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Liquid crystalline polymers with complex architectures

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Case Western Reserve University, 1993
LIQUID CRYSTALLINE POLYMERS WITH COMPLEX ARCHITECTURES

by

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Submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

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LIQUID CRYSTALLINE POLYMERS WITH COMPLEX
ARCHITECTURES

Abstract

by

MASAYA KAWASUMI

Novel classes of thermotropic liquid crystalline polyethers with linear, cyclic
and dendritic architectures are described. All the mesogenic units have the same
basic skeleton based on conformational isomerism, i.e., 1-(4-hydroxy-4'-
biphenyl)-2-(4-hydroxyphenyl)substituted or nonsubstituted alkanes which were
designed according to a simple thermodynamic scheme so that resulting
polyethers can exhibit an enantiotropic mesophase.

The synthesis and characterization of thermotropic linear polyethers based on
1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) and \( \alpha,\omega \)-
dibromoalkanes containing \( X \) methylenic units (TPB-X, \( X=4-20 \)) are described.
Most of TPB-X exhibit an enantiotropic nematic mesophase as predicted from the
simple thermodynamic scheme. The linear polyethers based on 1-(4-hydroxy-4'
biphenyl)-2-(4-hydroxyphenyl)decane (TPD) and \( \alpha,\omega \)-dibromoalkanes
containing \( X \) methylenic units (TPD-X, \( X=6-10 \)) were synthesized and the
thermal behavior was compared with that of TPB-X.

The molecular weight effect on the thermal behavior was studied with
synthesized oligomers and fractionated linear TPB-10 polyethers with number
average molecular weights from monomer to about 57,200.
The synthesis and characterization of the first thermotropic cyclic main chain oligomers based on TPB and α,ω-dibromoalkanes containing X methylenic units (TPB-X(c), X=4-14, 18) are presented. The cyclic oligomers were separated and were characterized by $^1$H-NMR, GPC, and DSC. Most of cyclic oligomers exhibit a nematic mesophase. The effect of the ring size and spacer length on the phase behavior was discussed.

The chiral linear and cyclic polyethers based on chiral (R)-TPB* and α,ω-dibromoalkanes containing X methylenic units (linear polyethers, TPB*-X, X=10, 12, 14, 16; cyclic polyethers, TPB*-X(c), X=10) were synthesized and characterized. The effect of chirality of the mesogenic unit on the phase behavior was studied.

The synthesis and characterization of the first thermotropic dendrimers based on 10-bromo-1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)decane (TPD-b) and 6-bromo-1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)hexane (TPH-b) are described. The dendrimers were synthesized by the homopolymerization of TPD-b or TPH-b followed by the alkylation with an alkyl bromide or benzyl chloride. Some of the resulting dendrimers exhibit an enantiotropic nematic mesophase. The effect of the chain end groups on their phase behavior was studied.
ACKNOWLEDGEMENTS

I would like to extend my thanks and deep appreciation to Professor Virgil Percece for his many contributions, kind, patient, and enthusiastic guidance towards the completion of this work, and for teaching me what is the real spirits for research.

I would like to thank Toyota Central Research and Development Laboratories, Inc., Japan, for providing all financial and mental supports for my studies.

I would like to express my deep gratitude to Professor G. Ungar, University of Sheffield, and Professor J. Blackwell for providing X-ray analysis of the samples, to Professor P. L. Linaldi and V. E. Litman for providing NMR analysis of cyclic oligomers. Special thanks are due to my coworkers in our research group for their cooperation and for the maintenance of all instruments.
# TABLE OF CONTENTS

Abstract

Acknowledgements

Table of Contents

List of Figures and Schemes

List of Tables

## CHAPTER 1: Introduction
- 1.1 Introduction 1
- 1.2 Techniques 2
- 1.3 References 15

## CHAPTER 2: Synthesis and Characterization of Linear Polyethers
- Based on a Laterally Substituted Semiflexible Mesogenic Unit and $\alpha,\omega$-Dibromoalkanes
- 2.1 Introduction 20
- 2.2 Experimental 21
- 2.3 Results and Discussion 23
- 2.4 Conclusions 39
- 2.5 References 55

## CHAPTER 3: The Effect of Molecular Weight on The Phase Behavior of Linear Polyethers
- 3.1 Introduction 58
- 3.2 Experimental 59
- 3.3 Results and Discussion 60
- 3.4 Conclusions 80
- 3.5 References 112

## CHAPTER 4: Synthesis and Characterization of Cyclic Oligopolyethers Based on a Semiflexible Mesogenic Unit and $\alpha,\omega$-Dibromoalkanes
- 4.1 Introduction 115
- 4.2 Experimental 116
- 4.3 Results and Discussion 118
- 4.4 Conclusions 129
- 4.5 References 255

References 257
CHAPTER 5: Synthesis and Characterization of Chiral Linear and Cyclic Polyethers Based on a Laterally Substituted Semiflexible Mesogenic Unit and α,ω-Dibromoalkanes

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>259</td>
</tr>
<tr>
<td>5.2 Experimental</td>
<td>260</td>
</tr>
<tr>
<td>5.3 Results and Discussion</td>
<td>263</td>
</tr>
<tr>
<td>5.4 Conclusions</td>
<td>274</td>
</tr>
<tr>
<td>5.5 References</td>
<td>297</td>
</tr>
</tbody>
</table>

CHAPTER 6: Synthesis and Characterization of Thermotropic Liquid Crystalline Dendritic Polyethers

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Introduction</td>
<td>301</td>
</tr>
<tr>
<td>6.2 Experimental</td>
<td>302</td>
</tr>
<tr>
<td>6.3 Results and Discussion</td>
<td>303</td>
</tr>
<tr>
<td>6.4 Conclusions</td>
<td>321</td>
</tr>
<tr>
<td>6.5 References</td>
<td>334</td>
</tr>
</tbody>
</table>

CHAPTER 7: Conclusions

BIBLIOGRAPHY
LIST OF FIGURES

Scheme 1.1 Classified architectures for thermotropic liquid crystalline polymers by Demus\(^1\) (\(\sim\), flexible chain; \(\bullet\), core (mainly ring systems); \(\circlearrowright\), discotic skeleton without flexible chain; \(\sim\), short connectors with low flexibility).

3

Scheme 1.2 Schematic representations of dendritic architecture.

6

Scheme 1.3 The semiflexible mesogenic units used to synthesize linear, cyclic, dendritic polyethers.

8

Scheme 1.4 (a) Rigid rod-like mesogens, (b) flexible rod-like mesogens based on conformational isomerism.

9

Figure 1.1 (a) Schematic plots of free energies, \(G_k\), \(G_{16}\), \(G_1\), versus temperature for a virtual system. Heavy line corresponds to the most stable state at a given temperature; (b) schematic plots of free energies vs temperature for an enantiotropic system transformed from the system 1.1 (a) by raising \(G_i\); (c) schematic plots of free energies vs temperature for an enantiotropic system transformed from the system 1.1 (a) by raising \(G_k\).

12

Scheme 2.1 Synthesis of 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane (TPB).

25

Scheme 2.2 Synthesis of 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (TPD).

33

Scheme 2.3 Synthesis of polyethers based on 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane and \(\alpha,\omega\)-dibromoalkanes containing \(X\) methylenic units (TPB-X).

37

Scheme 2.4 Synthesis of polyethers based on 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane and \(\alpha,\omega\)-dibromoalkanes containing \(X\) methylenic units (TPD-X).

38

Figure 2.1 Second heating (a) and first cooling (b) DSC thermograms (20\(^\circ\)C/min) of polyethers based on TPB and \(\alpha,\omega\)-dibromoalkanes containing \(X\) methylenic units (TPB-X).

44
Figure 2.2 Dependence of phase transition temperatures of TPB-X on the number of methylenic units in the flexible spacer (X): (a) data from the second heating scan (Tg data of TPB-11 to TPB-20 are from the first heating scan); (b) data from the first cooling scan.

Figure 2.3 Dependence of the enthalpy change (a) and the entropy change (b) associated with the nematic-isotropic transitions on the number of methylene units in the flexible spacer (X) of TPB-X.

Figure 2.4 Second heating (a) and first cooling (b) DSC thermograms (20°C/min) of polyethers based on TPD and α,ω-dibromoalkanes containing X methylene units (TPD-X).

Scheme 3.1 Synthesis of linear TPB-10 monomer and dimer.

Scheme 3.2 Synthesis of linear TPB-10 trimer.

Scheme 3.3 Synthesis of linear TPB-10 tetramer.

Scheme 3.4 Preparation of high molecular weight TPB-10 polyether with terminal decyl groups.

Scheme 3.5 Preparation of low molecular weight TPB-10 polyether with terminal decyl groups.

Figure 3.1 GPC chromatograms of linear TPB-10 oligomers.

Figure 3.2 Observed and calculated molecular weights of linear TPB-10 oligomers versus the degree of polymerization.

Figure 3.3 DSC thermograms of first heating scans (a), second heating (b), and cooling scans (c) of linear TPB-10 oligomers.

Figure 3.4 Typical polarized optical microscopic textures (x100) of linear TPB-10 oligomers: (a) linear TPB-10 trimer annealed at 55.3°C for 1 min; (b) linear TPB-10 tetramer annealed at 71.2°C for 4 min.

Figure 3.5 DSC thermograms of first heating (a), second heating (b), and cooling scans (c) of intermediate linear oligomers with one TPB unit in the structures (monomers).

Figure 3.6 DSC thermograms of first heating (a), second heating (b), and cooling scans (c) of intermediate linear oligomers with two TPB units in the structure (dimers).
Figure 3.7 GPC chromatograms of fractionated TPB-10 polyethers from the high molecular weight TPB-10. 97

Figure 3.8 Number average molecular weight (a) and polydispersity (b) of the fractionated polyethers from the high molecular weight TPB-10 versus CHCl₃ content in eluent. 98

Figure 3.9 Yield of the fractionated polyethers from the high molecular weight TPB-10 versus CHCl₃ content in eluent. 99

Figure 3.10 GPC chromatograms of fractionated TPB-10 polyethers from the low molecular weight TPB-10. 101

Figure 3.11 DSC thermograms of second heating (a) and cooling scans (b) of fractionated polyethers from the high molecular weight TPB-10 and of the original high molecular weight TPB-10 before the fractionation. 102

Figure 3.12 DSC thermograms of second heating (a) and cooling scans (b) of fractionated polyethers from the low molecular weight TPB-10 and of the original low molecular weight TPB-10 before the fractionation. 103

Figure 3.13 Nematic-isotropic transition temperatures (Tni and Tin) (a) and glass transition temperature (Tg) (b) of fractionated linear TPB-10 polyethers versus number average molecular weight (Mn). 105

Figure 3.14 Nematic-isotropic transition temperatures (Tni and Tin) (a) and glass transition temperature (Tg) (b) of fractionated linear TPB-10 polyethers versus reciprocal number average molecular weight (1/Mn). 106

Figure 3.15 Super cooling (Tni-Tin) versus number average molecular weight (Mn). 108

Figure 3.16 Ratio Tni/Tg (in K) versus number average molecular weight (Mn) (Data from second heating scan). 109

Figure 3.17a,b Typical polarized optical microscopic textures (x100) of the linear TPB-10 polyethers; (a) Mn=1.15 x 10⁴, annealed at 84.2°C for 22min; (b) Mn=3.58 x 10⁴, annealed at 95.4°C for 22min. 110

Figure 3.18 Enthalpy change (ΔH) associated with nematic-isotropic and isotropic-nematic transitions versus number average molecular weight (Mn) (a) and 1/Mn (b). 111
Scheme 4.1 Polyetherification of TPB with 1,10-dibromodecane at various concentrations.

Scheme 4.2 Cyclization of TPB with α,ω-dibromoalkanes (the number of methylenic units are 4-14, 18) followed by the separation of cyclic oligomers.

Scheme 4.3 Protonic assignments of TPB-10(c) oligomers.

Scheme 4.4 Schematic representation of the isotropic-nematic transition of TPB-10(c) tetramer.

Scheme 4.5 Schematic representation of the ideal conformation of cyclic trimers to form a nematic state.

Figures 4.1a GPC chromatograms of polymerization mixtures obtained at various polymerization time at initial monomer concentration, monomer (mmol) / solvent (ml) = 1/2.

Figures 4.1b GPC chromatograms of polymerization mixtures obtained at various polymerization time at initial monomer concentration, monomer (mmol) / solvent (ml) = 1/20.

Figures 4.1c GPC chromatograms of polymerization mixtures obtained at various polymerization time at initial monomer concentration, monomer (mmol) / solvent (ml) = 1/100.

Figures 4.2a,b The dependence of the average molecular weights on the polymerization time at various initial monomer concentrations [monomer (mmol) / solvent (ml) = 1/2, 1/20, and 1/100]: (a) the number average molecular weight (M_n); (b) the weight average molecular weight (M_w).

Figure 4.3 Effect of the monomer concentration on the weight fraction of oligomers versus the degree of polymerization.

Figure 4.4 GPC chromatograms of the reaction mixtures obtained by the polyetherifications of TPB with α,ω-dibromoalkanes with X methylenic unit (X = 4-14, 18) under high dilution conditions [monomer (mmol) / solvent (ml) = 1/100].
Figure 4.5 Weight fractions of cyclic oligomers in the polymerization mixtures obtained under high dilution conditions [monomer (mmol) / solvent (ml) = 1/100] versus the spacer length.

Figure 4.6 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,4-dibromobutane.

Figure 4.7 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,5-dibromopentane.

Figure 4.8 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,6-dibromohexane.

Figure 4.9 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,7-dibromoheptane.

Figure 4.10 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,8-dibromooctane.

Figure 4.11 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,9-dibromononane.

Figure 4.12 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,10-dibromodecane.

Figure 4.13 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,11-dibromoundecane.

Figure 4.14 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,12-dibromododecane.
Figure 4.15 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,13-dibromotridecane.

Figure 4.16 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,14-dibromotetradecane.

Figure 4.17 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,18-dibromoocadecane.

Figure 4.18 (a) The calculated and measured (GPC) molecular weights of the TPB-10(c) oligomers versus the ring size; (b) the comparison of the values [Mn(GPC)/Mn(calculated)] between the TPB-10(c) and the linear TPB-10 oligomers.

Figure 4.19 300 MHz $^1$H-NMR spectra of TPB-10(c) series: (a) cyclic monomer; (b) cyclic dimer; (c) cyclic trimer; (d) cyclic tetramer; (e) crude cyclic pentamer; (f) CHCl$_3$ eluted part (CDCl$_3$, TMS).

Figure 4.20 2-D 300 MHz $^1$H-NMR COSY spectrum of the cyclic TPB-10(c) monomer (CDCl$_3$, TMS).

Figure 4.21a 2-D 300 MHz $^1$H-NMR NOESY spectrum of the cyclic TPB-10(c) monomer (CDCl$_3$, TMS) in full scale.

Figure 4.21b 2-D 300 MHz $^1$H-NMR NOESY spectrum of the cyclic TPB-10(c) monomer (CDCl$_3$, TMS) in aromatic region.

Figure 4.21c 2-D 300 MHz $^1$H-NMR NOESY spectrum of the cyclic TPB-10(c) monomer (CDCl$_3$, TMS) in aromatic-aliphatic region.

Figure 4.22a,b The dependence of chemical shifts on the ring size: (a) aromatic protons (A1 - A6); (b) protons of lateral ethyl group (c and d).

Figure 4.22c,d The dependence of chemical shifts on the ring size: (c) methylenic protons next to the biphenyl ring (a and a') and methine proton (b); (d) methylenic protons in the spacer (1 - 10).
Figure 4.23 One of the lowest free energy conformation of the cyclic monomer.

Figure 4.24 200 MHz $^1$H-NMR spectra of TPB-4(c) series.

Figure 4.25 200 MHz $^1$H-NMR spectra of TPB-5(c) series.

Figure 4.26 200 MHz $^1$H-NMR spectra of TPB-6(c) series.

Figure 4.27 200 MHz $^1$H-NMR spectra of TPB-7(c) series.

Figure 4.28 200 MHz $^1$H-NMR spectra of TPB-8(c) series.

Figure 4.29 200 MHz $^1$H-NMR spectra of TPB-9(c) series.

Figure 4.30 200 MHz $^1$H-NMR spectra of TPB-11(c) series.

Figure 4.31 200 MHz $^1$H-NMR spectra of TPB-12(c) series.

Figure 4.32 200 MHz $^1$H-NMR spectra of TPB-13(c) series.

Figure 4.33 200 MHz $^1$H-NMR spectra of TPB-14(c) series.

Figure 4.34 200 MHz $^1$H-NMR spectra of TPB-18(c) series.

Figure 4.35a The dependence of chemical shifts of aromatic protons (A1 - A6), the protons of lateral ethyl group (c and d), methylene protons next to the biphenyl ring (a and a') and methine proton (b) versus the spacer length for the cyclic monomers.

Figure 4.35b The dependence of chemical shifts of aromatic protons (A1 - A6), the protons of lateral ethyl group (c and d), methylene protons next to the biphenyl ring (a and a') and methine proton (b) versus the spacer length for the cyclic dimers.

Figure 4.35c The dependence of chemical shifts of aromatic protons (A1 - A6), the protons of lateral ethyl group (c and d), methylene protons next to the biphenyl ring (a and a') and methine proton (b) versus the spacer length for the cyclic trimers.
Figure 4.35a The dependence of chemical shifts of aromatic protons (A1 - A6), the protons of lateral ethyl group (c and d), methylenic protons next to the biphenyl ring (a and a') and methine proton (b) versus the spacer length for the cyclic tetramers.

Figure 4.35b The dependence of chemical shifts of aromatic protons (A1 - A6), the protons of lateral ethyl group (c and d), methylenic protons next to the biphenyl ring (a and a') and methine proton (b) versus the spacer length for the linear polymers.

Figure 4.36 DSC thermograms of the linear TPB-10 polyethers (L), of the high molecular weight part of TPB-10(c) eluted with CHCl3 (H) and of the cyclic TPB-10(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 4.37a,b The textures of the cyclic TPB-10(c) oligomers observed under optical polarized microscope (x100): (a) fine nematic texture of the cyclic dimer after annealing at 42.3°C for 14 min; (b) crystalline texture of the cyclic dimer after annealing at 85.9°C for 5 min.

Figure 4.37c,d The textures of the cyclic TPB-10(c) oligomers observed under optical polarized microscope (x100): (c) homogeneous nematic texture of cyclic trimer after annealing at 79.6°C for 13 min; (d) schlieren nematic texture of cyclic tetramer after annealing at 114.3°C upon heating.

Figure 4.38 The transition temperatures of the TPB-10(c) oligomers obtained during second heating and first cooling scans versus the ring size and the comparison with their linear homologue.

Figure 4.39 The entropy change associated with the nematic-isotropic transitions of the cyclic oligomers obtained during second heating and first cooling scans versus ring size and the comparison with their linear homologue.

Figure 4.40 The comparison of cyclic oligomers versus linear oligomers; (a) nematic-isotropic transition temperature versus the degree of polymerization; (b) the entropy change associated with the nematic-isotropic transition versus the degree of polymerization.
Figure 4.41 DSC thermograms of the linear TPB-5 polyethers (L), of the high molecular weight part of TPB-5(c) eluted with CHCl₃ (H) and of the cyclic TPB-5(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 4.42 DSC thermograms of the linear TPB-7 polyethers (L), of the high molecular weight part of TPB-7(c) eluted with CHCl₃ (H) and of the cyclic TPB-7(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 4.43 DSC thermograms of the linear TPB-4 polyethers (L), of the high molecular weight part of TPB-4(c) eluted with CHCl₃ (H) and of the cyclic TPB-4(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 4.44 DSC thermograms of the linear TPB-6 polyethers (L), of the high molecular weight part of TPB-6(c) eluted with CHCl₃ (H) and of the cyclic TPB-6(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 4.45 DSC thermograms of the linear TPB-8 polyethers (L), of the high molecular weight part of TPB-8(c) eluted with CHCl₃ (H) and of the cyclic TPB-8(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 4.46 DSC thermograms of the linear TPB-9 polyethers (L), of the high molecular weight part of TPB-9(c) eluted with CHCl₃ (H) and of the cyclic TPB-9(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 4.47 DSC thermograms of the linear TPB-11 polyethers (L), of the high molecular weight part of TPB-11(c) eluted with CHCl₃ (H) and of the cyclic TPB-11(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.
Figure 4.48 DSC thermograms of the linear TPB-12 polyethers (L), of the high molecular weight part of TPB-12(c) eluted with CHCl₃ (H) and of the cyclic TPB-12(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 4.49 DSC thermograms of the linear TPB-13 polyethers (L), of the high molecular weight part of TPB-13(c) eluted with CHCl₃ (H) and of the cyclic TPB-13(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 4.50 DSC thermograms of the linear TPB-14 polyethers (L), of the high molecular weight part of TPB-14(c) eluted with CHCl₃ (H) and of the cyclic TPB-14(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 4.51 DSC thermograms of the linear TPB-18 polyethers (L), of the high molecular weight part of TPB-18(c) eluted with CHCl₃ (H) and of the cyclic TPB-18(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 4.52a The transition temperatures of the cyclic dimers obtained from the first heating scans versus the spacer length.

Figure 4.52b,c The transition temperatures of the cyclic dimers versus the spacer length obtained from: (b) the second heating scans; (c) the first cooling.

Figure 4.53a,b The transition temperatures of the cyclic trimers versus the spacer length obtained from: (a) the first heating scans; (b) the second heating scans and cooling scans.

Figure 4.54 The enthalpy change associated with nematic-isotropic transition of the cyclic trimers versus the spacer length obtained from second heating and cooling.

Figure 4.55a,b The representative textures of cyclic trimers observed under optical polarized microscope (x100): (a) TPB-7(c) trimer annealed at 78.4°C for 6 min; (b) TPB-11(c) trimer annealed at 92.5°C for 0.5 min.
Figure 4.56a,b The textures of cyclic TPB-14(c) trimers observed under cooling under optical polarized microscope (x100): (a) at 66.3°C, right above the second transition (nematic phase); (b) at 61.1°C for 1.5 min, below the second transition (smectic phase).

Figure 4.57a,b The transition temperatures of the cyclic tetramers versus the spacer length obtained from: (a) the first heating scans; (b) the second heating scans and cooling scans.

Figure 4.58 The enthalpy change associated with the nematic-isotropic transition of the cyclic tetramers versus the spacer length obtained from second heating and cooling.

Figure 4.59a,b The comparison of the nematic-isotropic transition temperatures (a) and the enthalpy changes (b) associated with nematic-isotropic transition between the cyclic tetramers and the corresponding high molecular weight linear polymers.

Figure 4.60 The representative textures of cyclic tetramers observed under optical polarized microscope (x100): (a) TPB-8(c) tetramer annealed at 131.1°C for 1 min; (b) TPB-12(c) tetramer annealed at 108.3°C for 1.5 min.

Figure 4.61a,b The transition temperatures (a) and enthalpy changes (b) associated with nematic-isotropic transition of the cyclic pentamers versus the spacer length obtained from second heating and cooling.

Figure 4.62 A possible molecular arrangement of cyclic oligomers in a crystalline phase.

Figure 4.63 DSC thermograms of TPB-8(c) tetramer, of the mixture of 50:50 TPB-8(c) tetramer and linear TPB-8 polymer, and of linear TPB-8 polymer: (a) second heating scan; (b) cooling scan.

Figure 4.64 DSC thermograms of TPB-8(c) trimer, of the mixture of 50:50 TPB-8(c) trimer and linear TPB-8 polymer, and of linear TPB-8 polymer: (a) second heating scan; (b) cooling scan.
Figure 4.65a,b The transition temperature (the line indicates the calculated value by simplified Schrödinger-van Laar equations) (a) and the enthalpy change (b) of the mixtures of TPB-8(c) tetramer and linear TPB-8 polymer versus the composition.

Figure 4.66a,b The transition temperature (the line indicates the calculated value by simplified Schrödinger-van Laar equations) (a) and the enthalpy change (b) of the mixtures of TPB-8(c) trimer and linear TPB-8 polymer versus the composition.

Figure 4.67 DSC thermograms of TPB-8(c) dimer, of the mixture of 50:50 TPB-8(c) dimer and linear TPB-8 polymer, and of linear TPB-8 polymer: (a) second heating scan; (b) cooling scan.

Scheme 5.1 Schematic representation of the structure of cholesteric phase. Molecules are shown as elliptical rods which stack in a single-twist structure.

Scheme 5.2 Synthesis of (R)-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane.

Scheme 5.3 Synthesis of chiral linear TPB*-X polymers and cyclic TPB*-10(c) oligomers based on (R)-TPB* with α,ω-dibromoalkanes.

Scheme 5.4 Supercoiled structure of chiral TPB*-10(c) tetramer and pentamer.

Figure 5.1a,b 200 MHz $^1$H-NMR spectra of the methoxy protons of 2-(4-methoxyphenyl)butanoic acid in the presence of the equal molar amount of (-)-cinchonidine in CDCl$_3$: (a) racemic 2-(4-methoxyphenyl)butanoic acid; (b) resolved (R)-2-(4-methoxyphenyl)butanoic acid.

Figure 5.2 GPC chromatograms of the reaction mixtures, of high molecular weight part eluted with CHCl$_3$, and of separated chiral cyclic oligomers [TPB*-10(c)].

Figure 5.3a-f 200 MHz $^1$H-NMR spectra of chiral cyclic TPB*-10(c) series: (a) CHCl$_3$ eluted part; (b) cyclic pentamer; (c) cyclic tetramer; (d) cyclic trimer; (e) cyclic dimer; (f)cyclic monomer (CDCl$_3$, TMS).
Figure 5.4a The comparison of DSC thermograms of chiral linear TPB*-X polymers with those of racemic TPB-X polymers obtained from the first heating scan.

Figure 5.4b The comparison of DSC thermograms of chiral linear TPB*-X polymers with those of racemic TPB-X polymers obtained from the second heating scan.

Figure 5.4c The comparison of DSC thermograms of chiral linear TPB*-X polymers with those of racemic TPB-X polymers obtained from the first cooling scan.

Figure 5.5a The comparison of DSC thermograms of chiral cyclic TPB*-10(c) oligomers with those of racemic cyclic TPB-10(c) oligomers obtained from the first heating scan (Numbers in the figure indicate the ring size. H indicates the part eluted with CHCl₃.).

Figure 5.5b The comparison of DSC thermograms of chiral cyclic TPB*-10(c) oligomers with those of racemic cyclic TPB-10(c) oligomers obtained from the second heating scan (Numbers in the figure indicate the ring size. H indicates the part eluted with CHCl₃.).

Figure 5.5c The comparison of DSC thermograms of chiral cyclic TPB*-10(c) oligomers with those of racemic cyclic TPB-10(c) oligomers obtained from the cooling scan (Numbers in the figure indicate the ring size. H indicates the part eluted with CHCl₃.).

Figure 5.6a,b The comparison of the texture of chiral cyclic TPB*-10(c) tetramer with that of racemic cyclic TPB-10(c) tetramer observed under optical polarized microscope (x100): (a) schlieren nematic texture of the racemic tetramer after annealing at 115.9°C for 3 min; (b) focal conic cholesteric texture of the chiral tetramer after annealing at 114.3°C upon heating.

Figure 5.7 The texture of chiral cyclic TPB*-10(c) pentamer observed under optical polarized microscope (x100) (annealing at 111.4°C for 2 min).

Figure 5.8a,b The textures of chiral cyclic TPB*-10(c) dimer and trimer observed under optical polarized microscope (x100): (a) the cyclic dimer quenched from isotopic melt; (b) the cyclic trimer after annealing at 86°C for 2 min.
Figure 5.9 UV and CD spectra of the dioxane solutions of the (R)-TPB, the chiral TPB*-10(c) oligomers, and chiral linear TPB*-10 polymer.

Figure 5.10 CD spectra of the films of chiral TPB*-10(c) oligomers and chiral linear TPB*-10 polymer on a cover glass (The films of the tetramer and pentamer are much thicker than those of the dimer, trimer, and linear polymer. Also the y-axis is more expanded for the tetramer and pentamer.).

Scheme 6.1 Synthesis of 10-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (TPD-b).

Scheme 6.2 Synthesis of 6-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)hexane (TPH-b).

Scheme 6.3 Synthesis of dendritic polyethers based on 10-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (TPD-b-X) and the schematic representation of the transformation between nematic and isotropic phases.

Figure 6.1 200 MHz \textsuperscript{1}H-NMR of TPD-b-8 (CDCl3).

Figure 6.2a,b Second heating (a) and first cooling (b) DSC thermograms (20°C/min) of dendritic polyethers based on TPD-b and alkylbromide or benzylchloride (TPD-b-X, X is the structure of the chain end groups, i.e., Bz=benzyl, 4=butyl, 6=hexyl and 8=octyl).

Figure 6.3 The representative nematic texture of TPD-b-8 after annealing at 35.5°C for 1 h 30 min (x100).

Figure 6.4a,b The transition temperatures and the enthalpy changes of TPD-b-X dendrimers versus the chain end groups (X) and the comparison with the linear model TPD-8 polymer: (a) the transition temperatures obtained from the second heating and cooling scans; (b) the enthalpy changes associated with the nematic-isotropic transitions.

Figure 6.5 200 MHz \textsuperscript{1}H-NMR of TPH-b-4 (CDCl3).

Figure 6.6a,b Second heating (a) and first cooling (b) DSC thermograms (20°C/min) of dendritic polyethers based on TPH-b and alkylbromide or benzylchloride (TPH-b-X, X is the structure of the chain end groups, i.e., Bz=benzyl, 4=butyl, 6=hexyl and 8=octyl).
LIST OF TABLES

Table 2.1 Characterization of polyethers based on TPB and α, ω-
dibromoalkanes (TPB-X) with different number of
methylenic units (X). Data collected from second heating
and first cooling DSC scans.

Table 2.2 Characterization of polyethers based on TPD and α, ω-
dibromoalkanes (TPB-X) with different number of
methylenic units (X). Data collected from second heating
and first Cooling DSC scans.

Table 3.1 Characterization of linear TPB-10 oligomers.

Table 3.2 Characterization of linear TPB-10 oligomers with various
terminal groups.

Table 3.3 Characterization of fractionated polyethers from high
molecular weight TPB-10.

Table 3.4 Characterization of fractionated polyethers from low
molecular weight TPB-10.

Table 4.1 Characterization of cyclic oligomers and corresponding linear
polymer based on TPB and 1,4-dibromobutane.

Table 4.2 Characterization of cyclic oligomers and corresponding linear
polymers based on TPB and 1,5-dibromopentane.

Table 4.3 Characterization of cyclic oligomers and corresponding linear
polymer based on TPB and 1,6-dibromohexane.

Table 4.4 Characterization of cyclic oligomers and corresponding linear
polymer based on TPB and 1,7-dibromohexane.

Table 4.5 Characterization of cyclic oligomers and corresponding linear
polymer based on TPB and 1,8-dibromooctane.

Table 4.6 Characterization of cyclic oligomers and corresponding linear
polymer based on TPB and 1,9-dibromononane.

Table 4.7 Characterization of cyclic oligomers and corresponding linear
polymer based on TPB and 1,10-dibromodecane.
Table 4.8 Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,11-dibromoundecane.  

Table 4.9 Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,12-dibromododecane.  

Table 4.10 Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,13-dibromotridecane.  

Table 4.11 Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,14-dibromotetradecane.  

Table 4.12 Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,18-dibromooctadecane.  

Table 4.13 \(^1\text{H-NMR}\) peak assignment of cyclic oligomers, of CHCl\(_3\) eluted part, and of linear polyether.  

Table 4.14 The length of TPB unit, spacers, and monomer unit in fully extended TPB-X.  

Table 4.15 Characterization of TPB-8(c) oligomers and linear TPB-8 mixtures.  

Table 5.1 Characterization of chiral polyethers based on chiral TPB and \(\alpha, \omega\)-dibromoalkanes (TPB-X) with different number of methylenic units (X).  

Table 5.2 Characterization of chiral TPB*-10(c) oligomers based on TPB* and 1-10-dibromodecane.  

Table 6.1 Characterization of dendritic polyethers (TPD-b-X) with different chain ends (X) and comparison with the linear model polyether (TPD-8).  

Table 6.2 Characterization of dendritic polyethers (TPH-b-X) with different chain ends (X).
CHAPTER 1

Introduction
1.1 INTRODUCTION

Since the discovery of the liquid crystals by Reinitzer\textsuperscript{1} and Lehmann\textsuperscript{2} about one hundreds years ago, more than 20,000 rod-like thermotropic liquid crystals have been synthesized and about 1,000 new liquid crystals are synthesized every year.\textsuperscript{3} Demus classified these numerous numbers of liquid crystals into about 70 types based on their architectures.\textsuperscript{3} Scheme 1.1 summarizes the architectures for polymeric systems classified by Demus.\textsuperscript{3} As seen from this scheme only four simplified basic units, i.e., flexible chain, core unit (mainly ring systems), discotic skeletons without flexible chains, short connectors with low flexibility, can represent most of the liquid crystalline polymers by connecting these basic units in a different way. The additional class of liquid crystalline polymers could be liquid crystalline networks.\textsuperscript{4} The simple combination of theses moieties still can lead to novel architectures of liquid crystalline polymers which are not listed in Scheme 1.1. Perhaps some of the most important missing structures could be cyclic and dendritic liquid crystalline polymers.

One of the goals of this thesis is to provide novel classes of liquid crystalline polymers with new architectures. The main targets are novel thermotropic main chain cyclic and dendritic liquid crystalline polymers and oligomers. Their mesomorphic behavior is studied and compared with that of the corresponding linear polymers. First, let us explain briefly the background of cyclic and dendritic polymers and the motivations for those structures.
Scheme 1.1 Classified architectures for thermotropic liquid crystalline polymers by Demus 3 (——, flexible chain; ●, core (mainly ring systems);
●, discotic skeleton without flexible chain; ——, short connectors with low flexibility).
Cyclic oligomers are generated both during step condensation and ring opening polymerization reactions. Therefore, unless removed they are available in many polymers synthesized by these synthetic methods. Also cyclic oligomers (i.e., ionophores) and polymers (i.e., DNA and peptides) are important compounds found in nature. Recently several groups have synthesized cyclic glassy oligomers and polymers i.e., polystyrene, poly(2-vinylpyridine), and polysiloxanes. The solution and bulk properties of the cyclic polymers have been studied and the following interesting conclusions were obtained. The cyclic polymers in solution generally have smaller radius of gyration (theoretically $\langle R^2 \rangle_{cyclic}/\langle R^2 \rangle_{linear} = 0.5$, the observed values for polydimethylsiloxane-benzene and polystyrene-toluene by neutron scattering experiments are close to this value). The glassy cyclic polymers exhibit opposite dependence of glass transition temperature on molecular weight from that of linear homologues. Namely, the glass transition temperature of cyclic polymers increases with decreasing their molecular weight. This has been theoretically supported. The cyclic oligomers of polyethylene were synthesized as a crystalline material and used to understand the crystallization mechanism of polyethylene. However, the differences and similarities between cyclic and linear polymers have not been clear yet. The liquid crystalline states of cyclic polymers should reveal the new aspects of cyclic polymers and help to understand the differences between cyclic and linear polymers since it is obvious that each state, i.e., crystalline, amorphous, isotropic melt, solution, and liquid crystalline states can provide different information of the molecules. There have been only two examples of cyclic side chain liquid crystalline polymers and no reports of
main chain liquid crystalline polymers. These background prompted us to explore the thermotropic main chain cyclic liquid crystalline polymers.

Besides cyclic polymers, there has been an increased interest in the synthesis and characterization of dendrimers or hyperbranched polymers, i.e., polymers containing a branching point in each structural unit as a polymeric system with novel architecture 15-26 (Scheme 1.2). To date most of the effort has been put on the synthetic aspect. Dendrimers display a spherical or tree-like architecture and are not expected to display liquid crystallinity. For example dendritic aromatic polyesters,21e,25b polyphenylenes20,25a and polybenzyl ethers21a,b were reported and they do not exhibit liquid crystallinity although their linear homologues do. There are only few examples of lyotropic systems. A dendrimer was used as solvent to generate a nonaqueous lamellar liquid crystal from octanoic acid.27 A lyotropic liquid crystalline dendritic aromatic polyamide was prepared in parallel with our work reported in this thesis.28 However, there has been no report of thermotropic dendrimers. The dendritic liquid crystalline polymers are very interesting for following reasons. First of all, compared to a linear architecture, a dendritic architecture has more variable structural units, i.e., core unit and its multiplicity, branching unit and its multiplicity, surface units, generation, etc (Scheme 1.2). Therefore, the thermotropic behavior can be molecularly engineered with many structural elements. Secondly, there is a possibility to show new mesophases. For example, dendritic architectures may exhibit an intramolecular mesophase, i.e., mesophase within a molecule.
Scheme 1.2 Schematic representations of dendritic architectures.
The mesogenic units which will be incorporated in linear, cyclic, and hyperbranched architectures have the same basic skeletons based on conformational isomerism so that the thermal behavior can be compared directly (Scheme 1.3). These mesogenic units are semiflexible. Let us explain first the concept of the mesogenic unit based on conformational isomerism\textsuperscript{29-32} and the molecular design of these semiflexible mesogenic units.

Traditional rigid rod-like mesogenic units, which have been employed in the preparation of main chain and side chain liquid crystalline polymers, are composed of linearly substituted aromatic or cycloaliphatic rings connected by rigid interconnecting groups (Scheme 1.4a).\textsuperscript{33-42} The free rotation about certain carbon-carbon single bonds of these compounds does not change the lineality. On the other hand, the mesogenic units based on the conformational isomerism consist of rings and flexible interconnecting groups such as ethylene or methylenedioxy (Scheme 1.4b). These flexible interconnecting groups can adopt a number of conformations. The two stable conformers are anti and gauche. Since the anti conformer has an extended shape which is similar to that of the rigid rod-like molecule, it is responsible for displaying liquid crystallinity. The gauche conformer is similar to a kinked unit which is generally used to depress phase transition temperatures. The anti and gauche conformers are in dynamic equilibrium and therefore provide a liquid crystalline polymers having a dynamic compositions. The mesogenic units based on conformational isomerism have been used to synthesize linear main-chain liquid crystalline polyethers and copolyethers without\textsuperscript{29} and with\textsuperscript{30,31} flexible spacers and proved the ability to exhibit liquid
Scheme 1.3 The semiflexible mesogenic units used to synthesize linear, cyclic, dendritic polyethers.
a) Rigid rod-like mesogens

\[
\begin{align*}
\text{Rigid rod-like mesogens} & : \\
\text{Flexible rod-like mesogens or rod-like mesogens based on conformational isomerism} & : \\
\text{anti} & \quad \text{gauche}
\end{align*}
\]

\[\oplus = -\text{CH}_2\text{-} \text{O}\]

**Scheme 1.4** (a) Rigid rod-like mesogens, (b) flexible rod-like mesogens based on conformational isomerism.
crystallinity and even to tailor-make nematic,\textsuperscript{30,31,43} smectic,\textsuperscript{44a} and hexagonal columnar\textsuperscript{44b} mesophases. The first examples of polymers exhibiting two nematic mesophases were also provided by these polymers.\textsuperscript{31b} To date the experiments reported by Percec et al. were performed with polyethers and copolymers based on 1-(4-hydroxyphenyl)-2-(2-R-4-hydroxyphenyl)ethane (RBPE, R = CH\textsubscript{3},\textsuperscript{30,31} F,\textsuperscript{45} Cl,\textsuperscript{45} Br,\textsuperscript{45} CF\textsubscript{3}\textsuperscript{45}) or 1,2-bis(4-hydroxyphenyl)ethane (BPE)\textsuperscript{44} and \(\alpha,\omega\)-dibromoalkanes. Most of the polyethers based on RBPE exhibited virtual (a potentially possible but thermodynamically unstable mesophase) or monotropic (a thermodynamically metastable mesophase with respect to the crystalline phase and which can be observed under certain kinetic conditions on cooling) which were determined by using a copolymerization technique elaborated by Percec et al.. In order to explore the mesomorphic polymers with various architectures we needed to design new mesogenic units which have much higher ability to exhibit an enantiotropic mesophase (a thermodynamically stable mesophase which can be observed reversibly both on heating and cooling) as well as the accessibility to cyclic and dendritic architectures.

Recently a thermodynamic scheme which correlates the thermodynamic stabilities of liquid crystalline (i.e., virtual, monotropic and enantiotropic), crystalline and isotropic phases has been reported.\textsuperscript{46,47} The thermodynamic equation required for this discussion is

\[
dG = Vdp - SdT \quad (1.1)
\]
where $G$, $S$, $V$, $p$, $T$ are the free energy, the entropy, the volume, the pressure and the temperature, respectively. Since the phase behavior under constant pressure will be considered, $dp = 0$. Therefore, the free energies of the crystal ($G_k$), liquid crystal ($G_{lc}$) and isotropic ($G_i$) phases decrease with increasing temperature. The decrease of $G_i$ is steeper than $G_{lc}$ and $G_k$, since:

$$S_i > S_{lc} > S_k$$

Figure 1.1a presents the $G$-$T$ relations of a virtual system in which a crystalline phase melts into an isotropic phase before reaching at the crystalline-liquid crystalline transition temperature. Therefore, the mesophase is unstable the entire range of temperature. As seen from Figure 1.1b and 1.1c, the virtual mesophase can be transformed into an enantiotropic phase by either raising $G_i$ (Figure 1.1b) or raising $G_k$ (Figure 1.1c). $G_i$ can be increased by increasing the rigidity of the system, i.e., by decreasing the entropy of the isotropic phase. $G_k$ can be increased by increasing the disorder of the system, i.e., by decreasing the perfection of the crystalline phase. The previously used flexible mesogens were based on substituted or unsubstituted 1-((4-hydroxyphenyl)-2-(4-hydroxyphenyl)ethane (BPE). The rigidity of this mesogen will be increased by substituting a phenyl unit for a biphenyl unit and its disorder will be increased by substituting the 1,2-ethane for a 1,2-alkane which is longer than the ethan unit. The replacements of the 1,2-ethane with the 1,2-alkane adds a lateral substituted or nonsubstituted alkyl chain to the BPE mesogen. This lateral substituent decreases the order of the mesogen in the crystalline phase and therefore, lowers
Figure 1.1 (a) Schematic plots of free energies, $G_k$, $G_{lc}$, $G_i$, versus temperature for a virtual system. Heavy line corresponds to the most stable state at a given temperature; (b) schematic plots of free energies vs temperature for an enantiotropic system transformed from the system 1.1 (a) by raising $G_i$; (c) schematic plots of free energies vs temperature for an enantiotropic system transformed from the system 1.1 (a) by raising $G_k$. 
its melting point. In addition, this new mesogen increases the number of constitutional isomeric structural units of the resulting polymer, from one to four arising from both the racemic nature of mesogenic units and the regiochemical structure due to the unsymmetrical structure of the mesogenic units along the chain. This may decrease even more the degree of order of the polymer chains in the crystalline phase. The resulting mesogenic units are semiflexible mesogenic units as shown in Scheme 1.3.

This thesis consists of seven chapters. In Chapter 2, the synthesis and characterization of linear thermotropic polyethers based on 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) and α,ω-dibromoalkanes containing an X number of methylenic units (TPB-X, X=4-20) (Scheme 1.3) are presented. The validity of the molecular design mentioned above is demonstrated. Secondly, the lateral chain length effect is discussed briefly with polyethers based on 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decanes (TPD) and α,ω-dibromoalkanes containing an X number of methylenic units (TPD-X, X=6-10). These linear polyethers are used as the model polymers for cyclic and dendritic polyethers.

In Chapter 3, the effect of the molecular weight of linear TPB-10 polyethers on their thermal behavior is discussed. The data presented in this chapter is the most accurate and complete molecular weight effect data available.
In Chapter 4, the synthesis and characterization of the first thermotropic cyclic main chain oligomers based on TPB and α,ω-dibromoalkanes containing $X$ methylenic units (TPB-X(c), $X=4$-14, 18) (Scheme 1.3) are presented. The mesogenic units based on conformational isomerism should be suitable for the preparation of cyclic polymers and oligomers since its gauche conformer prefers cyclization. First, the effect of dilution on the formation of the cyclic structure versus the linear one is studied. The effect of ring size and spacer length on the mesomorphic behavior of separated cyclic oligomers is studied. Also the phase behavior of cyclic oligomers is compared with that of corresponding linear polymers and oligomers.

In Chapter 5, the chiral linear and cyclic polyethers based on chiral TPB and α,ω-dibromoalkanes containing $X$ methylenic units (linear polyethers, TPB*-X, $X=10, 12, 14, 16$; cyclic polyethers, TPB*-X(c), $X=10$) are synthesized and characterized. The effect of chirality of mesogenic unit on their phase behavior is studied.

In Chapter 6, the synthesis and characterization of first thermotropic dendrimers based on 10-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (TPD-b) and 6-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)hexane (TPH-b) are described. These dendrimers were synthesized by the homopolymerization of TPD-b or TPH-b followed by the alkylation with an alkyl bromide or benzyl chloride (Scheme 1.3). The effect of the chain end
group is studied and the results are compared with that of the corresponding linear homologue. In Chapter 7, conclusion remarks are made.

1.2 TECHNIQUES

1-D $^1$H-NMR (200 MHz) spectra were recorded on a Varian XL-200 NMR spectrometer. All spectra were acquired at room temperature.

Relative molecular weights and purities were determined by gel permeation chromatography (GPC) and high pressure liquid chromatography (HPLC). GPC analyses were carried out with a Perkin-Elmer series 10 LC equipped with an LC-100 column oven, and a Nelson Analytical 900 series data station. The measurements were made by using the UV detector, chloroform as solvent (1 ml/min, 40°C), two PL gel columns of 5x10^2 and 10^4 Å, and a calibration plot constructed with polystyrene standards. HPLC analyses were performed with the same instrument with a PL gel column of 1x10^2 Å.

A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station Model 3600 was used to determine thermal transitions. Heating and cooling rates were 20°C/min in all cases. First-order transitions (crystalline-crystalline, crystalline-liquid crystalline, liquid crystalline-isotropic, etc.) were read at the maximum or minimum of the endothermic or exothermic peaks. Glass transition temperatures (Tg) were read at the middle of the change in the heat capacity. All heating and cooling scans after the first heating scan
produced perfectly reproducible data. We will report the transitions collected from first and second or subsequent heating scans and from first cooling scan.

A Carl Zeiss optical polarizing microscope (magnification 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe thermal transitions and to analyze anisotropic textures.48

1.3 REFERENCES


CHAPTER 2

Synthesis and Characterization of Linear Polyethers Based on a Laterally Substituted Semiflexible Mesogenic Unit and α,ω-Dibromoalkanes
2.1 INTRODUCTION

The traditional molecular design employed in the preparation of main-chain and side-chain liquid crystalline polymers is based on the use of the concept of rigid rodlike mesogenic unit.\textsuperscript{1-10} Additional classes of mesogenic groups were recently reviewed by Demus.\textsuperscript{11}

The concept of flexible rodlike mesogenic unit or rodlike mesogenic unit based on conformational isomerism has been advanced by Percec et al. and was used to synthesize main-chain liquid crystalline polyethers without\textsuperscript{12} and with\textsuperscript{13,14,15} flexible spacers. The flexible mesogenic concept is very important since it provides flexibility in the molecular design of mesogenic units. Also, these polymers can be used to tailor-make nematic,\textsuperscript{13,14,16} smectic,\textsuperscript{17a} and hexagonal columnar\textsuperscript{17b} mesophases. The first examples of polymers exhibiting two nematic mesophases were also provided by these polymers.\textsuperscript{14b} Additional examples of liquid crystalline polymers based on conformational isomerism were reported.\textsuperscript{18-21} To date most of the reported experiments were performed with polyethers and copolymers based on 1-(4-hydroxyphenyl)-2-(2-R-4-hydroxyphenyl)ethane (RBPE, R = CH\textsubscript{3},\textsuperscript{13,14} F\textsuperscript{15b}, Cl\textsuperscript{15a,b}, Br\textsuperscript{15b}, CF\textsubscript{3}\textsuperscript{15b}) or 1,2-bis(4-hydroxyphenyl)ethane (BPE)\textsuperscript{17} and \(\alpha,\omega\)-dibromoalkanes. Most of the polyethers based on RBPE exhibited virtual mesophases\textsuperscript{14b,15a,b} which were determined by using a copolymerization technique elaborated by Percec.\textsuperscript{13,14}
Recently a thermodynamic scheme which correlates the thermodynamic stabilities of liquid crystalline (i.e., virtual, monotropic and enantiotropic) and crystalline phases has been reported\textsuperscript{22,23} as discussed in Chapter 1. According to this scheme\textsuperscript{22,23} the transformation of a virtual or monotropic mesophase into an enantiotropic mesophase can be accomplished by increasing both the rigidity (i.e., by decreasing the entropy of the mesophase, increasing the free energy of the isotropic phase and therefore, by increasing the isotropization temperature) and the disorder (i.e., by decreasing the perfection of the crystalline phase which increases its free energy and therefore decreases the melting temperature) of the molecule. The goal of this chapter is to demonstrate this concept. The previously used flexible mesogens were based on substituted or unsubstituted 1-(4-hydroxyphenyl)-2-(4-hydroxyphenyl)ethane (BPE). The rigidity of this mesogen will be increased by substituting a phenyl unit for a biphenyl unit and its disorder will be increased by substituting the 1,2-ethane for a 1,2-butane or decane unit. The replacement of 1,2-ethane with 1,2-butane or decane adds a lateral ethyl or octyl substituent to the BPE mesogen. This lateral substituent decreases the order of the mesogen in the crystalline phase and therefore, lowers its melting point. In addition, as it will be discussed in more details later, this new mesogens increase the number of constitutional isomeric structural units of the resulting polymer, from one to four and this may decrease even more the degree of order of the polymer chains in the crystalline phase. The resulting mesogenic units are 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) and 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (TPD).
In this chapter, first, the synthesis, phase behavior and structure of polyethers based on TPB and \(\alpha,\omega\)-dibromoalkanes containing an \(X\) number of methylenic units (TPB-X, \(X=4-20\)) are described. Secondly, the lateral chain length effect is discussed briefly with polyethers based on TPD and \(\alpha,\omega\)-dibromoalkanes containing an \(X\) number of methylenic units (TPD-X, \(X=6-10\)).

2.2 EXPERIMENTAL

2.2.1 Materials

Boron tribromide (1.0M in \(\text{CH}_2\text{Cl}_2\)), thionyl chloride, lithium aluminum hydride (95+%), tetrabutylammonium hydrogen sulfate (TBAH) (97%), 4-methoxyphenylacetic acid (99%), 4-phenylphenol (98%), 1-iodooctane (98%) (all from Aldrich), iodoethane (Lancaster Synthesis), aluminium chloride, 48% hydrobromic acid (both from Fisher Scientific), acetic anhydride (J. T. Baker Chemical Co.) were used as received. Diethyl ether was dried by refluxing over \(\text{LiAlH}_4\) followed by distillation. Methylene chloride and chloroform were refluxed over \(\text{CaH}_2\) and then distilled from \(\text{CaH}_2\). \(\alpha\)-Dichlorobenzene was distilled under reduced pressure. 1,4-Dibromobutane (99%), 1,5-dibromopentane (97%), 1,6-dibromohexane (97%), 1,7-dibromoheptane (97%), 1,8-dibromooctane (98%), 1,9-dibromononane (97%), 1,10-dibromodecane (97%), 1,11-dibromoundecane (98%) (all from Aldrich) were fractionated by vacuum distillation. 1,12-Dibromododecane (technical, Aldrich) was purified by recrystallization from methanol. 1,16-Dibromohexadecane (Pfaltz and Bauer) and 1,18-dibromoocadecane (K and K Laboratories) were used as received. 1,13-
Dibromotridecane, 1,14-dibromotetradecane, 1,15-dibromopentadecane, and 1,17-dibromohexadecane, 1,19-dibromononadecane, and 1,20-dibromoicosane were synthesized as described in a previous publication and papers cited therein.\textsuperscript{14b} All other chemicals were commercially available and were used as received.

2.2.2 Synthesis of TPB

The synthesis of TPB is outlined in Scheme 2.1.

2.2.2.1 Synthesis of 4-hydroxyphenylacetic acid (4)

4 was prepared by the demethylation of 4-methoxyphenylacetic acid (3). 4-Methoxyphenylacetic acid 3 (49.9 g, 0.30 mol) was dissolved in a mixture of 48\% hydrobromic acid (113 ml, 1.0 mol) and acetic acid (400 ml) in a 1 l round bottom flask equipped with a reflux condenser and magnetic stirrer. The resulting solution was heated to reflux for 12 h (reflux temperature, 111°C) after which the reaction mixture was cooled to room temperature. The excess of hydrobromic acid and acetic acid were removed under reduced pressure in the presence of an appropriate amount of water to avoid esterification. White crystals precipitated out of the solution. They were separated by filtration and recrystallized from water (100 ml) to yield 42.7 g (93.6\%) of large needle-like crystals. mp, 146-152°C (lit.,\textsuperscript{24} mp, 148°C). \textsuperscript{1}H-NMR (Acetone-d\textsubscript{6}, TMS, δ, ppm): 3.51 (2H, -CH\textsubscript{2}-, s), 6.80 (2H, ortho to hydroxy of the phenyl ring, d, J=8.8Hz), 7.11 (2H, meta to hydroxy of the phenyl ring, d, J=6.9Hz) The \textsuperscript{1}H-NMR spectrum showed that the resulting 4 is free of unreacted methoxy groups.
Scheme 2.1 Synthesis of 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane (TPB).
2.2.2.2 Synthesis of 4-acetoxyphenylacetic acid (5)

4-Acetoxyphenylacetic acid (5) was prepared by the acetylation of 4-hydroxyphenylacetic acid (4). 4-Hydroxyphenylacetic acid (4) (42.7 g, 0.281 mol) and acetic anhydride (53 ml, 0.562 mol) were placed in a 250 ml round bottom flask equipped with a reflux condenser and magnetic stirrer. Few drops of sulfuric acid were added and the reaction mixture was stirred at 50°C for 2 h. It was allowed to cool to room temperature. Water (150 ml) were added and the mixture was stirred to produce a white precipitate. The precipitate was separated by filtration, washed with water, and dried to yield 37.2 g (68%) of white fine crystals. mp, 105-108°C (lit.,25 mp, 108-110°C). ¹H-NMR (CDCl₃, TMS, δ, ppm): 2.29 (3H, CH₃-, s), 3.59 (2H, -CH₂-, s), 7.08 (2H, ortho to acetoxy of the phenyl ring, d, J=8.3 Hz), 7.32 (2H, meta to acetoxy of the phenyl ring, d, J=8.3 Hz).

2.2.2.3 Synthesis of 4-acetoxybiphenyl (2)

4-Acetoxybiphenyl (2) was prepared by the acetylation of 4-phenylphenol (1). 4-Phenylphenol (1) (51.1 g, 0.30 mol) and acetic anhydride (42 ml, 0.45 mol) were placed in a 250 ml round bottom flask equipped with a reflux condenser and magnetic stirrer. After the addition of few drops of sulfuric acid, the reaction mixture was stirred at 60°C for 2 h. It was cooled to room temperature, 200 ml of water were added, and the mixture was stirred until a white solid separated. The precipitate was washed with water, and recrystallized from 95% ethanol to give
57.2 g (89.8%) of white crystals. Purity (HPLC), 100%. mp, 86-88°C (lit., 86-87°C). 1H-NMR (CDCl₃, TMS, δ, ppm): 2.32 (3H, CH₃, s), 7.19 (2H, ortho to acetoxy of the substituted phenyl ring, d, J=8.8Hz), 7.45 (3H, meta and para of the unsubstituted phenyl ring, m), 7.55 (2H, meta to acetoxy of the substituted phenyl ring, d, J=7.4Hz), 7.57 (2H, ortho of the unsubstituted phenyl ring, d, J=8.7Hz).

2.2.2.4 Synthesis of 1-(4-acetoxy-4'-biphenyl)-2-(4-acetoxyphenyl)ethanone (7)

4-Acetoxyphenylacetic acid (5) (29.1 g, 150 mmol) was dissolved in 150 ml of dry methylene chloride in a 500 ml three necks flask equipped with a dropping funnel, nitrogen inlet-outlet, and magnetic stirrer. Thionyl chloride (16.4 ml, 225 mmol) was added dropwise to this solution. The resulting mixture was refluxed for 16 h after which methylene chloride and excess thionyl chloride were removed under reduced pressure to produce a yellow liquid which was used directly in the acylation reaction. 4-Acetoxybiphenyl (2) (38.2 g, 180 mmol) was dissolved in 150 ml of methylene chloride in a 500 ml three necks flask equipped with a nitrogen inlet-outlet, thermometer, dropping funnel, and magnetic stirrer. The solution was cooled to below 10°C in an ice-water bath after which 72.0 g (540 mmol) of anhydrous AlCl₃ were added. 4-Acetoxyphenylacetyl chloride (6) was dissolved in 150 ml of dry methylene chloride. This solution was added dropwise to the solution of 4-acetoxybiphenyl so that the reaction temperature did not rise above 10°C. After the addition, the deep red solution was stirred at room temperature for 3 h. Then it was poured into a mixture of 75 ml concentrated HCl, 600 ml ice-water, and 300
ml of chloroform. The organic layer was separated and washed twice each time
with 500 ml of water, after which it was dried over anhydrous MgSO₄, filtered,
and the solvents were removed in a rotary evaporator to produce an orange solid.
The solid was washed twice each time with 200 ml of hot 95% ethanol, and dried to
yield 48.4 g (83.1%) of crystals. After recrystallization from 1.31 of toluene, 40.4
g (69.3%) of white crystals were obtained. Purity (HPLC), 92.7%. mp, 195-
1980°C. 1H-NMR (CDCl₃, TMS, δ, ppm): 2.29 (3H, CH₃COO-Ph-CH₂-, s), 2.33
(3H, CH₃COO-biphenyl, s), 4.30 (2H, -CH₂-, s), 7.09 (2H, ortho to acetoxy of
the monophenyl ring, d, J=9.3Hz), 7.22 (2H, ortho to acetoxy of the biphenyl
ring, d, J=7.9Hz), 7.28 (2H, meta to acetoxy of the monophenyl ring, d,
J=8.8Hz), 7.64 (4H, meta to acetoxy of the biphenyl ring and meta to acyl, 2d,
J=8.0Hz, J=8.9Hz), 8.06 (2H, para to acyl, d, J=9.3Hz).

2.2.2.5 Synthesis of 1-(4-ethoxy-4'-biphenyl)-2-(4-ethoxyphenyl)butanone (8)

1-(4-Acetoxy-4'-biphenyl)-2-(4-acetoxyphenyl)ethanone (7) (10.5 g, 97 mmol)
was dissolved in 160 ml of tetrahydrofuran in a 11 three necks flask equipped with
a reflux condenser and magnetic stirrer. To this solution were successively added
iodoethane (15.2 g, 97 mmol), tetrabutylammonium hydrogen sulfate (3.2 g, 9.4
mmol), and 160 ml of 50% (wt/wt) NaOH-water solution. The reaction mixture
was stirred vigorously at 60°C for 10 h. During the reaction the color of the
solution changed from orange to slight yellow. The organic and aqueous layers
were diluted with 400 ml of water and 400 ml of chloroform, respectively, after
which the organic layer was separated and washed with 200 ml of water. To this
organic layer was added a mixture of 100 ml concentrated HCl and 200 ml water. It was stirred for 30 min and the organic layer was separated, washed with 300 ml of water, and dried over magnesium sulfate. The solvents were removed in a rotary evaporator to give a yellow solid which was dissolved in 60 ml of tetrahydrofuran in a 1 neck flask equipped with a magnetic stirrer. To this solution were successively added iodoethane (4.21 g, 27 mmol), tetrabutylammonium hydrogen sulfate (1.08 g, 3.2 mmol), and 60 ml of 50% NaOH water solution. The reaction mixture was stirred vigorously at room temperature. After 1 h the product was extracted with 200 ml of chloroform and 200 ml of water. The organic layer was separated and washed sequentially with 200 ml of water, a mixture of 40 ml concentrated hydrochloric acid and 160 ml of water, and 2 times with 200 ml of water. It was dried over magnesium sulfate, filtered, and the solvents were removed on a rotary evaporator. The resulting white solid was recrystallized from 200 ml of methanol to yield 6.21 g (59.1%) of white crystals. Purity (HPLC), 97.3%. mp, 123-125°C. 1H-NMR (CDCl₃, TMS, δ, ppm): 0.87 (3H, -CH-CH₂-CH₃, t, J=7.1Hz), 1.40 (6H, -O-CH₂-CH₃, 2t, J=6.9Hz and J=6.9Hz), 2.01 (2H, -CH-CH₂-CH₃, m), 4.02 (4H, -O-CH₂-CH₃, 2q, J=6.8Hz and J=6.7Hz), 4.41 (1H, -CH-C=O, t, J=7.2Hz), 6.85 (2H, ortho to ethoxy of the monophenyl ring, d, J=8.3Hz), 6.99 (2H, ortho to ethoxy of the biphenyl ring, d, J=8.4Hz), 7.21 (2H, meta to ethoxy of the monophenyl ring, d, J=7.9Hz), 7.55 (4H, meta to ethoxy of the biphenyl ring and meta to acyl of the biphenyl ring, 2d, J=9.8Hz and J=9.3Hz), 7.99 (2H, ortho to acyl of the biphenyl ring, d, J=8.4Hz).

2.2.2.6 Synthesis of 1-(4-ethoxy-4'-biphenyl)-2-(4-ethoxyphenyl)butane (11)
was prepared by the reduction of 1-(4-ethoxy-4'-biphenyl)-2-(4-ethoxyphenyl)butanone (8) with LiAlH₄/AlCl₃. AlCl₃ (12.5 g, 94 mmol) was placed in a 100 ml three necks flask equipped with a dropping funnel, nitrogen inlet-outlet, and magnetic stirrer, and cooled in an ice-water bath, after which dry diethyl ether was added dropwise under nitrogen. LiAlH₄ (1.63 g, 43 mmol) was placed in a 250 ml three necks flask equipped with a dropping funnel, nitrogen inlet-outlet, and magnetic stirrer, and cooled in an ice-water bath. To the flask containing LiAlH₄ were added successively 35 ml dry diethyl ether, the solution of AlCl₃ diethyl ether complex, and 35 ml of dry chloroform. A solution of 8 (6.21 g, 16 mmol) in 35 ml of dry chloroform was added dropwise to the reducing agent solution maintained at 0°C. The resulting reaction mixture was stirred at room temperature for 3 h. To this mixture was added dropwise a solution of 40 ml concentrated HCl and 50 ml water. After the reaction mixture was stirred for 5 h, the product was extracted with 200 ml of chloroform. The organic layer was separated, washed twice with 300 ml of water, and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to give a white solid. The solid was recrystallized from 500 ml of methanol to yield 4.70 g (78.4%) of white needle-like crystals. Purity (HPLC), 99.8%. mp, 107-109°C. ¹H-NMR (CDCl₃, TMS, δ, ppm): 0.77 (3H, -CH₂-CH₃, t, J=7.3 Hz), 1.39 (6H, -O-CH₂-CH₃, 2t, J=6.9Hz), 1.64 (2H, -CH-CH₂-CH₃, m), 2.67 (1H, -CH-, m), 2.86 (2H, Ph-CH₂-CH-, d, J=7.0 Hz), 4.03 (4H, -O-CH₂-CH₃, 2q, J=7.4 Hz), 6.83 (2H, ortho to ethoxy of the monophenyl ring, d, J=8.9 Hz), 6.96 (2H, ortho to ethoxy of the biphenyl ring, d, J=9.4Hz), 7.05 (4H, ortho to methylene of the
biphenyl ring and meta to ethoxy of the monophenyl ring, 2d, J=7.9 Hz and J=8.9 Hz), 7.37 (2H, meta to methylene of the biphenyl ring, d, J=7.8 Hz), 7.46 (2H, meta to ethoxy of the biphenyl ring, d, J=8.8 Hz). The $^1$H-NMR spectrum showed that 11 is 100 % pure and therefore free of unreacted ketone 8.

2.2.2.7 Synthesis of TPB (12)

A 250 ml three necks flask equipped with a dropping funnel, nitrogen inlet-outlet, and magnetic stirrer was cooled in a dry-ice-acetone bath. To this flask were added 30 ml of dry methylene chloride and 30 ml of 1.0 M BBr$_3$ solution in methylene chloride (30 mmol). A solution of 11 (4.70 g, 12.5 mmol) in 60 ml of dry methylene chloride was added dropwise to the BBr$_3$ solution. After the addition, the mixture was stirred at room temperature for 16 h. To this reaction mixture were added slowly 30 ml of water and 200 ml of diethyl ether. The organic layer was separated, washed two times with 100 ml of water, and dried over anhydrous magnesium sulfate. The solvent was evaporated on a rotary evaporator to produce a white solid which was recrystallized two times from 100 ml of toluene to yield 3.11 g (78.1 %) of white needle-like crystals. Purity (HPLC), >99.8 %. mp, 145-146°C. $^1$H-NMR (CDCl$_3$, TMS, δ, ppm): 0.77 (3H, -CH$_3$, t, J=7.1 Hz), 1.69 (2H, CH$_3$-CH$_2$-, m), 2.68 (1H, -CH=, m), 2.85 (2H, Ph-CH$_2$-CH$_2$-, d of d, J=5.8 Hz and 8.3 Hz), 4.62 (1H, -CH-Ph-OH, s), 4.82 (1H, HO-biphenyl, s), 6.77 (2H, ortho to hydroxy of the monophenyl ring, d, J=8.5 Hz), 6.91 (2H, ortho to hydroxy of the biphenyl ring, d, J=9.3 Hz), 6.98 (2H, meta to hydroxy of the monophenyl ring, d, J=8.8 Hz), 7.09 (2H, ortho to methylene of the biphenyl
ring, d, J=8.9 Hz), 7.37 (2H, meta to methylene of the biphenyl ring, d, J=7.7 Hz), 7.43 (2H, meta to hydroxy of the biphenyl ring, d, J=8.6 Hz).

2.2.3 Synthesis of TPD

The synthesis of TPD is outlined in Scheme 2.2.

2.2.3.1 Synthesis of 1-(4-octyloxy-4′-biphenyl)-2-(4-octyloxyphenyl)decanone (13)

13 was prepared by the similar procedure to the one used for the synthesis of 8 except following conditions. 1-(4-Acetoxy-4′-biphenyl)-2-(4-acetoxyphenyl)ethanone (7) (19.4 g, 50 mmol), 1-iodooctane (32.5 ml, 180 mmol), tetrabutylammonium hydrogen sulfate (5.1 g, 15 mmol), 300 ml of tetrahydrofuran, and 300 ml of 50% (wt/wt) NaOH-water solution were used. After 7 h and 14 h, 9 ml (7 h) and 4.2 ml (14 h) of 1-iodooctane and 1.7 g (for both time) of TBAH were added. The total reaction time was 30 h. 1-Iodoctane (9.0 ml, 50 mmol), tetrabutylammonium hydrogen sulfate (2.0 g, 5 mmol), 100 ml of tetrahydrofuran, and 100 ml of 50% NaOH water solution were used for the second alkylation. The reaction time was 4 h. The resulting product was crystallized from ethanol followed by the purification by silica gel column chromatography. First only hexanes was used as eluent to remove the excess 1-iodooctane. Diethyl ether was gradually increased from 0 % to 16 % of the total amount of eluent to elute the desired product. After the evaporation of the solvent 13.8 g (43.1%) of a colorless liquid was obtained. The liquid was crystallized on standing. Purity (HPLC), 97%.
Scheme 2.2 Synthesis of 1-(4-hydroxy-4' -biphenyl)-2-(4-hydroxyphenyl)decane (TPD).
mp, 55-57°C. 1H-NMR (CDCl₃, TMS, δ, ppm): 0.89 (9H, CH₃-, m), 1.23-1.28 (32H, CH₃-(CH₂)₅-CH₂-CH₂-O- and CH₃-(CH₂)₆-CH₂-CH-CO-, m), 1.76 (5H, -O-CH₂-CH₂- and one of -CO-CH-CH₂-, m), 2.13 (1H, the other one of CO-CH-CH₂-, m), 3.89 and 3.99 (4H, -O-CH₂-, 2t, J=6.7Hz and J=6.2Hz), 4.50 (1H, -CO-CH-, t, J=7.1Hz), 6.83 (2H, ortho to octyloxy of the monophenyl ring, d, J=8.4Hz), 6.96 (2H, ortho to octyloxy of the biphenyl ring, d, J=8.9Hz), 7.23 (2H, meta to octyloxy of the monophenyl ring, d, J=7.8Hz), 7.52 and 7.57 (4H, meta to octyloxy of the biphenyl ring and meta to acyl of the biphenyl ring, 2d, J=9.3Hz and J=9.3Hz), 8.02 (2H, ortho to acyl of the biphenyl ring, d, J=7.8Hz).

2.2.3.2 Synthesis of 1-(4-octyloxy-4'-biphenyl)-2-(4-octylxyphenyl)decane (16)

16 was prepared by the similar procedure to the one used for the synthesis of 11 except following conditions. AlCl₃ (15.7 g, 117 mmol) 50 ml of diethyl ether complex, the suspension of LiAlH₄ (2.04 g, 54 mmol) in 50 ml of diethyl ether, a solution of 13 (12.8 g, 20 mmol) in 100 ml of dry diethyl ether were used for the reduction. The reaction was carried out for 4 h. The resulting solid was recrystallized from 1-butanol to yield 9.4 g (74.6 %) of white fine crystals. Purity (HPLC), >99%. mp, 50-51°C. 1H-NMR (CDCl₃, TMS, δ, ppm): 0.89 (9H, CH₃-, m), 1.19-1.30 (32H, CH₃-(CH₂)₅-CH₂-CH₂-O- and CH₃-(CH₂)₆-CH₂-CH-Phenyl, m), 1.57-1.77 (6H, -O-CH₂-CH₂- and Phenyl-CH-CH₂-CH₂-, m), 2.76 (1H, -CH-monophenyl, m), 2.85 (2H, biphenyl-CH₂-), d, J=6.9Hz), 3.92 and 3.98 (4H, -O-CH₂-, 2t, J=6.4Hz and J=6.0Hz), 6.80 (2H, ortho to octyloxy of the monophenyl ring, d, J=8.5 Hz), 6.94 (2H, ortho to octyloxy of the biphenyl ring,
d, J=7.9 Hz), 7.03 and 7.06 (4H, meta to octyloxy of the monophenyl ring and ortho to methylene of the biphenyl ring, 2d, J=6.9 Hz and J=6.4 Hz), 7.39 (2H, meta to methylene of the biphenyl ring, d, J=7.8 Hz), 7.49 (2H, meta to octyloxy of the biphenyl ring, d, J=8.0 Hz). The $^1$H-NMR spectrum showed that 11 is 100 % pure and therefore free of unreacted ketone 13.

2.2.3.3 Synthesis of TPD (17)

17 was prepared by the similar procedure to the one used for the synthesis of 12 except the following conditions. A solution of 16 (8.2 g, 13 mmol) in 65 ml of dry methylene chloride, 66 ml of 0.5 M BBr3 solution in methylene chloride (33 mmol) were used for the deprotection of octyl group. The reaction time was 25 h. The resulting product was purified on a silica gel column chromatography. First a mixture of hexanes and diethyl ether (1:1 v/v) was used to remove the 1-bromoocctane which was produced in the reaction. Then diethyl ether was used to flush out the product which was recrystallized from 70 ml of toluene to yield 3.4 g (65.0%) of white fine crystals. Purity (HPLC), >99 %. mp, 124-127°C. $^1$H-NMR (CDCl3, TMS, $\delta$, ppm): 0.85 (3H, -CH$_3$, t, J=6.8 Hz), 1.19 (12H, CH$_3$-(CH$_2$)$_6$-CH$_2$-), 1.65 (2H, CH$_3$-(CH$_2$)$_6$-CH$_2$-, m), 1.65 (2H, CH$_3$-(CH$_2$)$_6$-CH$_2$-, m), 2.77 (1H, -CH-monophenyl, m), 2.83 (2H, biphenyl-CH$_2$-, m), 4.67-4.80 (2H, -CH-Ph-OH and HO-biphenyl, 2 broad s), 6.73 (2H, ortho to hydroxy of the monophenyl ring, d, J=7.0 Hz), 6.88 (2H, ortho to hydroxy of the biphenyl ring, d, J=9.4 Hz), 6.99 (2H, meta to hydroxy of the monophenyl ring, d, J=8.8 Hz), 7.04 (2H, ortho to methylene of the biphenyl
ring, d, J=8.3 Hz), 7.38 (2H, meta to methylene of the biphenyl ring, d, J=8.0 Hz), 7.45 (2H, meta to hydroxy of the biphenyl ring, d, J=8.4 Hz).

2.2.4 Synthesis of Polyethers (TPB-X and TPD-X)

Scheme 2.3 and 2.4 outlines the polymerization of TPB and TPD with α,ω-dibromoalkanes. Conventional liquid-liquid two phase (organic solvent-aqueous NaOH solution) phase-transfer-catalyzed polyetherification conditions were used for the preparation of polyethers.\(^{13}\) The polyetherifications were carried out under a nitrogen atmosphere at 80°C in an o-dichlorobenzene-10N NaOH water solution (10 times molar excess of NaOH versus phenol groups) in the presence of tetrabutylammonium hydrogen sulfate (TBAH) as phase-transfer catalyst. The molar ratio of nucleophilic to electrophilic monomers was in every case 1.0/1.0. The ratio between the volume of o-dichlorobenzene and the total moles of monomers was also maintained constant in all polymerizations. An example of copolyetherification is as follows.

To a 25 ml single-neck flask equipped with a condenser and nitrogen inlet-outlet were successively added 0.191 g (0.600 mmol) of 12, 1.2 ml of o-dichlorobenzene, 0.163 g (0.600 mmol) of 1,8-dibromooctane, 1.2 ml of 10 N NaOH, and 0.0814 g (0.240 mmol, 20 mol% of phenol groups) of TBAH. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80°C under nitrogen. After 6 h of reaction, the organic and aqueous layers were diluted with chloroform and water, respectively, and the aqueous layer was separated. The organic layer was washed with water, followed by dilute hydrochloric acid, and
Scheme 2.3 Synthesis of polyethers based on 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane and α,ω-dibromoalkanes containing X methylenic units (TPB-X).
Scheme 2.4 Synthesis of polyethers based on 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane and α,ω-dibromoalkanes containing X methylenic units (TPD-X).
again with water three times. The polymer was separated by precipitation of its solution into methanol to obtain 0.251 g (98%) of white fibrous precipitate. The polymer was further purified by two successive precipitations from chloroform solution first into acetone and then into methanol.

2.3 RESULTS AND DISCUSSION

2.3.1 The Synthesis and Characterization of TPB-X

2.3.1.1 The Synthesis of TPB Mesogen

Scheme 2.1 outlines the synthesis of TPB (12). Monomer 12 has a chiral center. However, its synthesis by the sequence of the reactions from Scheme 2.1 results in a racemic mixture. There are only few experimental details concerning the synthesis of TPB which we would like to mention. Although 4 is commercially available, we prefer to prepare it from 3 since this route is less expensive. The alkylation of 7 with ethyl iodide was performed under various reaction conditions. Under any conditions, the cleavage of acetyl groups followed by the ethrification occurred to some extent. Therefore, we decided to complete not only C-alkylation but also etherification of the phenol groups for the sake of the purification. A relatively high yield of C alkylated product 8 (88%) versus O-alkylated product 9 was obtained under the experimental conditions described in the experimental part. By decreasing the reaction temperature from 60°C to 25°C the yield of the C alkylated product increases to 94%. However, at this temperature the etherification of the phenol groups is very slow and therefore we prefer to perform the reaction at
60\(^\circ\)C. Since the separation of O-alkylated product 9 from C-alkylated product 8 was very difficult, we cleaved the ethyl vinyl ether group of 9 with acid from the mixture containing both 9 and 8 to produce a mixture containing 8 and 10. The mixture of 8 and 10 was realkylated at room temperature to produce almost pure 8. After recrystallization from methanol, 8 was separated in 97.3% purity. It is very important that the keto group of 8 is reduced quantitatively to -CH\(_2\)-. This was accomplished by using LiAlH\(_4\)/AlCl\(_3\)-Et\(_2\)O reducing system\(^{27,28}\) in CHCl\(_3\). Compound 12 was obtained by the deethylation of 11 with BBr\(_3\) in CH\(_2\)Cl\(_2\).\(^{29}\) When 12 contains a small amount of unreacted keto groups, it leads to crosslinked polymers. This is due to the additional C-alkylation of the -CH- unit activated by the C=O group. Therefore, it is essential that 12 does not contain any product with unreacted C=O groups.

\[ \text{2.3.1.2 Synthesis of TPB-X} \]

Scheme 2.3 presents the polymerization of TPB with \(\alpha,\omega\)-dibromoalkanes under phase transfer catalyzed conditions. Table 2.1 presents the yields and the molecular weights of polyethers (TPB-X) obtained by the phase transfer catalyzed polyetherification of 12 with \(\alpha,\omega\)-dibromoalkanes containing from four to twenty methylenic units (X). The most of the number average molecular weights of TPB-X are higher than 20,000 above which phase transition temperatures are less dependent on a molecular weight (± 2 \(^\circ\)C) according to the results which will be presented in Chapter 3. Therefore, the phase transition temperatures of various
## Table 2.1

Characterization of polyethers based on TPB and α,ω-dibromoalkanes (TPB-X) with different number of methylenic units (X). Data collected from second heating and first cooling DSC scans.

<table>
<thead>
<tr>
<th>X</th>
<th>Yield (%)</th>
<th>(Mn)GPC</th>
<th>(Mw/Mn)GPC</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mr) in parentheses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Heating</td>
</tr>
<tr>
<td>4</td>
<td>80.1</td>
<td>14700</td>
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<td>g 82 n 154 (2.04) i</td>
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<td>5</td>
<td>87.3</td>
<td>15400</td>
<td>2.89</td>
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<td>6</td>
<td>94.6</td>
<td>32300</td>
<td>2.10</td>
<td>g 67 n 137 (2.16) i</td>
</tr>
<tr>
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<td>20500</td>
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<td>8</td>
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<td>30300</td>
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<td>g 52 n 123 (2.43) i</td>
</tr>
<tr>
<td>9</td>
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<td>39300</td>
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<td>g 43 k 52 n 74 (0.78) i&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>10</td>
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<td>11</td>
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<td>19800</td>
<td>2.12</td>
<td>g 40 k 54 (0.24) n 74 (1.08) i</td>
</tr>
<tr>
<td>12</td>
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<td>42600</td>
<td>2.38</td>
<td>g 39 k 69 n 104 (2.36) i</td>
</tr>
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<td>13</td>
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<td>2.08</td>
<td>g 41 k 57 (0.39) n 79 (1.48) i</td>
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<td>2.22</td>
<td>g 54 k 97 (6.50) i</td>
</tr>
<tr>
<td>17</td>
<td>99.4</td>
<td>38000</td>
<td>2.60</td>
<td>g 47 k 79 n 81 i</td>
</tr>
<tr>
<td>18</td>
<td>95.5</td>
<td>37100</td>
<td>3.88</td>
<td>g 37 k 91 (5.81) i</td>
</tr>
<tr>
<td>19</td>
<td>89.1</td>
<td>36700</td>
<td>2.22</td>
<td>g 40 k 86 (6.66) i</td>
</tr>
<tr>
<td>20</td>
<td>98.5</td>
<td>39200</td>
<td>2.45</td>
<td>g 36 k 93 (6.11) i</td>
</tr>
</tbody>
</table>

<sup>a</sup> Data from first heating scan
TPB-X can be compared directly as a function of the number of carbons in the flexible spacer X.

Regardless of the spacer length, both TPB-X containing odd and even number of methylenic units in the spacer are quite soluble at room temperature in solvents like chloroform, tetrahydrofuran, chlorobenzene, o-dichlorobenzene, methylene chloride etc. This is in contrast to polyethers and copolyethers based on α,ω-dibromomethanes and 4,4'-dihydroxybiphenyl which exhibit a very low solubility even at high temperature.\textsuperscript{30} Also, polyethers based on MBPE and α,ω-dibromoalkanes containing low numbers of even methylenic units and high numbers of both odd and even methylenic units are soluble only at high temperatures.\textsuperscript{14b} However, the solubility of copolyethers of both 4,4'-dihydroxybiphenyl\textsuperscript{30} and of MBPE\textsuperscript{14a} containing two or more than two flexible spacers increases versus that of the parent homopolymers. This effect is due to an increased entropy which decreases the ability of the polymer to crystallize.\textsuperscript{22,23}

An inspection of Scheme 2.3 may explain the high solubility of the "homopolyethers" TPB-X. First of all, the presence of laterally substituted ethyl group prevent the dense packing of mesogenic units, which result in low tendency toward the crystallization. Secondly, since TPB mesogen \textsuperscript{12} represents a racemic mixture of two enantiomers, the resulting "homopolymers" are in fact copolymers containing four different constitutional isomeric structural units. Such a structure may have a high configuration entropy and lead to TPB-X with low crystallization
tendency again and therefore, high solubility. However, the effect of the chirality was very small according to the result presented in Chapter 5.

2.3.1.3 Phase Behavior of TPB-X

Figure 2.1a presents second heating, while Figure 2.1b first cooling DSC scans of TPB-X. With the exception of TPB-9 and TPB-10 the first DSC heating scans are almost identical with the second and subsequent DSC scans. TPB-5 exhibits only a glass transition temperature (T_g). The other polymers from TPB-4 to TPB-10 exhibit an enantiotropic nematic mesophase. The nematic mesophase of TPB-7 is kinetically controlled since its isotropization temperature is very close to T_g. Therefore, both the temperature and the enthalpy associated with the isotropization of the nematic phase of TPB-7 are affected by the thermal history of the sample and are not as reliable as those of the other polymers. TPB-4 to TPB-10 do not crystallize on the second and subsequent heating scans and on the first and subsequent cooling scans. TPB-9 and TPB-10 exhibit a melting transition only on the first heating scan (Table 2.1). Since these crystalline phases are located in the close proximity of the glass transition temperature, they are kinetically controlled and do not appear on subsequent DSC scans. Polymers with more than ten methylenic units in the flexible spacer crystallize. Thus TPB-11 to TPB-15 and TPB-17 present an enantiotropic nematic mesophase and a crystalline phase. TPB-16 presents a monotropic nematic mesophase, while TPB-18 to TPB-20 are only crystalline. Compared to BPE or MBPE, it is apparent that the crystallinity of TPB-X polymers are drastically suppressed except TPB-X polymers with longer spacer.
Figure 2.1 Second heating (a) and first cooling (b) DSC thermograms (20°C/min) of polyethers based on TPB and α,ω-dibromoalkanes containing X methylenic units (TPB-X).
These results clearly demonstrate the validity of the molecular design mentioned in Chapter 1. The nematic mesophase of all these polymers was identified by thermal optical polarized microscopy and by X-ray diffraction experiments. After proper annealing on the optical polarized microscope all polymers exhibit a fine schlieren nematic texture.

The thermal transition temperatures and the corresponding enthalpy changes of TPB-X collected from second heating and first cooling scans are summarized in Table 2.1. Data from first heating scans are tabulated only for TPB-9 and TPB-10. The first and second DSC heating scans of the other polymers are almost identical. Some slight differences appear only for the enthalpy changes associated with the melting transitions and the presence of endothermic peaks before transitions. Figure 2.2a presents the dependence of the glass transition (T_g), melting (T_m) and nematic to isotropic (T_ni) transition temperatures versus the number of methyleneic units of the flexible spacer (X) of TPB-X. T_m and T_ni refer to data collected from the second DSC heating scan (Table 2.1). The T_g values of TPB-4 to TPB-10 plotted in Figure 2.2a were determined from the second DSC heating scan while those of the polymers with longer spacers from the first heating scan. This is due to the fact that the T_g of glassy polymers are more accurate when determined from second heating scan. However TPB-11 to TPB-20 are crystalline polymers and when separated by precipitation from solution, therefore when characterized during the first DSC scans, they have a lower degree of crystallinity than after heating and cooling scans. Therefore, for crystallizable polymers the T_g values determined from
Figure 2.2 Dependence of phase transition temperatures of TPB-X on the number of methylenic units in the flexible spacer (X): (a) data from the second heating scan (T_g data of TPB-11 to TPB-20 are from the first heating scan); (b) data from the first cooling scan.
the first DSC heating scan seem to be more accurate than those determined from second DSC scan.

The dependences of $T_{ni}$ and $T_{in}$ versus $X$ of TPB-X follow a similar trend as the corresponding virtual data reported for MBPE-X.\textsuperscript{14b} That is, in addition to the odd-even dependence of $T_{ni}$ and $T_{in}$, there is a continuous decrease of the transition temperatures for the polymers containing an even $X$, and a continuous increase for the polymers containing an odd $X$ (Figure 2.2a, b). This opposite trend provides a vanishing of the odd-even dependence at long flexible spacers. The same trend was observed for the series of polyethers based on 1-(4-hydroxyphenyl)-2-(2-chloro-4-hydroxyphenyl)ethane and $\alpha,\omega$-dibromoalkanes (CIBPE-X).\textsuperscript{15a} The continuous decrease of the $T_{ni}$ for the polymers with even spacer can be explained by using the thermodynamic scheme presented in Chapter 1. Namely, increasing spacer length corresponds to the increase in the flexibility of molecules. This increased flexibility decreases the free energy of the isotropic phase ($G_i$), therefore decreases the isotropization temperature. On the other hand, in the case of the polymers with odd spacers, not only the flexibility factor but also the ordering of mesogenic units seem to be affected. In the case of odd spacer, assuming fully extended conformation of the repeating units, there is a change of the direction of the mesogenic unit at each monomer unit, which decreases the nematic order significantly, while there is no such change in the case of even spacer.\textsuperscript{31} It is obvious that easiness of the adjustment of the mesogenic unit alignment to one direction increases with increasing spacer length. This should increase the transition temperature. Most probably this ordering effect prevails over the effect of flexibility
to result in the slight increase in the transition temperature of the polymers with odd spacers with increasing the spacer length.

Both $T_m$ and $T_k$ of TPB-X are increasing with the increase of $X$ (Figure 2.2a, b). At a certain value of $X$, $T_m$ and $T_k$ values are higher than the $T_{ni}$ (at $X=16$) and $T_{in}$ values (at $X=18$). Consequently, with the exception of TPB-5 which is glassy the polymers from TPB-4 to TPB-15 and TPB-17 exhibit an enantiotropic mesophase. TPB-16 displays only a monotropic mesophase, and TPB-18 to TPB-20 are crystalline and therefore exhibit only virtual mesophases. The increased crystallization tendency with increasing spacer length may be due to the following reason. The length of the spacer unit exceeds that of the mesogen above $X = 13 -14$ according to the molecular modeling results. The presence of the aromatic rings means that the mesogen is wider than spacer, and this is only partially compensated by adoption of a few gauche conformations in the lattice. However, once the length of the spacer unit exceeds that of the mesogen, the mesogen on adjacent chains can be staggered, making it possible for economic crystalline packing to occur. In conclusion, the opposite trends of the dependences $T_m$, $T_k$ versus those of $T_{ni}$, $T_{in}$ as a function of $X$ can explain the difference between the thermodynamic stability of the mesophase (i.e., enantiotropic, monotropic and virtual) versus that of the crystalline phase at various spacer lengths.

As expected, the $T_g$ of all polymers decreases by increasing the value of $X$ (Figure 2.2a, b). This trend is opposite to that of $T_{ni}$ and $T_{in}$ of the polymers with odd spacers and of $T_m$ and $T_k$ of polymers with both odd and even spacers. As a
consequence, at a certain value of $X$ there is an intercept of the dependence $T_{ni}$ and $T_{in}$ (of polymers containing odd spacers) versus $X$ with that of the dependence $T_g$ versus $X$. At this intercept the $T_{ni}$ and $T_{in}$ values are below $T_g$ and therefore, the corresponding polymer does not exhibit a mesophase since its formation is prohibited by the lack of motion of the glassy phase. This is the case of TPB-5 which is amorphous and therefore exhibits only a glass transition temperature (Figures 2.1 and 2.2, Table 2.1). TPB-7 exhibits a nematic mesophase which is kinetically controlled since it is located in the close proximity of $T_g$ (Figures 2.1 and 2.2). When $T_m$ and $T_k$ values are lower than the $T_g$ values the corresponding polymers can not crystallize and therefore, they should provide noncrystallizable nematic polymers. This is the case of TPB-4, and TPB-6 to TPB-8 which display an enantiotropic nematic mesophase and are noncrystallizable because their $T_k$ values are lower than their $T_g$ values. TPB-9 and TPB-10 exhibit a melting transition only in the first DSC heating scans (Table 2.1). Since their $T_m$ values are in the close proximity of their glass transition temperatures these polymers can not crystallize from the melt and therefore, on the second and subsequent heating scan they exhibit only an enantiotropic nematic mesophase (Figures 2.1, 2.2 and Table 2.1). However, during precipitation from solution and drying at room temperature they crystallize again.

The different dependences of $T_g$, $T_m$ and $T_{ni}$ versus $X$ from Figure 2.2a, b provide a clear picture on how their trends affect the difference between the various thermodynamic stabilities of the nematic mesophase of TPB-X as a function of spacer length. According to Figure 2.2a, b noncrystallizable enantiotropic nematic
polymers of TPB-X can be obtained when the melting temperature is below the glass transition temperature. This is the case of TPB-4, and TPB-6 to TPB-10.

Figure 2.3a plots the enthalpy changes associated with the nematic-isotropic (ΔH_{ni}) and isotropic-nematic (ΔH_{in}) phase transitions as a function of X. The corresponding entropy changes (ΔS_{ni} and ΔS_{in}) are plotted in Figure 2.3b. Both plots show an odd-even dependence of ΔH and ΔS versus spacer length. This dependance is strong for short spacers and tends to vanish with the increase in the spacer length. Both ΔH and ΔS for TPB-X with even spacer are higher than those for TPB-X with odd spacer. These results of TPB-X resemble those for MBPE-X\textsuperscript{14b} and CIBPE-X.\textsuperscript{15a} The higher ΔH_{ni} values for the even series could be explained by lower energy conformation and/or higher order in the mesophase (i.e., no change in the direction of mesogenic unit).

2.3.2 The Synthesis and Characterization of TPD-X

TPD was synthesized by the similar procedure to the one used for the synthesis of TPB. Scheme 2.4 outlines the polyetherification of TPD with α,ω-dibromoalkanes containing from six to ten methylenic units. As shown in Scheme 3, TPD has a chiral center as the same as TPB and therefore, since we use the racemic mixture of its two enantiomers, upon polyetherification with α,ω-dibromoalkanes we generate a copolymer (TPD-X) containing all four constitutional isomers of TPD. TPD-X are soluble in chloroform, methylene chloride, tetrahydrofuran, toluene, etc. The results on the synthesis and characterization of TPD-X with X=6 to 10 are summarized in Table 2.2. The relative number average
Figure 2.3 Dependence of the enthalpy change (a) and the entropy change (b) associated with the nematic-isotropic transitions on the number of methylenic units in the flexible spacer (X) of TPB-X.
Table 2.2
Characterization of polyethers based on TPD and α,ω-dibromoalkanes (TPB-X) with different number of methylenic units (X). Data collected from second heating and first Cooling DSC scans.

<table>
<thead>
<tr>
<th>X</th>
<th>Yield (%)</th>
<th>(Mn)GPC</th>
<th>(Mw/Mn) GPC</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mr) in parentheses</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>84.8</td>
<td>29800</td>
<td>1.63</td>
<td>g 31 n 71 (1.40) i</td>
</tr>
<tr>
<td>7</td>
<td>94.1</td>
<td>27900</td>
<td>1.75</td>
<td>g 21 i</td>
</tr>
<tr>
<td>8</td>
<td>92.2</td>
<td>27500</td>
<td>1.99</td>
<td>g 19 n 60 (1.58) i</td>
</tr>
<tr>
<td>9</td>
<td>96.8</td>
<td>41800</td>
<td>2.01</td>
<td>g 17 i</td>
</tr>
<tr>
<td>10</td>
<td>90.1</td>
<td>30800</td>
<td>1.78</td>
<td>g 15 n 55 (1.63 i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>i 58 (1.51) n 24 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>i 17 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>i 47 (1.58) n 13 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>i 10 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>i 42 (1.70) n 8 g</td>
</tr>
</tbody>
</table>
molecular weights of all TPD-X polymers are close to or higher than 30,000 and polydispersities range from 1.6 to 2.0.

The DSC traces of their second heating and first cooling scans are presented in Figure 2.4a and b. First, second, and subsequent DSC heating scans are almost identical. First and subsequent DSC cooling scans are also identical. As observed from these DSC traces polymers TPD-6, TPD-8 and TPD-10 display an noncrystallizable enantiotropic mesophase, which according to the characterization by optical polarized microscopy is nematic. The isotropization temperature increases with decreasing the spacer length X. The isotropization temperatures of TPD-6, TPD-8, and TPD-10 are lower than those of the corresponding TPB-6, TPB-8, and TPB-10 by 70-80 °C. The enthalpy changes of TPD-X are also lower than those of the corresponding TPB-X. These results indicate that longer lateral chain suppresses the liquid crystallinity most probably through increasing the entropy of nematic phase. TPD-7 and TPD-9 are glassy polymers. This behavior can be understood by analogy with the phase behavior of the TPB-X. Due to the odd-even effect of the isotropization transition temperatures, the isotropization values of the TPD-X with odd values of X are much lower than those of the polymers with even values of X, especially when the X value is relatively small. Therefore, the isotropization temperatures are either located in the close proximity of the glass transition temperatures or below it. Consequently, the formation of the mesophase is kinetically prohibited for the case of the polymers with X=7 and 9. These TPD-X series will be used as linear models of the mesomorphic dendritic polyethers which will be discussed in Chapter 6.
Figure 2.4 Second heating (a) and first cooling (b) DSC thermograms (20°C/min) of polyethers based on TPD and α,ω-dibromoalkanes containing X methylenic units (TPD-X).
2.4 CONCLUSIONS

As predicted from the simple thermodynamic scheme, TPB-X and TPD-X polyethers exhibit high tendency toward an enantiotropic nematic phase with low crystallization tendency. The TPB-X with X=4, 6-8 even do not undergo crystallization. These homologous series of TPB-X polyethers have demonstrated that the different dependence of Tg, Tni, and Tm versus the spacer length determines the nature of phase of the polyethers (i.e., amorphous, noncrystallizable enantiotropic, crystallizable enantiotropic, monotropic and virtual). The incorporation of longer lateral chain into the mesogenic unit suppresses the liquid crystallinity drastically.

2.5 REFERENCES


24. E. Salkowski and H. Salkowski, *Ber.* 12, 650 (1879)


CHAPTER 3

The Effect of Molecular Weight on The Phase Behavior of Linear Polyethers
3.1 INTRODUCTION

The study of molecular weight effect on the phase behavior of linear liquid crystalline polymers is very important subject in terms of both theoretical and practical aspects since molecular weight affects all the thermodynamic parameters (transition temperatures, enthalpy changes, the stability of mesophase) and sometimes even the nature of mesophase. The molecular weight effects on transition temperatures have been investigated by a few groups for both main chain\textsuperscript{1-8} and side chain liquid crystalline polymers.\textsuperscript{9-14} Also, the theory concerning the stability of mesophase has been developed to explain the molecular weight effect observed in the literatures.\textsuperscript{15} In order to obtain the accurate molecular weight effect on a phase behavior, the precise control of molecular weight and narrow polydispersity is essential. The development of living polymerization has allowed the precise control of molecular weight with narrow polydispersity for side chain liquid crystalline polymers such as polyvinyl ethers.\textsuperscript{9,10,14} Such liquid crystalline polymers have provided very interesting results and allowed detailed argument concerning molecular weight effect. Generally speaking, most of main chain liquid crystalline polymers posses a relatively larger polydispersity since main chain polymers are synthesized by a condensation polymerization in which the polydispersity is determined by the stoichiometry and conversion of monomers as a so called most probable distribution. In past, very few papers have reported polydispersity,\textsuperscript{2,6} although the values were relatively large. Polycondensates with narrow polydispersity can be obtained by fractionation methods\textsuperscript{16} such as fractional dissolution-precipitation\textsuperscript{5}, column separation, etc.
The goal of this chapter is to study the precise molecular weight effect on the phase behavior of the linear polyethers based on semiflexible 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) and 1,10-dibromodecane (TPB-10). The TPB-10 with number average molecular weight (Mn) from 5,200 to 57,200 and narrow polydispersity (1.16 - 1.47) were obtained from high and low molecular weight TPB-10 with decyl terminal groups by using column fractionation. Also, the TPB-10 oligomers from monomer to tetramer were synthesized by a stepwise syntheses. The thermal behavior of these TPB-10 polymers was measured by differential scanning calorimetry (DSC) and discussed. The intermediate compounds to synthesize TPB-10 oligomers were used to study the terminal group effect.

3.2 EXPERIMENTAL

3.2.1 Materials

1-Bromodecane (98%), carbon tetrabromide (99%), triphenyl phosphine (99%), tetrabutylammonium hydrogen sulfate (TBAH) (97%), 9-BBN [0.5 M solution in tetrahydrofuran (THF)], 9-decene-1-ol (98%) (all from Aldrich), potassium carbonate, 30% H₂O₂ (both from Fisher Scientific) were used as received.

1,10-Dibromodecane (97%) (from Aldrich) was purified by vacuum distillation. THF was dried by refluxing over LiAlH₄ followed by distillation. o-
Dichlorobenzene was distilled under reduced pressure. All other chemicals were commercially available and were used as received. TPB was synthesized as described in Chapter 1.

3.2.2 Synthesis of linear TPB-10 oligomers

Scheme 3.1 - 3.3 outlines the synthesis of linear oligomers.

3.2.2.1 Synthesis of linear TPB-10 monomer (3) and monodecyl TPB (4a and 4b)

3, 4a and 4b were prepared by the etherification of TPB (1) with 1-bromodecane (2). TPB (1.91 g, 6.0 mmol) was dissolved in 30 ml of absolute ethanol in a 100 ml one neck flask equipped with a reflux condenser and magnetic stirrer. After anhydrous potassium carbonate (0.83 g, 6.0 mmol) was added, it was stirred under nitrogen atmosphere at reflux temperature for 1.5 h. 1-Bromodecane (1.33 g, 6.0 mmol) was then added to this solution and the reaction mixture was stirred at reflux temperature for 24 h. After the evaporation of ethanol the remained solid was dissolved in 50 ml of CHCl₃. The organic layer was washed with water, dilute aqueous HCl and water, dried over anhydrous magnesium sulfate, and filtered. The solvent was evaporated to give a solid which contained TPB-10 monomer, monodecyl TPB, and TPB. It was separated into monodecyl TPB, and TPB-10 monomer by silicagel column chromatography with hexanes and diethyl ether (3:1) mixed solvent to yield 1.04 g (37.8 %) of monodecyl TPB and 0.589 g (16.4 %) of TPB-10 monomer. Purity (HPLC): Monodecyl TPB, >99 %; TPB-10 monomer, >99 %.¹H-NMR of monodecyl TPB (CDCl₃, TMS, δ, ppm): 0.77 (3H,
Scheme 3.1 Synthesis of linear TPB-10 monomer and dimer.
Scheme 3.2 Synthesis of linear TPB-10 trimer.
Scheme 3.3 Synthesis of linear TPB-10 tetramer.
Ph-CH-CH₂-CH₃, t, J=7.7 Hz), 0.89 (3H, -O-(CH₂)₉-CH₃, t, J=6.3 Hz), 1.28 (14H, CH₃-(CH₂)₇-, m), 1.63 (2H, Ph-CH-CH₂-CH₃, m), 1.76 (2H, -O-CH₂-CH₂-, m), 2.68 (1H, Ph-CH-, m), 2.86 (2H, Ph-CH₂-CH₂-, d, J=7.6 Hz), 3.92 and 3.98 (2H, -O-CH₂-, 2t), 4.67 and 4.88 (1H, -OH, 2s), 6.74 and 6.81 (2H, ortho to hydroxy or ether of the monophenyl ring, 2d, J=8.5 and 8.3 Hz), 6.87 and 6.94 (2H, ortho to hydroxy or ether of the biphenyl ring, 2d, J=8.5 and 9.3 Hz), 6.99 (2H, ortho to methine of the monophenyl ring, d, J=9.3 Hz), 7.06 (2H, ortho to methylene of the biphenyl ring, d, J=7.9 Hz), 7.40 (2H, meta to methylene of the biphenyl ring, d, J=8.4 Hz), 7.48 (2H, meta to hydroxy or ether of the biphenyl ring, d, J=8.5 Hz). The ratio of 4b to 4a was 79:21. ¹H-NMR of TPB-10 monomer (CDCl₃, TMS, δ, ppm): 0.76 (3H, Ph-CH-CH₂-CH₃, t, J=7.5 Hz), 0.88 (6H, -O-(CH₂)₉-CH₃, t, J=6.3 Hz), 1.27 (28H, CH₃-(CH₂)₇-, m), 1.63 (2H, Ph-CH-CH₂-CH₃, m), 1.76 (4H, -O-CH₂-CH₂-, m), 2.68 (1H, Ph-CH-, m), 2.86 (2H, Ph-CH₂-CH₂-, d, J=7.3 Hz), 3.90 (2H, monophenyl-O-CH₂-, t, J=6.2 Hz), 3.98 (2H, biphenyl-O-CH₂-, t, J=6.4 Hz), 6.81 (2H, ortho to ether of the monophenyl ring, d, J=8.2 Hz), 6.95 (2H, ortho to ether of the biphenyl ring, d, J=7.2 Hz), 7.03 (2H, ortho to methine of the monophenyl ring, d, J=7.4 Hz), 7.07 (2H, ortho to methylene of the biphenyl ring, d, J=7.3 Hz), 7.40 (2H, meta to methylene of the biphenyl ring, d, J=8.6 Hz), 7.48 (2H, meta to ether of the biphenyl ring, d, J=8.8 Hz).

3.2.2.2 Synthesis of linear TPB-10 dimer (6)

₆ was prepared by the etherification of monodecyl TPB (4a and 4b) with 1,10-dibromodecane (₅) using a similar procedure to the one used for 4a and 4b with the
following modifications. 4a and 4b (0.298 g, 0.65 mmol), 10 ml of absolute ethanol anhydrous potassium carbonate (0.099 g, 0.715 mmol), and 1,10-dibromodecane (0.098 g, 0.325 mmol) were used. The total reaction time was 23 h. The reaction mixture was worked up by using a similar procedure to the one used for 4a and 4b. The resulting product was purified twice by silicagel column chromatography with hexanes and diethyl ether (first 4:1, second 20:1) mixed solvent to yield 0.131 g (38.1 %) of linear TPB-10 dimer. Purity (HPLC): >99 %.

$^1$H-NMR (CDCl$_3$, TMS, δ, ppm): 0.76 (6H, Ph-CH$_2$-CH$_3$, t, J=7.4 Hz), 0.88 (6H, -O-(CH$_2$)$_9$-CH$_3$, t, J=5.9 Hz), 1.27 (28H, CH$_3$-(CH$_2$)$_7$, m), 1.33 (12H, -O-CH$_2$-CH$_2$-(CH$_2$)$_6$, m), 1.63 (4H, Ph-CH-CH$_2$-CH$_3$, m), 1.76 (8H, -O-CH$_2$-CH$_2$, m), 2.68 (2H, Ph-CH-, m), 2.87 (4H, Ph-CH$_2$-CH-, d, J=6.5 Hz), 3.92 (4H, monophenyl-O-CH$_2$-t, J=5.8 Hz), 3.98 (4H, biphenyl-O-CH$_2$-t, J=6.7 Hz), 6.81 (4H, ortho to ether of the monophenyl ring, d, J=8.3 Hz), 6.94 (4H, ortho to ether of the biphenyl ring, d, J=8.5 Hz), 7.03 (4H, ortho to methine of the monophenyl ring, d, J=7.7 Hz), 7.07 (4H, ortho to methylene of the biphenyl ring, d, J=7.0 Hz), 7.40 (4H, meta to methylene of the biphenyl ring, d, J=8.0 Hz), 7.48 (4H, meta to ether of the biphenyl ring, d, J=9.0 Hz).

3.2.2.3 Synthesis of 10-bromo-1-decene (8)

10-Bromo-1-decene (8) was synthesized by the bromination of 9-decene-1-ol (7) with carbon tetrabromide and triphenyl phosphine.$^{17}$ 9-Decene-1-ol (12.5 g, 80 mmol) and carbon tetrabromide (33.2 g, 100 mmol) were dissolved in dry THF in 50 ml three necks flask equipped with an additional funnel, nitrogen inlet-outlet, and magnetic stirrer. Triphenyl phosphine (26.2 g, 100 mmol) - dry THF (50 ml)
solution was added dropwise to the solution under cooling with an ice-water bath. The color of the reaction mixture changed to yellow and a precipitate occurred. The reaction mixture was stirred at room temperature for 4.5 h. The precipitate was removed by filtration and washed with THF. After the evaporation of THF, the product was extracted with about 300 ml of hexanes followed by the evaporation of hexanes. The resulting liquid was distilled two times under vacuum to yield a colorless liquid (14.0 g, 80.0%). Boiling point, 55-59°C/0.55 mmHg. 1H-NMR (CDCl3, TMS, δ, ppm): 1.31 (12H, Br-CH2-(CH2)6-, m), 1.86 (2H, Br-CH2-CH2-, m), 2.05 (2H, -CH2-CH=CH2, m), 3.43 (2H, Br-CH2-, t, J=6.8 Hz), 4.96 (2H, -CH=CH2, m), 5.83 (1H, -CH=CH2, m).

3.2.2.4 Synthesis of dideceny l TPB-10 monomer (9)

2 was prepared by the etherification of TPB (1) with 10-bromo-1-decene (8) by using a similar procedure to the one used for 4a and 4b. TPB (3.18 g, 10 mmol), 50 ml of absolute ethanol, anhydrous potassium carbonate (4.15 g, 30 mmol), 10-bromo-1-decene (5.26 g, 24 mmol) were used. The etherification was carried out for 23 h. The reaction mixture was worked up by using a similar procedure to the one used for 4a and 4b. The product was purified twice by silicagel column chromatography (first with hexanes, second with hexanes and diethyl ether (4:1 mixed solvent) to yield 4.56 g (76.6 %) of dideceny l TPB-10 monomer (9). Purity (HPLC): >99 %. 1H-NMR (CDCl3, TMS, δ, ppm): 0.77 (3H, Ph-CH-CH2-CH3, t, J=7.3 Hz), 1.33 (20H, -(CH2)5-CH2-CH=CH2, m), 1.76 (6H, Ph-O-CH2-CH2- and Ph-CH-CH2-CH3, m), 2.03 (4H, -CH2-CH=CH2, m), 2.69 (1H, Ph-CH-, m), 2.87 (2H, Ph-CH2-CH-, d, J=6.8 Hz), 3.92 (2H, monophenyl-O-CH2-,
t, J=6.3 Hz), 3.99 (2H, biphenyl-O-CH₂-, t, J=6.7 Hz), 4.96 (4H, -CH=CH₂, m), 5.81 (2H, -CH=CH₂, m), 6.81 (2H, ortho to ether of the monophenyl ring, d, J=8.3 Hz), 6.94 (2H, ortho to ether of the biphenyl ring, d, J=8.2 Hz), 7.04 (2H, ortho to methine of the monophenyl ring, d, J=7.6 Hz), 7.08 (2H, ortho to methylene of the biphenyl ring, d, J=7.4 Hz), 7.40 (2H, meta to methylene of the biphenyl ring, d, J=7.2 Hz), 7.49 (2H, meta to ether of the biphenyl ring, d, J=7.9 Hz).

3.2.2.5 Synthesis of dibhydroxydecyl TBP-10 monomer (10)

Monomer 10 was prepared by the hydroboration of monomer 9 according to the literature procedure. Monomer 9 (4.50 g, 7.56 mmol) was dissolved in 10 ml of dry THF in a 100 ml three necks flask equipped with an addition funnel, magnetic stirrer, and nitrogen inlet-outlet. 9-BBN (0.5M THF solution, 39.4 ml, 19.7 mmol) was added dropwise to the solution after which the reaction mixture was stirred at room temperature for 3 h under nitrogen atmosphere. The organoborane was treated with 12 ml of ethanol followed by 8 ml of 3 N NaOH. 30 % H₂O₂ (8.0 ml) was added dropwise slowly so that the temperature was maintained below 50°C. The reaction mixture was further stirred at 50°C for 1 h, cooled, and extracted with 100 ml of diethyl ether twice. The extract was washed two times with water, dried over anhydrous magnesium sulfate. After the evaporation of the solvents, the resulting solid was purified by silicagel column chromatography with hexanes and diethyl ether (3:1) mixed solvent to yield 3.70 g (yield, 77.5 %) of white solid. Purity (HPLC), 97.7 %. ¹H-NMR (CDCl₃, TMS, δ, ppm): 0.76 (3H, Ph-CH-CH₂-CH₃, t, J=7.1 Hz), 1.32 (24H, HO-(CH₂)₂-(CH₂)₆-, m), 1.56 (6H, HO-CH₂-CH₂- and
Ph-CH-CH₂-CH₃, m), 1.76 (4H, Ph-O-CH₂-CH₂-, m), 2.69 (1H, Ph-CH₂-, m), 2.87 (2H, Ph-CH₂-CH₂-, d, J=7.4 Hz), 3.64 (4H, HO-CH₂-, t, J=6.3 Hz), 3.92 (2H, monophenyl-O-CH₂-, t, J=6.3 Hz), 3.98 (2H, biphenyl-O-CH₂-, t, J=6.5 Hz), 6.81 (2H, ortho to ether of the monophenyl ring, d, J=8.1 Hz), 6.94 (2H, ortho to ether of the biphenyl ring, d, J=7.2 Hz), 7.03 (2H, ortho to methane of the monophenyl ring, d, J=7.6 Hz), 7.07 (2H, ortho to methylene of the biphenyl ring, d, J=7.5 Hz), 7.40 (2H, meta to methylene of the biphenyl ring, d, J=7.1 Hz), 7.49 (2H, meta to ether of the biphenyl ring, d, J=8.5 Hz).

3.2.2.6 Synthesis of dibromodecyl TBP-10 monomer (11)

(11) was synthesized by a similar method to the one used for 8 except the following conditions. Monomer 10 (3.46 g, 5.5 mmol), carbon tetrabromide (4.38 g, 13.2 mmol), triphenyl phosphine (3.46 g, 13.2 mmol), and dry THF (100 ml for carbon tetrabromide, 15 ml for triphenyl phosphine) were used. The reaction time was 3 h. The reaction mixture was worked up by using a similar procedure to the one used for 8. The resulting product was purified by silicagel column chromatography two times. First, only hexanes was used as eluent to remove excess of carbon tetrabromide. Hexanes and diethyl ether (1:1) mixed solvent was then used. The evaporation of solvent yielded a colorless liquid (3.43 g, 82.4 %) which solidified on standing. Purity (HPLC), 97.3 %. ¹H-NMR (CDCl₃, TMS, δ, ppm): 0.76 (3H, Ph-CH-CH₂-CH₃, t, J=7.2 Hz), 1.32 (24H, Br-(CH₂)₂-(CH₂)₆-, m), 1.56 (2H, Ph-CH-CH₂-CH₃, m), 1.82 (8H, Br(CH₂-CH₂- and Ph-O-CH₂-CH₂-, m), 2.68 (1H, Ph-CH₂-, m), 2.87 (2H, Ph-CH₂-CH₂-, d, J=7.0 Hz), 3.41 (4H, Br-CH₂-, t, J=6.8 Hz), 3.92 (2H, monophenyl-O-CH₂-, t, J=6.3 Hz), 3.98
(2H, biphenyl-O-CH2-, t, J=6.4 Hz), 6.81 (2H, ortho to ether of the monophenyl ring, d, J=8.4 Hz), 6.94 (2H, ortho to ether of the biphenyl ring, d, J=8.7 Hz), 7.04 (2H, ortho to methine of the monophenyl ring, d, J=7.8 Hz), 7.07 (2H, ortho to methylene of the biphenyl ring, d, J=6.9 Hz), 7.40 (2H, meta to methylene of the biphenyl ring, d, J=8.0 Hz), 7.49 (2H, meta to ether of the biphenyl ring, d, J=9.4 Hz).

3.2.2.7 Synthesis of linear TPB-10 trimer (12)

The TPB-10 trimer (12) was synthesized by the etherification of dibromodecyl TPB-10 monomer (11) with monodecyl TPB (4a, 4b). To a 25 ml single-neck flask equipped with a condenser and magnetic stirrer were added successively monodecyl TPB (0.321 g, 0.70 mmol), 3.0 ml of 10 N NaOH aqueous solution (30 mmol), 3.0 ml of o-dichlorobenzene, dibromodecyl TPB-10 monomer (0.265 g, 0.35 mmol), and TBAH (0.095 g, 0.28 mmol). A balloon filled with nitrogen was placed at the top of the condenser. The reaction mixture was stirred at 1100 rpm at 80°C. After 50 min, the reaction mixture was diluted with water and chloroform, and the aqueous layer was removed. The organic layer was washed with water, followed by dilute aqueous HCl, and two times with water. The product was precipitated in methanol. After dried under vacuum, the product was purified by silicagel column chromatography with hexanes and diethyl ether (10:1) mixed solvent to yield a white solid (0.338 g, 63.8 %). Purity (HPLC), >99 %. 1H-NMR (CDCl3, TMS, δ, ppm): 0.76 (9H, Ph-CH-CH2-CH3, t, J=7.2 Hz), 0.88 (6H, -O-(CH2)9-CH3, t, J=6.3 Hz), 1.27 and 1.33 (52H, CH3-CH2-(CH2)7-and -O-CH2-CH2-(CH2)6-, m), 1.63 (6H, Ph-CH-CH2-CH3, m), 1.76 (12H, -O-CH2-CH2-, m),
2.68 (3H, Ph-CH\textsubscript{-}, m), 2.87 (6H, Ph-CH\textsubscript{2}-CH\textsubscript{-}, d, J=7.3 Hz), 3.92 (6H, monophenyl-O-CH\textsubscript{2}-, t, J=6.0 Hz), 3.98 (6H, biphenyl-O-CH\textsubscript{2}-, t, J=6.2 Hz), 6.80 (6H, ortho to ether of the monophenyl ring, d, J=8.0 Hz), 6.93 (6H, ortho to ether of the biphenyl ring, d, J=8.3 Hz), 7.03 (6H, ortho to methine of the monophenyl ring, d, J=7.9 Hz), 7.07 (6H, ortho to methylene of the biphenyl ring, d, J=7.4 Hz), 7.39 (6H, meta to methylene of the biphenyl ring, d, J=7.9 Hz), 7.48 (6H, meta to ether of the biphenyl ring, d, J=8.3 Hz).

3.2.2.8 Synthesis of monodeceny TPB (13a, 13b)

The mixture of 13a with 13b was prepared by the etherification of TPB (1) with 10-bromo-1-decene (8) using the same method as that used for 4a and 4b. TPB (2.55 g, 8.0 mmol), 40 ml of absolute ethanol, anhydrous potassium carbonate (1.11 g, 8.0 mmol), and 10-bromo-1-decene (1.76 g, 8.0 mmol) were used. The etherification was carried out for 14.5 h. The reaction mixture was worked up by using a similar procedure to the one used for 4a and 4b. The mixture of 13a with 13b was separated from the reaction mixture by silicagel column chromatography with hexanes and diethyl ether (3:1) mixed solvent. The evaporation of solvent yielded 1.68 g (46.0 %) of white crystals. Purity (HPLC), >99 %. \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, TMS, \textit{δ}, ppm): 0.77 (3H, Ph-CH-CH\textsubscript{2}-CH\textsubscript{3}, t, J=7.4 Hz), 1.33 (12H, CH\textsubscript{2}=CH-(CH\textsubscript{2})\textsubscript{6}-, m), 1.63 (2H, Ph-CH-CH\textsubscript{2}-CH\textsubscript{3}, m), 1.76 (2H, -O-CH\textsubscript{2}-CH\textsubscript{2}-, m), 2.04 (2H, CH\textsubscript{2}=CH-CH\textsubscript{2}-, m), 2.68 (1H, Ph-CH\textsubscript{-}, m), 2.86 (2H, Ph-CH\textsubscript{2}-CH\textsubscript{-}, d, J=6.1 Hz), 3.92 and 3.98 (2H, -O-CH\textsubscript{2}-, 2t), 4.68 and 4.88 (1H, -OH, 2s), 4.76 (2H, CH\textsubscript{2}=CH-,-, m), 5.82 (1H, CH\textsubscript{2}=CH\textsubscript{-}, m), 6.74 and 6.81 (2H, ortho to hydroxy or ether of the monophenyl ring, 2d, J=8.2 and 8.3 Hz), 6.87 and
6.94 (2H, ortho to hydroxy or ether of the biphenyl ring, 2d, J=8.4 and 9.6 Hz),
6.99 (2H, ortho to methine of the monophenyl ring, d, J=9.5 Hz), 7.06 (2H, ortho
to methylene of the biphenyl ring, d, J=7.6 Hz), 7.39 (2H, meta to methylene of
the biphenyl ring, d, J=8.0 Hz), 7.48 (2H, meta to hydroxy or ether of the
biphenyl ring, d, J=8.0 Hz). The ratio of 13b to 13a could not be determined due to
the severe overlapping.

3.2.2.9 Synthesis of dideceny1 TBB-10 dimer (14)

Dimer 14 was synthesized by the etherification of 1,10-dibromodecane (5) with
the mixture of 13a and 13b using a similar method to the one used for 12 except the
following conditions. 13a and 13b (0.709 g, 1.55 mmol), 3.1 ml of 10 N NaOH
aqueous solution (31 mmol), 3.1 ml of o-dichlorobenzene, 1,10-dibromodecane
(0.225 g, 0.75 mmol), and TBAH (0.132 g, 0.39 mmol) were used. The reaction
time was 75 min. After working up by the same method as that used for 12, the
product was precipitated in methanol and dried under vacuum. It was purified by
silicagel column chromatography with hexanes and diethyl ether (3:1) mixed
solvent followed by the evaporation of solvents to yield a white solid (0.653 g,
82.7 %). Purity (HPLC), >99 %. 1H-NMR (CDCl3, TMS, δ, ppm): 0.76 (6H,
Ph-CH-CH2-CH3, t, J=7.1 Hz), 1.33 (32H, Ph-O-(CH2)2-(CH2)6-(CH2)2-O-Ph
and -(CH2)5-CH=CH2, m), 1.76 (12H, Ph-O-CH2-CH2- and Ph-CH-CH2-CH3,
m), 2.05 (4H, -CH2-CH=CH2, m), 2.69 (2H, Ph-CH-, m), 2.86 (4H, Ph-CH2-
CH-, d, J=7.3 Hz), 3.92 (4H, monophenyl-O-CH2-, t, J=6.1 Hz), 3.98 (4H,
biphenyl-O-CH2-, t, J=6.3 Hz), 4.96 (4H, -CH=CH2, m), 5.82 (2H, -CH=CH2,
m), 6.81 (4H, ortho to ether of the monophenyl ring, d, J=8.3 Hz), 6.94 (4H,
ortho to ether of the biphenyl ring, d, J=8.6 Hz), 7.04 (4H, ortho to methine of the monophenyl ring, d, J=7.3 Hz), 7.07 (4H, ortho to methylene of the biphenyl ring, d, J=6.6 Hz), 7.40 (4H, meta to methylene of the biphenyl ring, d, J=7.1 Hz), 7.48 (4H, meta to ether of the biphenyl ring, d, J=8.1 Hz).

3.2.2.10 Synthesis of dihydroxydecyl TPD-10 dimer (15)

15 was prepared by a similar procedure to the one used for 10 except the following conditions. Dimer 14 (0.631 g, 0.60 mmol) was dissolved in 4.8 ml of dry THF. 9-BBN (0.5M THF solution, 4.8ml, 2.4 mmol) was added dropwise to the solution after which the reaction mixture was stirred at room temperature for 6 h under nitrogen atmosphere. The organoborane was treated with 1.8 ml of ethanol followed by 1.1 ml of 3 N NaOH. 30 % H₂O₂ (1.1 ml) was added dropwise slowly. The reaction mixture became cloudy during the addition of H₂O₂ aqueous solution. Few ml of THF were added to the reaction mixture to maintain it homogeneous. It was further stirred at 50°C for 1.5 h, cooled, and extracted with 50 ml of CHCl₃. The extract was washed three times with water, dried over anhydrous magnesium sulfate. After the filtration and evaporation of the solvents, the resulting solid was purified by silicagel column chromatography three times with petroleum ether and diethyl ether (first, 1:1, second, 2:1, third, 3:1) mixed solvent followed by the evaporation of solvents to yield 0.448 g (68.7 %) of a white solid. Purity (HPLC), >99 %. ¹H-NMR (CDCl₃, TMS, δ, ppm): 0.76 (6H, Ph-CH-CH₂-CH₃, t, J=6.9 Hz), 1.32 (36H, HO-(CH₂)₂-(CH₂)₆-, m), 1.58 (8H, HO-CH₂-CH₂- and Ph-CH-CH₂-CH₃, m), 1.76 (8H, Ph-O-CH₂-CH₂-, m), 2.68 (2H, Ph-CH₂- m), 2.87 (4H, Ph-CH₂-CH-, d, J=7.4 Hz), 3.64 (4H, HO-CH₂-, t,
J=6.3 Hz), 3.92 (4H, monophenyl-O-CH$_2$-, t, J=6.3 Hz), 3.98 (4H, biphenyl-O-CH$_2$-, t, J=6.1 Hz), 6.81 (4H, ortho to ether of the monophenyl ring, d, J=8.5 Hz), 6.94 (4H, ortho to ether of the biphenyl ring, d, J=7.2 Hz), 7.04 (4H, ortho to methine of the monophenyl ring, d, J=7.7 Hz), 7.07 (4H, ortho to methylene of the biphenyl ring, d, J=7.3 Hz), 7.40 (4H, meta to methylene of the biphenyl ring, d, J=7.5 Hz), 7.48 (4H, meta to ether of the biphenyl ring, d, J=8.3 Hz).

3.2.2.11 Synthesis of dibromodecyl TPB-10 dimer (16)

16 was prepared by the same procedure as that used for 11 except the following conditions. Dimer 15 (0.421 g, 0.39 mmol) and carbon tetrabromide (0.308 g, 0.93 mmol) were dissolved in 20 ml of dry THF. Triphenyl phosphine (0.244 g, 0.93 mmol) - dry THF (7 ml) solution was added dropwise to the solution. The reaction mixture was stirred at room temperature overnight. After THF was evaporated, the resulting solid was dissolved in CHCl$_3$ and precipitated in methanol. After dried, the precipitant was purified by silicagel column chromatography. First, a mixture of hexanes and diethyl ether (2:1) was used as eluent to yield the pure and impure fractions. The impure fraction was further purified by silicagel column chromatography with hexanes and diethyl ether (1:1) mixed solvent to yield a pure compound. The combined pure part was dissolved in CHCl$_3$ and precipitated in methanol to yield a white solid (0.219 g, 46.6 %). Purity (HPLC), >99 %. $^1$H-NMR (CDCl$_3$, TMS, δ, ppm): 0.76 (6H, Ph-CH-CH$_2$-CH$_3$, t, J=7.6 Hz), 1.32 (40H, Br-(CH$_2$)$_2$-(CH$_2$)$_6$- and Ph-CH-CH$_2$-CH$_3$, m), 1.79 (10H, -O-CH$_2$-CH$_2$- and -CH$_2$-CH$_2$-Br, m), 2.68 (2H, Ph-CH$_2$-, m), 2.87 (4H, Ph-CH$_2$-CH-, d, J=7.4 Hz), 3.41 (4H, Br-CH$_2$-, t, J=6.8 Hz), 3.92 (4H,
monophenyl-O-CH$_2$-, t, J=6.1 Hz), 3.98 (4H, biphenyl-O-CH$_2$-, t, J=6.2 Hz),
6.81 (4H, ortho to ether of the monophenyl ring, d, J=8.1 Hz), 6.94 (4H, ortho to ether of the biphenyl ring, d, J=7.9 Hz), 7.04 (4H, ortho to methine of the monophenyl ring, d, J=7.3 Hz), 7.07 (4H, ortho to methylene of the biphenyl ring, d, J=7.5 Hz), 7.40 (4H, meta to methylene of the biphenyl ring, d, J=7.6 Hz),
7.49 (4H, meta to ether of the biphenyl ring, d, J=8.4 Hz).

3.2.2.12 Synthesis of linear TPB-10 tetramer (17)

The linear tetramer (17) was synthesized by the etherification of dibromodecyl
TPB-10 dimer (16) with monodecyl TPB (4a, 4b) using the same method for the linear TPB-10 trimer (12). To a 25 ml single-neck flask equipped with a condenser and magnetic stirrer were added successively monodecyl TPB (0.159 g, 0.347 mmol), 2.0 ml of 10 N NaOH aqueous solution (20 mmol), 2.0 ml of o-
dichlorobenzene, dibromodecyl TPB-10 dimer (0.200 g, 0.165 mmol), and TBAH (0.030 g, 0.087 mmol). A balloon filled with nitrogen was placed at the top of the condenser. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at
80°C. After 30 min, the reaction mixture was diluted with water and chloroform, and the aqueous layer was removed. The organic layer was washed with water, followed by dilute hydrochloric acid, and three times with water. The product was precipitated in methanol. After dried under vacuum, the product was purified by silicagel column chromatography with hexanes and CHCl$_3$ (1:1) mixed solvent. The solid was again precipitated in methanol from the CHCl$_3$ solution to yield a white solid (0.192 g, 56.2 %). Purity (HPLC), >99 %. $^1$H-NMR (CDCl$_3$, TMS,
δ, ppm): 0.76 (12H, Ph-CH-CH$_2$-CH$_3$, t, J=7.2 Hz), 0.88 (6H, -O-(CH$_2$)$_9$-CH$_3$,
t, J=6.0 Hz), 1.27 and 1.33 (64H, CH3-(CH2)7- and -O-CH2-CH2-(CH2)6-, m),
1.63 (8H, Ph-CH2-CH2-CH3, m), 1.76 (16H, -O-CH2-CH2-, m), 2.68 (4H, Ph-
CH-, m), 2.86 (8H, Ph-CH2-CH-, d, J=6.7 Hz), 3.92 (8H, monophenyl-O-CH2-
t, J=5.9 Hz), 3.97 (8H, biphenyl-O-CH2-, t, J=6.2 Hz), 6.81 (8H, ortho to ether
of the monophenyl ring, d, J=8.2 Hz), 6.94 (8H, ortho to ether of the biphenyl
ring, d, J=8.1 Hz), 7.03 (8H, ortho to methine of the monophenyl ring, d, J=7.6
Hz), 7.07 (8H, ortho to methylene of the biphenyl ring, d, J=7.2 Hz), 7.39 (8H,
meta to methylene of the biphenyl ring, d, J=7.1 Hz), 7.48 (8H, meta to ether of
the biphenyl ring, d, J=9.5 Hz).

3.2.3 Synthesis of linear TPB-10 polyethers for fractionation

Scheme 3.4 and 3.5 present the preparation of high and low molecular weight
TPB-10 polyethers for fractionations. Conventional liquid-liquid two phase
(organic solvent-aqueous NaOH solution) phase-transfer-catalyzed
polyetherification conditions were used for the preparation of TPB-10 polyethers.
The polyetherifications were carried out under a nitrogen atmosphere at 80°C in an
o-dichlorobenzene-10N NaOH water solution (10 times molar excess of NaOH
versus phenol groups) in the presence of TBAH as a phase-transfer catalyst.

3.2.3.1 High molecular weight TPB-10

To a 25 ml single-neck flask equipped with a condenser were successively
added 0.325 g (1.02 mmol) of TPB (1), 2.0 ml of 10 N NaOH, 2.0 ml of o-
dichlorobenzene, 0.300 g (1.00 mmol) of 1,10-dibromodecane (5), and 0.136 g
Scheme 3.4 Preparation of high molecular weight TPB-10 polyether with terminal decyl groups.
Scheme 3.5 Preparation of low molecular weight TPB-10 polyether with terminal decyl groups.
(0.40 mmol, 20 mol% of phenol groups) of TBAH. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80°C under nitrogen. After 1 h, 1-bromodecane (2) was added to the reaction mixture so that polyethers with only decyl chain ends are obtained. After 1 h, the organic and aqueous layers were diluted with chloroform and water, respectively, and the aqueous layer was separated. The organic layer was washed with water, followed by dilute aqueous HCl, and again three times with water. The polymer was separated by precipitation of its solution into methanol to obtain 0.436 g (93%) of white fibrous precipitate. The polymer was further purified by two precipitations from THF solution into water.

3.2.3.2 Low molecular weight TPB-10

The procedure was the same as that used for the high molecular weight TPB-10 except the following conditions. TPB (0.319 g, 1.00 mmol) and 1,10-dibromodecane (0.276 g, 0.92 mmol) were polymerized in the presence of 1-bromodecane (0.0354 g, 0.16 mmol) for 30 min followed by the addition with 1-bromodecane (0.136 g, 0.40 mmol) to complete the alkylation of the terminal phenolates. The yield was 0.407 g (89%).

3.2.4 Fractionation of TPB-10

The high molecular weight TPB-10 (0.367 g) was dissolved in chloroform. Silica gel (12.6 g) was added to this solution and the chloroform was evaporated. The polymer absorbed on the silica gel was charged on the top of a column
containing silicagel and was flushed 11 times with 100 ml of solvents. The solvents were acetone-CHCl₃ mixed solvents whose ratios (acetone/CHCl₃) were 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, and 0/100, and changed from 100/0 to 0/100. The each eluted fraction was collected and the solvents were evaporated on a rotary evaporator to give fractionated TPB-10s based on molecular weight. Each fraction was dissolved in CHCl₃, filtered, precipitated in methanol, and dried under vacuum.

The procedure used for the low molecular weight TPB-10 was the same as that used for the high molecular weight TPB-10 except the following conditions. The amount of polymer and silicagel were 0.230 g and 26.0 g, respectively. The solvents ratios (acetone/CHCl₃) were 100/0, 90/10, 80/20, 70/30, 60/40, 55/45, 50/50, 45/55, 40/60, and 30/70 and changed from 100/0 to 30/70.

3.3 RESULTS AND DISCUSSION

3.3.1 Syntheses of TPB-10 oligomers

Scheme 3.1- 3.3 outline the synthesis of linear TPB-10 monomer, dimer, trimer, and tetramer. All the oligomers have decyl terminal groups at the both chain ends so that the effect of terminal group change can be excluded. The monomer and dimer syntheses are rather simple. The etherification of TPB (1) with an equal molar 1-bromodecane (2) yielded TPB-10 monomer (3), monodecyl TPB (4a, 4b), and with unreacted TPB (1). These compounds were separated by silicagel column chromatography without any difficulty. The reactivity of the phenol group in the
biphenyl group was higher than that in the monophenyl group according to the $^1$H-
NMR spectrum of the separated monodecyl TPB (4a, 4b). The ratio of $\text{4b} / \text{4a}$ was
79/21.

The linear TPB-10 dimer was synthesized by the etherification of monodecyl
TPB (4a, 4b) with 1,10-dibromodecane (5). Therefore, there are three possible
constitutional isomers due to the regiochemical structure as indicated in Scheme 1.
The most dominant structure must be 6a. The yield was not very high most
probably due to the low solubility of dibromide reacted with one monodecyl TPB,
which is an intermediate compound to the dimer and precipitated out during the
reaction.

The linear TPB-10 trimer and tetramer were synthesized by the same sequence
of reactions, i.e., etherification with 10-bromo-1-decene, hydroboration followed
by oxidation, bromination, and etherification with monodecyl TPB except that, in
the case of the tetramer, the etherification of monodecyl TPB was carried out with
1,10-dibromodecane to yield didecenyl TPB-10 dimer (14). Again, in the synthesis
of the tetramer, monodecyl TPB contained higher content of biphenyl alkylated
product (13b). The exact ratio could not be calculated due to the peak overlapping.
However, the ratio should not be far different from the ratio for the monodecyl TPB
(4a, 4b). The preferential alkylation to the biphenyl phenol group again leads to the
preferential sequence of regiochemical structure of the trimer and tetramer. In the
hydroboration, bromination, and etherification steps, the reactions proceeded to
high conversion. However, the yield of TPB-10 dimer 6 (38.1%), TPB-10 trimer
12 (64%), dihydroxydecyl TPB-10 dimer 15 (69%), dibromodecyl TPB-10 dimer 16 (47%), TPB-10 tetramer 17 (56%) were low. These low yields are due to the fact that minor impurities were severely overlapped with the desired products in the silicagel column and the products with impurities were excluded to obtain pure products.

3.3.2 Characterization of TPB-10 oligomers

Figure 3.1 presents the GPC chromatograms of synthesized linear TPB-10 oligomers. Table 3.1 presents the calculated and measured molecular weight determined by GPC and purities by HPLC. The purity of each oligomer was higher than 99%. The observed molecular weight was proportional to the degree of polymerization as indicated in Figure 3.2. The molecular weights obtained by GPC were higher than the calculated ones. This indicates the larger hydrodynamic volume of TPB-10 in CHCl₃ compared to polystyrene standards.

Figure 3.3a-3.3c presents the DSC thermograms of the first heating, second heating, and cooling scans of TPB-10 oligomers. Thermal transition temperatures and the corresponding enthalpy changes were tabulated in Table 3.1. All TPB-10 oligomers exhibit only melting transitions during first heating scans as seen in Figure 3.3a. The dimer, trimer and tetramer exhibit isotropic-nematic transitions during cooling scans (Figure 3.3c). Therefore, these nematic phases are monotropic. The mesophase was identified by polarized optical microscopy. These oligomers exhibit a typical schlieren nematic texture. Figure 3.4a and 3.4b presents the typical textures obtained from the trimer and tetramer. The monomer exhibits
Figure 3.1 GPC chromatograms of linear TPB-10 oligomers.
### Table 3.1
Characterization of linear TPB-10 oligomers.

<table>
<thead>
<tr>
<th>M_n x 10^3 (Calculated)</th>
<th>M_n x 10^3 (Observed)</th>
<th>Purity (%)</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mole) in parentheses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating</td>
<td>Cooling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monomer</td>
<td>0.599</td>
<td>0.96</td>
<td>&gt;99%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimer</td>
<td>1.056</td>
<td>1.67</td>
<td>&gt;99%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimer</td>
<td>1.512</td>
<td>2.42</td>
<td>&gt;99%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetramer</td>
<td>1.969</td>
<td>3.07</td>
<td>&gt;99%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.

**Overlapped peaks.

*Data obtained by heating before crystallizing on cooling.
Figure 3.2 Observed and calculated molecular weights of linear TPB-10 oligomers versus the degree of polymerization.
Figure 3.3 DSC thermograms of first heating scans (a), second heating (b), and cooling scans (c) of linear TPB-10 oligomers (The nematic-isotropic transition of the dimer could be observed during second heating scan by heating right after the isotropic-nematic transition on cooling).
Figure 3.4 Typical polarized optical microscopic textures (x100) of linear TPB-10 oligomers: (a) linear TPB-10 trimer annealed at 55.3 °C for 1 min; (b) linear TPB-10 tetramer annealed at 71.2 °C for 4 min.
several exothermic peaks during cooling scan. However, these phases could not be identified. The trimer and tetramer did not crystallize during both cooling and second heating scans. In the case of the dimer, the nematic-isotropic transition on heating scan could be observed by heating right after the isotropic-nematic transition on cooling scan. Both nematic-isotropic and isotropic-nematic transition temperatures ($T_{ni}$ and $T_{in}$) increase with increasing molecular weight. Crystallization tendency decreases with increasing molecular weight.

Figure 3.5a-3.5c presents the DSC thermograms of the first heating, second heating, and cooling scans of intermediate compounds with one TPB unit in the structures (monomers), while Figure 3.6a-3.6c presents those with two TPB units (dimers). Table 3.2 summarizes the purities and thermal transition temperatures and the corresponding enthalpy changes of all the intermediate compounds to synthesize linear TPB-10 oligomers. It is interesting to see how the terminal groups alter the phase behavior of the oligomers by inspecting the DSC thermograms of these intermediate compounds. All monomers with various chain ends show one melting peak during the first heating scans. The melting temperature decreases depending on the terminal groups by the following order.

Monodeceny1 TPB (13a, 13b) = Monodecyl TPB (4a, 4b)

> Dihydroxydecyl TPB-10 monomer (10) > TPB-10 monomer (2)

= Dibromodecyl TPB-10 monomer (11) > Dideceny1 TPB-10 monomer (9)
Figure 3.5 DSC thermograms of first heating (a), second heating (b), and cooling scans (c) of intermediate linear oligomers with one TPB unit in the structures (monomers).
Figure 3.6 DSC thermograms of first heating (a), second heating (b), and cooling scans (c) of intermediate linear oligomers with two TPB units in the structure (dimers).
### Table 3.2
Characterization of linear TPB-10 oligomers with various terminal groups.

<table>
<thead>
<tr>
<th>Oligomers</th>
<th>Purity (%)</th>
<th>Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monododecyl TPB</td>
<td>&gt;99%</td>
<td>k 82 (11.2) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>g 5 n 18 (0.58) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 (-3.11) k 42 (-3.88) k 75 k 80 (9.32b) i</td>
</tr>
<tr>
<td>Monodecenyl TPB</td>
<td>&gt;99%</td>
<td>k 83 (9.33) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>g 8 n 4 (1.06) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11 k 19 k 38 (6.54b) k 80 k 85 (9.06) i</td>
</tr>
<tr>
<td>Didecenyl TPB-10 monomer</td>
<td>96.0%</td>
<td>k 49 (9.82) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>k 31 k 38 (6.43b) i</td>
</tr>
<tr>
<td>Dihydroxydecyd TPB-10 monomer</td>
<td>97.7%</td>
<td>k 70 (11.8) k 84 (0.34) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>k 52 k 58 k 65 (3.01b) k 85 (6.35) i</td>
</tr>
<tr>
<td>Dibromodecyd TPB-10 monomer</td>
<td>97.3%</td>
<td>k 57 (9.69) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>k 13 k 31 (3.04b) k 54 (8.27) i</td>
</tr>
<tr>
<td>Didecenyl TPB-10 dimer</td>
<td>&gt;99%</td>
<td>k 52 k 69 k 81 k 90 (8.53b) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>g -9 n 8 (-4.10) k 60 k 89 (5.86b) i</td>
</tr>
<tr>
<td>Dihydroxydecyd TPB-10 dimer</td>
<td>&gt;99%</td>
<td>k 54 k 92 (7.38b) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>k 62 (0.79) k 81 k 90 (5.75b) i</td>
</tr>
<tr>
<td>Dibromodecyd TPB-10 dimer</td>
<td>&gt;99%</td>
<td>k 83 k 98 k 113 (8.00b) k</td>
</tr>
<tr>
<td></td>
<td></td>
<td>k 16 (0.46) k 82 k 112 (8.68b) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i 12 (1.48) n -5 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i -1 (0.67) n -11 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i 10 (5.86) k</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i 60 (2.06) n 35 (2.32) k</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i 13 (0.65) n -16 k</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i 50 (1.25) n 18 (0.15) k 6.2 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i 68 (2.48) n 48 (1.90) k</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i 51 (1.13) n 35 (3.59) k</td>
</tr>
</tbody>
</table>

---

1 Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.
2 Overlapped peaks.
The same trend was observed during second heating scans. During cooling scans, a nematic mesophase was observed for all monomers except didecenylic TPB-10 (9) monomer and TPB-10 monomer (3). TPB-10 monomer shows a small shoulder and two peaks. However, it is not yet known if these peaks correspond to the mesophase transitions as mentioned above. Dihydroxydecal TPB-10 monomer (10) exhibits higher isotropic-nematic transition temperature (60°C) than those of the other oligomers. Also the enthalpy change was very high compared to those of the other monomers. This may be explained by the stabilization of mesophase through a hydrogen bonding. Although phenol groups which can undergo hydrogen bonding exist in the monodecenylic and monodecyl TPB (13a and 13b, 4a and 4b), these exhibit relatively low Tni which are almost the same as that of dibromodecyl TPB-10 monomer (11). The lack of one alkyl group may decrease the stability of mesophase. It is interesting that monodecenylic TPB (13a, 13b) shows lower Tni and enthalpy change compared to monodecyl TPB (4a, 4b) since the only difference is the presence of vinyl groups.

All the dimers with various terminal groups show a monotropic nematic mesophase. During first heating scans, all the dimers exhibit rather broad melting peaks. The order of melting temperature is as follows.

Dibromodecyl TPB-10 Dimer (16) > Didecyl TPB-10 Dimer (6) > Dihydroxydecal TPB-10 Dimer (15) = Didecenylic TPB-10 Dimer (14)
This order of the melting temperature was different from that found in the monomers. During cooling scans, in all cases, isotropic-nematic and nematic-crystal transitions were observed. The order of $T_{in}$ is as follows.

Dihydroxydecyl TPB-10 Dimer (11) > Didecyl TPB-10 Dimer (6) > dibromodecyl TPB-10 Dimer =Didecenyl TPB-10 Dimer

This order was opposite to that for the melting temperature except didecenyl TPB-10 dimer and similar to the order of $T_{in}$ found in the TPB monomers. Again, hydrogen bonding must be responsible for the higher transition temperature of dihydroxydecyl TPB-10 dimer.

The arguments indicated above clearly demonstrate that, although it becomes less important with increasing molecular weight, the terminal groups apparently affect the phase behavior. Therefore, it is very important to maintain the terminal groups consistent through entire molecular weight range in order to extract only molecular weight effect on phase transitions.

3.3.3 Fractionation of TPB-10 polyethers

Scheme 3.4 and 3.5 present the polymerization schemes for high molecular weight TPB-10 and low molecular weight TPB-10, respectively. The polyether with high molecular weight was synthesized to obtain relatively high molecular weight fractions of TPB-10. The polymerization was carried out with slight excess of TPB (2 mol%) so that most of polymer chain ends remain as phenolate anion at
the end of polymerization. Following the polymerization, the phenolate chain ends were endcapped with 1-bromodecane in situ. The low molecular weight TPB-10 was synthesized by replacing the 8 mol% of the dibromide for 16 mol% of 1-bromodecane. The polymerization was followed by the addition of 1-bromodecane to make sure that no unreacted phenol chain ends existed. The number average molecular weight (Mn) and polydispersity (Mw/Mn) of resulting TPB-10 polyethers were $1.33 \times 10^4$ and $3.54$, $0.59 \times 10^4$ and $2.43$, respectively. Both polydispersities are significantly higher than the values expected from the most probable distribution. This is due to the formation of cyclic oligomers during polymerization, which can not propagate further.

Fractionations of these polymers were carried out by a conventional column method with chloroform as a solvent and acetone as a nonsolvent. Table 3.3 and 3.4 summarize the yields, number average molecular weights, polydispersities, phase transition temperatures and the corresponding enthalpy changes, for the high molecular weight and low molecular weight TPB-10, respectively. Figure 3.7 presents the GPC chromatograms of fractionated TPB-10 from the high molecular weight TPB-10. As seen in Figure 3.7, each fraction shows a sharp peak. In Figure 3.8a and 3.8b, the number average molecular weights and polydispersities were plotted versus CHCl$_3$ content in eluent. The molecular weight of fractionated polymers increases with increasing the CHCl$_3$ content until 70 % and the polydispersity remained lower than 1.5 except the acetone only fraction which probably contains cyclic oligomers. The yield was also plotted versus the CHCl$_3$ content in Figure 3.9. The plot shows maximum yield around 60 % CHCl$_3$ content.
Table 3.3
Characterization of fractionated polyethers from high molecular weight TPB-10.

<table>
<thead>
<tr>
<th>Solvents (CHCl3/Acetone)</th>
<th>Yield (%)</th>
<th>$M_n \times 10^3$</th>
<th>$M_D/M_W$</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mmol) in parentheses$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Heating</td>
</tr>
<tr>
<td>Original</td>
<td>-</td>
<td>1.33</td>
<td>3.54</td>
<td>g 38.3 n 111.3 (2.76) l</td>
</tr>
<tr>
<td>0/100</td>
<td>4.2</td>
<td>0.16</td>
<td>2.63</td>
<td>g 26.9 n 96.4 (2.24) l</td>
</tr>
<tr>
<td>20/80</td>
<td>2.1</td>
<td>0.555</td>
<td>1.16</td>
<td>g 35.5 k 41.2 (0.16) n 103.5 (2.64) l</td>
</tr>
<tr>
<td>40/60</td>
<td>4.6</td>
<td>1.13</td>
<td>1.18</td>
<td>g 32.6 n 103.8 (2.69) l</td>
</tr>
<tr>
<td>50/50</td>
<td>13.5</td>
<td>2.09</td>
<td>1.20</td>
<td>g 38.1 k 44.7 (0.10) k 60.0 (0.08) n 108.0 (2.78) l</td>
</tr>
<tr>
<td>60/40</td>
<td>23.2</td>
<td>3.58</td>
<td>1.28</td>
<td>g 39.0 n 44.9 (-0.04) n 112.2 (2.86) l</td>
</tr>
<tr>
<td>70/30</td>
<td>20.2</td>
<td>5.63</td>
<td>1.34</td>
<td>g 40.9 n 112.6 (2.85) l</td>
</tr>
<tr>
<td>80/20</td>
<td>9.8</td>
<td>5.72</td>
<td>1.47</td>
<td>g 47.5 n 52.8 (0.76)$^b$ n 114.4 (2.82) l</td>
</tr>
<tr>
<td>90/10</td>
<td>1.0</td>
<td>5.49</td>
<td>1.48</td>
<td>g 44.1 n 114.4 (2.88) l</td>
</tr>
<tr>
<td>100/0</td>
<td>0.4</td>
<td>5.73</td>
<td>1.44</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.

$^b$Overlapped peaks.
Table 3.4
Characterization of fractionated polyethers from low molecular weight TPB-10.

<table>
<thead>
<tr>
<th>Solvents (CHCl₃/Acetone)</th>
<th>Yield (%)</th>
<th>Mn x 10⁴</th>
<th>Mw/Mn</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mru) in parentheses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>Heating</strong></td>
</tr>
<tr>
<td>Original</td>
<td>0.59</td>
<td>2.43</td>
<td></td>
<td>g 46.7 h 50.0 k 56.6 (1.56) n 100.6 (2.49) l</td>
</tr>
<tr>
<td>0/100</td>
<td>19.9</td>
<td>0.30</td>
<td>1.40</td>
<td>I 88.6 (2.39) n 19.8 g</td>
</tr>
<tr>
<td>10/90</td>
<td>2.1</td>
<td>0.52</td>
<td>1.16</td>
<td>g 26.5 k 44.1 (0.40) n 95.1 (2.40) l</td>
</tr>
<tr>
<td>20/80</td>
<td>4.0</td>
<td>0.66</td>
<td>1.16</td>
<td>g 26.6 n 95.6 (2.39) l</td>
</tr>
<tr>
<td>30/70</td>
<td>5.5</td>
<td>0.82</td>
<td>1.18</td>
<td>g 24.7 k 60.8 k 70.8 n 95.3 (6.74b) l</td>
</tr>
<tr>
<td>40/60</td>
<td>7.8</td>
<td>1.01</td>
<td>1.28</td>
<td>g 32.6 k 36.3 (0.12) n 101.0 (2.51) l</td>
</tr>
<tr>
<td>45/55</td>
<td>7.9</td>
<td>1.43</td>
<td>1.21</td>
<td>g 31.3 n 101.5 (2.64) l</td>
</tr>
<tr>
<td>50/50</td>
<td>8.0</td>
<td>1.18</td>
<td>1.56</td>
<td>g 37.8 k 41.7 (0.21) n 105.4 (2.65) l</td>
</tr>
<tr>
<td>55/45</td>
<td>17.3</td>
<td>1.13</td>
<td>1.50</td>
<td>g 35.0 n 105.1 (2.66) l</td>
</tr>
<tr>
<td>60/40</td>
<td>4.4</td>
<td>1.25</td>
<td>1.75</td>
<td>g 40.6 k 43.9 (0.21) n 106.0 (2.74) l</td>
</tr>
<tr>
<td>70/30</td>
<td>5.1</td>
<td>1.85</td>
<td>1.49</td>
<td>g 35.8 n 105.9 (2.81) l</td>
</tr>
</tbody>
</table>

Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.

b Overlapped peaks.
Figure 3.7 GPC chromatograms of fractionated TPB-10 polyethers from the high molecular weight TPB-10.
Figure 3.8 Number average molecular weight (a) and polydispersity (b) of the fractionated polyethers from the high molecular weight TPB-10 versus CHCl₃ content in eluent.
Figure 3.9 Yield of the fractionated polyethers from the high molecular weight TPB-10 versus CHCl₃ content in eluent.
and the yield becomes significantly low above 70% CHCl₃ content since there was only little polymer remained in the column. The total recover yield was 79.0%.

On the other hand, the fractionation of low molecular weight TPB-10 was not as successful as that of high molecular weight TPB-10. Figure 3.10 presents the GPC traces of fractionated TPB-10. The perfect fractionation occurred up to 45% CHCl₃ contents. The molecular weights of polymers fractionated with the solvents containing 20% and 40% of CHCl₃ were almost the same as those of polymers fractionated with the same solvents from the high molecular weight TPB-10. However, the fraction at 50% showed a bimodal distribution. The polydispersity remained relatively high (>1.5) above 50%. This is due to the fact that occurrence of the crystallization of the charged polymer during solvent evaporation or fractionation prevented the smooth fractionation since low molecular weight TPB-10 is more crystallizable than high molecular weight one, especially from the solution. The fractionated polyethers with narrow polydispersity were used to evaluate the molecular weight effect.

3.3.4 Phase transition of TPB-10 polymers

Figure 3.11a-3.11b presents the DSC thermograms of the second heating and cooling scans of fractionated polymers from the high molecular weight TPB-10 and of the original high molecular weight TPB-10 before the fractionation while Figure 3.12a-3.12b presents those of the fractionated polymers from the low molecular weight TPB-10 and of the the original low molecular weight TPB-10. The DSC data including first heating scans are tabulated in Table 3.3 and 3.4. The
Figure 3.10 GPC chromatograms of fractionated TPB-10 polyethers from the low molecular weight TPB-10.
Figure 3.11 DSC thermograms of second heating (a) and cooling scans (b) of fractionated polyethers from the high molecular weight TPB-10 and of the original high molecular weight TPB-10 before the fractionation.
Figure 3.12 DSC thermograms of second heating (a) and cooling scans (b) of fractionated polyethers from the low molecular weight TPB-10 and of the original low molecular weight TPB-10 before the fractionation.
fractionated polyethers with molecular weight lower than 40,000 show a small melting transition on the first heating scans (Table 3.3 and 3.4) below the nematic-isotropic transition. Therefore, these polymers exhibit an enantiotropic nematic mesophase. Since the tetramer, trimer, and dimer exhibit a monotropic nematic phase, the monotropic phase is transformed into an enantiotropic phase by increasing molecular weight of TPB-10. This behavior has been observed for both main chain\textsuperscript{4-6} and side chain liquid crystalline polymers.\textsuperscript{12,13} As seen in Figure 3.11 and 3.12, on cooling and second heating scans, only glass and nematic-isotropic transitions were observed. All fractionated polyethers with narrow polydispersities exhibit very sharp nematic-isotropic transitions regardless of molecular weight. On the other hand, the original TPB-10 before fractionation exhibits relatively broad transitions. In Figure 3.13a and 3.13b, \(T_{ni}\) and \(T_{in}\), \(T_g\) (glass transition temperature) for heating and cooling scans were plotted versus number average molecular weight (\(M_n\)) obtained by GPC. Both \(T_{ni}\) and \(T_{in}\) increase abruptly in low molecular weight region with increasing molecular weight followed by leveling off at high molecular weight region. \(T_g\) follows the same trend. \(T_{ni}\) and \(T_{in}\), \(T_g(\text{heating})\) and \(T_g(\text{cooling})\) were plotted versus reciprocal \(M_n\) in Figure 3.14a and 3.14b, respectively. The linear relationships of \(T_{ni}\), \(T_{in}\), \(T_g(\text{heating})\), and \(T_g(\text{cooling})\) versus \(1/M_n\) were obtained except high molecular weight region. For the glass transition, this relation can be expected from Fox-Flory equation which is based on a free-volume theory.\textsuperscript{19} Detailed inspection of Figure 3.14a and 3.14b leads to very interesting phenomena. In Figure 3.14a, \(T_{ni}\) deviates from the linear relation to upper side above \(M_n=20,000\) while \(T_{in}\) deviates to lower side above \(M_n=20,000\). This phenomena can be explained by
Figure 3.13: Nematic-isotropic transition temperatures (Tni and Tin) (a) and glass transition temperature (Tg) (b) of fractionated linear TPB-10 polyethers versus number average molecular weight (Mn).
Figure 3.14 Nematic-isotropic transition temperatures (Tni and Tin) (a) and glass transition temperature (Tg) (b) of fractionated linear TPB-10 polyethers versus reciprocal number average molecular weight (1/Mn).
supercooling and superheating due to the high viscosity of the system in high molecular weight region. The super cooling (T_{ni}-T_{in}) was plotted versus Mn in Figure 3.15. Actually, it increases linearly with increasing molecular weight. On the other hand, both Tg on cooling and heating deviate from the linear relations to upper side (Figure 3.14b). Another interesting phenomena is that the ratio T_{ni}/Tg (in K) is remained almost constant throughout the entire molecular weight range as indicated in Figure 3.16.

Although all the polyethers exhibit typical schlieren nematic textures, there is a difference in the texture evolution rate depending on the molecular weight. Namely, the evolution rate increases significantly with decreasing molecular weight. Figure 3.17a and 3.17b presents examples. The texture (Figure 3.17b) exhibited by the high molecular weight sample (Mn = 3.58 x 10^4) is much smaller than that (Figure 3.17a) of the low molecular weight sample (Mn = 1.13 x 10^4) at the same evolution time although the former was annealed at higher temperature.

In Figure 3.18a and 3.18b, the enthalpy change (ΔH) associated with the nematic-isotropic and isotropic-nematic transitions were plotted versus Mn and 1/Mn. Again, ΔH increases with increasing molecular weight and levels off above 20,000 molecular weight. ΔH also shows the linear relationship up to 1/Mn=2x10^{-4}. However, ΔH deviates to upper side below tetramer region. This tend may be due to the fact that ΔH was calculated based on the molecular weight of repeating unit. However, the contribution from chain ends to ΔH may not be negligible for low molecular weight oligomers such as trimer and tetramer.
Figure 3.15 Super cooling ($T_{ni}-T_{in}$) versus number average molecular weight (Mn).
Figure 3.16 Ratio $T_{ni}/T_g$ (in K) versus number average molecular weight ($M_n$)
(Data from second heating scan).
Figure 3.17a and 3.17b Typical polarized optical microscopic textures (x100) of the linear TPB-10 polyethers; (a) $M_n=1.13 \times 10^4$, annealed at 84.2°C for 22 min; (b) $M_n=3.58 \times 10^4$, annealed at 95.4°C for 22 min.
Figure 3.18 Enthalpy change ($\Delta H$) associated with nematic-isotropic and isotropic-nematic transitions versus number average molecular weight (Mn) (a) and $1/Mn$ (b).
3.4 CONCLUSIONS

The molecular weight effect on the phase behavior of linear polyethers TPB-10 has been intensively studied by DSC with the synthesized oligomers from monomer to tetramer and fractionated polymers. All the polymers and oligomers have the same terminal groups and those molecular weights range from monomer to 57,200 with narrow polydispersities. From the phase diagrams obtained with these well defined polymers, many interesting features were revealed, as follows. The glass transition and nematic-isotropic transition temperatures increase rapidly at low molecular weight region and level off at high molecular weight region (Mn > 20,000). There are linear relationships of both the glass transition and nematic-isotropic transition temperatures with reciprocal number average molecular weight up to Mn = 20,000. The super cooling increases with increasing molecular weight linearly. The ratio of nematic-isotropic transition temperature to glass transition temperature (T_{ni}/T_G) is constant and equal to 1.22-1.24 within the entire range of molecular weight. The enthalpy change associated with the nematic-isotropic transition increases rapidly at low molecular weights region and levels off at high molecular weights region.

The molecular weight effect data presented in this chapter is one of the most accurate sets of data available in the literature. These data will help to solve the theoretical problems in this field.
3.5 REFERENCES


CHAPTER 4

Synthesis and Characterization of Cyclic Oligopolyethers Based on a Semiflexible Mesogenic Unit and \( \alpha,\alpha' \)-Dibromoalkanes
4.1 INTRODUCTION

Cyclic oligomers are generated both during step condensation and ring opening polymerization reactions.\textsuperscript{1} Therefore, unless removed they are available in many polymers synthesized by these synthetic methods. In addition, cyclic oligomers (i.e., ionophores)\textsuperscript{2} and polymers (i.e., DNA and peptides)\textsuperscript{1a} are important natural compounds. However, there is very little understanding of the differences and similarities between cyclic and linear oligomers and polymers. This is due to the lack of reliable preparative methods for their syntheses. Three major synthetic procedures have been used for the preparation of cyclic polymers and oligomers. First, ring-chain equilibrium method has been used for the preparation of cyclic polycondensates such as polysiloxanes.\textsuperscript{1,3} This method utilizes the backbiting reactions in an equilibrium process of polycondensation reactions to obtain a cyclic structure. Secondly, nonequilibrium process of polycondensations has been used for the preparation of cyclic oligomeric polycarbonates,\textsuperscript{4} which were produced in a remarkably high selectivity over linear polymers through a pseudo-high dilution nature of the reaction. Also some of few cyclic condensates were synthesized.\textsuperscript{5} On the other hand, the chain polymerization of vinyl, acryl, and diene monomers do not involve a cyclic formation process since there are no functional links in their chain ends. Therefore, a ring closure reaction of a linear \( \alpha,\omega \)-difunctional precursor with a coupling agent has been used for the preparation of cyclic polymers of this type of monomers. Presently, cyclic glassy oligomers and polymers, i.e., polystyrene,\textsuperscript{1,6} and poly(2-vinylpyridine)\textsuperscript{7} were synthesized and characterized. Cyclic oligomers of polyethylene were synthesized and used to understand the crystallization mechanism of polyethylene.\textsuperscript{1a,8}
To date the combination of liquid crystalline polymers with cyclic geometry has not been reported except two examples of cyclic side chain liquid crystalline oligomers and polymers.\textsuperscript{9} They found that isotropization temperatures of cyclic polymers are higher than those of the corresponding linear polymers.\textsuperscript{9b}

The goal of this paper is to describe the synthesis and characterization of the first examples of cyclic main chain liquid crystalline oligomers. We will use two strategies for obtaining cyclic main chain liquid crystalline oligomers.

1) Mesogenic units based on conformational isomerism.

2) High dilution conditions.

The concept of liquid crystalline polyethers based on conformational isomerism has been developed by Percet et al.\textsuperscript{10-12} Mesogenic units based on conformational isomerism such as 1-(4-hydroxy-4',biphenyl)-2-(4-hydroxyphenyl)butane (TPB)\textsuperscript{12} are ideal structures for the synthesis of cyclic main chain liquid crystalline polymers since their gauche conformer favors the cyclization reaction. On the other hand, high dilution conditions have been widely used to synthesize many kinds of cyclic compounds\textsuperscript{13} and polymers,\textsuperscript{5,7} and can be applied for the phase transfer catalyzed polyetherification of TPB and \(\alpha,\omega\)-dibromoalkanes to synthesize cyclic polyethers.

This chapter will report the synthesis and characterization of cyclic oligopolyethers based on TPB and \(\alpha,\omega\)-dibromoalkanes containing \(X\) methylenic
units in the flexible spacer [TPB-X(c), (c) indicates the cyclic structure]. All molecular receptors with at least one aromatic ring bridged by at least one aliphatic n-membered bridge (n ≥ 0) may be called cyclophanes. Therefore, TPB-X(c) reported in this chapter represent the first examples of liquid crystalline cyclophanes.

### 4.2 EXPERIMENTAL

#### 4.2.1 Materials

Tetrabutylammonium hydrogen sulfate (TBAH) (97%) (Aldrich) was used as received. 1,4-Dibromobutane (99%), 1,5-dibromopentane (97%), 1,6-dibromohexane (97%), 1,7-dibromohexeptane (97%), 1,8-dibromooctane (98%), 1,9-dibromononane (97%), 1,10-dibromodecane (97%), 1,11-dibromoundecane (98%) (all from Aldrich) were purified by vacuum distillation. 1,12-Dibromododecane (technical, Aldrich) and 1,18-dibromoocotadecane (K and K Laboratories) were purified by recrystallization from methanol. 1,13-Dibromotridecane and 1,14-dibromotetradecane were synthesized as described in a previous publication and papers cited therein. o-Dichlorobenzene was distilled under reduced pressure. 1-(4-Hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) (purity, >99% by HPLC) was synthesized according to the procedure described in Chapter 2. Silicagel plates with fluorescent indicator (Eastman Kodak) were used for thin layer chromatography (TLC) analyses. All other chemicals were commercially available and were used as received.
4.2.2 Phase transfer catalyzed polymerization of TPB with 1,10-dibromodecane at various monomer concentrations

Scheme 4.1 presents the scheme of polyetherification of TPB with 1,10-dibromodecane at various concentrations followed by GPC analyses. The polyetherifications of TPB with 1, 10-dibromodecane were carried out at various concentrations [monomer (mmol) / organic solvent (ml) = 1/2, 1/20, and 1/100] under nitrogen atmosphere at 80°C in an o-dichlorobenzene - 10N NaOH aqueous solution mixture in the presence of tetrabutylammonium hydrogen sulfate (TBAH) as a phase-transfer catalyst. Samples of the reaction mixture were collected at various reaction times and analyzed by gel permeation chromatography. The procedure used in each concentration is as follows.

4.2.2.1 Concentration 1 [monomer (mmol) / solvent (ml) = 1/2]

To a 25 ml single-neck flask equipped with a condenser were added successively 0.318 g (1.00 mmol) of TPB, 2.0 ml of 10 N NaOH aqueous solution (20 mmol), 2.0 ml of o-dichlorobenzene, 0.300 g (1.00 mmol) of 1,10-dibromodecane, and 0.136 g (0.40 mmol, 20 mol% of phenol groups) of TBAH. A balloon filled with nitrogen was placed at the top of the condenser. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80°C. After 15 min, 30 min, 45 min, 1 h, 2 h, 4 h, and 6 h, a part of reaction mixture was collected. Each reaction mixture was diluted with water and chloroform, and the aqueous layer was removed. The organic layer was washed with water, followed by dilute hydrochloric acid, and again three times with water. The solvents were evaporated
Scheme 4.1 Polyetherification of TPB with 1,10-dibromodecane at various concentrations.
on a rotary evaporator to give a polymer as a solid. The obtained polyether was precipitated in water from a THF solution two times to remove completely the inorganic salts. After dried in vacuo, the product was analyzed by gel permeation chromatography.

4.2.2.2 Concentration 2 [monomer (mmol) / solvent (ml) = 1/20]

The procedure was the same as that used in Concentration 1 except the following conditions. A 100 ml single neck flask was used. The amounts of 10 N NaOH aqueous solution (200 mmol) and o-dichlorobenzene were 20 ml each. The sampling times were 1 h, 2 h, 3 h, 4 h, 6 h, 8 h, and 10 h.

4.2.2.3 Concentration 3 [monomer (mmol) / solvent (ml) = 1/100]

The procedure is the same as that used in Concentration 1 except the following conditions. A 500 ml single neck flask was used. The amounts of 10 N NaOH aqueous solution (1.0 mol) and o-dichlorobenzene were both 100 ml. The sampling times were 1 h, 3 h, 6 h, 9 h, 12 h, 24 h, and 72 h. After the dilution of the reaction mixture with water and chloroform, the aqueous layer was separated in a separatory funnel. The organic layer was washed with water, followed by dilute hydrochloric acid, and again six times with water. The solvents were evaporated on a rotary evaporator to give a mixture of solid and liquid products. The products were analyzed directly by gel permeation chromatography without precipitation.

4.2.3 Preparation of cyclic oligomers with various spacer length
Scheme 4.2 presents the cyclization of TPB with α,ω-dibromoalkanes (the number of methylenic units are 4-14, 18) followed by the separation of cyclic oligomers. The polyetherifications of TPB with α,ω-dibromoalkanes were carried out under high dilution conditions [monomer (mmol) / solvent (ml) = 1/100] under nitrogen atmosphere at 80°C in an o-dichlorobenzene-10N NaOH aqueous solution in the presence of TBAH as a phase-transfer catalyst. The reaction mixture was then separated into cyclic oligomers and higher molecular weight part. The procedures for the preparation of cyclic polyethers are as follows.

4.2.3.1 Preparation of TPB-10(c) oligomers

To a 500 ml single-neck flask equipped with a condenser were successively added 0.318 g (1.00 mmol) of TPB, 100 ml of 10 N NaOH aqueous solution (1.0 mol), 100 ml of o-dichlorobenzene, 0.300 g (1.00 mmol) of 1,10-dibromodecane, and 0.136 g (0.40 mmol, 20 mol% of phenol groups) of TBAH. A balloon filled with nitrogen was placed at the top of the condenser. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80°C. After 40 h, the reaction mixture was diluted with water and chloroform. The organic layer was washed two times with water, with dilute hydrochloric acid, and three times with water. After the evaporation of the solvents, the product was dissolved in chloroform. To this solution silicagel was added and the chloroform was evaporated. The product absorbed on silicagel was charged on the top of a column containing silicagel and was flushed with acetone to separate the mixture of cyclic oligomers. The remaining product at the top of the column was flushed with chloroform to separate the higher molecular weight part. The mixture of cyclic oligomers was separated into about 50
Scheme 4.2 Cyclization of TPB with α,ω-dibromoalkanes (the number of methylenic units are 4-14, 18) followed by the separation of cyclic oligomers.
fractions by silica gel column chromatography with a mixture of acetone and hexanes (1:20 v/v). Each fraction was checked by TLC [developed by a mixture of acetone and hexanes (1:15 - 1:20 v/v) and detected with a UV lamp]. The fraction containing each cyclic oligomer was collected and the solvents were evaporated on a rotary evaporator to give a separated cyclic oligomer. The cyclic dimer and trimer were further purified by recrystallization from hexanes.

4.2.3.2 Preparation of TPB-4(c) oligomers

The same procedure as the TPB-10(c) oligomers was used except the following conditions. 1,4-Dibromobutane (0.216 g, 1.00 mmol) was used. The ratio of acetone and hexanes was 1:10 v/v. The cyclic oligomers were further purified by the filtration of its chloroform solution followed by the precipitation in methanol.

4.2.3.3 Preparation of TPB-5(c) oligomers

The same procedure as the TPB-4(c) oligomers was used except the following condition. 1,5-Dibromopentane (0.230 g, 1.00 mmol) was used.

4.2.3.4 Preparation of TPB-6(c) oligomers

The same procedure as the TPB-4(c) oligomers was used except the following conditions. 1,6-Dibromohexane (0.244 g, 1.00 mmol) was used. The ratio of acetone and hexanes was 1:15 v/v. The column fractionation was repeated for the tetramer and pentamer with the same solvents mixture.
4.2.3.5 Preparation of TPB-7(c) oligomers

The same procedure as the TPB-4(c) oligomers was used except the following conditions. 1,7-Dibromooctane (0.258 g, 1.00 mmol) was used. The ratio of acetone and hexanes was 1:15 v/v.

4.2.3.6 Preparation of TPB-8(c) oligomers

The same procedure as the TPB-4(c) oligomers was used except the following conditions. 1,8-Dibromooctane (0.272 g, 1.00 mmol) was used. The ratio of acetone and hexanes was 1:15 v/v.

4.2.3.7 Preparation of TPB-9(c) oligomers

The same procedure as the TPB-4(c) oligomers was used except the following conditions. 1,9-Dibromononane (0.286 g, 1.00 mmol) was used. The ratio of acetone and hexanes was 1:20 v/v.

4.2.3.8 Preparation of TPB-11(c) oligomers

The same procedure as the TPB-4(c) oligomers was used except the following conditions. TPB (0.478 g, 1.50 mmol), 1,11-dibromoundecane (0.471 g, 1.50 mmol), TBAH (0.204 g, 0.60 mmol), 150 ml of o-dichlorobenzene, and 150 ml of 10 N NaOH aqueous solution were used. The ratio of acetone and hexanes was 1:30 v/v.
4.2.3.9 Preparation of TPB-12(c) oligomers

The same procedure as the TPB-11(c) oligomers was used except the following conditions. 1,12-Dibromododecane (0.492 g, 1.50 mmol) was used. The trimer and tetramer were further purified by the column with the acetone and hexanes (1:30 v/v).

4.2.3.10 Preparation of TPB-13(c) oligomers

The same procedure as the TPB-11(c) oligomers was used except the following conditions. 1,13-Dibromotridecane (0.513 g, 1.50 mmol) was used. The ratio of acetone and hexanes was 1:30 v/v. The dimer and monomer were further purified by column with the mixture of acetone and hexanes (1:50 v/v).

4.2.3.11 Preparation of TPB-14(c) oligomers

The same procedure as the TPB-4(c) oligomers was used except the following condition. 1,14-Dibromotetradecane (0.356 g, 1.00 mmol) was used. The ratio of acetone and hexanes was 1:50 v/v.

4.2.3.12 Preparation of TPB-18(c) oligomers

The same procedure as the TPB-4(c) oligomers was used except the following conditions. TPB (0.637 g, 2.00 mmol), 1,18-dibromoocotadecane (0.825 g, 2.00 mmol), TBAH (0.272 g, 0.800 mmol), 200 ml of o-dichlorobenzene, and 200 ml of 10 M NaOH aqueous solution were used. First, the mixture of chloroform and
acetone (1:2 v/v) was used for the rough separation of cyclic oligomers from the high molecular weight part. The mixture of acetone and hexanes (1:50 v/v) was used for the fractionations of each cyclic oligomer. Only the cyclic monomer and dimer were obtained in high purity.

4.2.4 Miscibility study of cyclic oligomers and linear polymer

The miscibility tests of TPB-8(c) dimer, trimer, and tetramer with linear TPB-8 (Mn=30,300, Mw/Mn=2.13) were carried out by using DSC. Each cyclic oligomer was mixed with linear polymer at weight ratio 50/50. The mixed samples were dissolved in CH₂Cl₂ and placed in DSC pans. After the evaporation of solvent, it was completely dried in vacuo and the amounts of the samples were obtained by weighing. DSC thermograms of mixed samples were obtained at 20 °C/min heating and cooling rate.

The transition temperatures were predicted by simplified Schroeder-van Laar equations.¹⁶ For a binary solution of components 1 and 2 in equilibrium between α phase and β phase, the equilibrium phase composition can be calculated by these two Schroeder-van Laar equations, (4.1) and (4.2).

\[
\ln\left(\frac{\chi_{1\beta}}{\chi_{1\alpha}}\right) = \frac{\Delta H_{1\alpha}^0 (T-T_1)}{RT_1} = H_1 \tag{4.1}
\]

\[
\ln\left(\frac{\chi_{2\beta}}{\chi_{2\alpha}}\right) = \frac{\Delta H_{2\alpha}^0 (T-T_2)}{RT_2} = H_2 \tag{4.2}
\]
Where $\Delta H^o_{\alpha\beta}$ is the $\alpha \leftrightarrow \beta$ transition enthalpy at $T_1$, assumed independent of temperature. If $H_1$ and $H_2$ were small enough to expand the exponential, the equations (4.1) and (4.2) can be simplified and solved for the composition of $\chi_{1\alpha}$ as indicated in the equation (4.3). The transition temperatures of mixed samples were predicted by using this equation.

$$\chi_{1\alpha} = \left[ 1 - \frac{\Delta H^o_{1\alpha\beta} T_2 (T - T_1)}{\Delta H^o_{2\alpha\beta} T_1 (T - T_2)} \right]^{-1}$$ (4.3)

4.2.5 Techniques

1-D and 2-D $^1$H-NMR (300 MHz) spectra were recorded on a VXR 300 NMR spectrometer at 299.949 MHz using a 5 mm $^1$H-$^{19}$F/broad band switchable probe. Data were collected at ambient temperature without sample spinning. COSY spectra were acquired with 512 fid's, which were acquired with 16 transients and 8 dummy sets of pulses at the beginning of the experiment to establish a steady state, 20.8 $\mu$s 90° pulse width, 0.189 - 0.407 acquisition time (1024 - 2048 data points), 1s relaxation delay, and 2715.9 Hz spectrum window in f1 and f2. The COSY spectra were processed with floating point transforms, zerofilling to 2048 or 4096 in t2 and 1024 in t1, sinebell weighting. Phase sensitive 2-D NOESY spectra were collected at ambient temperature without sample spinning. At the beginning of the experiment 8 dummy fid's were collected to establish a steady state, 512 fid's were acquired with 16 transients, 20.8 $\mu$s 90° pulse width, 0.377 - 0.407 acquisition time (2048
data points), 1s relaxation delay, and 2647.6 Hz spectral window in f1 and f2. The NOESY spectra were processed with floating point transforms.

Molecular modeling and energy minimization experiments were carried out with an ALCHEMY II software (Tripos Associates) on a Macintosh IIci personal computer.

4.3 RESULTS AND DISCUSSION

4.3.1 Cyclization of TPB with α,ω-dibromoalkanes

TPB is a mesogenic unit based on conformational isomerism (Scheme 4.1). Its gauche conformer should prefer intramolecular cyclization to intermolecular extension. TPB has a chiral center and therefore, since we use the racemic mixture of its two enantiomers, upon polymerization with α,ω-dibromoalkane we generate cyclic copolymers containing all four constitutional isomers of TPB as discussed for the linear polyethers in Chapter 2 except cyclic monomers which have only two constitutional isomers.

4.3.1.1 Effect of monomer concentrations on a formation of cyclic oligomers versus linear polymers

Figures 4.1a - c presents the GPC chromatograms of polymerization mixtures obtained at various polymerization time at various monomer concentrations. The
Figures 4.1a GPC chromatograms of polymerization mixtures obtained at various polymerization time at initial monomer concentration, monomer (mmol) / solvent (ml) = 1/2.
Figures 4.1b GPC chromatograms of polymerization mixtures obtained at various polymerization time at initial monomer concentration, monomer (mmol) / solvent (ml) = 1/20.
Figures 4.1c GPC chromatograms of polymerization mixtures obtained at various polymerization time at initial monomer concentration, monomer (mmol) / solvent (ml) = 1/100.
Figures 4.2a and 4.2b The dependence of the average molecular weights on the polymerization time at various initial monomer concentrations \([\text{monomer (mmol)} / \text{solvent (ml)} = 1/2, 1/20, \text{and} 1/100]\): (a) the number average molecular weight \((M_n)\); (b) the weight average molecular weight \((M_w)\).
number average molecular weight ($M_n$) and weight average molecular weight ($M_w$) are plotted versus time in Figures 4.2 a and b.

The polyetherification at the concentration [monomer (mmol) / solvent (ml) = 1/2] proceeded very fast. The average $M_n$ and $M_w$ reached those maximum values after 30 min (Figure 4.2a and b). A very little amount of oligomers was formed at this concentration as seen from Figure 4.1a. Decreasing the concentration to [monomer (mmol) / solvent (ml) = 1/20] slowed down the polymerization rate. However, $M_w$ of the polymer reached the same level as that obtained at the concentration [monomer (mmol) / solvent (ml) = 1/2] after 8 h (Figure 4.2b) while the maximum $M_n$ was lower than that at monomer (mmol) / solvent (ml) = 1/2 (Figure 4.2a). This is due to the formation of oligomers as seen in Figure 4.1b. As the concentration of monomer decreased to real high dilution level [monomer (mmol) / solvent (ml) = 1/100], the amount of oligomers increased even more. The highest $M_w$ of the polymer did not reach the same level as that obtained at monomer (mmol) / solvent (ml) = 1/2 (Figure 4.2). The oligomers were formed at the beginning of the polymerization and the amount and the ratio of oligomers did not change during the polymerization. Figure 4.3 presents the effect of the monomer concentration on the weight fraction of oligomers obtained from GPC chromatograms versus the degree of polymerization. In this figure, peak assignments were carried out based on the molecular weight obtained by GPC. The weight fractions of oligomers increase with decreasing the concentration of the monomer in the reaction mixture as clearly seen in Figure 4.3. These two observations, (1) increase in the formation of oligomers with decreasing
Figure 4.3 Effect of the monomer concentration on the weight fraction of oligomers versus the degree of polymerization.
concentrations, (2) the fact that the formed oligomers do not propagate, suggest that these oligomers are cyclic oligomers. The preferential formation of cyclic oligomers under dilute conditions is attributed to the preferential intramolecular cyclization versus intermolecular reaction under dilution conditions. The intramolecular cyclization involves only a single molecule and therefore, it is a first order reaction on the concentration of the growing species. On the other hand, the intermolecular reaction which leads to linear extension is a second order reaction on the concentration of the growing species. Therefore, the intramolecular cyclization becomes more favorable than the linear polymerization with decreasing the monomer concentration.

4.3.1.2 Spacer length effect of the weight fraction of cyclic oligomers

Scheme 4.2 presents the cyclization of TPB with $\alpha,\omega$-dibromoalkanes. Figure 4.4 presents the GPC chromatograms of the reaction mixtures obtained by the polyetherifications of TPB with $\alpha,\omega$-dibromoalkanes with $X$ methylenic units ($X = 4-14, 18$) under high dilution conditions [monomer (mmol) / solvent (ml) = 1/100]. The weight fraction of each cyclic oligomer was estimated from these GPC chromatograms and plotted versus the spacer length in Figure 4.5. No cyclic monomer was formed at the spacer length below $X = 6$. This is due to the fact that the spacer length is not long enough to form a cyclic structure. The weight fraction of cyclic monomers increases abruptly as the spacer length increases from $X = 6$ and becomes larger than that of cyclic dimers above $X = 11$. This abrupt increase in the weight fraction of cyclic monomers corresponds to the decrease in the strain energy of the ring structure with increasing the spacer length. The weight fraction
Figure 4.4 GPC chromatograms of the reaction mixtures obtained by the polyetherifications of TPB with α,ω-dibromoalkanes with X methylenic unit (X = 4-14, 18) under high dilution conditions [monomer (mmol) / solvent (ml) = 1/100].
Figure 4.5 Weight fractions of cyclic oligomers in the polymerization mixtures obtained under high dilution conditions [monomer (mmol) / solvent (ml) = 1/100] versus the spacer length.
of dimers decreases with increasing spacer length. It is interesting that the weight
fraction of dimers shows odd-even effect versus the spacer length, which vanishes
as the spacer length becomes longer. Odd spacers tend to yield higher weight
fraction of dimers compared to even spacers. This may be due to the favorable
conformation for the phenolate to attack the α carbon of bromide group in the case
of odd spacer. The weight fractions of trimers, tetramers, and pentamers including
dimers decrease as the spacer length increases. This is simply due to the fact that the
cyclic monomer is formed at the expense of higher oligomers.

4.3.2 Characterization of separated cyclic oligomers

The characterization of separated cyclic oligomers was carried out with GPC,
$^1$H-NMR, DSC, and optical polarized microscopy.

4.3.2.1 GPC analyses of cyclic oligomers

Figure 4.6-4.17 show the GPC chromatograms of the reaction mixtures, of the
high molecular weight parts eluted with chloroform, and of the individual cyclic
oligomers for all cyclic series. The purity and molecular weight at the peak top of
each cyclic oligomer are presented in Table 4.1 - 4.12 with other characterization
results. The purity of each cyclic oligomer is higher than 93 % except some cases.
Most of the contaminations are cyclic oligomers with different ring size. The purity
tends to be lower as the ring size increases. This is due to the fact that the difference
between the cyclic oligomers with degree of polymerization n and that with n+1
becomes more subtle with increasing n number. The calculated and measured
Figure 4.6 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,4-dibromobutane.
Figure 4.7 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,5-dibromopentane.
Figure 4.8 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,6-dibromohexane.
Figure 4.9 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,7-dibromoheptane.
Figure 4.10 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,8-dibromo-octane.
Figure 4.11 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,9-dibromononane.
Figure 4.12 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,10-dibromodecane.
Figure 4.13 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,11-dibromoundecane.
Figure 4.14 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,12-dibromododecane.
Figure 4.15 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,13-dibromotridecane.
Figure 4.16 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,14-dibromotetradecane.
Figure 4.17 GPC chromatograms of the reaction mixture, of the high molecular weight part eluted with chloroform, and of the individual cyclic oligomers separated from the cyclization mixture of TPB and 1,18-dibromooctadecane.
Table 4.1
Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,4-dibromobutane.

<table>
<thead>
<tr>
<th>Ring size</th>
<th>Yield (%)</th>
<th>Purity by GPC (%)</th>
<th>Molecular weight at peak top</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mrų) in parentheses (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td></td>
<td>Heating</td>
</tr>
<tr>
<td>2</td>
<td>9.9</td>
<td>98.7</td>
<td>877</td>
<td>k 181 (2.24) (i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>745</td>
<td>g 621</td>
</tr>
<tr>
<td>3</td>
<td>4.7</td>
<td>97.1</td>
<td>1336</td>
<td>k 140 (2.12) k 152 (-1.44) 176 (1.36) (i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1118</td>
<td>g 70 i</td>
</tr>
<tr>
<td>4</td>
<td>3.2</td>
<td>95.8</td>
<td>1807</td>
<td>g 59 k 123 (-1.85) k 188 (1.75) (i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1490</td>
<td>g 60 n 114 (0.23) (i)</td>
</tr>
<tr>
<td>CHCl₃ Eluted Part</td>
<td>23.1</td>
<td>68c</td>
<td>Mn = 6.05 x 10³</td>
<td>g 83 (-1.21) n 143 (1.64) (i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mw/Mn = 1.57</td>
</tr>
<tr>
<td>Linear</td>
<td>-</td>
<td>-</td>
<td>Mn = 1.47 x 10⁴</td>
<td>g 88 n 99 (-0.32) n 154 (2.04) (i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mw/Mn = 1.82</td>
</tr>
</tbody>
</table>

\(^a\) Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan. \(^b\) Overlapped peaks. \(^c\) Mole % of cyclic polymers.
Table 4.2
Characterization of cyclic oligomers and corresponding linear polymers
based on TPB and 1,5-dibromopentane.

<table>
<thead>
<tr>
<th>Ring size</th>
<th>Yield (%)</th>
<th>Purity by HPLC</th>
<th>MW by GPC at the peak top</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (kcal/mrur) in parentheses$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td>Heating</td>
<td>Cooling</td>
</tr>
<tr>
<td>2</td>
<td>10.4</td>
<td>97</td>
<td>810</td>
<td>773 k 163 (-1.36) k 179 k 183 (5.79b) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 61 k 104 (-2.28) k 173 (4.23) i</td>
</tr>
<tr>
<td>3</td>
<td>3.5</td>
<td>95</td>
<td>1293</td>
<td>1160 g 60 k 68 (0.26) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 63 i</td>
</tr>
<tr>
<td>4</td>
<td>1.4</td>
<td>94</td>
<td>1733</td>
<td>1546 g 66 k 73 k 80 (0.37b) n 103 (0.08) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 64 n 103 (0.11) i</td>
</tr>
<tr>
<td>5</td>
<td>1.3</td>
<td>92</td>
<td>2299</td>
<td>1933 g 64 k 68 (0.10) k 80 (0.30) n 94 (0.07) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 63 n 93 (0.10) i</td>
</tr>
<tr>
<td>CHCl₃ Eluted Part</td>
<td>$60^c$</td>
<td>Mn=1.02 x $10^4$</td>
<td>g 61 i</td>
<td>i 62 g</td>
</tr>
<tr>
<td>Linear</td>
<td></td>
<td>Mw/Mn=1.37</td>
<td>g 68 i</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn= 1.54 x $10^4$</td>
<td>g 67 i</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mw/Mn=2.89</td>
<td>g 67 i</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.
$^b$Overlapped peaks. $^c$Mole % of cyclic polymers.
Table 4.3

Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,6-dibromohexane.

<table>
<thead>
<tr>
<th>Ring size</th>
<th>Yield (%)</th>
<th>Purity by GPC (%)</th>
<th>Molecular weight</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mru) in parentheses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Heating</td>
<td>Cooling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.9</td>
<td>&gt;99</td>
<td>845</td>
<td>k 196 (8.94) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 55 k 101 (-1.01) k 158 (-2.67) k</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 192 k 197 k 203 (8.34) i</td>
</tr>
<tr>
<td>3</td>
<td>2.7</td>
<td>95.2</td>
<td>1344</td>
<td>k 132 k 148 (3.46) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 63 s 80 (0.35) i</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>95.5</td>
<td>1812</td>
<td>g 55 k 75 (0.13) n 148 (0.90) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 61 n 149 (0.79) i</td>
</tr>
<tr>
<td>CHCl₃ Eluted Part</td>
<td>21.8</td>
<td>63c</td>
<td>Mₙ = 7.24 x 10³</td>
<td>g 51 n (-0.44) n 131 (2.12) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mₘ/Mₙ = 1.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 62 n 130 (1.59) i</td>
</tr>
<tr>
<td>Linear</td>
<td>-</td>
<td>-</td>
<td>Mₙ = 3.23 x 10⁴</td>
<td>g 71 n 81 (-0.21) n 137 (2.21) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mₘ/Mₙ = 2.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 67 n 137 (2.16) i</td>
</tr>
</tbody>
</table>

a Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.
bOverlapped peaks. cMole % of cyclic polymers.
<table>
<thead>
<tr>
<th>Ring size</th>
<th>Yield (%)</th>
<th>Purity by HPLC</th>
<th>MW by GPC at the peak top</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (kcal/mr) in parentheses$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td>Heating</td>
<td>Cooling</td>
</tr>
<tr>
<td>2</td>
<td>5.9</td>
<td>&gt;99</td>
<td>901 829</td>
<td>k 171 k 180 (6.84b) i k 150 (-0.99) k 166 k 172 k 180 (5.53b) i</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>92</td>
<td>1453 1244</td>
<td>g 52 n 81 (0.07) i g 49 n 81 (0.08) i</td>
</tr>
<tr>
<td>4</td>
<td>1.9</td>
<td>93</td>
<td>1884 1658</td>
<td>g 52 k 64 (0.12) n 115 (0.28) i g 50 n 114 (0.34) i</td>
</tr>
<tr>
<td>5</td>
<td>2.1</td>
<td>89</td>
<td>2650 2073</td>
<td>g 47 n 108 (0.29) i g 51 n 107 (0.36) i</td>
</tr>
<tr>
<td>CHCl3 Eluted Part</td>
<td>27$^c$</td>
<td>Mn=1.01 x 10$^4$</td>
<td>g 53 n 69 (0.26) i</td>
<td>i 62 (0.15) n 48 g</td>
</tr>
<tr>
<td>Linear</td>
<td></td>
<td>Mw/Mn=1.40</td>
<td>g 53 n 67 (0.10) i</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn=2.05 x 10$^4$</td>
<td>Mw/Mn=2.07</td>
<td>g 47 n 74 (0.83$^b$) i</td>
<td>i 60 (0.10) n 48 g</td>
</tr>
</tbody>
</table>

$^a$Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.

$^b$Overlapped peaks. $^c$Mole% of cyclic polymers.
Table 4.5
Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,8-ditromoocetane.

<table>
<thead>
<tr>
<th>Ring size</th>
<th>Yield (%)</th>
<th>Purity (%)</th>
<th>Molecular weight by GPC</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mru) in parentheses(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td>Heating</td>
<td>Cooling</td>
</tr>
<tr>
<td>1</td>
<td>6.6</td>
<td>98.0</td>
<td>479</td>
<td>429</td>
</tr>
<tr>
<td>2</td>
<td>8.8</td>
<td>98.5</td>
<td>983</td>
<td>857</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>91.9</td>
<td>1523</td>
<td>1286</td>
</tr>
<tr>
<td>4</td>
<td>2.7</td>
<td>95.4</td>
<td>2106</td>
<td>1715</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>76.5</td>
<td>2736</td>
<td>2143</td>
</tr>
<tr>
<td>CHCl₃ Eluted Part</td>
<td>32.8</td>
<td>44(^c)</td>
<td>(M_n = 8.73 \times 10^3)</td>
<td>(42 \pm 61 (-0.26) \times 115 (2.18))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(M_w/M_n = 1.62)</td>
<td>(47 \pm 114 (2.12))</td>
</tr>
<tr>
<td>Linear</td>
<td>-</td>
<td>-</td>
<td>(M_n = 3.03 \times 10^4)</td>
<td>(46 \pm 124 (2.39))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(M_w/M_n = 2.13)</td>
<td>(52 \pm 123 (2.43))</td>
</tr>
</tbody>
</table>

\(^a\) Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan. \(^b\) Overlapped peaks. \(^c\) Mol% of cyclic polymers.
Table 4.6

Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,9-dibromononane.

<table>
<thead>
<tr>
<th>Ring size</th>
<th>Yield (%)</th>
<th>Purity (%)</th>
<th>Molecular weight (g/mol)</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mrunit) in parenthesesa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td></td>
<td>Heating</td>
</tr>
<tr>
<td>1</td>
<td>4.8</td>
<td>98.2</td>
<td>549</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>13.7</td>
<td>97.8</td>
<td>1121</td>
<td>g 42 k 134 (4.61) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>885</td>
<td>k 97 (-0.54) k 117 k 121 (2.17) k 134 (1.62) i</td>
</tr>
<tr>
<td>3</td>
<td>3.4</td>
<td>95.2</td>
<td>1743</td>
<td>g 43 n 96 (0.19) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1328</td>
<td>g 40 n 96 (0.19) i</td>
</tr>
<tr>
<td>4</td>
<td>2.7</td>
<td>93.9</td>
<td>2429</td>
<td>g 41 n 121 (0.47) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1771</td>
<td>g 40 n 121 (0.48) i</td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>90.9</td>
<td>3025</td>
<td>g 46 n 110 (0.32) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2213</td>
<td>g 44 n 110 (0.35) i</td>
</tr>
<tr>
<td>CHCl₃ Eluted Part</td>
<td>23.4</td>
<td>41c</td>
<td>Mₙ = 1.04 x 10⁴</td>
<td>g 48 n 74 (0.54) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mₘ/Mₙ = 1.62</td>
<td>g 46 n 73 (0.78) i</td>
</tr>
<tr>
<td>Linear</td>
<td>-</td>
<td>-</td>
<td>Mₙ = 3.93 x 10⁴</td>
<td>g 43 k 52 n 74 (1.16b) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mₘ/Mₙ = 2.29</td>
<td>g 47 n 74 (0.78) i</td>
</tr>
</tbody>
</table>

a Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan. b Overlapped peaks. c Mole% of cyclic polymers.
<table>
<thead>
<tr>
<th>Ring Size</th>
<th>Yield (%)</th>
<th>Purity (%)</th>
<th>MW by GPC at the peak top</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes Kcal/mrL in parentheses&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td>Heating</td>
<td>Cooling</td>
</tr>
<tr>
<td>1</td>
<td>2.4</td>
<td>99</td>
<td>542</td>
<td>g &lt; -10&lt;sup&gt;i&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>92</td>
<td>1154</td>
<td>g 53 k 90 k 113 (5.78&lt;sup&gt;b&lt;/sup&gt;) i</td>
</tr>
<tr>
<td>3</td>
<td>1.6</td>
<td>95</td>
<td>1845</td>
<td>g 23 n 46 (0.15) i</td>
</tr>
<tr>
<td>4</td>
<td>2.3</td>
<td>96</td>
<td>2343</td>
<td>g 50 k 55 k 82 k 121 n 130 (3.13&lt;sup&gt;b&lt;/sup&gt;) i</td>
</tr>
<tr>
<td>5</td>
<td>0.8&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td>3100</td>
<td>g 29 n 127 (1.21) i</td>
</tr>
<tr>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt; Eluted Part</td>
<td></td>
<td></td>
<td></td>
<td>g 36 k 45 (0.09) n 127 (1.21) i</td>
</tr>
<tr>
<td>Linear</td>
<td></td>
<td></td>
<td></td>
<td>g 33 n 128 (1.14) i</td>
</tr>
<tr>
<td></td>
<td>Mn=1.18 x 10&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>g 49 k 57 k 71 n 97 (2.69&lt;sup&gt;b&lt;/sup&gt;) i</td>
</tr>
<tr>
<td></td>
<td>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;=1.53</td>
<td></td>
<td></td>
<td>g 28 n 98 (2.31) i</td>
</tr>
<tr>
<td></td>
<td>Mn=3.77 x 10&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>g 42 k 48 (0.03) n 112 (2.54) i</td>
</tr>
<tr>
<td></td>
<td>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;=2.22</td>
<td></td>
<td></td>
<td>g 43 n 112 (2.54) i</td>
</tr>
</tbody>
</table>

<sup>a</sup>Data on the first line are from first heating and cooling scan. Data on the second line are from second heating scan.

<sup>b</sup>Overlapped peaks. It contains trimer, tetramer, and higher cyclics. However, each cyclics is overlapped severely and purity could not be determined.

<sup>d</sup>Mole% of cyclic polymers.
Table 4.8
Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,11-dibromoundecane.

<table>
<thead>
<tr>
<th>Ring size</th>
<th>Yield (%)</th>
<th>Purity by GPC (%)</th>
<th>Molecular weight (g) by GPC at peak top</th>
<th>Thermal transitions (ºC) and corresponding enthalpy changes (Kcal/mole) in parenthesesa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.4</td>
<td>&gt;99</td>
<td>508</td>
<td>k 88 (6.24) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 64 i</td>
</tr>
<tr>
<td>2</td>
<td>2.8</td>
<td>&gt;99</td>
<td>1043</td>
<td>k 110 k 132 (6.81) b k 144 (0.64) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>k 112 k 132 (4.63) b i</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>90.6</td>
<td>1675</td>
<td>g 35 n 105 (0.56) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 33 n 104 (0.48) i</td>
</tr>
<tr>
<td>4</td>
<td>2.2</td>
<td>91.5</td>
<td>2317</td>
<td>g 38 k 59 (-1.20) k 81 (0.52) k 103 n 116 (1.77) b i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 34 n 67 (-0.76) k 83 (0.55) n 116 (0.71) i</td>
</tr>
<tr>
<td>5</td>
<td>1.2</td>
<td>90.7</td>
<td>3014</td>
<td>g 39 n 108 (0.76) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 35 X 47 (0.02) n 109 (0.81) i</td>
</tr>
<tr>
<td>CHCl3 Eboned Part</td>
<td>11.4</td>
<td>37c</td>
<td>M_n = 7.05 x 10³</td>
<td>g 44 n 82 (1.07) i</td>
</tr>
<tr>
<td>Linear</td>
<td>-</td>
<td>-</td>
<td>M_n = 1.98 x 10⁴</td>
<td>g 41 k 49 k 55 n 74 (1.36) b i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 40 k 54 (0.24) n 74 (1.08) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 105 (0.89) n 39 (0.06) X 31 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 112 (0.73) n 27 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 94 (3.94) k</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 -11 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 74 (-0.98) n 47 (0.16) k 34 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 64 (1.09) n 47 (0.15) k 34 g</td>
</tr>
</tbody>
</table>

a Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan. b Overlapped peaks. c Mol% of cyclic polymers.
Table 4.9
Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,12-dibromododecane.

<table>
<thead>
<tr>
<th>Ring size</th>
<th>Yield (%)</th>
<th>Purity by GPC (%)</th>
<th>Molecular weight by GPC (Kcal/mmol)</th>
<th>Thermal transitions (OC) and corresponding enthalpy changes (Kcal/mol) in parentheses*a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td>Heating</td>
<td>Cooling</td>
</tr>
<tr>
<td>1</td>
<td>14.7</td>
<td>&gt;99</td>
<td>541</td>
<td>k 102 (8.31) l</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g -7 i</td>
</tr>
<tr>
<td>2</td>
<td>8.5</td>
<td>97.0</td>
<td>1184</td>
<td>k 110 k 130 (7.40b) l</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 16 n 61 (0.22) l 75 (-0.30) k 111 (0.30) l</td>
</tr>
<tr>
<td>3</td>
<td>3.6</td>
<td>94.7</td>
<td>1834</td>
<td>g 27 n 103 (0.62) l</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 27 n 103 (0.62) l</td>
</tr>
<tr>
<td>4</td>
<td>2.2</td>
<td>94.5</td>
<td>2474</td>
<td>g 44 n 66 k 89 (-2.51b) 115 n 124 (3.89b) l</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 29 n 54 k 82 (-2.29b) k 115 n 125 (3.78b) l</td>
</tr>
<tr>
<td>GCH3 Eluted Part</td>
<td>22.4</td>
<td>67c</td>
<td>Mn = 6.47 x 10³</td>
<td>i 121 (1.38) n 23 g</td>
</tr>
<tr>
<td>Linear</td>
<td></td>
<td></td>
<td>Mn = 4.26 x 10⁴</td>
<td>i 92 (2.59) n 25 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MW/Mn = 1.82</td>
<td>i 88 (2.69) n 31 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>g 45 k 59 (0.39) n 65 (-0.28) n 104 (2.56) l</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>g 39 k 69 n 104 (2.56) l</td>
<td></td>
</tr>
</tbody>
</table>

*a Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan. b Overlapped peaks. c Mole% of cyclic polymers.
<table>
<thead>
<tr>
<th>Ring size</th>
<th>Yield (%)</th>
<th>Purity by GPC (%)</th>
<th>Molecular weight by GPC at peak top</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mru) in parentheses&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td>Heating</td>
<td>Cooling</td>
</tr>
<tr>
<td>1</td>
<td>6.4</td>
<td>&gt;99</td>
<td>518</td>
<td>k 96 (6.75) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>g -4 i</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>94.8</td>
<td>1146</td>
<td>g 67 k 90 (-0.55) 115 k 133 (6.84)&lt;sup&gt;b&lt;/sup&gt; i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>k 109 k 129 (4.09)&lt;sup&gt;b&lt;/sup&gt; i</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.3</td>
<td>93.3</td>
<td>1806</td>
<td>g 31 s 58 (0.05) n 106 (0.69) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>g 31 s 37 (0.06) n 106 (0.71) i</td>
<td></td>
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<tr>
<td>4</td>
<td>1.4</td>
<td>92.2</td>
<td>2499</td>
<td>g 62 k 89 (2.24) n 115 (0.91) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>g 34 k 48 (1.03) k 88 (1.65) n 115 (0.88) i</td>
<td></td>
</tr>
<tr>
<td>CHCl₃ Eluted Part</td>
<td>21.8</td>
<td>67&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear</td>
<td>-</td>
<td>-</td>
<td>M&lt;sub&gt;n&lt;/sub&gt; = 7.42 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>M&lt;sub&gt;W&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt; = 1.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>g 39 k 45 (0.37) n 79 (1.20) i</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>g 37 k 50 (0.20) n 79 (1.32) i</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>M&lt;sub&gt;n&lt;/sub&gt; = 3.29 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>g 32 k 48 n 78 (2.47)&lt;sup&gt;b&lt;/sup&gt; i</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>g 41 k 47 (0.39) n 79 (1.48) i</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan. <sup>b</sup> Overlapped peaks.  
<sup>c</sup> Mole% of cyclic polymers.
<table>
<thead>
<tr>
<th>Ring size</th>
<th>Yield (%)</th>
<th>Purity by GPC (%)</th>
<th>Molecular weight by GPC at peak top</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/m mole) in parentheses(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Heating</td>
<td>Cooling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>93.2</td>
<td>563</td>
<td>g 11 k 19 k 29 k 53 (-2.98) k 98 (5.82) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>513</td>
<td>g -51</td>
</tr>
<tr>
<td>2</td>
<td>1.3</td>
<td>95.7</td>
<td>1209</td>
<td>k 95 k 105 k 121 (7.68) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1026</td>
<td>g 18 n 62 (-5.21) k 100 k 111 k 119 (6.41) i</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>98.3</td>
<td>1930</td>
<td>g 32 k 44 k 56 (0.77) e 70 (0.01) n 107 (0.71) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1538</td>
<td>g 29 e 70 (0.02) n 107 (0.72) i</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
<td>86.7</td>
<td>2590</td>
<td>k 59 (1.96) e 119 (1.43) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2051</td>
<td>i 108 (1.27) n 46 (1.57) k</td>
</tr>
<tr>
<td>CHCl₃ Eluted Part 23.7</td>
<td>58(^c)</td>
<td>Mn = 6.12 x 10³</td>
<td>Mₙ/Mₚ = 1.67</td>
<td>g 36 k 48 (0.43) k 75 n 85 (4.53) i</td>
</tr>
<tr>
<td>Linear</td>
<td>.</td>
<td>.</td>
<td>Mn = 3.02 x 10⁴</td>
<td>g 41 k 74 n 84 (4.36) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mₙ/Mₚ = 2.16</td>
<td>g 38 k 58 (0.26) k 64 (-0.34) k 84 n 96 (3.97) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>i 83 (2.71) n 60 (1.85) k 43 g</td>
</tr>
</tbody>
</table>

\(^a\)Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan. \(^b\)Overlapped peaks. \(^c\)Mole% of cyclic polymers.
Table 4.12
Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,18-dibromo-octadecane.

<table>
<thead>
<tr>
<th>Ring size</th>
<th>Yield (%)</th>
<th>Purity (%)</th>
<th>Molecular weight by GPC measured</th>
<th>Molecular weight by GPC calculated</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mole) in parentheses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.0</td>
<td>&gt;99</td>
<td>646</td>
<td>569</td>
<td>Heating: 64 (10.32) i, 1 - 11 g, Cooling: 178 (0.36) a 44 k 35 (5.22) k</td>
</tr>
<tr>
<td>2</td>
<td>1.87</td>
<td>91.5</td>
<td>1371</td>
<td>1138</td>
<td>Heating: 54 k 102 k 111 (9.97) i, 59 (-0.98) k 112 k 118 (8.61) i, 169 (5.36) k 28 g, Cooling: 34 k 65 k 91 (3.56) i, 37 (5.81) i</td>
</tr>
<tr>
<td>CHCl3 Eluted Part</td>
<td>20.9</td>
<td>62c</td>
<td>$M_n = 5.77 \times 10^3$</td>
<td>$M_w/M_n = 1.80$</td>
<td>Heating: 39 (-.97) k 84 (5.40) i, 43 k 84 (5.89) i, 172 (5.61) a 35 g</td>
</tr>
<tr>
<td>Linear</td>
<td>-</td>
<td>-</td>
<td>$M_n = 3.71 \times 10^4$</td>
<td>$M_w/M_n = 3.88$</td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{a Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan. b Overlapped peaks. c Mole\% of cyclic polymers.} \]
molecular weights of the cyclic oligomers are plotted versus the ring size in Figure 4.18a in the case of TPB-10(c) as an example. The measured molecular weight is proportional to the ring size and is higher than the calculated value. This linear dependence is the proof of the correct assignment of the ring size. The higher measured values compared to the calculated ones suggest larger hydrodynamic volumes of the cyclic oligomers than those of the linear polystyrenes with the same molecular weight in chloroform most probably due to the presence of the semirigid mesogenic unit. The similar results were obtained for all other cyclic oligomers. Figure 4.18b presents the comparison of the ratios of the number average molecular weight obtained by GPC to the calculated one between TPB-10(c) oligomers and the linear TPB-10 oligomers synthesized in Chapter 3. The values of cyclic oligomers are lower than those of the linear oligomers. The values of the cyclic oligomers tend to increase with increasing the ring size while the ones of the linear oligomers stay constant. These results indicate that the hydrodynamic volumes of the cyclic oligomers are lower than those of the linear oligomers and increase with increasing the ring size.

4.3.2.2 Characterization of cyclic oligomers by $^1$H-NMR spectroscopy

4.3.2.2.1 1D and 2D $^1$H-NMR analyses of TPB-10(c)

Figure 4.19a-4.19f presents the 300 MHz $^1$H-NMR spectra of cyclic monomer, dimer, trimer, tetramer, pentamer, and of the high molecular weight part eluted with chloroform of TPB-10(c) while Scheme 4.3 presents the protonic assignments of the TPB-10(c) oligomers. The $^1$H-NMR spectrum of the linear polyether is almost
Figure 4.18 (a) The calculated and measured (GPC) molecular weights of the TPB-10(c) oligomers versus the ring size; (b) the comparison of the values [Mn(GPC)/Mn(calculated)] between the TPB-10(c) and the linear TPB-10 oligomers.
Figure 4.19 300 MHz $^1$H-NMR spectra of TPB-10(c) series: (a) cyclic monomer; (b) cyclic dimer; (c) cyclic trimer; (d) cyclic tetramer; (e) crude cyclic pentamer; (f) CHCl$_3$ eluted part (CDCl$_3$, TMS).
Scheme 4.3 Protonic assignments of TPB-10(c) oligomers.

X+Y = Ring Size
identical to the spectrum of the high molecular weight part eluted with chloroform which will be discussed in more detail later. There are two significant features in these $^1$H-NMR spectra. First, no peaks corresponding to the expected terminal groups (such as Br-CH$_2$-, CH$_2$=CH-, HO-CH$_2$-, HO-Ph, etc.) for linear structures can be observed in these spectra. Secondly, the patterns of NMR spectra are highly dependant on the ring size. These features of the spectra are the proof of the cyclic structure of the separated oligomers. Let us explain more detailed results of NMR of these cyclic oligomers.

Figure 4.20 presents the 300 MHz 2-D $^1$H-NMR COSY spectrum of the TPB-10(c) monomer while Figure 4.21 a, b, and c presents the 300 MHz 2-D $^1$H-NMR NOESY spectra of TPB-10(c) monomer as a example. These COSY and NOESY 2-D $^1$H-NMR techniques allowed the complete peak assignments of the NMR spectra of cyclic oligomers. COSY and NOESY spectra provide us with the information about the presence of through bond coupling and through space coupling interactions, respectively. Both spectra contain diagonal peaks corresponding to the shifts in the normal $^1$H-NMR spectra; off diagonal peaks at the intersection of two chemical shifts indicate coupling between two protons in the COSY spectrum or the proximity (<5Å) of two protons if present in the NOESY spectrum. An example of the peaks assignment process is demonstrated with COSY and NOESY spectra of cyclic monomer as follows.

The interpretation of COSY spectrum of the cyclic monomer shown in Figure 4.20 started with the aromatic region. This area exhibits three crosspeaks which
Figure 4.20 2-D 300 MHz $^1$H-NMR COSY spectrum of the cyclic TBP-10(c) monomer (CDCl$_3$, TMS).
Figure 4.21b 2-D 300 MHz $^1$H-NMR NOESY spectrum of the cyclic TPB-10(c) monomer (CDCl$_3$, TMS) in aromatic region.
Figure 4.21c 2-D 300 MHz $^1$H-NMR NOESY spectrum of the cyclic TPB-10(c) monomer (CDCl$_3$, TMS) in aromatic-aliphatic region.
correspond to the presence of through bond couplings. Crosspeak A correlates peaks A1 and A2. Crosspeak B correlates peaks A3 and A4 while crosspeak C correlates peaks A5 and A6. Therefore, the protons corresponding to A1 and A2 peaks, the protons corresponding to A3 and A4 peaks, and the protons corresponding to A5 and A6 peaks should be on the same phenyl ring respectively. In the aliphatic region, crosspeak D shows the correlation between peaks 1 and 2, while crosspeak E shows the correlation for peaks 10 and 9. The methylene protons next to the aromatic ether usually show up around 4 ppm. Therefore, peaks 1 and 10 can be assigned to these protons and the protons corresponding to peaks 2 and 9 should be from the methylene groups next to these protons. Crosspeak F correlates peaks a and a'. Crosspeak G shows correlation between peaks a and b. Crosspeak H shows through bond coupling for peaks a' and b. Crosspeak I shows correlation between peaks b and c, while crosspeak J shows correlation between c and d. Peak d is apparently due to the protons of methyl group. Therefore, peak c can be assigned to the methylene protons next to the methyl group. From the correlation between the peaks b and c, the peak b is assigned to the methine proton next to the monophenyl ring while a and a' are assigned to the methylene protons next to the biphenyl ring. Peaks 2 and 3 are correlated by crosspeak K. Therefore, the protons corresponding to peak 3 should be next to the protons corresponding to peak 2.

Interpretation of the NOESY spectrum of the cyclic monomer started with the aromatic region (Figure 4.21b). Crosspeak A shows the proximity of protons with responsible for peaks A2 and A3; crosspeak B correlates peaks A2 and A1; crosspeak C correlates peaks A3 and A4; and crosspeak D correlates peaks A5 and
A6. However, the protons corresponding to A2 and A3 peaks are not on the same ring as discussed in the COSY spectrum. Therefore, it is possible to assign these protons to the biphenyl protons ortho to the phenyl rings. There are also crosspeaks correlating the aromatic and the aliphatic region (Figure 4.21c). Crosspeak E correlates peaks A1 and 1 while crosspeak F correlates peaks A6 and 10, indicating that the protons producing peaks A1 and A6 should be ortho to the ether linkages. This discussion provided enough information about the relative position of aromatic protons. Namely, A1 is due to the protons ortho to the ether group on the biphenyl ring while A2 is due to the protons ortho to the ether group on the same ring. A3 is due to the protons meta to the methylene group on the biphenyl ring while A4 is due to the protons ortho to the methylene group on the same ring. Furthermore, A5 is due to the protons meta to the ether group on the monophenyl ring while A6 is due to the protons ortho to the ether group on the same ring. There are other crosspeaks correlating the aromatic and the aliphatic region: crosspeak G shows the correlation between peaks A5 and b, and crosspeak I which correlates peaks A4 and a'. Therefore, the peak a' should be assigned to one of the protons of methylene group next to the biphenyl ring and the peak b should be assigned to the methine proton. These assignments are consistent with those made from COSY spectrum. Crosspeak K shows correlation between peaks A5 and c which was assigned to methylene protons next to the methyl group. In the aliphatic region there is crosspeak L correlating peaks a and a' (Figure 4.21a). The assignments of the proton resonances of the other cyclic oligomers of TPB-10(c) were accomplished by the same process with both COSY and NOESY spectra.
The assignments of all peaks are summarized in Table 4.13. As mentioned previously, the patterns of the $^1$H-NMR spectra change drastically by increasing the size of the macrocyclic ring from monomer to pentamer. Figure 4.22a presents the chemical shifts of aromatic protons (A₁-A₆) versus ring size. Most of the protons shift to a lower field with increasing the ring size except the protons (A₁) ortho to the ether group on the biphenyl ring whose chemical shift does not change with the ring size. The differences between the chemical shifts of various protons of the cyclic monomer and the linear polymer are summarized as $\Delta \delta$ in Table 4.13. As the position of protons on the phenyl rings moves further from the ethylene unit connecting the monophenyl ring and the biphenyl ring, $\Delta \delta$ becomes smaller. This behavior can be explained as follows. Figure 4.23 presents the lowest free energy conformation of the cyclic monomer obtained by a computer modeling. In the cyclic monomer TPB is considered to primarily adopt a gauche conformation due to the restricted length of the spacer. In this conformation the monophenyl ring and the phenyl ring next to methylene group of biphenyl ring become close to each other and shield the protons of each phenyl ring. This shielding effect shifts them to the upper field. However, the A₁ protons are too far away to be affected by the monophenyl ring. The A₂ protons have relatively a smaller effect. In the case of the dimer the anti conformation becomes possible. However, it should still adopt a gauche conformation to some extent since both conformers are in a dynamic equilibrium. As the the ring size becomes larger, the anti conformation of the mesogen becomes more favorable, and the chemical shifts move to the lower field as the proton experience the environment of the anti conformation for a larger fraction of time. On the other hand, the methyl protons (d) and the methylene
Table 4.13

*H-NMR peak assignment of cyclic oligomers, of CHCl₃ eluted part, and of linear polyether.

| Ring Size | A1  | A2  | A3  | A4  | A5  | A6  | a   | a'  | b   | c   | d   | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1         | 6.91| 7.36| 7.14| 6.68| 6.64| 6.54| 3.13| 2.44| 2.62| 1.83| 0.92| 4.18| 1.66| 1.37| 1.07| 1.07| 1.07| 1.07| 1.24| 1.54| 3.82|
| 2         | 6.90| 7.43| 7.29| 6.88| 6.87| 6.72| 2.95| 2.74| 2.66| 1.75| 0.82| 3.97| 1.75| 1.43| 1.30| 1.30| 1.30| 1.30| 1.43| 1.75| 3.87|
| 3         | 6.90| 7.44| 7.33| 6.99| 6.93| 6.75| 2.87| 2.80| 2.63| 1.76| 0.77| 3.95| 1.76| 1.44| 1.30| 1.30| 1.30| 1.30| 1.44| 1.76| 3.89|
| 4         | 6.90| 7.44| 7.34| 7.01| 6.96| 6.76| 2.83| 2.83| 2.66| 1.73| 0.75| 3.95| 1.73| 1.41| 1.30| 1.30| 1.30| 1.30| 1.41| 1.73| 3.87|
| 5         | 6.90| 7.44| 7.35| 7.01| 6.98| 6.76| 2.84| 2.84| 2.64| 1.74| 0.77| 3.95| 1.74| 1.42| 1.30| 1.30| 1.30| 1.30| 1.42| 1.74| 3.88|
| CHCl₃ Eluted part | 6.91| 7.45| 7.37| 7.05| 7.01| 6.78| 2.84| 2.84| 2.67| 1.74| 0.73| 3.95| 1.74| 1.44| 1.31| 1.31| 1.31| 1.31| 1.44| 1.74| 3.90|
| Linear    | 6.92| 7.46| 7.37| 7.05| 7.01| 6.79| 2.84| 2.84| 2.67| 1.75| 0.74| 3.96| 1.75| 1.44| 1.32| 1.32| 1.32| 1.32| 1.44| 1.75| 3.90|
| (M₆=37700)|    |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Δδb       | 0.01| 0.10| 0.23| 0.37| 0.37| 0.25| -0.29| 0.40| 0.05| -0.08| -0.18| -0.22| 0.09| 0.07| 0.25| 0.25| 0.25| 0.25| 0.20| 0.21| 0.08|

aThere are also minor peaks which are assigned to terminal groups. (t1, 5.79 ppm, -CH₂CH₂; t2, 4.95 ppm, -CH₂CH₂; t3, 0.0036 ppm, -CH₂OH)

bΔδ is the chemical shift difference between cyclic monomer and linear polyether: (δlinear polymer - δcyclic monomer)
Figure 4.22a and 4.22b The dependence of chemical shifts on the ring size: (a) aromatic protons (A1 - A6); (b) protons of lateral ethyl group (c and d).
Figure 4.22c and 4.22d The dependence of chemical shifts on the ring size: (c) methylenic protons next to the biphenyl ring (a and a') and methine proton (b); (d) methylenic protons in the spacer (1 - 10).
Figure 4.23 One of the lowest free energy conformation of the cyclic monomer.
protons (c) of the ethyl group of the mesogenic unit shift to a higher field with increasing the ring size as presented in Figure 4.22b since the anti conformation places these protons over the shielding regions of phenyl rings for a large fraction of time. The chemical shifts of the methylene protons (a and a') next to the biphenyl ring also change drastically as shown in Figure 4.22c. These protons are diastereomeric protons since they are next to the chiral center. Therefore, these protons have a different chemical shift in the cyclic oligomers. These are getting closer with increasing ring size and become a simple doublet in the linear polymer. This phenomena can also be explained by the dynamic conformational change between the gauche and anti conformers and their ratio. The chemical shift of the methine proton (b) is not affected by the ring size. The chemical shift of methylene protons (1-10) in the spacer shifts differently depending on those positions, as presented in Figure 4.22d. The methylene protons next to the biphenyloxy group shift to a higher field with increasing ring size, while the other protons shift to a lower field. This can be explained as follows; in the cyclic monomer the methylene protons next to the biphenyl ring are aside of the phenyl ring while the other methylene protons are placed mostly above the biphenyl ring. These NMR results demonstrate that the conformation of the mesogenic unit is highly dependent of the ring size. Namely, the semiflexibility of the TPB mesogenic unit affects and contributes to the formation of cyclic oligomers and polymers as expected.

Two kinds of terminal groups (t1, t2, t3), i.e., -CH2-OH, -CH=CH2, were detected in the 1H-NMR spectrum of the high molecular weight part eluted with chloroform (Figure 4.19f, Table 13). If we assume that there are no other terminal
groups and the number average molecular weight is correct, the mole fraction of cyclic molecule in this part can be calculated by using following equations.

\[ \text{The total concentration of terminal groups detected by NMR (mol/g)} = 2L \quad (4.4) \]

\[ \text{The total mole of cyclic and linear molecules (mol/g)} = L + C = 1/Mn \quad (4.5) \]

\[ \text{Mole fraction of cyclic molecule (mol%)} = 100C/(L + C) \quad (4.6) \]

where L and C are the total moles of linear and cyclic molecules in the sample (mol/g), respectively. For the Mn the value obtained by GPC was used. In order to calculate the total concentration of terminal groups, the NMR peak ratios of methylene protons next to the oxygens as a main chain unit versus all terminal groups detected were used. Consequently, the chloroform eluted fraction contains about 50 mol% of larger cyclic polyethers although this is only an estimation. The vinyl groups originate from the elimination of HBr from the bromide chain ends of the spacer, while the alcohol groups are produced by the hydrolysis of the bromide groups. These side reactions apparently limit the possibility to obtain high molecular weight macrocyclics without the contamination of linear polymers in this system.

4.3.2.2.2. \text{1H-NMR analyses of other cyclic oligomers}

200 MHz $^1$H-NMR spectra of all the TPB-X(c) series are presented in Figure 4.24-4.34. The similar dependences of chemical shifts on a ring size to that of
Figure 4.24 200 MHz $^1$H-NMR spectra of TPB-4(c) series.
Figure 4.25 200 MHz $^1$H-NMR spectra of TPB-5(c) series.
Figure 4.26 200 MHz $^1$H-NMR spectra of TPB-6(c) series.
Figure 4.27 200 MHz $^1$H-NMR spectra of TPB-7(c) series.
Figure 4.28 200 MHz $^1$H-NMR spectra of TPB-8(c) series.
Figure 4.29 200 MHz $^1$H-NMR spectra of TPB-9(c) series.
Figure 4.30 200 MHz $^1$H-NMR spectra of TPB-11(c) series.
Figure 4.31 200 MHz $^1$H-NMR spectra of TPB-12(c) series.
Figure 4.32 200 MHz $^1$H-NMR spectra of TPB-13(c) series.
Figure 4.33 200 MHz $^1$H-NMR spectra of TPB-14(c) series.
Figure 4.34 200 MHz $^1$H-NMR spectra of TPB-18(c) series.
TPB-10(c) series are observed. Some of the cyclic oligomers show peak splittings which are due to either the constitutional isomers or the restricted conformations with the slow rate of isomerization.

The effect of the spacer length on chemical shifts are plotted for each ring size including the linear polymers in Figure 4.35a-e. The dependences of chemical shifts (aromatic protons, methylene and methine protons next to phenyl rings, and methyl proton) on the spacer length decrease with increasing ring size. The effect of spacer length on chemical shifts for the cyclic monomers in Figure 4.35a resembles to the effect of ring sizes on chemical shifts as presented in Figure 4.22a-4.22c although those X axis is the ring size instead of the spacer length. It means that the increasing spacer length has the similar effect to increasing the ring size on a conformation of TPB mesogenic unit since the chemical shifts of those protons are mainly determined by its conformation as discussed in 4.3.2.2.1. This is quite reasonable since longer spacer allows the mesogen to adopt conformations more close to anti conformer in a cyclic monomer. The chemical shifts of the dimers and trimers are less dependent on the spacer length than those of the monomers. However, there are still some dependence. It means that the conformations of the dimers and trimers change to some extent with changing the spacer length. On the other hand, for the tetramers and linear TPB-X polymers, there is almost no dependence of chemical shifts on the spacer length, which suggests very little change in the conformation of the mesogenic unit with the spacer length.
Figure 4.35a The dependence of chemical shifts of aromatic protons (A1 - A6), the protons of lateral ethyl group (c and d), methylenic protons next to the biphenyl ring (a and a') and methine proton (b) versus the spacer length for the cyclic monomers.
Figure 4.35b The dependence of chemical shifts of aromatic protons (A1 - A6), the protons of lateral ethyl group (c and d), methylenic protons next to the biphenyl ring (a and a') and methine proton (b) versus the spacer length for the cyclic dimers.
Figure 4.35c The dependence of chemical shifts of aromatic protons (A1 - A6), the protons of lateral ethyl group (c and d), methylenic protons next to the biphenyl ring (a and a') and methine proton (b) versus the spacer length for the cyclic trimers.
Figure 4.35d The dependence of chemical shifts of aromatic protons (A1 - A6), the protons of lateral ethyl group (c and d), methylenic protons next to the biphenyl ring (a and a') and methine proton (b) versus the spacer length for the cyclic tetramers.
Figure 4.35e The dependence of chemical shifts of aromatic protons (A1 - A6), the protons of lateral ethyl group (c and d), methylenic protons next to the biphenyl ring (a and a') and methine proton (b) versus the spacer length for the linear polymers.
In a expanded $^1$H-NMR spectra of the high molecular weight parts eluted with chloroform, there are several minor peaks which correspond to the terminal groups of linear polymers, i.e., -CH=CH$_2$, -CH$_2$-OH, and -CH$_2$-Br. The mole fractions of cyclic polymers were estimated by the same procedure presented in 4.3.2.2.1 and presented in Table 4.1-4.12. These were 27% - 68%. Therefore, these fractions represent the mixture of cyclic and linear polymers.

4.3.2.3 Phase behavior of cyclic oligomers

The phase behavior of cyclic oligomers are highly dependent on the ring size and spacer length. The discussion will be focused on the comparison of cyclic oligomers and linear oligomers and polymers, the effect of ring size, the change of mesophase nature via cyclization, the effect of spacer length, and miscibility of cyclic oligomers with a linear polymer.

4.3.2.3.1 The comparison of TPB-10(c) oligomers vs linear TPB-10 oligomers and polymers

Figure 4.36a-4.36c present the first heating, second heating, and first cooling DSC thermograms of TPB-10(c) oligomers, of the high molecular weight part eluted with chloroform and of corresponding linear TPB-10 polymer. The thermal transition temperatures and the corresponding enthalpy changes collected from the first heating, second heating, and first cooling scans are summarized in Table 4.7. TPB-10(c) monomer, which at room temperature is a liquid, does not show any phase transition between -10 and 155 °C. The cyclic dimer exhibits glass transition temperature ($T_g$) and melting transitions during the first heating scan. Isotropic-
Figure 4.36a-4.36c DSC thermograms of the linear TPB-10 polyethers (L), of the high molecular weight part of TPB-10(c) eluted with CHCl₃ (H) and of the cyclic TPB-10(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.
nematic, nematic-isotropic, and glass transitions are observed on the cooling and second heating scans. Figure 4.37a illustrates the fine nematic texture of the cyclic dimer obtained after annealing at 42.3°C for 14 min upon cooling from the isotropic phase. $T_m$ observed on the first heating scan is higher than $T_{ni}$ observed on the second heating scan. Actually, upon heating above $T_{ni}$ the crystallization of the dimer started around 60°C. After annealing at 85.9°C for 5 min the needle like crystalline texture was observed as presented in Figure 4.37b. Therefore, under equilibrium conditions the nematic mesophase of the dimer is monotropic.

The cyclic trimer shows a glass, melting, and enantiotropic nematic-isotropic transitions on the first heating scan. However, only the isotropic-nematic, nematic-isotropic, and glass transitions are observed during the cooling and second heating scans. The nematic phase is enantiotropic since the melting temperature is lower than that of the nematic-isotropic transition temperature. Figure 4.37c presents the homogeneous nematic texture of the cyclic trimer obtained after annealing at 79.8°C for 13 min.

The cyclic tetramer shows a complicated DSC thermogram during its first heating scan. After glass transition, two melting followed by crystallization and a melting into a nematic phase followed by isotropization are observed. However, only isotropic-nematic, nematic-isotropic, and glass transitions are observed on the cooling and second heating scans. Again, the nematic phase is enantiotropic. Figure 4.37d presents the schlieren texture of the nematic phase of the cyclic tetramer obtained at 114.3°C on heating.
Figure 4.37a,b The textures of the cyclic TPB-10(c) oligomers observed under optical polarized microscope (x100): (a) fine nematic texture of the cyclic dimer after annealing at 42.3°C for 14 min; (b) crystalline texture of the cyclic dimer after annealing at 85.9°C for 5 min.
Figure 4.37c,d The textures of the cyclic TPB-10(c) oligomers observed under optical polarized microscope (x100): (c) homogeneous nematic texture of cyclic trimer after annealing at 79.8°C for 13 min; (d) schlieren nematic texture of cyclic tetramer after annealing at 114.3°C upon heating.
The crude cyclic pentamer also exhibits glass, melting, and nematic-isotropic transitions during the first heating scan. Only isotropic-nematic, nematic-isotropic transitions and glass transition are observed during the cooling and second heating scans. The nematic phase is enantiotropic.

The chloroform eluted part represents a mixture of larger cyclic and linear polymers as discussed in NMR part and shows glass, melting and nematic-isotropic transitions during the first heating scan. Only isotropic-nematic, nematic-isotropic transitions and glass transition are observed during the cooling and second heating scans. The peaks of nematic-isotropic transitions are relatively broad. In this case the polymer is actually a mixture of both linear and cyclic polymers which may have different isotropization transition temperatures and therefore, this mixture broadens the isotropization transition peaks.

Figure 4.38 presents the transition temperatures collected during second heating and cooling scans versus the ring size. As the ring size increases, the glass transition temperature increases slightly while $T_{ni}$ and $T_{in}$ increase rapidly with the increase in the ring size. However, $T_{ni}$ of the CHCl$_3$ eluted part which represents a mixture of linear and cyclic polyethers is lower than those of the cyclic tetramer and pentamer. $T_{ni}$ of tetramer and pentamer are even higher than that of the linear TPB-10 with $M_n = 37,700$. The entropy change associated with the nematic-isotropic transition during second heating and cooling scans tends to increase with increasing
Figure 4.38 The transition temperatures of the TPB-10(c) oligomers obtained during second heating and first cooling scans versus the ring size and the comparison with their linear homologue.
the ring size as presented in Figure 4.39. However, the entropy change of all the cyclic oligomers are much lower than that of high molecular weight linear TPB-10.

We can make a direct comparison of linear oligomers and cyclic oligomers by using the data obtained in Chapter 3. As discussed in Chapter 3, all the linear oligomers exhibit a monotropic nematic phase while the cyclic trimer and tetramer show an enantiotropic nematic phase. Therefore, the crystallizability of cyclic oligomers is lower than that of linear oligomers with the same degree of polymerization. The transition temperature of cyclic oligomers increases more rapidly than that of the linear oligomers does as indicated in Figure 4.40a. Consequently, although the cyclic dimer shows lower nematic-isotropic transition temperature, the cyclic trimer and tetramer show higher transition temperatures than those of the corresponding linear trimer and tetramer. On the other hand, the enthalpy changes of cyclic oligomers are much lower than those of linear oligomers regardless of degree of polymerization as presented in Figure 4.40b.

Scheme 4.4 presents the schematic representation of the isotropic-nematic transition of the cyclic tetramer as an example. Due to the cyclic nature and the molecular recognition of mesogens, these cyclic oligomers have distorted conformation of spacers or mesogens which is highly dependent on the ring size and parity of the ring size. In linear oligomers and polymers the middle spacers are extended while their chain ends are melted. In cyclic oligomers there are no chain ends, and although in the fold these are both cis and trans conformers of the methylenic units, they are rigid. Simultaneously, the cyclic structure has a lower
Figure 4.39 The entropy change associated with the nematic-isotropic transitions of the cyclic oligomers obtained during second heating and first cooling scans versus ring size and the comparison with their linear homologue.
Figure 4.40a-4.40b The comparison of cyclic oligomers versus linear oligomers; (a) nematic-isotropic transition temperature versus the degree of polymerization; (b) the entropy change associated with the nematic-isotropic transition versus the degree of polymerization.
Scheme 4.4 Schematic representation of the isotropic -nematic transition of TPB-10(c) tetramer.
entropy in the isotropic phase than that of the homologous linear oligomer. Therefore, the entropy change of cyclic oligomers is lower than that of corresponding linear compounds. At the same time since the chain ends (i.e., the fold) of cyclic oligomers are rigid, they can explain their higher isotropization transition temperatures versus those of the corresponding linear oligomers with similar molecular weights. Nevertheless, the difference between the rigidity of the chain ends of cyclic oligomers and high molecular weight linear polymer can not explain completely the difference between their isotropization transition temperatures. Therefore, we can assume that the overall rigidity of the cyclic oligomers is higher than that of the high molecular weight linear polymer.

The detailed inspection of Scheme 4.4 leads to some interesting aspects of these cyclic oligomers. While linear compounds exhibiting nematic mesophases show translational and rotational motions, cyclic liquid crystals provide most probably the translational motion of their mesogenic group mostly via a jump reptation motion which changes the conformation of the mesogen and spacer when they pass through the fold.

4.3.2.3.2 Transformation of a kinetically prohibited mesophase of a Linear polymer into an enantiotropic mesophase one via cyclization\textsuperscript{17a}

As demonstrated above, some of the cyclic oligomers have higher transition temperatures than those of the corresponding linear polymers even with high molecular weight. Therefore, it may be possible for a amorphous polymer, whose mesophase transition temperature is below its glass transition temperature, to
exhibit an enantiotropic mesophase via cyclization provided that the increase in mesophase transition temperature is much higher than that in glass transition temperature. Namely, the kinetically prohibited mesophase of the linear polymer is expected to get transformed into an enantiotropic one via cyclization. This is the case for TPB-5 series.

Figure 4.41a-c presents DSC traces obtained during the first, second heating and first cooling scans of TPB-5(c) oligomers, of the high molecular weight part eluted with chloroform, and of linear TPB-5. Table 4.2 summarizes the data available for linear and cyclic oligomers and polymer of TPB-5 series. TPB-5 is glassy since its glass transition temperature is higher than the isotropization temperature as discussed in Chapter 2. Namely, the nematic phase of TPB-5 is kinetically prohibited by its own glass transition temperature. The cyclic dimer is crystalline, while the cyclic trimer is amorphous. However, the cyclic tetramer and pentamer exhibit an enantiotropic nematic mesophase. This enantiotropic mesophase is achieved since the nematic transition temperatures increase by more than 36 °C for the tetramer and 27 °C for the pentamer (calculated by subtracting the glass transition temperature of the linear polymer from the nematic-isotropic transition temperatures of cyclic oligomers) via cyclization while the glass transition temperature does not change so much (Tg of the linear polymer is 67 °C while Tg of tetramer and pentamer are 64 °C).

4.3.2.3.3 Transformation of a kinetically controlled nematic phase of a linear polymer into a thermodynamically controlled one via cyclization17b
Figure 4.41a-4.41c DSC thermograms of the linear TPB-5 polyethers (L), of the high molecular weight part of TPB-5(c) eluted with CHCl₃ (H) and of the cyclic TPB-5(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.
The same concept mentioned above can be applied to the transformation of a kinetically controlled nematic phase of a linear polymer into a thermodynamically controlled one via cyclization. This is the case for TPB-7 series. The high molecular weight linear TPB-7 exhibits a nematic mesophase whose isotropization temperature is in the very close proximity of its glass transition temperature. Therefore, this nematic phase is kinetically controlled.

Figure 4.42a-c presents representative DSC traces exhibited during the first, second heating, and first cooling scans of TPB-7(c) oligomers, of chloroform eluted part, and of linear TPB-7. Table 4.4 summarizes the data available for TPB-7 series. As we can observe from the Figure 4.42a-c, the cyclic dimer is crystalline, while the cyclic trimer, tetramer and pentamer exhibit an enantiotropic nematic mesophase whose isotropization transition temperatures are higher than that of linear high molecular weight linear TPB-7 polymer. The peaks of the nematic mesophase of the linear TPB-7 polymer and of chloroform eluted fraction are located in the close proximity of their glass transition temperatures. Therefore, their nematic phase is formed with difficulties since it is kinetically controlled due to the close proximity of the glass transition. In fact, the isotropic-nematic transition peak can not be observed clearly on the cooling DSC scan (Figure 4.42c). However, this nematic phase can be seen on the optical microscope. In the case of the cyclic trimer, tetramer and pentamer the nematic mesophase becomes thermodynamically controlled since its isotropization temperature is located further away from the glass transition temperature.
Figure 4.42c: DSC thermograms of the linear TPB-7 polyethers (L), of the high molecular weight part of TPB-7(c) eluted with CHCl3 (H) and of the cyclic TPB-7(c) oligomers (the numbers in the figure indicate the ring size); (a) first heating scans; (b) second heating scans; (c) first cooling scans
4.3.2.3.4 Spacer length effect on phase behavior

Figure 4.43-4.51 present the DSC thermograms of the first heating, second heating, and first cooling scans of the cyclic oligomers, of the high molecular weight part eluted with chloroform, and of the corresponding linear polymers for the rest of TPB-X(c) series with X=4, 6, 8, 9, 11, 12, 13, 14, and 18. All the DSC data are summarized in Table 4.1-4.12.

4.3.2.3.4.1 General trend of cyclic monomer

As seen from Table 4.1-4.12, all cyclic monomers obtained are liquid or crystalline which do not crystallize on the cooling and subsequent heating scans. No mesophase was observed with the cyclic monomers. This is quite reasonable since the cyclic monomers have the conformation of the mesogenic unit close to gauche conformer as discussed in the NMR part. TPB unit with such a conformation is no longer a rod-like molecule and can not align.

4.3.2.3.4.2 General trend of cyclic dimer

Figure 4.52a-c presents the phase diagrams phase diagrams obtained from the first heating, second heating, and cooling scans of the TPB-X(c) dimers. The general trends of the dimers are as follows. Most of the dimers exhibit several melting peaks on their first heating scans. The clearing temperature decreases with increasing spacer length. Some of the dimers with spacer length longer than X=9 exhibit a monotropic nematic mesophase during cooling scans. The dimers with the spacer length below X=9 do not exhibit such a mesophase due to the following
Figure 4.43a-4.43c DSC thermograms of the linear TPB-4 polyethers (L), of the high molecular weight part of TPB-4(c) eluted with CHCl₃ (H) and of the cyclic TPB-4(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.
Figure 4.44a-4.44c DSC thermograms of the linear TPB-6 polyethers (L), of the high molecular weight part of TPB-6(c) eluted with CHCl₃ (H) and of the cyclic TPB-6(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.
Figure 4.45a-4.45c DSC thermograms of the linear TPB-8 polyethers (L), of the high molecular weight part of TPB-8(c) eluted with CHCl3 (H) and of the cyclic TPB-8(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.
Figure 4.46a-4.46c DSC thermograms of the linear TPB-9 polyethers (L), of the high molecular weight part of TPB-9(c) eluted with CHCl₃ (H) and of the cyclic TPB-9(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.
Figure 4.47a-4.47c DSC thermograms of the linear TPB-11 polyethers (L), of the high molecular weight part of TPB-11(c) eluted with CHCl₃ (H) and of the cyclic TPB-11(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.
Figure 4.48a-4.48c DSC thermograms of the linear TPB-12 polyethers (L), of the high molecular weight part of TPB-12(c) eluted with CHCl₃ (H) and of the cyclic TPB-12(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.
Figure 4.49a, b, c: DSC thermograms of the linear TPB-13 polyethers (L.), of the high molecular weight part of TPB-13(c) eluted with CHCl₃ (H) and of the cyclic TPB-13(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.
Figure 4.50a-4.50c. DSC thermograms of the linear TPB-14 polyethers (L), of the high molecular weight part of TPB-14(c) cluted with CHCl₃ (H) and of the cyclic TPB-14(c) oligomers (the numbers in the figure indicate the ring size); (a) first heating scans; (b) second heating scans; (c) first cooling scans.
Figure 4.51a-4.51c DSC thermograms of the linear TPB-18 polyethers (L), of the high molecular weight part of TPB-18(c) eluted with CHCl₃ (H) and of the cyclic TPB-18(c) oligomers (the numbers in the figure indicate the ring size): (a) first heating scans; (b) second heating scans; (c) first cooling scans.
Figure 4.52a The transition temperatures of the cyclic dimers obtained from the first heating scans versus the spacer length.
Figure 4.52b and 4.52c The transition temperatures of the cyclic dimers versus the spacer length obtained from: (b) the second heating scans; (c) the first cooling.
reasons. First, these dimers are more crystallizable and crystallize at relatively higher temperatures during cooling scans than the expected isotropic-nematic transition temperatures. Secondly, as expected from the opposite trend of isotropic-nematic transition temperature \(T_{ni}\) to glass transition temperature \(T_g\) on a spacer length, \(T_{ni}\) becomes lower than \(T_g\) at spacer length \(X=8\) and the mesophase formation is kinetically prohibited. The exhibited isotropic-nematic transitions of the dimers with even spacers increase with increasing spacer length. There is only one data point of the dimer with odd spacer \(X=13\). Although the trend is not clear, since the TPB-13(c) dimer exhibits higher transition temperature than those of the dimers with even spacers, \(T_{in}\) transition temperature of the dimers may show inverse odd-even effect compared to the odd-even effect of linear TPB-X discussed in Chapter 2. The glass transition temperature decreases with increasing spacer length as linear homologues do. During the second heating scans, most of the dimers exhibit glass transition and crystallization followed by melting. TPB-10(c) and TPB-12(c) exhibited a nematic mesophase since these dimers did not crystallize on cooling scans.

4.3.2.3.4.3. General trend of cyclic trimer

Figure 4.53a presents the phase diagram obtained from the first heating scan of the TPB-X(c) trimers while 4.53b presents the phase diagram obtained from the second heating and cooling scans of the TPB-X(c) trimers. Most trimers exhibit a nematic phase with very little tendency toward crystallization. Even on these first heating scans, only TPB-4(c), TPB-6(c), and TPB-10(c) trimers exhibit a melting peak. Upon cooling and second heating scans, all the trimers do not exhibit
Figure 4.53a and 4.53b The transition temperatures of the cyclic trimers versus the spacer length obtained from: (a) the first heating scans; (b) the second heating scans and cooling scans.
crystallization or melting transitions. TPB-4(c) trimer exhibits glass transition during first cooling and second heating scans. TPB-6(c) show a transition to a monotropic mesophase during cooling and second heating scans. This phase was hard to identify since the texture obtained on the optical polarized microscope is very fine and upon annealing crystallization occurs due to the monotropic mature. However, this may be a higher order phase than a nematic phase since the enthalpy change of this transition is much higher than the value expected from the trend presented in Figure 4.54. The nematic-isotropic transition temperature increases as the spacer length increases with slight opposite odd-even effect to that of linear TPB-X series as shown in Figure 4.53a and b. Also, the enthalpy change associated with the nematic-isotropic transition increases drastically with increasing spacer length as shown in Figure 4.54. This can be explained as follows. From the X-ray and molecular modeling results,\textsuperscript{18} in a nematic phase, the anti conformer of TPB mesogenic unit is dominant species and these are aligned parallel to each other. Therefore, the ideal conformation of a trimer to form a nematic state should contain the anti conformer of mesogenic unit which is fully aligned to one direction as shown in Scheme 4.5. The length of mesogenic unit and spacers obtained by a computer modeling are listed in Table 4.14. The minimum length of the spacer to obtain the ideal conformation in a trimer was roughly estimated by equation which was written assuming that at the minimum length the length of two mesogen and one spacer should be equal to the length of the part of two spacers (The rest of the part of spacer is needed to make a fold. The minimum number of carbons of spacers to achieve the 180° turn in the fold may be two or more, namely 2.5 Å or
Figure 4.54 The enthalpy change associated with nematic-isotropic transition of the cyclic trimers versus the spacer length obtained from second heating and cooling.
Scheme 4.5 Schematic representation of the ideal conformation of cyclic trimers to form a nematic state.

- $L_s$: Length of spacer
- $L_f$: Length of mesogen
- $2L_f' + L_f$: Length to make a fold
- $L_m$: Length of mesogen
- : Mesogenic Unit
  - Anti Conformer
- : Spacer
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*The length measured from oxygen to oxygen by Alchemy II.
longer. However, we assume here it is 2.5 Å.) and one mesogen as shown in Scheme 4.5.

\[ 2L_m + L_s = 2(L_s-2.5) + L_m \quad (4.7) \]

where \( L_m \) is the length of the mesogen while \( L_s \) is the length of the spacer (Scheme 4.5). Table 4.14 lists the length of mesogenic unit and spacers obtained by a computer modeling. From the equation 4.7 and the the length of mesogen, the minimum length of the spacer for the ideal conformation is 21 Å. Therefore, the ideal conformation is almost impossible in a cyclic trimer unless the spacer length is longer than \( X=15 \). The cyclic trimers with spacer length shorter than \( X=15 \) should have a distorted conformation from the ideal one. The extent of distortion should be dependent on the spacer length. Namely, as the spacer length increases the conformation of the trimer should approach the ideal one. Naturally, the transition temperature and the enthalpy change associated with this transition should increase with increasing spacer length. This speculative explanation is supported by the NMR analysis. As discussed in Chapter 4.3.2.2.2, the average conformation of cyclic trimers in solution changes from gauche to anti with increasing the spacer length. Even in nematic state this tendency should be reflected. Although the opposite odd-even effect can not be explained clearly at this stage, most probably the shape of molecules with even spacers somehow are further distorted from the ideal one than those with odd spacers. The some of the nematic texture observed in cyclic trimers are presented in Figure 4.55a and b.
Figure 4.55a and 4.55b The representative textures of cyclic trimers observed under optical polarized microscope (x100): (a) TPB-7(c) trimer annealed at 78.4°C for 6 min; (b) TPB-11(c) trimer annealed at 92.5°C for 0.5 min.
Another interesting feature of the cyclic trimer is that some of the trimers exhibit second phases below the nematic phase as shown in Figure 4.53a,b. Figure 4.56a and b presents the textures of TPB-14(c) trimer above and below the second transitions. Most of the textures in a second phase are characterized by the presence of striped lines. The long time annealing did not change the texture so much. X ray experiments\(^{19}\) were carried out with TPB-13(c) trimer which shows a second phases between 31 °C - 57 °C. The second phase was found to be smectic. The smectic layer spacing is 47 Å, which fits remarkably well with 3/2 times 33.5 Å extended TPB-13 monomer length in the linear TPB-13. Hence this phase is most probably a \(S_A\) phase.

The trend of second phase observed for the trimers does not seem to be consistent. TPB-14(c) and TPB-13(c) trimers show a clear second peak on heating and cooling scans of DSC as seen in Figure 4.49 and 4.50. TPB-12(c) trimer shows the similar texture change around 47 °C on cooling although DSC thermograms did not show clear peak (Figure 4.48). For TPB-11(c), TPB-10(c), and TPB-9(c) trimers, neither the change of texture nor the peak in DSC thermograms were observed (Figure 4.46, 4.36, and 4.48). The speculative explanation of the smectic phase for the trimers with longer spacers is as follows. As discussed in Chapter 2, once the spacer length gets close or exceeds the length of the mesogen, the mesogen on adjacent chain can be staggered, making a rigid molecule. Such a rigid molecule somehow prefers a smectic phase at a lower temperature. As seen in Figure 4.4, TPB-8(c) trimer shows a relatively large second peak which corresponds to the transition from a nematic to smectic phase.
Figure 4.56a and 4.56b The textures of cyclic TPB-14(c) trimers observed under cooling under optical polarized microscope (x100): (a) at 66.3°C, right above the second transition (nematic phase); (b) at 61.1°C for 1.5 min, below the second transition (smectic phase).
according to X-ray experiments. As discussed before the peak shown by TPB-6(c) during cooling and second heating scans may be due to the same phase as the second phase of TPB-8(c). However, the explanation mentioned above can not explain the smectic phase displayed by these trimers.

4.3.2.3.4.4 General trend of cyclic tetramer

Figure 4.57a presents the phase diagram obtained from the first heating scans of the TPB-X(c) tetramers while Figure 4.57b presents that from the second heating and first cooling scans of the TPB-X(c) tetramers. The cyclic tetramers exhibit a nematic phase with higher tendency toward crystallization than that of the cyclic trimers, especially with longer spacers (X > 9). During first heating scans, most of the tetramers exhibit melting or crystallization followed by melting and nematic-isotropic transition except TPB-4(c) tetramer. TPB-4(c) tetramer exhibits a monotropic nematic mesophase on cooling and second heating scans. During cooling scans, tetramers with spacer length shorter than X=13 do not show crystallization. TPB-13(c) and TPB-14(c) tetramers show small crystallization peaks close proximity of glass transitions. On second heating scans, the tetramers with spacer length shorter than X=11 do not crystallize while those with spacers above X=10 exhibit crystallization followed by melting. Apparently the longer spacer facilitated the crystallization most probably due to the increased molecular flexibility and better packing.

Unlike the trimers, the tetramers show very similar dependence of both nematic-isotropic transition temperatures and the enthalpy changes on the spacer length to
Figure 4.57a and 4.57b The transition temperatures of the cyclic tetramers versus the spacer length obtained from: (a) the first heating scans; (b) the second heating scans and cooling scans.
that of the linear TPB-10 polyethers. That is, in addition to the odd-even
dependence of $T_{ni}$ and $T_{in}$, there is a continuous decrease of the nematic-isotropic
transition temperature for the tetramers with even spacers with increasing spacer
length, and a continuous slight increase followed by slightly decrease for the
polymers containing an odd spacer. TPB-4(c) tetramer is a exception. It exhibits
lower transition temperature and the enthalpy change expected from the trend
observed for the other tetramers with even spacers. This is most probably due to the
fact that the short spacer of TPB-4(c) tetramer does not allow the proper
conformation and alignment of a mesogenic unit. The enthalpy change of the
tetramers with both even and odd spacers increases with increasing spacer length
and shows strong odd-even effect as shown in Figure 4.58. The similarity of the
phase behavior of these cyclic tetramers to those of linear homologues suggests that
there are some similarities in their structures. Although at least two spacers should
have fold to form a cyclic structure, four mesogens and two spacers can adopt
almost the same conformation as that of linear TPB-X as schematically drawn in
Scheme 4.4.

As discussed before frequently, the cyclic tetramers show higher transition
temperatures with smaller enthalpy changes than those of linear homologues as seen
in Figure 4.59a and 4.59b. Higher transition temperature is most probably due to
the lack of the chain ends and the higher rigidity of cyclic structure (lower entropy
of the structure) while the lower enthalpy change of the nematic isotropic transition
is attributed to the lower entropy of the isotropic phase of the cyclic structure.
Figure 4.58 The enthalpy change associated with the nematic-isotropic transition of the cyclic tetramers versus the spacer length obtained from second heating and cooling.
Figure 4.59a,b The comparison of the nematic-isotropic transition temperatures (a) and the enthalpy changes (b) associated with nematic-isotropic transition between the cyclic tetramers and the corresponding high molecular weight linear polymers.
Figure 4.60 presents the representative textures of the cyclic tetramers. Most of the tetramers exhibit a schlieren texture.

4.3.2.3.4.5 General trend of cyclic pentamer

The pentamers again exhibit a nematic phase with very low tendency toward crystallization. The dependences of the nematic-isotropic transition temperature and the enthalpy change on a spacer length are quite similar to those of the tetramers as indicated in Figure 4.61. The larger ring structures again allow to adopt the similar structure to those of the linear polymers. TPB-11(c) pentamer show second phase which has not been identified yet.

4.3.2.3.4.6 Some consideration of an odd-even effect of the ring size on crystallizability

As discussed above the crystallization tendency has odd even effect on a ring size. Namely, odd rings have lower tendency toward crystallization than even rings. A speculative explanation for the odd-even effect is as follows. The cyclic oligomers with an even degree of polymerization, i.e., the dimer and the tetramer, can pack in a crystalline phase containing only the anti conformer of the mesogen, while the cyclic oligomers with an odd degree of polymerization i.e., the trimer and the pentamer, require both the anti and gauche conformers of the mesogen in their structure if the spacer length is not long enough as discussed in 4.3.2.3.4.3. This last situation may generate a crystalline phase with a lower degree of order (Figure 4.62). Therefore, the cyclic oligomers with an even degree of polymerization may
Figure 4.60 The representative textures of cyclic tetramers observed under optical polarized microscope (x100): (a) TPB-8(c) tetramer annealed at 131.1°C for 1 min; (b) TPB-12(c) tetramer annealed at 108.3°C for 1.5 min.
Figure 4.61a and 4.61b The transition temperatures (a) and enthalpy changes (b) associated with nematic-isotropic transition of the cyclic pentamers versus the spacer length obtained from second heating and cooling.
Figure 4.62 A possible molecular arrangement of cyclic oligomers in a crystalline phase.
have a lower entropy in the crystalline phase and a higher melting temperature than
the cyclic oligomers with an odd degree of polymerization do. Elucidation of the
crystalline structures of these cyclic oligomers is nevertheless required in order to
confirm this speculative explanation. It is interesting that even for the case in which
the corresponding homopolymers exhibit high crystallization tendency, the odd
rings exhibit very little tendency toward crystallization. Therefore, the crystalline
phase is suppressed via cyclization to odd rings.

4.3.2.3.4.7 General trend of high molecular weight part eluted with chloroform

As discussed in the NMR part, these fractions represent the mixture of linear
and cyclic polymers. The phase behavior is summarized in Table 4.1-12 and quite
similar to that of high molecular weight linear TPB-X series except that the
transition temperatures and the enthalpy changes are slightly lower than those of
linear polymers and peaks are broader in most cases. This is due to both the mixture
nature of these fractions and their lower molecular weights.

4.3.2.4 Miscibility of cyclic oligomers with linear polymer

For low molar mass liquid crystals, miscibility rules have developed\textsuperscript{20-22} and
used to identify mesophases. The rules are following. If two liquid crystalline
phases are miscible, they are isomorphic, and therefore belong to the same type of
mesophase. If two liquid crystalline phases are immiscible, they are not
isomorphic, but still may belong to the same type of phase. To date there are few
examples where the isomorphism of polymer chains was investigated. The nematic
phases displayed by several different pairs of main-chain liquid-crystalline polymers were miscible and therefore the nematic phases of these polymers were isomorphic in some cases. In both cases investigated, the binary polymer mixtures were based on homopolymers containing either even or odd flexible spacers with small difference of their spacer lengths. However, recently, the immiscibility of homopolymers and copolymers in which the only difference is the length of flexible spacers has been reported. They found that, in the case of mixtures of homopolymers, the tendency towards isomorphism increases with the decrease of the difference between the spacer length and parity. In the case of mixtures of copolymers, the tendency towards isomorphism increases by increasing the number of flexible spacers from the copolymers.

There are several motivations for studying the miscibilities. First, the isomorphism of two different polymers in a certain liquid crystalline phase can be used to tailor-make phase transition temperatures and polymer properties. Secondly, if two polymer chains are isomorphic within a virtual mesophase, their virtual mesophase can be determined from the phase diagram of the corresponding polymer mixtures.

The miscibility study of cyclic oligomers with the corresponding linear polymers is interesting since the only structural difference is those geometries, i.e., degree of polymerization and cyclic versus linear structures.
The DSC thermograms of mixtures of 50:50 TPB-8(c) oligomers with linear TPB-8 polymer are presented in Figure 4.63, 4.64, and 4.67 with DSC thermograms of homocyclic oligomers and homolinear TPB-8. The transition temperatures and corresponding enthalpy changes are also tabulated in Table 4.15. As seen in Figure 4.63, the mixture of the cyclic tetramer and linear polymer exhibits a single peak both in second heating and cooling scans, which corresponds to isotropic-nematic transition. The peak width of the mixture is wider than that of the linear polymer but narrower than that of the cyclic tetramer. In Figure 4.64, the mixture of the cyclic trimer and linear polymer exhibits a single peak both in second heating and cooling scans although the cyclic trimer exhibits a smectic phase which disappears after mixing. The transition temperatures and the corresponding enthalpy changes for both the tetramer-linear polymer and trimer-linear polymer mixtures are plotted in Figure 4.65a and b, 4.66a and b. The lines indicate the calculated transition temperatures from the transition temperatures and the enthalpy changes of pure components by simplified Schroeder-van Laar equations. The negative deviation of the transition temperatures from the calculated values was observed for both systems. It indicates the deviation of this binary system from the ideality. Nevertheless, for both systems the glass transition temperatures and the enthalpy changes show linear dependence which suggests that the cyclic trimer and tetramer are miscible with linear polymer and the mixtures are isomorphic within a nematic phase.

In Figure 4.67a, the mixture of the cyclic dimer and linear polymer exhibits very broad glass and nematic-isotropic transitions on second heating. During
Table 4.15
Characterization of TPB-8(c) oligomers and linear TPB-8 mixtures.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Second heating</th>
<th>First cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear TPB-8 + TPB-8(c) Tetramer (50/50 Wt/ Wt)</td>
<td>g 42 n 120 (1.79) i</td>
<td>i 113 (1.77) n 40 g</td>
</tr>
<tr>
<td>TPB-8(c) Tetramer</td>
<td>g 36 n 141 (0.95) i</td>
<td>i 133 (0.84) n 31 g</td>
</tr>
<tr>
<td>Linear TPB-8 + TPB-8(c) Trimer (50/50 Wt/ Wt)</td>
<td>g 47 n 100 (1.24) i</td>
<td>i 91 (1.16) n 39 g</td>
</tr>
<tr>
<td>TPB-8(c) Trimer</td>
<td>g 43 S 69 (0.15) n 83 (0.08) i</td>
<td>i 79 (0.07) n 66 (0.15) S 37 g</td>
</tr>
<tr>
<td>Linear TPB-8 + TPB-8(c) Dimer (50/50 Wt/ Wt)</td>
<td>g 29 n 89 (1.01) i</td>
<td>i 84 n 77 (0.89a) n 27 g</td>
</tr>
<tr>
<td>TPB-8(c) Dimer</td>
<td>g 37 i 90 k 121 (4.58a) k 142 k 147 (4.41a) i</td>
<td>i 31 g</td>
</tr>
<tr>
<td>Linear TPB-8</td>
<td>g 52 n 123 (2.43) i</td>
<td>i 107 (2.45) n 43 g</td>
</tr>
</tbody>
</table>

a Overlapping peaks
Figure 4.63 DSC thermograms of TPB-8(c) tetramer, of the mixture of 50:50 TPB-8(c) tetramer and linear TPB-8 polymer, and of linear TPB-8 polymer: (a) second heating scan; (b) cooling scan.
Figure 4.64 DSC thermograms of TPB-8(c) trimer, of the mixture of 50:50 TPB-8(c) trimer and linear TPB-8 polymer, and of linear TPB-8 polymer: (a) second heating scan; (b) cooling scan.
Figure 4.65a, b The transition temperature (the line indicates the calculated value by simplified Schroeder-van Laar equations) (a) and the enthalpy change (b) of the mixtures of TPB-8(c) tetramer and linear TPB-8 polymer versus the composition.
Figure 4.66a,b The transition temperature (the line indicates the calculated value by simplified Schroeder-van Laar equations) (a) and the enthalpy change (b) of the mixtures of TPB-8(c) trimer and linear TPB-8 polymer versus the composition.
Figure 4.67 DSC thermograms of TPB-8(c) dimer, of the mixture of 50:50 TPB-8(c) dimer and linear TPB-8 polymer, and of linear TPB-8 polymer: (a) second heating scan; (b) cooling scan.
cooling scans it exhibits two peaks as seen in Figure 4.67b. Although this phase is nematic according to the optical polarized microscopic observation, this system seems to be partially miscible or immiscible.

In conclusion, the preliminary miscibility study showed that TPB-8(c) trimer and tetramer are miscible with linear TPB-8 while the dimer is partially miscible or immiscible.

4.4 CONCLUSIONS

The first example of cyclic main chain liquid crystalline oligomers were synthesized by utilizing the mesogenic unit based on conformational isomerism and high dilution conditions. The effect of dilution on the formation of cyclic oligomers was studied. The resulting reaction mixtures were separated into individual cyclic oligomers. Their cyclic nature was demonstrated by intensive 1D and 2D $^1H$-NMR spectroscopies. The chemical shifts of protons in mesogenic units are highly dependent on the ring size and these are due to the change between anti and gauche conformers depending on the ring size. From these results, it is demonstrated that the conformational isomerism of the mesogenic unit affects and contributes to the formation of cyclic oligomers. The thermal properties of these cyclic oligomers have an odd-even effect not only with the spacer length but also with the ring size. Namely, the odd rings show a low tendency toward crystallization while the even rings have a relatively high tendency toward crystallization. The nematic-isotropic temperatures and corresponding enthalpy changes of the tetramers and pentamers
with different spacer length behave similarly to those of the corresponding linear polyethers. Namely, there is an odd-even effect of the nematic-isotropic transition temperatures on the spacer length. On the other hand, the transition temperatures and the enthalpy changes of the trimers do not exhibit such an odd-even effect and increases constantly with increasing spacer length. This is most probably due to the deformed conformation of the cyclic trimers from the ideal one in which the mesogens with anti conformers are aligned parallel to each other in a cyclic molecule. This deviation is released with increasing spacer length and the transition temperature and the corresponding enthalpy change increase. Some of the trimers exhibit both nematic and smectic phases although corresponding linear polyethers do not. The most interesting result of the cyclic oligomers is that some cyclic oligomers show higher transition temperatures than those of the corresponding high molecular weight linear polymers although the enthalpy changes associated with the transition are much lower than those of the linear polymers. This can be explained by the total rigidity of cyclic molecules and lower difference between their entropy in the isotropic and liquid crystalline phases. By using this behavior, the kinetically prohibited mesophase of linear TPB-5 polyether was transformed into an enantiotropic mesophase via cyclization while the kinetically controlled mesophase of linear TPB-7 polyether was converted to a thermodynamically controlled mesophase via cyclization. It was found that the TPB-8(c) trimer and tetramer are miscible with the corresponding linear polymer.

Although numerous experiments are still requested to elucidate the mesomorphic behavior of cyclic oligomers and polymers, the experiments
described here are nevertheless opening numerous new synthetic opportunities for
cyclic liquid crystalline polymers and oligomers.

4.5. REFERENCES


19. V. Percec, M. Kawasumi and G. Ungar, to be published.


CHAPTER 5

Synthesis and Characterization of Chiral Linear and Cyclic Polyethers Based on a Laterally Substituted Semiflexible Mesogenic Unit and α,ω-Dibromoalkanes

259
5.1 INTRODUCTION

Mesomorphic chiral compounds have been drawn a considerable attention,\textsuperscript{1-3} both scientifically and technologically, because of their special physical properties such as the selective reflection of polarized light\textsuperscript{4} or ferroelectricity.\textsuperscript{5} Most of these properties come from their unique unsymmetrical or helical structures in a mesophase induced by the chirality of the molecules. In a chiral polymeric system, the chirality may be enhanced due to the helical conformation of backbone through a cooperativity effect among the chiral monomers.\textsuperscript{6-8} Also, such a helical structure has been found in chiral rigid polymers such as polyisocyanates\textsuperscript{9} and polyisocyanides.\textsuperscript{10} In the mesomorphic state of the chiral polymers a chirality is further introduced into a mesomorphic structure through the helical arrangement of polymer backbones.\textsuperscript{1}

The introduction of chiral group into nematic polymers by using either copolymerization or mixing with low or high molecular weight chiral molecules causes twisting of the nematic layer, which ends into a cholesteric phase as shown in Scheme 5.1. There have been some examples of main chain cholesteric homopolymers and copolymers composed of a mesogenic unit and a chiral flexible spacers.\textsuperscript{11-15} One of the interesting properties of cholesteric materials is that, under certain conditions, they exhibit the selective reflection of polarized light whose wave length is related to the helical pitch of the cholesteric phase. The helical pitch can be controlled by either external conditions such as temperature or structural factors such as the composition of chiral and nonchiral monomers.
Scheme 5.1 Schematic representation of the structure of cholesteric phase.

Molecules are shown as elliptical rods which stack in a single-twist structure.
The linear and cyclic polyethers based on 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxybiphenyl)butane (TPB) and α,ω-dibromoalkanes were synthesized and their phase behavior was studied and discussed in Chapter 2, 3, and 4. Most of the linear polymers and cyclic oligomers exhibit a nematic phase and some of them do not crystallize. The noncrystallizability of the cholesteric materials could be advantageous for applications such as thermosensors or display devices, since crystallization can destroy the cholesteric phase.

As mentioned in those chapters, linear and cyclic TPB-X series contain chiral center in the mesogenic unit. Therefore, since we used the racemic mesogen, the resulting polymers and oligomers contain four constitutional isomers depending on the configuration of the chiral center and the regiochemical structure (direction of TPB unit along the polymer chain). If we replace racemic TPB unit for the chiral one, we can introduce the chirality without any change of the backbone structure except the configuration, and simultaneously reduce the backbone entropy by decreasing the number of constitutional isomers from four to two. This system is interesting since the chiral center is introduced not in a flexible spacer but in a mesogenic unit and the direct comparison of the chiral polymers with the racemic polymers can be made since the only difference in those structures are the chirality. The main goal of this short chapter is to clarify the effect of the chirality on the phase behavior of linear and cyclic TPB-X series. Then, we would like to discuss the chiroptic properties of these new chiral polymers and oligomers to obtain the information of their phase structures.
5.2 EXPERIMENTAL

5.2.1 Materials

Thionyl chloride, lithium aluminum hydride (95+%), tetrabutylammonium hydrogen sulfate (TBAH) (97%), 4-methoxyphenylacetic acid (99%), (-)-cinchonidine (98%) (all from Aldrich), aluminium chloride, 48% hydrobromic acid (both from Fisher Scientific), iodoethane (Lancaster Synthesis), naphthalene (Matheson Coleman & Bell), acetic anhydride (J. T. Baker Chemical Co.) were used as received. 1,10-Dibromodecane (97%) (Aldrich) was purified by vacuum distillation. 1,12-Dibromododecane (Lancaster Synthesis) and 1,16-dibromohexadecane (Pfaltz & Bauer) were recrystallized from methanol. Tetrahydrofuran (THF) and diethyl ether were dried by refluxing over LiAlH₄ and distilled from LiAlH₄. Methylene chloride and chloroform were refluxed over CaH₂ and then distilled from CaH₂. o-Dichlorobenzene was distilled under reduced pressure. 4-Acetoxybiphenyl was synthesized by the same procedure discussed in Chapter 2. 1,14-Dibromotetradecane was synthesized as described in a previous publication. All other chemicals were commercially available and were used as received.

5.2.2 Synthesis of (R)-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane [(R)-9]
Scheme 5.2 outlines the synthesis of (R)-1-((4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl))butane.

5.2.2.1 Synthesis of 2-(4-methoxyphenyl)butanoic acid (Racemic-2)

The alkylation of 4-methoxyphenylacetic acid (1) with iodoethane was carried out according to the literature procedure.\(^{17}\) Naphthalene (55.4 g, 0.432 mol) was dissolved in 250 ml of dry THF. After the addition of sodium (10.5 g, 0.457 mol), the mixture was stirred for 8 h at room temperature under nitrogen flow. The obtained sodium naphthalide-THF solution was added carefully (exothermic) to a vigorously stirred solution of 4-methoxyphenylacetic acid (1, 31.1 g, 0.188 mol) in 250 ml of dry THF. After the solution was stirred for 3 h at room temperature, iodoethane was added dropwise via a dropping funnel over 12 min and stirred at room temperature over night. Water (90 ml) was added to the reaction mixture. Alkylated acid salt was extracted with 180 ml of 10% Na\(_2\)CO\(_3\) aqueous solution, and 400 ml of water, successively. The water layer was washed two times with 200 ml of diethyl ether followed by the acidification with hydrochloric acid. The acid was extracted with diethyl ether and dried over MgSO\(_4\). The solvent was evaporated to yield a liquid which was distilled under reduced pressure. Crystallization from hexanes yielded white crystals (28.7 g, 78.6 %): mp 66-68°C (lit.\(^{17}\) mp 51-58°C); \(^1\)H-NMR (CDCl\(_3\), TMS, \(\delta\), ppm): 0.89 (3H, \(\text{CH}_3\)-CH\(_2\)-, t, J=7.1 Hz), 1.77 and 2.08 (2H, -CH\(_2\)-, 2m), 3.40 (1H, -CH-COOH, t, J=7.1 Hz), 3.78 (3H, \(\text{CH}_3\)-O-, s), 6.86 (2H, ortho to the methoxy, d, J=8.3 Hz), 7.24 (2H, meta to the methoxy, d, J=8.2 Hz).
Scheme 5.2 Synthesis of (R)-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane.
5.2.2.2 Resolution of (S)-2-(4-methoxyphenyl)butanoic acid [(S)-2]

(S)-2-(4-Methoxyphenyl)butanoic acid [(S)-2] was resolved by the fractional recrystallization of the salts of racemic 2-(4-methoxyphenyl)butanoic acid with (-)-cinchonidine followed by the regeneration of the acid according to a literature procedure.\textsuperscript{17} 2-(4-Methoxyphenyl)butanoic acid (28.5 g, 0.147 mol) and (-)-cinchonidine (44.1 g, 0.150 mol) were dissolved in the mixture of 95 % ethanol (300 ml) and water (75 ml) and crystallized at room temperature. After filtration, 24.2 g of the fibril like crystals of the salts were obtained. The optical purity (enantio excess) monitored by the ratio of methoxy peaks (S-diastreomer, 3.70 ppm; R-diastereomer, 3.64 ppm) in \textsuperscript{1}H-NMR spectrum of the diastereomeric salt (CDCl\textsubscript{3}) was 44.8%. The rest of the salts remained in the solution was precipitated by adding a large amount of water. It was collected by the filtration. The main fraction of the salts was recrystallized from the mixture of 95 % of ethanol and water (first, 100 ml ethanol / 25 ml water; second, 50 ml ethanol / 12.5 ml water) two times to yield 8.49 g of fibril-like crystals (optical purity, 76 %). The salts recovered from the solutions were also recrystallized several times until the optical purity reached to around 77 % and combined with the main fraction. The total yield of the salt was 22.2 g (59%).

The salt was dissolved in CHCl\textsubscript{3} (600ml) and acidified with the mixture of concentrated sulfuric acid (40 ml) and water (220 ml). The organic layer was washed two times with 300 ml of water and dried over MgSO\textsubscript{4}. After the filtration followed by the evaporation of the solvents, the acid was recrystallized from hexanes to yield white crystals (7.12g, 47.6 % calculated on the (S)-acid basis;
Optical purity measured by $^1$H-NMR with (-)-cinchonidine, 89%: mp 83-86°C (lit. $^{17}$ mp 85-86°C); $^1$H-NMR (CDCl$_3$, TMS, δ, ppm): 0.89 (3H, CH$_3$-CH$_2$-, t, J=7.1 Hz), 1.77 and 2.08 (2H, -CH$_2$-, 2m), 3.40 (1H, -CH-COOH, t, J=7.1 Hz), 3.78 (3H, CH$_3$O-, s), 6.86 (2H, ortho to the methoxy, d, J=8.3 Hz), 7.24 (2H, meta to the methoxy, d, J=8.2 Hz).

5.2.2.3 Synthesis of (S)-2-(4-hydroxyphenyl)butanoic acid [(S)-3]

(S)-2-(4-Hydroxyphenyl)butanoic acid [(S)-3] was prepared by the demethylation of (S)-2-(4-methoxyphenyl)butanoic acid [(S)-2] by the same procedure described in Chapter 2. (S)-2-(4-Methoxyphenyl)butanoic acid (6.86 g, 35 mmol) was dissolved in a mixture of 48% hydrobromic acid (13.3 ml) and acetic acid (47 ml). The solution was heated to reflux for 23 h (reflux temperature, 111°C) after which the reaction mixture was cooled to room temperature and 100 ml of water was added. The product was extracted two times with 100 ml of diethylether. The ether layer was washed two times with 100 ml of water and dried over MgSO$_4$. After the evaporation of solvents, the remained solid was recrystallized from water to yield 5.17 g (82.0%) of needle-like crystals. mp 136-138°C. $^1$H-NMR (Dimethysulfoxide-d$_6$, TMS, δ, ppm): 0.81 (3H, CH$_3$-CH$_2$-, t, J=7.4 Hz), 1.58 and 1.91 (2H, -CH$_2$-, 2m), 3.24 (1H, -CH-COOH, t, J=8.1 Hz), 6.72 (2H, ortho to the hydroxy, d, J=7.9 Hz), 7.08 (2H, meta to the hydroxy, d, J=9.3 Hz), 9.24 (1H, -COOH, broad peak). The $^1$H-NMR spectrum showed that the resulting acid is free of unreacted methoxy group.

5.2.2.4 Synthesis of (S)-2-(4-acetoxyphenyl)butanoic acid [(S)-4]
(S)-2-(4-Acetoxyphenyl)butanoic acid [(S)-4] was prepared by the acetylation of (S)-2-(4-hydroxyphenyl)butanoic acid [(S)-3]. (S)-2-(4-Hydroxyphenyl)butanoic acid (5.04 g, 28 mmol), acetic anhydride (5.71 g, 56 mmol), and few drops of sulfuric acid diluted with acetic anhydride were stirred at 50°C for 1.5 h. After it was cooled to room temperature, 25 ml of water was added and the mixture was stirred over night. After the addition of 200 ml of water the product was extracted with 200 ml of diethyl ether. The ether layer was washed three times with water and dried over MgSO₄. After the evaporation of the solvent, it was crystallized from water to yield 5.40 g (86.8%) of white fine crystals. mp 64-68°C. ¹H-NMR (CDCl₃, TMS, δ, ppm): 0.92 (3H, CH₃-CH₂-, t, J=7.5 Hz), 1.79 and 2.10 (2H, -CH₂-, 2m), 2.29 (3H, CH₃CO-, s), 3.46 (1H, -CH-COOH, t, J=7.4 Hz), 7.05 (2H, ortho to the acetoxy, d, J=9.2 Hz), 7.33 (2H, meta to the acetoxy, d, J=8.5 Hz)

5.2.2.5 Synthesis of (S)-1-(4-acetoxy-4'-biphenyl)-2-(4-acetoxyphenyl)butanone[(S)-8]

The mixture of (S)-2-(4-acetoxyphenyl)butanoic acid [(S)-4, 5.33 g, 24 mmol], thionyl chloride (3.0 ml, 41 mmol), and few drops of dimethylformamide were stirred for 1.5 h at room temperature under nitrogen flow. The excess thionyl chloride was removed under reduced pressure to produce a pale yellow liquid which was used directly in the acylation reaction. 4-Acetoxybiphenyl (7, 6.11 g, 29 mmol) was dissolved in 30 ml of dry methylene chloride and cooled to below 10°C in an ice-water bath after which 11.5 g (86 mmol) of anhydrous AlCl₃ was added.
(S)-2-(4-Acetoxyphenyl)butanoic acid chloride [(S)-5] was dissolved in 30 ml of dry methylene chloride. This solution was added dropwise to the solution of 4-acetoxybiphenyl over 35 min under cooling. After the addition, the deep red solution was stirred under cooling for 50 min. It was poured into a mixture of 20 ml concentrated HCl and 60 ml ice-water. The organic layer was separated and washed two times with water, after which it was dried over anhydrous MgSO4, filtered, and the solvents were removed in a rotary evaporator to produce a viscous orange oil. The product was crystallized from diethyl ether solution and purified by silicagel column chromatography (hexanes and diethyl ether). After recrystallization from ethanol, 3.2 g (32%) of white crystals were obtained. Purity (HPLC), 98.9%. mp, 140-141°C. 1H-NMR (CDCl3, TMS, δ, ppm): 0.92 (3H, CH3-CH2-, t, J=7.4 Hz), 1.86 and 2.22 (2H, -CH2-, 2m), 2.27 (3H, CH3COO-Ph-CH-, s), 2.34 (3H, CH3COO-biphenyl, s), 4.50 (1H, -CH-, t, J=6.9 Hz), 7.04 (2H, ortho to acetoxy of the monophenyl ring, d, J=9.5Hz), 7.18 (2H, ortho to acetoxy of the biphenyl ring, d, J=8.7Hz), 7.35 (2H, meta to acetoxy of the monophenyl ring, d, J=7.6Hz), 7.59 (4H, meta to acetoxy of the biphenyl ring and meta to acyl, 2d, J=8.5 Hz), 8.04 (2H, ortho to acyl, d, J=8.6 Hz).

5.2.2.6 Synthesis of (R)-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane [(R)-9]

(R)-2 was prepared by the reduction of (S)-1-(4-acetoxy-4'-biphenyl)-2-(4-acetoxyphenyl)butanone [(S)-8] with LiAlH4/AlCl3. AlCl3 (26.7 g, 200 mmol) was placed in a 100 ml three necks flask equipped with a dropping funnel, nitrogen inlet - outlet, and magnetic stirrer, and cooled in an ice-water bath, after which 35 ml of
dry diethyl ether was added dropwise under nitrogen. LiAlH₄ (1.73 g, 46 mmol) was placed in a 250 ml three necks flask equipped with a dropping funnel, nitrogen inlet-outlet, and magnetic stirrer, and cooled in an ice-water bath. To the flask containing LiAlH₄ were added successively 25 ml dry diethyl ether, the solution of AlCl₃ diethyl ether complex, and 25 ml of dry chloroform. A solution of (S)-8 (3.17 g, 7.6 mmol) in 50 ml of dry chloroform was added dropwise to the reducing agent solution maintained at 0°C. The resulting reaction mixture was stirred at room temperature over night. To this mixture cooled by ice-water bath was added dropwise a solution of 50 ml concentrated HCl and 60 ml water. After the reaction mixture was stirred for several hours, the product was extracted with 300 ml of chloroform. The organic layer was separated, washed two times with 300 ml of water, and dried over anhydrous MgSO₄. After filtration, the solvent was evaporated to give a viscous liquid. The liquid was crystallized from toluene to yield 1.61 g (66.5 %) of white crystals. Purity (HPLC), 99.3 %, mp, premelted at 140-142°C followed by the crystallization and melting at 159-160°C. ¹H-NMR (CDCl₃, TMS, δ, ppm): 0.77 (3H, -CH₃, t, J=7.1 Hz), 1.69 (2H, CH₃-CH₂-, m), 2.68 (1H, -CH₂-, m), 2.85 (2H, Ph-CH₂-CH₂-, d of d, J=5.8 Hz and 8.3 Hz), 4.62 (1H, -CH-Ph-OH, s), 4.82 (1H, H₂O-biphenyl, s), 6.77 (2H, ortho to hydroxy of the monophenyl ring, d, J=8.5 Hz), 6.91 (2H, ortho to hydroxy of the biphenyl ring, d, J=9.3 Hz), 6.98 (2H, meta to hydroxy of the monophenyl ring, d, J=8.8 Hz), 7.09 (2H, ortho to methylene of the biphenyl ring, d, J=8.9 Hz), 7.37 (2H, meta to hydroxy of the biphenyl ring, d, J=7.7 Hz), 7.43 (2H, meta to methylene of the biphenyl ring, d, J=8.6 Hz).
5.2.3 Preparation of chiral linear polyethers (TPB*-X) based on chiral TPB* [(R)-91 and α,ω-dibromoalkanes

Scheme 5.3 outlines the synthesis of chiral linear TPB*-X polymers. The similar procedure described in Chapter 2 was used to synthesize chiral linear TPB*-X containing X (X=10,12,14, and16) methylenic units in their flexible spacers. The example of the procedure is as follows.

To a 25 ml single-neck flask equipped with a condenser and nitrogen inlet-outlet were successively added 0.159 g (0.50 mmol) of (R)-2, 1.0 ml of o-dichlorobenzene, 0.150 g (0.50 mmol) of 1,10-dibromodecane, 1.0 ml of 10 N NaOH, and 0.0679 g (0.20 mmol, 20 mol% of phenol groups) of TBAH. The ratio between the volume of o-dichlorobenzene and the total moles of monomers was maintained constant in all polymerizations. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80°C under nitrogen. After 30 min of reaction, the organic and aqueous layers were diluted with chloroform and water, respectively, and the aqueous layer was separated. The organic layer was washed with water, followed by dilute hydrochloric acid, and three times again with water. The polymer was separated by precipitation of its solution into methanol to obtain 0.226 g (98.8 %) of white fibrous precipitate. The polymer was further purified by four successive precipitations from chloroform solution first into acetone and then into methanol followed by the two precipitations from THF solution into water.
Scheme 5.3 Synthesis of chiral linear TPB*-X polymers and cyclic TPB*-10(c) oligomers based on (R)-TPB* with α,ω-dibromoalkanes.
5.2.4 Preparation of chiral cyclic oligopolyethers [TPB*-10(c)] based on chiral TPB* (R)-9 and 1,10-dibromodecane

Scheme 5.3 outlines the synthesis of TPB*-10(c) oligomers. The same procedure described in Chapter 4 was used to synthesize TPB*-10(c) oligomers. The example of the procedure is as follows.

To a 500 ml single-neck flask equipped with a condenser were successively added 0.318 g (1.00 mmol) of (R)-2, 100 ml of 10 N NaOH aqueous solution (1.0 mol), 100 ml of o-dichlorobenzene, 0.300 g (1.00 mmol) of 1,10-dibromodecane, and 0.136 g (0.40 mmol, 20 mol% of phenol groups) of TBAH. A balloon filled with nitrogen was placed at the top of the condenser. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80°C. After 40 h, the reaction mixture was diluted with water and chloroform. The organic layer was washed two times with water, with dilute hydrochloric acid, and three times with water. After the evaporation of the solvents, the product was dissolved in chloroform. To this solution silicagel was added and the chloroform was evaporated. The product absorbed on silica gel was charged on the top of a column containing silica gel and was flushed with acetone to separate the mixture of cyclic oligomers. The remaining product at the top of the column was flushed with chloroform to separate a higher molecular weight part. The mixture of cyclic oligomers was separated into about 50 fractions by silicagel column chromatography with a mixture of acetone and hexanes (1:20 v/v). Each fraction was checked by TLC [developed by a mixture of acetone and hexanes (1:15 - 1:20 v/v) and detected with a UV lamp]. The fraction containing each cyclic oligomer was collected and the solvents were evaporated on a
rotary evaporator to give a separated cyclic oligomer. The cyclic trimer, tetramer, and pentamer were further purified by repeating the column chromatography.

5.2.5 Techniques

UV spectra were recorded on Varian DMS 200 UV-VIS spectrophotometer at room temperature. CD spectra were obtained by using JASCO J-40A automatic recording spectropolarimeter at room temperature. The film samples for solid state CD measurement were prepared as follows. A sample was placed between a slide glass and thin cover slide glass and heated up to cholesteric temperature or above isotropization temperature. The thin film was obtained by pushing the cover glass without shearing. It was quenched to room temperature by contacting on a cold surface. The temperatures from which the samples were quenched are as follows. TPB*-10(c) dimer, above isotropization temperature; TPB*-10(c) trimer, 82°C; TPB*-10(c) tetramer, 108°C; TPB*-10(c) pentamer, 104°C; linear TPB*-10 polymer, about 100°C.

5.3 RESULTS AND DISCUSSIONS

5.3.1 Synthesis (R)-TPB monomer

Scheme 5.2 presents the synthesis of chiral TPB* [(R)-2]. In this scheme, all the reaction steps after the alkylation of 4-methoxyphenylacetic acid do not involve the racemization or inversion of the chiral center. Therefore, the configuration signs of the compounds change as indicated in Scheme 5.2.
Figure 5.1 presents \(^1\)H-NMR spectra of the methoxy protons of racemic and resolved 2-(4-methoxyphenyl)butanoic acid in the presence of an equal molar amount of (−)-cinchonidine in CDCl\(_3\). Since 2-(4-methoxyphenyl)butanoic acid forms a diastereomeric salt with (−)-cinchonidine in CDCl\(_3\), the protons of (S)-acid and (R)-acid have different chemical shifts. Therefore, optical purity can be monitored by using the intensity of the methoxy protons of the acids as shown in Figure 5.1. Three times successive recrystallization of the salt of 2-(4-methoxyphenyl)butanoic acid with (−)-cinchonidine followed by the acidification yielded (S)-2-(4-methoxyphenyl)butanoic acid with 89 % optical purity (Figure 5.1). Although the optical purity can be increased further by increasing the recrystallization time, the yield becomes much lower. At the acylation step, when 4-methoxy compounds were used instead of (S)-2-(4-acetoxyphenyl)butanoic and 4-acetoxybiphenyl, the conversion to the desired product was very low according to the \(^1\)H-NMR of the reaction mixture. This is most probably due to the occurrence of the acylation on the ortho positions to the methoxy groups of the phenyl rings and the biphenyl rings since those positions are activated by the methoxy groups which are an electron donating group. Therefore, acetoxy compounds were used in this case.

### 5.3.2 Characterization of chiral linear TPB*-X and cyclic TPB*-10(c) oligomers

Scheme 5.3 presents the linear polymerization and cyclization of (R)-TPB* with \(\alpha,\alpha\)-dibromoalkanes. As indicated in the scheme, both linear polymers and cyclic oligomers mostly contain two (R)-constitutional isomers with minor amount of two
Figure 5.1a,b 200 MHz $^1$H-NMR spectra of the methoxy protons of 2-(4-methoxyphenyl)butanoic acid in the presence of the equal molar amount of (-)-cinchonidine in CDCl$_3$: (a) racemic 2-(4-methoxyphenyl)butanoic acid; (b) resolved (R)-2-(4-methoxyphenyl)butanoic acid.
(S)-constitutional isomers. Therefore, the entropy of the backbone should be less than that of racemic polymers.

All the characterization results of TPB*-X and TPB*-X(c) oligomers were presented in Table 5.1 and 5.2, respectively. The resulting chiral linear polymers and cyclic oligomers are soluble in conventional solvents such as chloroform, THF, dioxane, and methylene chloride. No difference in solubility between racemic compounds and chiral compounds was observed. The molecular weights of TPB*-X were more than 24,000 and are comparable with the molecular weights of racemic polymers (30,200-42,600) discussed in Chapter 2.

Figure 5.2 presents GPC chromatograms of chiral cyclic oligomers. The purity of each cyclic oligomer is higher than 92%. The ring size assignments were performed based on the molecular weight obtained by GPC. Figure 5.3 presents the ¹H-NMR spectra of cyclic oligomers and of the high molecular weight part eluted with CHCl₃. No differences were detected compared to those of racemic cyclic oligomers which was discussed in Chapter 4. These spectra proved the cyclic nature of these oligomers since no terminal groups are present in the spectra except that of high molecular weight part eluted with chloroform and the chemical shifts are dependent on the ring size. Detailed discussion of the chemical shift dependence on a ring size has been already made in Chapter 4. The higher molecular weight part eluted with chloroform represents the mixture of cyclic and linear polymers and contains 41 mol% of cyclic polymers according to the same analysis of ¹H-NMR spectrum described in Chapter 4.
Table 5.1
Characterization of chiral polyethers based on chiral TPB and α,ω-dibromoalkanes (TPB-X) with different number of methylenic units (X).

<table>
<thead>
<tr>
<th>X</th>
<th>Yield (%)</th>
<th>(Mn)GPC</th>
<th>(Mw/Mn)GPC</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mru) in parentheses</th>
</tr>
</thead>
</table>
| TPB*-10 | 98.8     | 29400   | 1.98       | Heating: 197 (2.59) ch 36 g  
         |           |         |            | Cooling: 197 (2.59) ch 36 g |
| TPB*-12 | 97.5     | 31800   | 2.08       | Heating: 189 (2.70) ch 31 g  
         |           |         |            | Cooling: 189 (2.70) ch 31 g |
| TPB*-14 | 91.0     | 24600   | 2.26       | Heating: 183 (2.94) ch 38 (1.37) k 46 g  
         |           |         |            | Cooling: 183 (2.94) ch 38 (1.37) k 46 g |
| TPB*-16 | 91.7     | 27600   | 2.10       | Heating: 179 ch 70 (6.36b) k 48 g  
         |           |         |            | Cooling: 179 ch 70 (6.36b) k 48 g |

*a Data from first heating scan*
Table 5.2
Characterization of chiral TPB*-10(c) oligomers based on TPB* and 1-10-dibromodecane.

<table>
<thead>
<tr>
<th>The ring size</th>
<th>Yield (%)</th>
<th>Purity (%)</th>
<th>MW by GPC (g)</th>
<th>Thermal transitions (°C) and corresponding enthalpy changes Kcal/mr in parentheses^a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td>Heating</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6.5</td>
<td>98.5</td>
<td>566</td>
<td>457</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g &lt; -10 i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>i &lt; -10 g</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>95.9</td>
<td>1211</td>
<td>913</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 50 k 63 k 79(-0.95^b) k 114</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(4.56) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 24 ch 43 (0.13) l 75 (-0.36) k</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>110 k 125 (0.36^b) i</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>94.9</td>
<td>1858</td>
<td>1370</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>g 37 ch 94 (0.33) i</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 34 ch 94 (0.34) i</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
<td>92.4</td>
<td>2556</td>
<td>1827</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 37 k 64 k 83 (-2.13^b) k 130</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(3.25) i</td>
</tr>
<tr>
<td>5</td>
<td>0.7</td>
<td>93.4</td>
<td>3027</td>
<td>2283</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 42 ch 124 (1.28) i</td>
</tr>
<tr>
<td>CHCl_3</td>
<td>25.4</td>
<td>41^c</td>
<td>Mn=8.81 x 10^3</td>
<td></td>
</tr>
<tr>
<td>eluted part</td>
<td></td>
<td></td>
<td></td>
<td>g 49 ch 54 (-0.41) ch 105 (2.48) l</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mw/Mn=1.68</td>
<td>g 39 ch 105 (2.39) i</td>
</tr>
</tbody>
</table>

^aData on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.
^bOverslapped peaks. ^cMole% of cyclic polymers.
Figure 5.2 GPC chromatograms of the reaction mixtures, of high molecular weight part eluted with CHCl₃, and of separated chiral cyclic oligomers [TPB*-10(c)].
Figure 5.3a-5.3f 200 MHz $^1$H-NMR spectra of chiral cyclic TPB$^+$-10(c) series:
(a) CHCl$_3$ eluted part; (b) cyclic pentamer; (c) cyclic tetramer; (d) cyclic trimer; (e) cyclic dimer; (f) cyclic monomer (CDCl$_3$, TMS).
5.3.3 The comparison of phase behavior between racemic and chiral compounds

The DSC thermograms obtained from the first heating, second heating and first cooling scans of TPB*-10, TPB*-12, TPB*-14, and TPB*-16 are compared with those of the corresponding racemic TPB-X in Figure 5.4a, 5.4b, and 5.4c, respectively. Also the data obtained by DSC for chiral polymers are tabulated in Table 5.1. As discussed in Chapter 2 and seen in Figure 5.4a, 5.4b, and 5.4c, racemic TPB-10 shows a noncrystallizable enantiotropic nematic phase during its cooling and second heating scans. The crystallizability of TPB-X increases with increasing spacer length and TPB-16 exhibits only a monotropic nematic phase. Therefore, the effect of chirality of the mesogenic unit can be seen on both nematic and crystalline phases. As clearly seen from these DSC thermograms and Table 5.1, there are no differences of phase behavior between the chiral and racemic TPB-X series not only in the nematic phase but also in the crystalline phase. This results indicate that the effect of chirality of TPB is subtle on the phase behavior due to the absence of chiral recognition in racemic TPB-X although the phase must be cholesteric rather than nematic.

The DSC thermograms obtained from the first heating, second heating and cooling scans of TPB*-10(c) oligomers are compared with those of the corresponding racemic TPB-10(c) oligomers in Figure 5.5a, 5.5b, and 5.5c. Also the data obtained by DSC are tabulated with the yields and GPC results in Table 5.2. Again, there are slight differences between chiral and racemic TPB-10(c) oligomers. The differences are as follows. First, the melting temperature (130 °C)
Figure 5.4a The comparison of DSC thermograms of chiral linear TPB*-X polymers with those of racemic TPB-X polymers obtained from the first heating scan.
Figure 5.4b The comparison of DSC thermograms of chiral linear TPB*-X polymers with those of racemic TPB-X polymers obtained from the second heating scan.
Figure 5.4c The comparison of DSC thermograms of chiral linear TPB*-X polymers with those of racemic TPB-X polymers obtained from the first cooling scan.
Figure 5.5a The comparison of DSC thermograms of chiral cyclic TPB*-10(c) oligomers with those of racemic cyclic TPB-10(c) oligomers obtained from the first heating scan (Numbers in the figure indicate the ring size. H indicates the part eluted with CHCl₃.).
Figure 5.5b The comparison of DSC thermograms of chiral cyclic TPB*-10(c) oligomers with those of racemic cyclic TPB-10(c) oligomers obtained from the second heating scan (Numbers in the figure indicate the ring size. H indicates the part eluted with CHCl₃.).
Figure 5.5c: The comparison of DSC thermograms of chiral cyclic TPB*-10(c) oligomers with those of racemic cyclic TPB-10(c) oligomers obtained from the cooling scan (Numbers in the figure indicate the ring size. H indicates the part eluted with CHCl₃.).
of the chiral tetramer is higher than that of the racemic tetramer (120 °C) while the isotropization temperatures (128 °C) are equal. Consequently, the mesophase of chiral tetramer is transformed from an enantiotropic mesophase of racemic TPB-10(c) tetramer into a monotropic mesophase. Secondly, the enthalpy changes of the isotropization of the chiral tetramers and pentamers are slightly higher than those of the corresponding racemic oligomers. The second heating scan of the chiral dimer exhibits crystallization after the isotropization while the racemic dimer did not. This slight increased crystallizability may be attributed to the decrease in the entropy of the backbone.

Although the DSC thermograms between the chiral and racemic oligomers are not very different, the textures and appearances are quite different for some oligomers. The thin film obtained from the chiral trimer is transparent and displays the strong reflection of purple color at the temperature of the cholesteric phase (the color changes slightly depending on the temperature. Near isotropization temperature, it is purple. It changes to blue upon cooling.). The color can be retained even after cooling to room temperature and no color change was observed for more than three months. Also, the chiral dimer displays the reflection of slight blue color when the thin film was prepared by quenching from its isotropic melt. The reflection of color should be attributed to the cholesteric structure. Therefore, the helical pitch of the cholesteric phase is close to the wavelength of visible light. The chiral tetramer and pentamer did not show such a strong cholesteric color.
Figure 5.6 compares the textures between the chiral cyclic tetramer and the racemic tetramer. The chiral tetramer displays a simple focal conic texture while the racemic tetramer exhibits a schlieren texture. The simple focal conic texture indicates that the phase of the chiral tetramer is either cholesteric or smectic A. However, the transition temperature and the enthalpy change of the chiral tetramer was similar to that of the racemic tetramer whose phase is nematic. Therefore, this simple focal conic texture is most probably attributed to a cholesteric structure since the smectic-isotropic phase transition should be accompanied by a much higher enthalpy change. The focal conic texture of cholesteric phase is generally obtained when the cholesteric phase is strongly twisted (the helical pitch of cholesteric phase is very short). This is consistent with the fact that the chiral tetramer does not display a reflection of color. The chiral pentamer exhibits the focal conic texture as indicated in Figure 5.7. Again, this should be a cholesteric phase with strong twist. On the other hand, the chiral cyclic dimer and trimer do not exhibit such a texture as shown in Figure 5.8. It is obvious that the helical pitch of the chiral cyclic oligomers is highly dependent on the ring size. The linear TPB*-10 polymer exhibits only a schlieren texture which is quite similar to that of the racemic TPB-10 polymer. A reflection of slight blue light was observed for the TPB*-10 polymer only when it was prepared by quenching from the isotropic melt.

Figure 5.9 presents the UV and CD spectra of the dioxane solutions of the (R)-TPB*, TPB*-10(c) oligomers, and TPB*-10 polymers. The UV spectra of all the compounds are characterized by the presence of strong absorption bands at 213-219 nm (A1) and 265-268 nm (A2). The A1 band is ascribed to the π-π* electronic
Figure 5.6a and 5.6b The comparison of the textures of chiral cyclic TPB*-10(c) tetramer with racemic cyclic TPB-10(c) tetramer observed under optical polarized microscope (x100): (a) schlieren nematic texture of racemic tetramer after annealing at 115.9°C for 3 min; (b) focal conic cholesteric texture of chiral tetramer after annealing at 114.3°C upon heating.
Figure 5.7 The texture of chiral cyclic TPB*-10(c) pentamer observed under optical polarized microscope (x100) (annealing at 111.4°C for 2 min).
Figure 5.8a and 5.8b The textures of chiral cyclic TPB*-10(c) dimer and trimer observed under optical polarized microscope (x100): (a) the cyclic dimer quenched from isotopic melt; (b) the cyclic trimer after annealing at 86°C for 2 min.
Figure 5.9 UV and CD spectra of the dioxane solutions of the (R)-TPB\(^*\), the chiral TPB\(^*\)-10(c) oligomers, and chiral linear TPB\(^*\)-10 polymer.
transition of the monophenyl ring in the mesogen while the A2 peak is due to the \( \pi- \pi^* \) electronic transition of the biphenyl ring. All the chiral TPB monomer, cyclic oligomers, and linear polymers show negative CD signals around 260 nm which is close to the UV absorption maxima of the A2 peaks as shown in Figure 5.9. Also there is a small shoulder besides the main peak. The presence of CD signals clearly indicates that the aromatic groups in a mesogens are located in a chirally perturbed environment. However, the CD spectra do not change so much with changing the ring size or architecture except the cyclic monomer which does not have a little shoulder besides the main peak.

Figure 5.10 shows the CD spectra of the films of chiral TPB*-10(c) oligomers and chiral linear TPB*-10 polymers on a cover glass. The glass itself has UV absorbance below 315 nm. Therefore, these results are reliable only above 315 nm. The samples were prepared by quenching from the cholesteric state without shearing. The film was rotated around the axis parallel to the incident light and no change in spectra was observed. The cyclic dimer and trimer exhibit very strong and broad CD signal with peak maxima at 330-340 nm. These peaks were not observed in the CD spectrum of the solutions. Therefore, these are due to the induced chirality in the supermolecular structure, of the cholesteric phase. On the other hand, the cyclic tetramer and pentamer exhibit a very weak CD signal above 315 nm (The CD spectra of the tetramer and pentamer were obtained with much thicker films than those of the dimer and trimer. Also the spectra of the tetramer and pentamer are more expanded. Therefore, the peaks for the tetramer and pentamer are exaggerated in Figure 5.10.). As discussed above, if the tetramer and pentamer
Figure 5.10 CD spectra of the films of chiral TPB*-10(c) oligomers and chiral linear TPB*-10 polymer on a cover glass (The films of the tetramer and pentamer are much thicker than those of the dimer, trimer, and linear polymer. Also the y-axis is more expanded for the tetramer and pentamer.).
have very high twist in its cholesteric structure, this result is quite reasonable since the main CD signals should exist far below the measured region. On the other hand, the linear polymer exhibits very broad negative CD signal with peak maximum at 430 nm.

Although in solution state the chirality of the cyclic oligomers and linear polymers is not so different according to the CD experiments, in the solid state, the drastic change in the helical pitch, i.e., chirality, of mesophase was observed according to the texture observation and CD spectra. These observations strongly suggest that the cyclic tetramer and pentamer have an enhanced chirality of their structure in the mesomorphoric state compared to those of the dimer, trimer and the linear polymer. The speculative structure of the tetramer and pentamer may be a supercoiled structure of molecules (Scheme 5.4) which is similar to the structure observed in cyclic DNA.\textsuperscript{19} The supercoiled structure itself has a higher chirality due to the secondary coiled structure and may cause strong twist of the mesophase, namely the cholesteric phase with a strong twist. Elucidation of such a structure of these cyclic oligomers is required in order to confirm this speculative explanation.

5.4 CONCLUSIONS

Chiral linear TPB*-X polymers and cyclic TPB*-10(c) oligomers were synthesized. These chiral polymers and oligomers exhibit almost similar DSC thermograms with those of the racemic polymers and oligomers. The cyclic dimer
Scheme 5.4 Supercoiled structure of chiral TPB*-10(c) tetramer and pentamer.
and trimer display selective reflections of polarized light. It was suggested that the chirality of the mesophase is highly dependent on the ring size and architecture of molecules from the observation of the textures and the results of solid state CD experiments. Based on these results a supercoiled structure was proposed for the cyclic tetramer and pentamer.

5.5 REFERENCES


CHAPTER 6

Synthesis and Characterization

of

Thermotropic Liquid Crystalline Dendritic Polyethers
6.1 INTRODUCTION

In the last decade there has been an increased interest in the synthesis and characterization of polymers exhibiting complex architectures. Such a novel class of macromolecules was provided by dendrimers or hyperbranched polymers, i.e., polymers containing a branching point in each structural unit.1-12 Dendrimers display a spherical or a tree-like architecture and are not expected to display liquid crystallinity. For example dendritic aromatic polyesters,7c,11b polyphenylenes6,11a and polybenzyl ethers7a,b were reported and they do not exhibit liquid crystallinity although their linear homologues do. A dendrimer was used as solvent to generate a nonaqueous lamellar liquid crystal from octanoic acid.13 A lyotropic liquid crystalline dendritic aromatic polyamide was prepared in parallel with our work reported here.14

Two major synthetic approaches,1b i.e., a controlled step growth approach1a,3a,7e and uncontrolled chain growth approach,6,7d have been employed to construct dendritic architecture. The controlled step growth approach generally involves iterative reaction sequence (deprotection, propagation, etc.) with purification at each step. Such a procedure is tedious and time consuming although it allows the precise control of the structure. On the other hand, uncontrolled chain growth approach, in which the polymerization of \( \text{AB}_n \) type multifunctional monomer leads to the hyperbranched structure, can overcome the shortcomings of the former approach.
This chapter will present the synthesis and characterization of the first thermotropic liquid crystalline dendrimer. Its synthesis was accomplished by the phase transfer catalyzed polyetherification of trifunctional AB$_2$ type monomers, 10-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (TPD-b) and 6-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)hexane (TPH-b). These monomers represent mesogenic units based on conformational isomerism. The phase behavior of the resulting dendrimers with different chain ends (TPD-b-X and TPH-b-X, whose X indicates the structure of the chain end) was studied and compared to that of those linear model compounds synthesized by the polyetherification of 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (TPD) with 1,8-dibromooctane (TPD-8) which was described in Chapter 2.

6.2 EXPERIMENTAL

6.2.1 Materials

Boron tribromide (1.0M in CH$_2$Cl$_2$), thionyl chloride, lithium aluminum hydride (95+%), dimethyl sulfate (99%), triphenyl phosphine (99%), tetrabutylammonium hydrogen sulfate (TBAH) (97%), 4-methoxyphenylacetic acid (99%), 8-bromooctanoic acid (97%), benzyl chloride (97%), 1-bromohexane (98%), 1-bromooctane (99%), 4-phenylphenol (98%) (all from Aldrich), aluminium chloride, bromine, sodium thiosulfate, trifluoroacetic acid (all from Fisher Scientific), 1-bromobutane (Pfaltz &Bauer), sodium iodide (Matheson Coleman & Bell) were used as received. Diethyl ether was dried by refluxing over
LiAlH₄ followed by distillation. Methylene chloride was refluxed over CaH₂ and then distilled from CaH₂. o-Dichlorobenzene was distilled under reduced pressure. Dimethylformamide was dried over calcium hydride and distilled under reduced pressure. All other chemicals were commercially available and were used as received.

6.2.2 Synthesis of 10-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (13, TPD-b)

Scheme 6.1 outlines the synthesis of TPD-b (13).

6.2.2.1 Synthesis of 4-methoxybiphenyl (2)

4-Methoxybiphenyl (2) was prepared by the methylation of 4-phenylphenol (1). 4-Phenylphenol (1) (68.0 g, 0.40 mol) was dissolved in a sodium hydroxide (16.0 g, 0.40 mol)-water (240 ml) solution in a 500 ml Erlenmeyer flask equipped with a magnetic stirrer at 80°C. Dimethyl sulfate (53.0 g, 0.82 mmol) was added to this solution slowly via a syringe and the reaction mixture was stirred for 15 min. It was cooled to room temperature to give a solid. The solid was washed with 10% sodium hydroxide water solution and water, and recrystallized from 95% ethanol to give 58.8 g (79.8%) of white crystals. Purity (HPLC), >99%. mp, 86-88°C. ¹H-NMR (CDCl₃, TMS, δ, ppm): 3.84 (3H, CH₃-, s), 6.98 (2H, ortho to methoxy of the substituted phenyl ring, d, J=9.1Hz), 7.30-7.57 (7H, 5H of the unsubstituted phenyl ring and 2H meta to methoxy of the substituted phenyl ring, m).
Scheme 6.1 Synthesis of 10-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (TPD-b).
6.2.2.2 Synthesis of 1-(4-methoxy-4'-biphenyl)-2-(4-methoxyphenyl)ethanone (5)

4-Methoxyphenylacetic acid (2) (33.2 g, 0.20 mol), thionyl chloride (17.5 ml, 0.24 mol), and few drops of DMF were placed in a 250 ml three necks flask equipped with a nitrogen inlet-outlet and magnetic stirrer, and the mixture was stirred for 4 h. The excess thionyl chloride was removed under reduced pressure to produce a pale yellow liquid which was used directly in the acylation reaction. 4-Methoxybiphenyl (2) (40.0 g, 0.22 mol) was dissolved in 300 ml of dry methylene chloride in a 1 l three necks flask equipped with a nitrogen inlet-outlet, thermometer, dropping funnel, and magnetic stirrer. The solution was cooled to below 10°C in an ice-water bath after which 82.7 g (0.62 mol) of anhydrous AlCl₃ was added. 4-Methoxyphenylacetyl chloride (4) was dissolved in 200 ml of dry methylene chloride. This solution was added dropwise to the solution of 4-methoxybiphenyl so that the reaction temperature did not rise above 10°C. After the addition, the solution was stirred below 10°C for 5.5 h. It was poured into a mixture of 100 ml concentrated HCl, 600 ml ice-water, and 300 ml of chloroform. The resulting compound was not very soluble in the organic layer. The organic solvents were evaporated on a rotary evaporator. The obtained solid was separated and washed twice each time with 1.5 l of water. It was dried, recrystallized first from chloroform, and subsequently from toluene, and dried to yield 26.1 g (39.3%) of fine crystals. The product was recovered from chloroform solution, and recrystallized first from chloroform, and then from toluene to yield 8.70 g of crystals. The combined yield was 34.8 g (52.3 %). Purity (HPLC), 98 %. mp, 197-199°C. ¹H-NMR (CDCl₃, TMS, δ, ppm): 3.80 (3H, CH₃O-monophenyl, s), 3.86 (3H, CH₃O-biphenyl, s), 4.24 (2H, -CH₂-, s), 6.88 (2H, ortho to methoxy
of the monophenyl ring, d, $J=9.3\text{Hz}$), 7.00 (2H, ortho to methoxy of the biphenyl ring, d, $J=9.3\text{Hz}$), 7.22 (2H, meta to methoxy of the monophenyl ring, d, $J=7.4\text{Hz}$), 7.58 (2H, meta to methoxy of the biphenyl ring, d, $J=9.3\text{Hz}$), 7.64 (2H meta to acyl, d, $J=7.9\text{Hz}$), 8.06 (2H, ortho to acyl, d, $J=7.9\text{Hz}$).

6.2.2.3 Synthesis of 8-bromoocutan-1-ol (8)

8-Bromoocutan-1-ol (8) was synthesized by the esterification of 8-bromoocutanoic acid (6) with ethanol followed by the reduction of the resulted ethylester (7) with LiAlH₄/AlCl₃. 8-Bromoocutanoic acid (6) (27.0 g, 0.121 mol) was dissolved in absolute ethanol (180 ml) in a 1 neck flask equipped with a reflux condenser and magnetic stirrer. Few drops of sulfuric acid were added and the solution was refluxed for 21 h. The reaction mixture was cooled to room temperature and the ethanol was evaporated on a rotary evaporator to give an orange liquid. This liquid was mixed with diethyl ether and the resulting solution was washed with water, 10 \% NaHCO₃ water solution, and water three times and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to give the ester (7) as a liquid. The ester (7) was reduced without further purification. $^1$H-NMR spectrum showed the complete esterification. $^1$H-NMR (CDCl₃, TMS, δ, ppm): 1.25 (3H, CH₃CH₂O-, t, $J=6.9\text{Hz}$), 1.33 (6H, -(CH₂)₃-(CH₂)₂-Br, m), 1.63 (2H, Et-OCO-CH₂-CH₂-, m), 1.85 (2H, -CH₂-CH₂-Br, m), 2.29 (2H, Et-OCO-CH₂-, t, $J=7.4\text{Hz}$), 3.41 (2H, -CH₂-Br, t, $J=7.1\text{Hz}$), 4.13 (2H, CH₃-CH₂-O-, q, $J=7.2\text{Hz}$).

AlCl₃ (32.3g, 0.242 mol) was placed in a 250 ml three necks flask equipped with a dropping funnel, nitrogen inlet-outlet, and magnetic stirrer, and cooled in an
ice-water bath, after which dry diethyl ether was added dropwise under nitrogen. LiAlH₄ (9.2 g, 0.24 mol) was placed in a 1 l three necks flask equipped with a dropping funnel, nitrogen inlet-outlet, and magnetic stirrer, and cooled in an ice-water bath. To the flask containing LiAlH₄ were added successively 120 ml dry diethyl ether and the solution of AlCl₃ diethyl ether complex. A solution of Z (30.4 g, 0.121 mol) in 120 ml of dry diethyl ether was added dropwise to the reducing agent solution maintained at 0°C. The resulting reaction mixture was stirred at room temperature for 16 h. It was cooled by an ice-water bath and to this mixture was added successively a mixture of 40 ml methanol and 40 ml diethyl ether and a mixture of 100 ml concentrated HCl and 120 ml water. After the mixture was stirred for several hours, 300 ml diethyl ether and 300 ml water were added. The organic layer was separated, washed three times with 300 ml of water, and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to yield 21.4 g (84.6%) of the alcohol (8) as a liquid. ¹H-NMR (CDCl₃, TMS, δ, ppm): 1.34 (8H, -(CH₂)₄-(CH₂)₂-Br, m), 1.55 (2H, HO-CH₂-CH₂-, m), 1.85 (2H, -CH₂-CH₂-Br, m), 2.38 (1H, HO-CH₂-, s), 3.41 (2H, -CH₂-Br, t, J=6.5Hz), 3.61 (2H, HO-CH₂-, t, J=7.0Hz).

6.2.2.4 Synthesis of 8-iodooctan-1-ol (9)

8-Bromoocutan-1-ol (8) (21.4 g, 0.102 mol) and anhydrous sodium iodide (45.9 g, 0.306 mol) were dissolved in acetone (250 ml) in a 500 ml one neck flask equipped with a condenser and magnetic stirrer. The reaction mixture was stirred at room temperature for 66 h. Then the solvent was evaporated. The obtained reaction mixture was extracted with 200 ml of diethyl ether and 200 ml of water. The
organic layer was washed three times with water and dried over anhydrous magnesium sulfate. The solvent was evaporated to give a brown liquid which was purified by silica gel column chromatography with a mixture of diethyl ether and hexanes (1:2 v/v) as a eluent to yield 23.0 g (88.2%) of a colorless liquid. \(^1\)H-NMR (CDCl\(_3\), TMS, 8, ppm): 1.34 (8H, -(CH\(_2\))\(_4\)-(CH\(_2\))\(_2\)-I, m), 1.56 (2H, HO-CH\(_2\)-CH\(_2\)I, m), 1.59 (1H, HO-CH\(_2\)-I, s), 1.82 (2H, -CH\(_2\)-CH\(_2\)-I, m), 3.19 (2H, -CH\(_2\)-I, t, J=7.4Hz), 3.64 (2H, HO-CH\(_2\)-I, t, J=6.4Hz).

6.2.2.5 Synthesis of 10-hydroxy-1-(4-methoxy-4'-biphenyl)-2-(4-methoxyphenyl)decanone (10)

1-(4-Methoxy-4'-biphenyl)-2-(4-methoxyphenyl)ethanone (5) (26.1 g, 79 mmol), toluene (280 ml), 8-iodooctanol (9) (22.2 g, 86 mmol), tetrabutylammonium hydrogen sulfate (1.34 g, 3.9 mmol), and 50 % (wt/wt) sodium hydroxide-water solution (280 ml) were placed in a 1 l three necks flask equipped with a reflux condenser and magnetic stirrer. A balloon filled with N\(_2\) was placed at the top of the reflux condenser. The reaction mixture was stirred vigorously at 60°C for 4 h. During the reaction the color of the solution changed from yellow to orange. The organic and aqueous layers were diluted with 600 ml of water and 300 ml of chloroform, respectively, after which the organic layer was separated and washed with 300 ml of water. To this organic layer was added a mixture of 200 ml concentrated HCl and 400 ml water. The mixture was stirred for 2 h and the organic layer was separated, washed with 600 ml of water twice, and dried over anhydrous magnesium sulfate. After filtration, the solvents were removed in a rotary evaporator to give a solid which was dissolved in methanol at
reflux temperature. The insoluble part, which was the ketone (5) converted from the O-alkylated product by the acid, was removed by filtration and the solution was put in a refrigerator to give white crystals. These crystals were recrystallized from 95 % ethanol to yield 13.4 g (36.9 %) of white crystals. The product was recovered from the ethanol solution and recrystallized from ethanol to give 7.9 g of crystals as a second crop. The combined yield was 21.4 g (58.8 %). Purity (HPLC), 98%. m.p., 78-80°C. 1H-NMR (CDCl₃, TMS, δ, ppm): 1.28 (10H, -(CH₂)₅-CH₂-CH₂-OH, m), 1.53 (2H, -CH₂-CH₂-OH, m), 1.79 and 2.13 (2H, CO-CH-CH₂-, 2m), 3.62 (2H, -CH₂-OH, t, J=6.7Hz), 3.75 and 3.84 (6H, CH₃O-monophenyl and CH₃O-biphenyl, 2s), 4.51 (1H, -CO-CH-, t, J=7.4Hz), 6.84 (2H, ortho to methoxy of the monophenyl ring, d, J=8.3Hz), 6.97 (2H, ortho to methoxy of the biphenyl ring, d, J=8.9Hz), 7.25 (2H, meta to methoxy of the monophenyl ring, d, J=8.8Hz), 7.53 (2H, meta to methoxy of the biphenyl ring, d, J=9.3Hz), 7.57 (2H, meta to acyl of the biphenyl ring, d, J=8.0Hz), 8.02 (2H, ortho to acyl of the biphenyl ring, d, J=8.3Hz).

6.2.2.6 Synthesis of 10-hydroxy-1-(4-methoxy-4'-biphenyl)-2-(4-methoxyphenyl)decane (11)

11 was prepared by the reduction of 10-hydroxy-1-(4-methoxy-4'-biphenyl)-2-(4-methoxyphenyl)decanone (10) with LiAlH₄/AlCl₃. AlCl₃ (33.3g, 0.25 mol) was placed in a 250 ml three necks flask equipped with a dropping funnel, nitrogen inlet-outlet, and magnetic stirrer, and cooled in an ice-water bath, after which dry diethyl ether was added dropwise under nitrogen. LiAlH₄ (1.63 g, 43 mmol) was placed in a 250 ml three necks flask equipped with a dropping funnel, nitrogen
inlet-outlet, and magnetic stirrer, and cooled in an ice-water bath. To the flask containing LiAlH₄ were added successively 60 ml dry diethyl ether, the solution of AlCl₃ diethyl ether complex, and 60 ml of dry chloroform. A solution of 10 (11.5 g, 25 mmol) in 60 ml of dry chloroform was added dropwise to the reducing agent solution maintained at 0°C. The resulting reaction mixture was stirred at room temperature for 12 h. The reaction mixture was cooled with an ice-water bath and a mixture of 80 ml concentrated HCl and 100 ml water was added dropwise. After the mixture was stirred for 5 h, the organic layer was separated and washed two times with 200 ml of water, and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to give a colorless liquid. The liquid was purified by the flush column chromatography with chloroform as a eluent and silicagel as a stationary phase. The obtained liquid crystallized on standing. Purity (HPLC), 99 %. mp, 56-59°C. ¹H-NMR (CDCl₃, TMS, δ, ppm): 1.20 (10H, -(CH₂)₅-CH₂-CH₂-OH, m), 1.51 (4H, -CH₂-CH₂-OH and biphenyl-CH₂-CH-CH₂-, m), 3.62 (2H, -CH₂-OH, t, J=6.7Hz), 2.78 (1H, -CH-monophenyl, m), 2.86 (2H, biphenyl-CH₂-CH-, d, J=5.8 Hz), 3.60 (2H, -CH₂-OH, t, J=6.7Hz), 3.79 and 3.84 (6H, CH₃O-monophenyl and CH₃O-biphenyl, 2s), 6.82 (2H, ortho to methoxy of the monophenyl ring, d, J=8.9Hz), 6.96 (2H, ortho to methoxy of the biphenyl ring, d, J=9.3Hz), 7.05 (2H, meta to methoxy of the monophenyl ring, d, J=9.9Hz), 7.06 (2H, ortho to methylene of the biphenyl ring, d, J=7.9Hz), 7.40 (2H, meta to methylene of the biphenyl ring, d, J=8.0Hz), 7.50 (2H, meta to methoxy of the biphenyl ring, d, J=9.2Hz). The ¹H-NMR spectrum showed that 11 is free of unreacted ketone 10.
6.2.2.7 Synthesis of 10-bromo-1-(4-methoxy-4'-biphenyl)-2-(4-methoxyphenyl)decane (12)

Triphenyl phosphine (4.13 g, 15.7 mmol) was dissolved in dry DMF (30 ml) in a 100 ml three necks flask equipped with a dropping funnel, nitrogen inlet-outlet, and magnetic stirrer. Bromine (2.62 g, 16.4 mmol) was added dropwise to the solution cooled by an ice-water bath. To the resulting triphenyl phosphine-bromine complex was added dropwise a solution of 11 in 30 ml of dry DMF. The reaction mixture was stirred for 12 h at room temperature after which DMF was evaporated on a rotary evaporator. The obtained liquid was extracted 4 times with 125 ml of hexanes. The solvents were evaporated to give a crude product as a liquid. It was purified by column chromatography with silicagel as a stationary phase and a mixture of petroleum ether and diethyl ether (19:1 V/V) as a eluent to yield 3.1 g (61%) of a colorless liquid. Purity (HPLC), >99 %. 1H-NMR (CDCl3, TMS, δ, ppm): 1.19 and 1.35 (10H, -CH2-(CH2)5-CH2-CH2-Br, m), 1.61 (2H, -CH-CH2-(CH2)7-Br, m), 1.80 (2H, -CH2-CH2-Br, m), 2.76 (1H, -CH-monophenyl, m), 2.86 (2H, biphenyl-CH2-, d, J=6.2Hz), 3.37 (2H, -CH2-Br, t, J=6.8Hz), 3.78 and 3.84 (6H, CH3-O-Ph-CH- and CH3-O-biphenyl, 2s), 6.81 (2H, ortho to methoxy of the monophenyl ring, d, J=8.5Hz), 6.96 (2H, ortho to methoxy of the biphenyl ring, d, J=8.8Hz), 7.04 (2H, meta to methoxy of the monophenyl ring, d, J=8.7Hz), 7.06 (2H, ortho to methylene of the biphenyl ring, d, J=8.3Hz), 7.40 (2H, meta to methylene of the biphenyl ring, d, J=7.9Hz), 7.50 (2H, meta to methoxy of the biphenyl ring, d, J=9.4Hz).
6.2.2.8 Synthesis of 10-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (13)

A 100 ml three necks flask equipped with a dropping funnel, nitrogen inlet-outlet, and magnetic stirrer was cooled in a dry-ice-acetone bath. To this flask were added 15 ml of dry methylene chloride and 15 ml of 1.0 M. BBr₃ solution in methylene chloride.¹⁹ A solution of 12 (3.1 g, 6.1 mmol) in 30 ml of dry methylene chloride was added dropwise to the BBr₃ solution. After the addition, the mixture was stirred at room temperature for 5 h. To this reaction mixture were added slowly 15 ml of water, 200 ml of diethyl ether, and 100 ml of water. The organic layer was separated, washed three times with 100 ml of water, and dried over anhydrous magnesium sulfate. The solvent was evaporated on a rotary evaporator to produce a white solid which was recrystallized from toluene to yield 1.9 g (64 %) of fine crystals. Purity (HPLC), >99%. mp, 115-117°C. ¹H-NMR (CDCl₃, TMS, δ, ppm): 1.18 and 1.35 (10H, -CH₂-(CH₂)₅-CH₂-CH₂-Br, m), 1.64 (2H, -CH-CH₂-(CH₂)₇-Br, m), 1.80 (2H, -CH₂-CH₂-Br, m), 2.76 (1H, -CH-monophenyl, m), 2.82 (2H, biphenyl-CH₂-, m), 3.36 (2H, -CH₂-Br, t, J=6.7Hz), 4.62 and 4.82 (2H, HO-Ph-CH- and HO-biphenyl, 2s), 6.72 (2H, ortho to hydroxy of the monophenyl ring, d, J=8.2Hz), 6.84 (2H, ortho to hydroxy of the biphenyl ring, d, J=8.4Hz), 6.97 (2H, meta to hydroxy of the monophenyl ring, d, J=8.3Hz), 7.03 (2H, ortho to methylene of the biphenyl ring, d, J=7.7Hz), 7.37 (2H, meta to methylene of the biphenyl ring, d, J=8.4Hz), 7.44 (2H, meta to hydroxy of the biphenyl ring, d, J=8.6Hz).
6.2.3 Synthesis of 6-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-
hydroxyphenyl)hexane (19)

Scheme 6.2 outlines the synthesis of TPH-b (19).

6.2.3.1 Synthesis of 1-(4-biphenyloxy)-4-bromobutane(15)

15 was prepared by the etherification of 4-hydroxybiphenyl (1) with 1,4-
dibromobutane (14). 1 (17.0 g, 0.10 mol) was dissolved in 200 ml of absolute
ethanol in a 500 ml one neck flask equipped with a reflux condenser and magnetic
stirrer. After anhydrous potassium carbonate (13.8 g, 0.10 mol) was added, it was
stirred at reflux temperature for 2.5 h under nitrogen atmosphere. 14 (32.4 g, 0.15
mol) was then added to this solution and the reaction mixture was stirred at reflux
temperature for 16 h. After the evaporation of ethanol, the remained solid was
dissolved in 200 ml of CHCl₃. The organic layer was washed with water, dilute
HCl aqueous solution and water, dried over anhydrous magnesium sulfate. After
filtration, the solvent was evaporated to give a solid which was dissolved in hot
ethanol. The insoluble part [1,4-bis(4-biphenyloxy)butane] was removed by
filtration. The product was recrystallized from the ethanol solution at room
temperature to yield 11.6 g (38.0 %) of fine crystals. Purity (HPLC): 99 %, mp,
75-76°C. ¹H-NMR (CDCl₃, TMS, δ, ppm): 2.03 (4H, Br-CH₂-(CH₂)₂-, m),
3.51 (2H, Br-CH₂-, t, J=6.4 Hz), 4.04 (2H, -CH₂-O-, t, J=5.4 Hz), 6.97 (2H ,
ortho to ether of the biphenyl ring, d, J=9.1 Hz), 7.31 and 7.43 (3H, meta and para
to phenyl ring of the monosubstituted phenyl ring, m), 7.54 (4H, meta to ether of
the phenyl ring and ortho to phenyl ring of the monosubstituted phenyl ring, m).
Scheme 6.2 Synthesis of 6-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)hexane (TPH-b).
6.2.3.2 Synthesis of 1-(4-biphenyloxy)-4-iodobutane (16)

1-(4-Biphenyloxy)-4-bromobutane (15, 11.6 g, 0.038 mol) and anhydrous sodium iodide (8.52 g, 0.057 mol) were dissolved in dry acetone (50 ml) in a 100 ml one neck flask equipped with a condenser and magnetic stirrer. The reaction mixture was stirred at room temperature for 21 h. After the evaporation of the solvent the obtained reaction mixture was extracted with 200 ml of CHCl₃ and 200 ml of water. The organic layer was washed with water, 5 % sodium thiosulfate water solution, and water, and dried over anhydrous magnesium sulfate. The solvent was evaporated to give a solid which was crystallized from ethanol (200 ml) to yield 11.2 g (84.1 %) of white crystals. Purity (HPLC), 98.7 %. mp, 89-90°C. ¹H-NMR (CDCl₃, TMS, δ, ppm): 1.98 (4H, 1-CH₂-(CH₂)₂-, m), 3.27 (2H, 1-CH₂-, t, J=6.7 Hz), 4.02 (2H, -CH₂-O-, t, J=5.6 Hz), 6.95 (2H, ortho to ether of the biphenyl ring, d, J=8.5 Hz), 7.29 and 7.41 (3H, meta and para to phenyl ring of the monosubstituted phenyl ring, m), 7.53 (4H, meta to ether of the phenyl ring and ortho to phenyl ring of the monosubstituted phenyl ring, m).

6.2.3.3 Synthesis of 6-(4-biphenyloxy)-1-(4-methoxy-4'-biphenyl)-2-(4-methoxyphenyl)hexanone (17)

To a 1 l three necks flask equipped with a reflux condenser and magnetic stirrer were successively added 1-(4-methoxy-4'-biphenyl)-2-(4-methoxyphenyl)ethanone (5, 13.3 g, 40 mmol), toluene (150 ml), 1-(4-biphenyloxy)-4-iodobutane (16, 14.1 g, 40 mmol), TBAH (1.36 g, 4.0 mmol), and 50 % (wt/wt) sodium hydroxide-
water solution (100 ml). A balloon filled with nitrogen was placed at the top of the reflux condenser. The reaction mixture was stirred vigorously at 60°C for 2 h. The color of the solution changed from yellow to almost white during the reaction and most of the product was precipitated out. The reaction mixture was diluted with 500 ml of water and filtered to collect the precipitated product. The product was suspended in THF and treated with 20 % HCl to cleave ether linkage of O-alkylated product. The mixture was filtered and washed with water and methanol, dried under vacuum. The obtained white solid was recrystallized from 400 ml of toluene to yield 16.3 g (73.1 %) of fine crystals. Purity (HPLC), >99 %. mp, 181-182°C. 1H-NMR (CDCl3, TMS, δ, ppm): 1.49 (2H, Ph-CH-CH2-CH2-, m), 1.85 (3H, -O-CH2-CH2- and one of Ph-CH-CH2-, m), 2.24 (1H, one of Ph-CH-CH2-, m), 3.76 (3H, CH3-O-phenyl, s), 3.85 (3H, CH3-O-biphenyl, s), 3.97 (2H, -O-CH2-, t, J=6.4 Hz), 4.56 (1H, -CO-CH-, t, J=6.9 Hz), 6.85 (2H, ortho to ether of the monophenyl ring, d, J=8.3Hz), 6.93 and 6.97 (4H, ortho to ether of the biphenyl rings, d, J=8.3Hz), 7.26 (2H, meta to methoxy of the monophenyl ring, d, J=9.1Hz), 7.41 - 7.54 (9H, protons of the monosubstituted phenyl ring, meta to ether of the biphenyl rings and meta to carbonyl of the biphenyl ring, m), 8.02 (2H, ortho to carbonyl of the biphenyl ring, d, J=9.0 Hz).

6.2.3.4 Synthesis of 6-(4-biphenyloxy)-1-(4-methoxy-4'-biphenyl)-2-(4-methoxyphenyl)hexane (18)

To a 250 ml three necks flask equipped with a reflux condenser and dropping funnel, were added 6-(4-biphenyloxy)-1-(4-methoxy-4'-biphenyl)-2-(4-methoxyphenyl)hexanone (17, 8.35 g, 15 mmol) and trifluoroacetic acid (110 ml).
The compound did not dissolve in the solvent completely. After heated up to reflux temperature, \((\text{CH}_3\text{CH}_2)_3\text{SiH}\) (3.84 g, 33 mmol) was added dropwise to the reaction mixture and stirred under reflux for 50 min. The reaction mixture was allowed to cool to room temperature and poured into 300 ml of methanol and the precipitate was filtered and washed with methanol. The compound was dried under vacuum to yield white fine powder (7.63 g, 93.7 %). Purity (HPLC), >99 %. mp, 150-151°C. \(^1\text{H}-\text{NMR}\) (CDCl\(_3\), TMS, \(\delta\), ppm): 1.33 (2H, Ph-CH-CH\(_2\)-CH\(_2\)-, m), 1.73 (4H, -O-CH\(_2\)-CH\(_2\)- and Ph-CH-CH\(_2\)-, m), 2.87 (3H, Ph-CH-CH\(_2\)-Ph, m), 3.79 (3H, CH\(_3\)-O-monophenyl, s), 3.83 (3H, CH\(_3\)-O-biphenyl, s), 3.89 (2H, -O-CH\(_2\)-, t), 6.83 (2H, ortho to ether of the monophenyl ring, d, \(J=8.5\) Hz), 6.90 and 6.95 (4H, ortho to ether of the biphenyl rings, d, \(J=8.9\) Hz), 7.07 (4H, meta to methoxy of the monophenyl ring and ortho to methylene of the biphenyl ring, 2d, \(J=8.2\) Hz), 7.30 - 7.55 (11H, protons of the monosubstituted phenyl ring, meta to ether of the biphenyl rings and meta to methylene of the biphenyl ring, m).

6.2.3.5 Synthesis of 6-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)hexane (19)

To a 500 ml three necks flask equipped with a dropping funnel, nitrogen inlet-outlet, and magnetic stirrer were added 200 ml of dry methylene chloride and 6-(4-biphenyloxy)-1-(4-methoxy-4'-biphenyl)-2-(4-methoxyphenyl)hexane (18, 7.33 g, 13.5 mmol). The flask was cooled in a dry-ice-acetone and 60 ml of 1.0 M BBr\(_3\) solution in methylene chloride was added dropwise to the suspension. The solution color was changed first to orange and then to red. The reaction mixture was stirred at room temperature over night after which 100 ml of water was added slowly. The
reaction product was extracted with 300 ml of diethyl ether, washed three times with water, and dried over anhydrous magnesium sulfate. After the evaporation of the solvent, the resulting viscous solid was purified by silicagel column chromatography. First, hexanes-diethyl ether (2:1) was used to remove deprotected 4-hydroxybiphenyl. The desired product was eluted with hexanes-diethyl ether (1:1). After the evaporation of the solvent remained solid was recrystallized from toluene (30 ml) and hexanes (10 ml) mixture to yield 2.97 g (63.7%) of white crystals. Purity (HPLC), > 99 %. mp, 103-110°C. 1H-NMR (CDCl3, TMS, δ, ppm): 1.27 (2H, Ph-CH-CH2-CH2-, m), 1.74 and 1.77 (4H, Br-CH2-CH2- and Ph-CH-CH2-, m), 2.78 (1H, Ph-CH-CH2-Ph, m), 2.84 (2H, Ph-CH-CH2-Ph, m), 3.30 (2H, Br-CH2-, t, J=7.0 Hz), 4.64 and 4.80 (2H, H-O-, 2s), 6.74 (2H, ortho to hydroxy of the monophenyl ring, d, J=8.3 Hz), 6.88 (2H, ortho to hydroxy of the biphenyl ring, d, J=7.6 Hz), 6.99 (2H, meta to hydroxy of the monophenyl ring, d, J=8.7 Hz), 7.05 (2H, ortho to methylene of the biphenyl ring, d, J=8.2 Hz), 7.39 (2H, meta to methylene of the biphenyl ring, d, J=7.9 Hz), 7.45 (2H, meta to hydroxy of the biphenyl ring, d, J=7.9Hz).

6.2.4 Synthesis of dendritic polyethers

Scheme 6.3 outlines the synthesis of the TPD-b-X (where X is the structure of the chain ends). Conventional liquid-liquid two phase (organic solvent-aqueous NaOH solution) phase-transfer-catalyzed polyetherification conditions were used for the preparation of dendritic polyethers. The polyetherifications of the AB2 type monomer TPD (13) or TPH (19) were carried out under a nitrogen atmosphere at 80°C in an o-dichlorobenzene-10N NaOH water solution (10 times molar excess of
Scheme 6.3 Synthesis of dendritic polyethers based on 10-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (TPD-b-X) and the schematic representation of the transformation between nematic and isotropic phases.
NaOH versus phenol groups) in the presence of tetrabutylammonium hydrogen sulfate (TBAH) as a phase-transfer catalyst followed by the alkylation of unreacted phenolate chain ends with alkyl bromide or benzyl chloride. An example of polyetherification is as follows.

To a 25 ml single-neck flask equipped with a condenser and nitrogen inlet-outlet were successively added TPD-b \( (13) \) (0.144 g, 0.300 mmol), 10 N NaOH (0.6 ml), o-dichlorobenzene (0.6 ml), and TBAH (0.204 g, 0.600 mmol, 100 mol% of phenol groups). The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80°C under nitrogen for 30 min. Then, benzyl chloride (0.0418 g, 0.33 mmol) and o-dichlorobenzene (0.6 ml) were added to the reaction mixture. After 30 min of reaction at 80°C, the organic and aqueous layers were diluted with chloroform and water, respectively, and the aqueous layer was separated. The organic layer was washed with water, followed by dilute hydrochloric acid, and again three times with water. The polymer was separated by the precipitation of its solution into methanol to obtain 0.116 g (79%) of a white precipitate. The polymer (TPD-b-Bz) was further purified by two successive precipitations from THF solution into water and dried in vacuo.

6.3 RESULTS AND DISCUSSION

6.3.1 Synthesis of TPD-b \( (13) \)

Scheme 6.1 outlines the synthesis of TPD-b \( (13) \). In this case, 1-(4-methoxy-4'-biphenyl)-2-(4-hydroxyphenyl)butanone \( (5) \) was used for the alkylation instead
of 1-(4-acetoxy-4'-biphenyl)-2-(4-acetoxy)butanone (2-7) which was used for the synthesis of TPB and TPD as described in Chapter 2. The disadvantages of using 5 are as follows. First, the yield (about 40 %) of 5 is lower than that of 2-7 (about 70 %). The lower yield of 5 is probably due to the attack of electrophile on not only the para position of the biphenyl ring but also the ortho positions to methoxy of the biphenyl and monophenyl ring during Friedel-Crafts acylation. Secondly, 5 is hardly soluble in most of solvents at room temperature. This makes it difficult to work up after the acylation. In spite of these shortcomings, 5 was used for the synthesis of TPD-b since iodooctanol is rather expensive. When we use 2-7 for the alkylation, alkyl halide is needed three times as much as the case for 5 to complete the reaction since the alkylation occurs not only α carbon of the ketone but also the phenol oxygens following the cleavage of the acetyl groups.

6.3.2 Synthesis of TPH-b (19)

Scheme 6.2 outlines the synthesis of TPH-b (19). The direct alkylation of 5 with 4-bromobutan-1-ol was tried to result in no alkylation. This is most probably due to the intramolecular cyclization of 4-bromobutan-1-ol to tetrahydrofuran. Therefore, biphenyl protecting group was used to avoid the cyclization. The biphenyl group was used as a protecting group since the etherification of 4-phenylphenol with 1,4-dibromobutane proceeded without any difficulty and the dialkylated compound, 1,4-bis(4-biphenyloxy)butane, was easy to remove from the desired monoalkylated compound (15) by using solubility difference. The purity of 15 was 99 % by HPLC after the recrystallization. The solubility of compounds 17 and 18 is low at room temperature even in halogenated solvents or aromatic
solvents. However, the reduction of 17 with (C$_2$H$_5$)$_3$SiH in CF$_3$COOH proceeded rapidly. The direct bromination occurred during the deprotection of methoxy and biphenyloxy groups to yield 64% of TPH-b, 19.

6.3.3 The synthesis and characterization of TPD-b-X

Scheme 6.3 outlines the synthesis of the TPD-b-X (where X is the structure of the chain ends) dendrimers by the homopolyetherification of TPD-b which is a tri functional mesogenic monomer based on conformational isomerism. 15,16 The homopolymer with X=H, i.e., the polymer containing phenol chain ends could not be characterized since it is insoluble in halogenated and aromatic solvents, and in its deprotonated form is soluble only in water. Therefore, at the end of the polymerization, the phenol chain ends of the TPD-b-X dendrimer were endcapped in the same reaction flask and the resulted polymers were characterized. The phenol chain ends of TPD-b-X were reacted with benzyl chloride (TPD-b-Bz), 1-butylobromide (TPD-b-4), 1-hexylbromide (TPD-b-6) and 1-octylbromide (TPD-b-8), respectively. The characterization of TPD-b-X polymers is summarized in Table 6.1. As we can observe from Table 6.1, the molecular weights of the dendrimers are low. This is most probably due to an intramolecular alkylation of a phenol group by the alkylbromide chain end of TPD-b. This reaction represents a chain termination and therefore, limits the molecular weight of the polymer. For the range of molecular weights of TPD-b-X from Table 6.1 we did expect to observe the -CH$_2$Br chain end of the polymer. Figure 6.1 shows a representative 200 MHz $^1$H-NMR spectrum of TPD-b-8 together with its protonic assignments, which demonstrates the absence of -CH$_2$Br chain end.
Table 6.1
Characterization of dendritic polyethers (TPD-b-X) with different chain ends (X) and comparison with the linear model polyether (TPD-8).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>X</th>
<th>Yield (%)</th>
<th>$M_n$</th>
<th>$M_w/M_n$ (GPC)</th>
<th>Thermal transitions ($^\circ$C) and corresponding enthalpy changes (Kcal/mru) in parentheses(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Heating</td>
</tr>
<tr>
<td>TPD-b-Bz</td>
<td>benzyl</td>
<td>79.2</td>
<td>4700</td>
<td>3.8</td>
<td>g 48 n 60 (0.10) i i 53 (0.15) n 43 g</td>
</tr>
<tr>
<td>TPD-b-4</td>
<td>butyl</td>
<td>70.3</td>
<td>4400</td>
<td>3.5</td>
<td>g 40 i i 34 g</td>
</tr>
<tr>
<td>TPD-b-6</td>
<td>hexyl</td>
<td>82.2</td>
<td>4700</td>
<td>3.9</td>
<td>g 24 n 39 (0.15) i i 30 (0.18) n 18 g</td>
</tr>
<tr>
<td>TPD-b-8</td>
<td>octyl</td>
<td>80.0</td>
<td>7900</td>
<td>2.6</td>
<td>g 20 n 40 (0.75) i i 30 (0.70) n 15 g</td>
</tr>
<tr>
<td>TPD-8</td>
<td>octane</td>
<td>92.2</td>
<td>27500</td>
<td>2.0</td>
<td>g 19 n 60 (1.58) i i 47 (1.58) n 13 g</td>
</tr>
</tbody>
</table>

\(^a\)Data from the second heating and cooling scans.
Figure 6.1 200 MHz $^1$H-NMR of TPD-b-8 (CDCl$_3$).
The second heating and first cooling DSC traces of TPD-b-X dendrimers are presented in Figure 6.2. First, second and subsequent heating DSC traces are almost identical except the presence of the peak due to the excess heat capacity in the first heating scan. First and subsequent cooling DSC traces are identical. Most of the TPD-b-X exhibit an enantiotropic nematic mesophase with very narrow temperature range except TPD-b-4 which is glassy. Figure 6.3 presents the representative texture of TPD-b-8. None of TPD-b-X crystallize. The transition temperatures and the corresponding entropy changes were plotted versus the chain end structure in Figure 6.4. As we can observe from Figure 6.4 and Table 6.1, the nature of the polymer chain ends affects the glass transition temperatures of the dendrimer. By decreasing the alkyl length of the chain end from octyl to butyl the glass transition temperature of the dendrimer increases from 20°C to 40°C. The isotropization temperatures of TPD-b-6 and TPD-b-8 are identical and therefore are not affected by the nature of the polymer chain ends. As a consequence, TPD-b-4 is only glassy, while TPD-b-6 and TPD-b-8 display enantiotropic nematic mesophases. The breadth of the temperature range of the mesophase is therefore determined by the glass transition temperature of the dendrimer. This result can be easily explained if we recall that in the liquid crystalline phase of the liquid crystalline polymers with flexible spacers the spacers intercalated between two mesogens are extended while the spacers from the polymer chain end are melted. Consequently, the spacers between the mesogens determine the thermodynamic stability of the mesophase while the aliphatic chain ends being melted are lowering the glass transition temperature of the polymer. The TPD-b-X dendrimers have
Figure 6.2a and 6.2b Second heating (a) and first cooling (b) DSC thermograms (20°C/min) of dendritic polyethers based on TPD-b and alkylbromide or benzylchloride (TPD-b-X, X is the structure of the chain end groups, i.e., Bz=benzyl, 4=butyl, 6=hexyl and 8=octyl).
Figure 6.3 The representative nematic texture of TPD-b-8 after annealing at 35.5°C for 1 h 30 min (x100).
Figure 6.4a and 6.4b The transition temperatures and the enthalpy changes of TPD-b-X dendrimers versus the chain end groups (X) and the comparison with the linear model TPD-8 polymer: (a) the transition temperatures obtained from the second heating and cooling scans; (b) the enthalpy changes associated with the nematic-isotropic transitions.
always the same spacer length between the mesogenic groups but different aliphatic chain ends. Therefore, the isotropization temperature should always be the same, while the glass transition should be affected drastically by the nature of the chain ends. An exception is provided by the dendrimer with benzyl chain ends (TPD-b-Bz) which exhibits a very narrow enantiotropic mesophase which undergoes isotropization at a higher temperature than that of the other TPD-b-X polymers with alkyl chain ends. At the same time its glass transition temperature is also higher than those of the other TPD-b-X dendrimers. This behavior also can be explained if we consider that the benzyl ether chain end increases the length of the mesogenic unit and therefore, has an opposite effect from that of the aliphatic chain ends. That is, it increases both the glass transition and the isotropization temperature of the dendrimer. The entropy change increases with increasing the length of the chain ends as seen from Figure 6.4b. This is most probably due to the kinetically controlled nature of the mesophase. Namely, if the nematic-isotropic transition is located in the close proximity of the glass transition, the mesophase is formed with difficulty. Consequently, the entropy change gets lower than the expected value from the thermodynamically equilibrated state.

Linear TPD-8 polymer which was described in Chapter 2 can be considered as the model linear polymers for these dendrimers. All TPD-b-X dendrimers exhibit a lower isotropization transition temperature and the entropy change than those of their linear model TPD-8 (Figure 6.4 and Table 6.1). In other words, dendrimers prefer isotropic phase to nematic phase compared to the linear polymers. This is most probably due to the fact that the number of trans methylenic units of the
flexible spacer of TPD-b-X is lower than that of the trans methylenic units of the flexible spacer of TPD-8. Also the molecular weights of the TPD-b-X dendrimers are lower than that of the linear model TPD-8.

Scheme 6.3 outlines the mechanism responsible for the generation of the conventional nematic mesophase exhibited by the TPD-b-X dendrimers. In solution and in the isotropic phase the TPD-b mesogenic unit of the dendrimers is most probably in its gauche conformer or in a dynamic equilibrium between the gauche and anti conformers and therefore, generates the conventional architecture characteristic for dendrimers. On lowering the temperature of the isotropic melt, the TPD-b mesogen displays mostly the anti conformer. This conformational change transforms the architecture of the polymer to that which can accommodate a conventional nematic mesophase.

6.3.4 Synthesis and Characterization of TPH-b-X

The results of the homopolyetherification of TPH-b are summarized in Table 6.2. The molecular weights of TPH-b-X are even lower than those of TPD-b-X. Figure 6.5 shows a representative 200 MHz ¹H-NMR spectrum of TPH-b-4 together with its protonic assignments, which shows minor peaks corresponding to a vinyl group and methylene group next to hydroxy group. This NMR result suggests that the molecular limiting factor is not only intramolecular cyclization but also the side reactions such as the elimination or hydrolysis of the bromide group in this case. This is most probably due to the fact that the nucleophilic attack of phenolate anion to the methylenic carbon next to the bromine leaving group is more
<table>
<thead>
<tr>
<th>Polymer</th>
<th>X</th>
<th>Yield (%)</th>
<th>M_n (GPC)</th>
<th>M_w/M_n (GPC)</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPH-b-Bz</td>
<td>benzyl</td>
<td>94.1</td>
<td>2520</td>
<td>1.69</td>
<td>g 50 k 61 (0.30) k 74 (0.02) l</td>
<td>144 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 51 l</td>
<td></td>
</tr>
<tr>
<td>TPH-b-4</td>
<td>butyl</td>
<td>71.9</td>
<td>3140</td>
<td>1.51</td>
<td>g 47 k 54 (0.50) k 69 (0.05) l</td>
<td>139 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 44 l</td>
<td></td>
</tr>
<tr>
<td>TPH-b-6</td>
<td>hexyl</td>
<td>65.1</td>
<td>3170</td>
<td>1.57</td>
<td>g 34 k 43 (6.18) l</td>
<td>130 (0.02) n 26 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 34 n 45 (0.04) l</td>
<td></td>
</tr>
<tr>
<td>TPH-b-8</td>
<td>octyl</td>
<td>75.7</td>
<td>3220</td>
<td>1.58</td>
<td>g 27 n 45 (0.36) l</td>
<td>134 (0.41) n 21 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g 27 n 44 (0.44) l</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\text{Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.}\)
Figure 6.5 200 MHz $^1$H-NMR of TPH-b-4 (CDCl$_3$).
sterically hindered due to the shorter spacer length than that of TPD-b monomer and facilitate the side reactions.

The second heating and first cooling DSC traces of TPH-b-X dendrimers are presented in Figure 6.6. The data from the first heating scan are tabulated in Table 6.2. TPH-b-6, TPH-b-4 and TPH-b-Bz exhibit endothermic peaks right after the glass transition on their first heating scans (Table 6.2). These peaks most probably a melting transition since they do not reproduce during cooling and subsequent heating scans. As we can observe from Figure 6.6 and Table 6.2, the phase behavior of TPH-b-X is similar to that of TPD-b-X. TPH-b-6 and TPH-b-8 show an enantiotropic nematic phase. No mesophase can been seen on cooling and second heating scans of TPH-b-4 and TPH-b-Bz. The glass transition temperature of TPH-b-X increases from 27 °C to 44 °C as the alkyl length of the chain end decreases from octyl to butyl. On the other hand, the nematic-isotropic transition temperature stays around 44-45 °C. Consequently, TPH-b-4 is glassy. These results confirm the argument made in the TPD-b-X part. Unlike TPD-b-Bz, TPH-b-Bz did not exhibit a mesophase. This is most probably due to the shorter spacer which does not accommodate the molecule in a nematic phase. All TPH-b-X have higher glass and nematic-isotropic transition temperatures compared to those of TPD-b-X with the same chain end.

6.4 CONCLUSIONS
Figure 6.6a and 6.6b Second heating (a) and first cooling (b) DSC thermograms (20°C/min) of dendritic polyethers based on TPH-b and alkylbromide or benzylchloride (TPH-b-X, X is the structure of the chain end groups, i.e., Bz=benzyl, 4=butyl, 6=hexyl and 8=octyl).
The first example of thermotropic dendrimers with various terminal groups, TPD-b-X and TPH-b-X, were synthesized by the homopolymerizations of trifunctional AB₂ type monomers, TPD-b and TPH-b, followed by the alkylation. Depending on the terminal group, some of the TPD-b-X exhibit a nematic mesophase with narrow temperature range. If the terminal group is an alkyl group the terminal group affects only the glass transition temperature of the resulting dendrimer. If bezyl ether group is introduced as a terminal group both the glass transition and nematic isotropic transition temperatures increase due to the extended nature of the mesogenic unit in the case of TPD-b-X. Similar behavior was observed for TPH-b-X except TPH-b-Bz. The comparison of the thermal behavior of dendrimers with the corresponding linear polymer (TPD-8) was made. The liquid crystallinity seems to be depressed in the dendritic architecture.

These results have demonstrated that it is possible to synthesize dendrimers which exhibit a thermotropic liquid crystalline phase by using a suitable selection of their structural unit. We think this is a very rewarding result since it generates both a novel class of liquid crystalline polymers and a novel phase exhibited by dendritic polymers. Therefore, these results open new synthetic and theoretical opportunities both in the area of liquid crystalline polymers and of dendritic polymers.

6.5 REFERENCES


20. Sigaud, G., to be published.
CHAPTER 7

Conclusions
New semiflexible mesogenic units based on conformational isomerism, i.e., 1- (4-hydroxyphenyl)-2-(4-hydroxy-4'-biphenyl)alkane and bromo-1-(4- hydroxyphenyl)-2-(4-hydroxy-4'-biphenyl)alkane, were designed according to the simple thermodynamic scheme. They were used to synthesize novel series of thermotropic linear, cyclic, and dendritic polyethers. Compared to the previously used flexible mesogenic units, 1-(4-hydroxyphenyl)-2-(2-R-4- hydroxyphenyl)ethane (RBPE, R = CH₃, F, Cl, Br, CF₃) and 1,2-bis(4- hydroxyphenyl)ethane (BPE), these mesogenic units have an additional phenyl ring which enhances the liquid crystallinity and a lateral substituent which suppresses the crystallinity and enhance the solubility of resulting polymers.

The mesogenic units with an ethyl or octyl lateral group, i.e., 1-(4- hydroxyphenyl)-2-(4-hydroxy-4'-biphenyl)butane (TPB) and 1-(4- hydroxyphenyl)-2-(4-hydroxy-4'-biphenyl)decane (TPD), have been used to synthesize the homologous series of linear thermotropic polyethers (TPB-X or TPD-X) based on TPB or TPD, and α,ω-dibromoalkanes containing X methylenic units. Most of these linear polyethers exhibit an enantiotropic nematic mesophase as expected from the simple thermodynamic scheme. The phase diagrams of these linear polyethers demonstrate that the nature of the mesophase (amorphous, noncrystallizable nematic, crystallizable nematic, monotropic, and virtual) is simply determined by the different dependence of the transition temperatures (glass transition, nematic-isotropic transition, melting transition temperatures) on the spacer length. This observation may be generalized as follows. Any kinds of compounds may have an ability to show liquid crystallinity. For example an
amorphous compound does not exhibit liquid crystallinity since the glass transition
temperature is higher than the mesomorphic transition temperature and the
mesophase formation is kinetically prohibited. By decreasing the glass transition
temperature or increasing the mesophase transition temperature the mesophase may
be observed. One of this example is provided in this dissertation. The kinetically
prohibited nematic phase of TPB-7 was converted to an enantiotropic nematic phase
via cyclization. On the other hand, by suppressing the crystallinity, a virtual
mesophase can be transformed into an enantiotropic mesophase.

The molecular weight effect on the phase behavior of linear polyethers TPB-10
has been intensively studied by DSC with the synthesized oligomers from monomer
to tetramer and fractionated polymers. All the polymers and oligomers have the
same terminal group and those molecular weights range from monomer to 57,200
with narrow polydispersities. From the phase diagrams obtained with these well
defined polymers, many interesting features were revealed, as follows. The glass
transition and nematic-isotropic transition temperatures increase rapidly at low
molecular weight region and level off at high molecular weight region (Mn >
20,000). There are linear relationships between both the glass transition and
nematic-isotropic transition temperatures and the reciprocal number average
molecular weight up to Mn = 20,000. The super cooling increases with increasing
molecular weight linearly. The ratio of nematic-isotropic transition temperature to
glass transition temperature (T_m/T_g) is constant and equal to 1.22-1.24 within the
entire range of molecular weights. The enthalpy change associated with the nematic-
isotropic transition increases rapidly at low molecular weights region and levels off
at high molecular weights region. The molecular weight effect data presented in this chapter is one of the most accurate sets of data available in the literature. These data will help to solve the theoretical problems in this field.

The first example of cyclic main chain liquid crystalline oligomers based on TPB and α,ω-dibromoalkanes were synthesized by utilizing the mesogenic unit based on conformational isomerism and high dilution conditions. The effect of dilution on the formation of cyclic oligomers was studied. The resulting reaction mixtures were separated into individual cyclic oligomers whose cyclic nature was demonstrated by intensive 1D and 2D ¹H-NMR spectroscopies. The chemical shifts of protons in mesogenic units are highly dependant on the ring size and these are due to the conformational change between anti and gauche conformers depending on ring size. From these results, it was demonstrated that the conformational isomerism of the mesogenic unit affects and contributes to the formation of cyclic oligomers. The thermal transitions of these cyclic oligomers display an odd-even effect not only with the spacer length but also with the ring size. Namely, the odd rings show quite a low tendency toward crystallization while the even rings display a relatively higher tendency toward crystallization. The nematic-isotropic temperatures and corresponding enthalpy changes of the tetramers and pentamers change similarly to those of the corresponding linear polyethers with changing the spacer length. Namely, there is an odd-even effect on a spacer length. On the other hand, the nematic-isotropic transition temperatures and the enthalpy changes of trimers do not exhibit such an odd-even effect and increases constantly with increasing spacer length. This is most probably due to the deformed conformation
of the cyclic trimers from the ideal one in which the mesogens with anti conformers are aligned parallelly each other in the cyclic molecule. The deformed conformation is released with increasing spacer length and the transition temperature and the corresponding enthalpy change increase. Some of the trimers exhibit both nematic and smectic phases although the corresponding linear polyethers do not. The most interesting result of the cyclic oligomers is that some cyclic oligomers show higher transition temperatures than those of the corresponding high molecular weight linear polymers although the enthalpy changes associated with the transition are much lower than those of the linear polymers. This can be explained by the total rigidity of cyclic molecules and lower entropy in the isotropic phase. By using this phenomena, the kinetically prohibited mesophase of linear TPB-5 polyether was transformed into an enantiotropic mesophase via cyclization while the kinetically controlled mesophase of the linear TPB-7 polyether was converted to the thermodynamically controlled mesophase via cyclization. It was found that the TPB-8(c) trimer and tetramer are miscible with the corresponding linear polymer.

Chiral linear polymers and cyclic oligomers based on (R)-TPB* and α,ω-dibromoalkanes exhibit a quite similar thermal behavior to that of the racemic polymers and oligomers although the phase is cholesteric rather than nematic. The cyclic dimer and trimer display the selective reflection of polarized light while the cyclic tetramer and pentamer do not. It was suggested that the chirality of mesophase, i.e., the pitch of cholesteric phase, is highly dependent on the ring size and architecture of molecule in the mesomorphic state. Based on these results, a supercoiled structure was proposed for the cyclic tetramer and pentamer.
Finally, the first example of thermotropic dendrimers (TPD-b-X and TPH-b-X) with various terminal groups (X) were synthesized by using the homopolyetherification of trifunctional monomers, 10-bromo-1-(4-hydroxy-4'\text{-}biphenyl)-2-(4-hydroxyphenyl)decane (TPD-b) and 6-bromo-1-(4-hydroxy-4'\text{-}biphenyl)-2-(4-hydroxyphenyl)hexane (TPH-b), followed by the alkylation of the phenolate chain ends with alkyl bromide or bezyl chloride. If the terminal group is an alkyl group the terminal group affects only the glass transition temperature of the resulting dendrimer. If a bezyl ether group is introduced as a terminal group both the glass and nematic-isotropic transitions increase due to the extended nature of the mesogenic units in the case of TPD-b-X. Similar behavior was observed with TPH-b-X. The comparison of the thermal behavior of dendrimers with the corresponding linear polymers (TPD-X) was made. The liquid crystallinity seems to be depressed in the dendritic architecture.

As seen from all chapters, the architecture of polymers or oligomers affect the mesomorphic behavior drastically. The cyclic architecture seems to enhance liquid crystallinity while the dendritic architecture depresses it compared to the linear architecture. As pointed out in Chapter 1, there are still many kinds of architectures which have not been explored yet. This thesis has opened numerous synthetic opportunities for such novel liquid crystalline polymers with new architectures.
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CHAPTER 2


CHAPTER 3


### CHAPTER 4


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**CHAPTER 6**


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