SYNTHESIS OF HYPERBRANCHED SIDE-CHAIN LIQUID CRYSTALLINE POLYACRYLATES: EFFECT OF THE ARCHITECTURE ON THE RHEOLOGICAL PROPERTIES

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SYNTHESIS OF HYPERBRANCHED SIDE-CHAIN LIQUID CRYSTALLINE POLYACRYLATES: EFFECT OF THE ARCHITECTURE ON THE PHYSICAL PROPERTIES

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ABSTRACT

A new class of inimer (a molecule containing an initiating site and a polymerizable group in the same molecule) was synthesized from a key halohydrin-based intermediate, which was obtained from serine by a diazotization synthetic route. Polymerization of these inimers resulted in hyperbranched polyacrylates using the concepts of self-condensing vinyl polymerization (SCVP) and atom transfer radical polymerization (ATRP). These hyperbranched polyacrylates contain an ester group attached to every other carbon atom along the polymer backbone, with a non-initiator-containing alkyl ester attached as a free side chain. This is in contrast to previously reported hyperbranched polyacrylates, which have these ester groups along the polymer backbone upon reaction. The architecture of our new polymers is therefore more chemically analogous to linear polyacrylates. We have synthesized and characterized polyacrylates with different ester functional side chains such as alkyl, perfluoro, siloxane, oligo(oxyethylene) and mesogenic side chains. The hyperbranched side-chain liquid crystalline polyacrylates (SCLCPs) were synthesized and characterized intensively by $^1$H, $^{13}$C and 2D nuclear magnetic resonance (NMR) spectroscopy, matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry, differential scanning calorimetry (DSC), polarized optical microscopy (POM), gel permeation chromatography (GPC), light scattering (LS), solution viscosity and rheological techniques. In this work, the structure was qualitatively analyzed by $^1$H, $^{13}$C and 2D
NMR techniques to obtain the branching units. Solution properties, e.g. radius of gyration and intrinsic viscosity, thermal properties (glass transition and isotropization temperatures) and rheological properties (isotropic and anisotropic viscosity) of the hyperbranched side-chain liquid crystalline polyacrylate were compared with those of the linear, three-arm star, six-arm star and comb analogues.

This work provides greater flexibility of synthesizing a variety of hyperbranched functional polyacrylates in a single-pot, single-step reaction and helps us in our understanding of the effect on the physical properties due to architectural differences of the polymers.
DEDICATION

I dedicate this dissertation to all my teachers, friends, family and individuals who have helped, guided and supported me during my education in the past and present. I have been a part of an educational society that strives for the growth and brings out the best in you. I am obligated to have encountered some of the best teachers and scientists in my life. Their constant support and guidance led me to be a scientist and I dedicate my dissertation to all of them.
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CHAPTER I
INTRODUCTION

The present work is directed to the synthesis of inimers (an inimer contains an initiating site and monomeric group in the same molecule) and hyperbranched\textsuperscript{2} polymers based on 2-halo-3-hydroxypropionic acid, 2-halo-3-hydroxybutyric acid and their derivatives\textsuperscript{5}. Polycrylates synthesized by this route can have a variety of functional groups attached as free ester side chains. Polycrylates, an important class of polymers, are used in a variety of applications, and by having different functional groups can provide utility as, for example, ingredients in paints, coatings, textiles, adhesives, superabsorbent materials, contact lenses, display devices, polyelectrolytes and hydrogels. The studies of architectural effects on the physical properties of polycrylates will provide an in depth understanding of the benefits and increased performance for a number of applications for such polymers.

The polycrylates were obtained by using the inimers of the current work in which the intermediate is a key halohydrin-based material. The halohydrins were synthesized from serine using a diazotization\textsuperscript{1} synthetic route. The ester substituents can be synthesized from any alcohol, and therefore include aliphatic or non-aliphatic, linear or branched, mesogenic or non-mesogenic, chiral or achiral, and hydrocarbon or non-hydrocarbon [such as fluorocarbon, oligo(oxyethylene), and siloxane] substituents\textsuperscript{6}. 
This research work provides a flexible approach for synthesizing a variety of hyperbranched functionalized polyacrylates in a single pot, single step reaction. The polymers were prepared by a self-condensing vinyl polymerization (SCVP)\textsuperscript{3} using atom transfer radical polymerization (ATRP)\textsuperscript{4}. Although, a variety of hyperbranched polyacrylates have been previously synthesized by different synthetic routes,\textsuperscript{11} they do not involve a free ester unit in the branch regions. Our hyperbranched polyacrylates contain an ester group attached to every other carbon atom along the polymer backbone, with a non-initiator-containing alkyl ester attached as a free side chain. The architecture of these polymers is therefore chemically analogous to linear polyacrylates, such that the physical properties can be compared with more precision.

Side-chain liquid crystalline polyacrylates (SCLCPs) have been considered for applications based on either electro-thermo-optical effects or separation effects, where the structural integrity, structural flexibility and/or high thermal stability of a polymer may be advantageous over the properties of lower molar mass liquid crystals (LMMLCs). For example, liquid crystals are commercially available as the stationary phase for gas chromatography to separate solutes based on their molecular shape, with SCLCPs having much higher thermal stability and column efficiency than LMMLCs.\textsuperscript{12} However, few applications based on electrical, thermal and/or optical effects have materialized, primarily because of the higher viscosities and slower switching rates of polymeric mesophases. Therefore, a highly branched architecture with a much lower viscosity might offer a superior polymer for applications that would combine the fluidity of a liquid crystalline phase with the ability of polymers to freeze an anisotropic arrangement below the glass transition temperature.
Although hyperbranched polymers have been synthesized with mesogens attached at their periphery no hyperbranched side-chain-liquid crystalline polyacrylates have been synthesized by SCVP from an inimer producing polymers that have a mesogenic unit as part of each repeat unit. This dissertation reports hyperbranched side-chain-liquid crystalline polyacrylates synthesized by SCVP\textsuperscript{3} from an inimer to produce polymers with a mesogenic unit in each repeat unit. The chemical structures of the mesogenic hyperbranched polyacrylates were studied in detail by nuclear magnetic resonance (NMR) spectroscopy, matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry and tandem mass spectrometry techniques. The solution and thermal properties were extensively by gel permeation chromatography (GPC), light scattering (LS), solution viscosity, differential scanning calorimetry (DSC) and polarized optical microscopy (POM). We also studied the rheological behavior of these polymers using a parallel plate rheometer in both the isotropic and anisotropic states of the polymers. The solution, thermal and rheological properties of the hyperbranched side-chain liquid-crystalline polyacrylates were also compared with those of the corresponding linear\textsuperscript{7}, three-arm star\textsuperscript{8}, six-arm star\textsuperscript{9} and comb\textsuperscript{10} polymers to understand the effect of the architecture on their physical properties.
CHAPTER II
LITERATURE REVIEW

2.1 Hyperbranched Polymers

Hyperbranched\(^2\) polymers are highly branched macromolecules with three-dimensional dendritic architectures\(^{11}\). These polymers possess different chemical and physical properties and are different from conventional architectures, such as linear, branched and cross-linked architectures. Differences in the properties are attributed to the presence of branching and a large number of terminal functional groups.

Hyperbranched polymers can be classified as a subclass of dendritic polymers. Dendritic architectures consist of six subclasses: (a) dendrons and dendrimers; (b) linear-dendritic hybrids; (c) dendrigrafts or dendronized polymers; (d) hyperbranched polymers; (e) multi-arm star polymers; and (f) hypergrafts or hypergrafted polymers.\(^{13}\) The first three subclasses exhibit perfect structures and have regular branching. They are monodisperse molecules with well-defined and perfectly branched structures. These structures with high structural regularity and controlled molecular weight are prepared step-by-step via convergent and divergent approaches. The well-defined architecture, high number of functional groups on the surface, excellent solubility in a variety of solvents, and lower viscosity of dendrimers make them good candidates for a wide range of applications, from viscosity modifiers to catalyst supports and drug carriers.\(^{11}\)
Hyperbranched polymers are randomly and less regularly branched than dendrimers. They are prepared by a single pot reaction. Similar to dendrimers, these polymers have a high degree of functionality, improved solubility and low viscosity. The final physical and chemical properties of these polymers are in between those of linear polymers and dendrimers. The comparative ease of manufacturing hyperbranched polymers at lower cost and comparable physical properties make them suitable and alternative candidates to dendrimers.

2.2 History of Highly Branched Polymers

The history of highly branched polymers goes back to the late 19\textsuperscript{th} century and early 20\textsuperscript{th} century.\textsuperscript{11} At the end of the 19\textsuperscript{th} century, Berzelius reported the formation of a resin from tartaric acid (A\textsubscript{2}B\textsubscript{2} monomer) and glycerol (B\textsubscript{3}) monomers.\textsuperscript{14} Following the Watson Smith report of the reaction between phthalic anhydride (latent A\textsubscript{2} monomer) or phthalic acid (A\textsubscript{2} monomer) and glycerol (B\textsubscript{3} monomer) in 1901, Kienle, et al.\textsuperscript{14,15,16} studied that reaction further, obtaining results and conclusions that are still used today. For example, Kienle\textsuperscript{15} showed that the specific viscosity of samples made from phthalic anhydride and glycerol was lower than numerous values given by Staudinger for linear synthetic polymers, such as polystyrene. In 1909, Baekeland\textsuperscript{17} introduced the first commercial synthetic plastics, phenolic polymers, commercialized through his Bakelite Company. The cross-linked phenolic polymers were obtained by the polymerization of soluble resole precursors made from formaldehyde (latent A\textsubscript{2} monomer) and phenol (latent B\textsubscript{3} monomer). Just prior to gelation, these polymers have a so-called random hyperbranched structure. In the mid 20\textsuperscript{th} century, Flory et al.\textsuperscript{18,19,20,21,22} used statistical mechanics to calculate the molecular weight distribution of three-dimensional polymers.
and developed a statistical theory to produce highly branched polymers by condensation polymerization of ABₙ monomer without gelation. In 1982, Kricheldorf²³ obtained highly branched polyesters by copolymerization of AB and AB₂ type monomers.¹¹

The term ‘hyperbranched polymer’ was first coined by Kim and Webster² when the authors intentionally synthesized soluble highly branched polyphenylene. Since then, research on hyperbranched polymers has grown rapidly.¹¹

2.3 Methods of Synthesis of Hyperbranched Polymers

In their review paper, Gao and Yan¹¹ categorized the synthesis of hyperbranched polymers into single monomer methodologies (SMM) and double monomer methodologies (DMM). In a single monomer methodology, hyperbranched polymers are synthesized from ABₙ monomers. SMM categories include polycondensation of ABₙ monomers, SCVP, self-condensing ring-opening polymerization (SCROP), and proton-transfer polymerization (PTP). In a DMM method, two types of monomers or a monomer pair are polymerized to generate hyperbranched polymers¹¹. (SCVP is discussed in subsection 2.4, as this is the method we have chosen to synthesize hyperbranched polyacrylates.)

Hyperbranched polymers produced from polycondensation of ABₙ monomers (including AB₂, AB₃, AB₄ and AB₆) have been widely investigated. A vast variety of polymers have been synthesized, including polyphenylenes,²,²⁴,²⁵ polyethers,²⁶,²⁷,²⁸,²⁹ polyesters,³⁰,³¹,³²,³³,³⁴,³⁵,³⁶,³⁷,³⁸,³⁹,⁴⁰,⁴¹,⁴²,⁴³,⁴⁴,⁴⁵,⁴⁶,⁴⁷,⁴⁸,⁴⁹,⁵⁰,⁵¹,⁵² polyamides,⁵³,⁵⁴,⁵⁵,⁵⁶,⁵⁷,⁵⁸ polycarbonates⁵⁹, poly (ether ketone)s,⁶⁰,⁶¹,⁶²,⁶³ polycarbosilanes,⁶⁴,⁶⁵,⁶⁶,⁶⁷,⁶⁸,⁶⁹,⁷⁰,⁷¹,⁷² and polyacetophenones.
Scheme 2.1: Examples of new AB$_2$ monomers used for the production of branched polymers

Scheme 2.2: Hyperbranched polymers synthesized via a combination of A$_2$ and B$_3$ monomer
More recently, several groups reported that AB$_2$ monomers that are not commercially available can be substituted with a combination of conventional A$_2$ and B$_3$ monomers$^{72,73,74,75}$. Schemes 2.1 and 2.2 show some of AB$_2$ monomers and A$_2$ and B$_3$ monomers that were reported to produce branched polymers. Hyperbranched polyamides and polyethers were obtained by stopping the reaction prior to the gel point. However, the critical conversion in these condensations depends on many factors, including the ratio of functionalities, purity of solvents and reagents, reaction time, and temperature. It is difficult to fully control the reaction and to obtain hyperbranched polymers with high molar mass without having to separate the solution from a gel fraction.

A new strategy introduced separately by Gao and Yan$^{76,77}$ and DSM research$^{78,79}$ uses commercial available monomers and avoids gelation by couple-monomer methodology (CMM) (Scheme 2.3). Their A$_2$ + B$_3$ methodology assumed equal reactivity of all A or B groups at a given stage of the reaction. In contrast, CMM is based on the non-equal reactivity of the functional groups in specific monomer pairs. In CMM, one type of AB$_n$ intermediate is preferably generated in the initial stage of the polymerization to produce hyperbranched macromolecules without gelation.
Scheme 2.3: AA’ + BB_2’ approach to hyperbranched polymers as a typical example for the basic principle descriptive of CMM

If A is identical to A’, and B is identical to B’, ‘A_2+B_3’ polymerization is obtained from AA’ + BB_2’ monomers. Asymmetric monomers, AA’ or B’B_2, avoid the cross-linking reaction. Different polymerization systems are obtained depending on the reactivities of A and A’ and B and B’. CMM affords AA’+B_3 polymerization (A’ more reactive than A), A_2+B’B_2 (B’ is more active than B), AC+DB_2 (both A and B groups are different from A’ and B’ groups). In all of the polymerization systems, AB_2 intermediates are generated in situ and further reaction of the AB_2 species results in hyperbranched macromolecules. As an example, if the reactivity of the B’ group in the B’B_2 monomer is greater than that of the two B groups, AB_2 intermediates are formed in situ in the initial stage of the reaction. Further self-polycondensation of the formed AB_2 species produces hyperbranched polymers and avoids gelation. In contrast, a molecule containing four B groups will be generated if the formed AB_2 further reacts with a B’B_2 molecule due to higher reactivity of B’ group. The species B_4 functions as a core.
molecule in the preparation of hyperbranched polymers with narrower molecular weight distribution.

Several kinds of hyperbranched polymers have been synthesized using coupled monomer methodology, including poly(sulfone amine)s and poly(ester amine)s, poly(urea urethane)s, poly(amine ester)s, poly(amide amine)s, poly(ester amide)s, and polyesters. Highly branched copolymers have also been reported in the literature.

Apart from the above mentioned addition reactions, self-condensing, ring-opening and proton transfer polymerizations were used to obtain hyperbranched polymers, including polyethers and polyesters. Hyperbranched polyesters with epoxy or hydroxyl end groups and hyperbranched polysiloxanes were synthesized through proton transfer polymerization. Proton transfer ring-opening polymerization, introduced by Fréchet and Chang, involves proton transfer in each propagation step for the activation of a nucleophile used in epoxide ring-opening. The polymerization of H-AB₂ monomer 1 (Scheme 2.4) is initiated by the addition of a catalytic amount of initiator such as hydroxide ion, which abstracts a proton and produces a reactive nucleophile 2. Coupling of 2 with another monomer unit produces dimer 3, which undergoes a thermodynamically driven proton exchange with another monomer 1 to produce nucleophile 2 and neutral dimer 4 (Scheme 2.4). Subsequent nucleophilic additions and proton transfers produce a polymeric product. Given the multiplicity of reactive B species in each growing molecule that contains a single H-A group, the polymerization proceeds with branching and a hyperbranched structure is obtained.
Scheme 2.4: Proton transfer polymerization of H-AB₂ monomer\textsuperscript{113}

Scheme 2.5: Some monomers for ring-opening multibranching polymerizations

Commercial branched poly(ethyl eneime)\textsuperscript{114} was prepared by self-condensing, ring-opening reaction of aziridine, which occurs due to reactions of NH groups in the formed polymer chain with the cyclic monomer. Penczek et al.\textsuperscript{115} and Hult et al.\textsuperscript{116} published the successful cationic ring-opening polymerization of 3-ethyl-3-
(hydroxymethyl)oxetane (see Scheme 2.6) leading to hyperbranched aliphatic polyethers. The reaction proceeds via protonation of the oxygen in the oxetane ring, followed by ring opening by nucleophilic attack of a second monomer (active chain end mechanism, ‘ACE’). However, in addition, two hydroxyl-methylene functions can be condensed under acid catalysis, forming an ether bond (activated monomer mechanism, ‘ACM’), which results in identical repeating units.

Scheme 2.6: Ring-opening multibranching polymerization, (a) ACE (b) AMM

As discussed earlier, in addition to the classical polycondensation reactions, addition reactions have also been employed to obtain the hyperbranched structures.
Scheme 2.7: AB₂ monomers in addition reactions to obtain branched polymers

Scheme 2.7 presents some AB₂ monomers that are used in addition reactions to obtain branched polymers. The AB₂ monomer can undergo a Diels-Alder [2+4] cycloaddition reactions to generate hyperbranched polyphenylenes\(^{117,118}\). When the triple bond was protected by triisopropylsilyl substituents, a perfect polyphenylene dendrimer was obtained.\(^{99}\) Weber et al. used the ruthenium-catalyzed addition of ortho C-H bonds of acetophenone across the triple bond\(^{119}\) or a vinyl group\(^{120}\). Hobson and Feast\(^{121}\) followed a Michael addition reaction of the AB₂ molecule by melt polymerization of N-acryloyl-alpha, beta-diaminoalkane hydrochlorides. The resulting structure was a
perfectly branched polymer. Voigt et al. synthesized hyperbranched poly(ether-amide)s via nucleophilic ring-opening addition reaction of phenols on oxazolines using the monomer (iv). The reaction was thermally induced proceeded in N-methylcaprolactame solution above 190°C.

2.4 Self-Condensing Vinyl Polymerizations (SCVP)

SCVP was invented by Fréchet and coworkers in 1995. This polymerization method is quite versatile, since hyperbranched polymers can be obtained via polymerization of AB* vinyl monomers.

Scheme 2.8: Polymerization of an inimer, AB*, via SCVP

Müller et al. established a nomenclature in which the inimer is designated AB* (Scheme 2.8), in which B* is the group capable of initiating the polymerization of vinyl groups, A. The chain is initiated by addition of a B* group to the vinyl group of another monomer, forming a dimer with two active sites and one double bond. Both the initiating center, B*, and the newly created propagating center, A*, can react with the vinyl group of another molecule (monomer, oligomer or polymer) in the same way with rate constants, k_B and k_A, respectively. In SCVP, the reactivities of the initiating and the propagating centers, A* and B*, may be different. If the reactivity of one of these two
sites is very large compared to the other site, a linear polymer is obtained. The reactivity ratio \( r = \frac{k_A}{k_B} \) represents the relative reactivities of sites \( A^* \) and \( B^* \);

\[
    r = \frac{1 - x - B^*}{1 + \ln B^* - B^*}
\]

in which,

- \( x \) is the conversion of A groups (vinyl), and
- \( B^* \) is the fraction of active B groups.

The degree of branching (DB) in a polymerizing system (inimer and polymer both together) is defined as:

\[
    DB = \frac{2B}{1 - M - 2A'}
\]

in which,

- \( DB \) is the average degree of branching,
- \( B \) is the fraction of branch points,
- \( M \) is the fraction of residual monomer,
- \( A' \) is the fraction of unreacted vinyl groups for the polymer only.

In SCVP, the activities of the growth sites and initiating sites often differ. A weakly branched polymer or a linear polymer resembling a polycondensate is formed if \( r \gg 1 \) or \( r \ll 1 \). Branched polymers with different values of DB are obtained depending on the value of \( r \). The statistics of SCVPs of inimers is discussed in the section 2.6.4.

2.5 Hyperbranched Side-Chain Liquid Crystalline Polymers

Side-chain liquid crystalline polymers (SCLCP)s with flexible backbones are of considerable interest to science and industry because they combine the unique properties
of low-molar-mass liquid crystals with the ability to form films of macromolecular compounds. The standard description of the molecular architecture of an SCLCP given in liquid-crystal textbooks is a flexible backbone plus a spacer and a mesogenic group (Scheme 2.9). SCLCPs are categorized into terminally attached and laterally attached polymers in which the mesogenic unit is attached terminally or laterally to the polymer backbone via a spacer group. Since the first introduction of SCLCPs by Bacceredda and coworkers in 1971, there have been many studies on the effects of polymer backbone, spacer group, and mesogens on the thermal and physical properties of the polymers. Furthermore, many studies have been reported on the applications of such polymers in areas such as ferroelectric display devices, nonlinear optics, optical storage data, pyroelectric detectors, and artificial muscles.

Side-chain liquid-crystalline polymers

![Scheme 2.9: A schematic diagrams of the side-chain liquid-crystalline polymers](image)

In recent years, there have been major advances in the development of living radical polymerization processes in terms of both the degree of polymerization and the polydispersity index (PDI = $M_w/M_n$). Most of this research has focused on the polymerization of common styrene, acrylate and methacrylate monomers with very little
work on the synthesis of novel SCLCP architectures. In principle, living polymerization techniques allow more precise studies to be undertaken to establish the role of the effect of molecular structure on the thermal and physical properties of SCLCPs.

The work published to date on the living polymerization of liquid-crystalline (LC) monomers includes anionic\textsuperscript{138,139,140}, cationic\textsuperscript{138,139,141}, ring-opening metathesis\textsuperscript{139,142} and group-transfer polymerization techniques\textsuperscript{143}, as well as nitroxide-mediated radical polymerization,\textsuperscript{144} and atom transfer radical polymerization\textsuperscript{139,145,146,147} and reversible addition fragmentation chain transfer polymerization\textsuperscript{148}.

2.6 Controlled Radical Polymerizations

The development of new polymeric materials with well-defined compositions, architectures, and functionalities are based primarily on living polymerizations. Living polymerization proceeds without irreversible chain-transfer and chain termination.\textsuperscript{148,149,150,151} Some of the examples of living polymerizations employed are anionic, cationic, coordination, and ring-opening polymerizations.

Living anionic polymerization of vinyl monomers requires nucleophilic initiators. Living anionic polymerization is often not suitable for the controlled synthesis of SCLCPs because the reactive anionic initiator and propagating chain ends react with functional groups within the mesogen. The initiator and/or propagating chain end attack any electron-deficient part of the polymerization system, including carbonyl-carbons (acrylates and methacrylates), or other functional groups. These side reactions are minimized by using bulky initiators at low temperatures in more polar solvents.\textsuperscript{152}

Group transfer polymerization (GTP) is also used to synthesize SCLCPs\textsuperscript{143,153}. It is an anionic polymerization involving an equilibrium between active enolate anions and
inactive silyl ketene acetal chain ends. GTP is also therefore also not tolerant of many
impurities and functionalities present in the SCLCPs. Low temperature is often required
to produce polymers with controlled molecular weights and low polydispersities. Similar
difficulties are present in living cationic polymerization of vinyl monomers; a
propagating carbenium ion is extremely reactive and chain transfer and termination are
difficult to avoid. Only mesogenic vinyl ethers have been polymerized via living cationic
vinyl polymerization to produce a broad range of SCLCPs. As in anionic
polymerizations, stringent reagent purification and often low temperature are necessary to
produce well-controlled polymerizations.

Ring-opening metathesis polymerization (ROMP) is used to produce SCLCPs
with controlled molecular weights and narrow polydispersities. Different metals
including tungsten-, molybdenum-, and ruthenium-based complexes have been used to
obtain controlled molecular weight and molecular weight distribution. Pugh and
Arehart synthesized norbornene-based polymer using Schrock’s molybdenum
alkylidene initiator. Even though the initiator is sensitive to air and moisture, it
tolerates many different functional groups such as nitriles, esters and trifluoromethyl
groups. Grubbs and coworkers reported polymerization of mesogenic cyclobutenes
with controlled molecular weight and molecular weight distribution, but at the expense of
chain termination via decomposition of the ruthenium alkylidene.

Free-radical polymerization is also an important technique for obtaining polymers
due to less stringent requirements for monomer and reagent purity, facile polymerization,
and the option of performing the reaction in either bulk, solution, suspension or emulsion.
However, conventional free radical polymerizations are generally poorly controlled,
producing high molecular weight polymers with larger molecular weight distributions, in contrast to living polymerization techniques. The problems associated with conventional radical polymerization have been overcome by using, "living" radical polymerizations.

Scheme 2.10: Thermodynamic equilibrium in the controlled radical polymerization (case 1: NMP, case 2: ATRP, case 3: RAFT)
Otsu, Yoshida and Tazaki first presented the concept for a living radical polymerization via reversible termination in 1982.\textsuperscript{162,163} The controlled/living polymerization methods, including nitroxide-mediated stable free radical polymerization (NMP), radical addition fragmentation chain transfer polymerization (RAFT), and atom transfer radical polymerization (ATRP) are based on establishing a rapid dynamic equilibrium between a minute amount of growing free radicals and a large concentration of the dormant species. The dormant chains may be alkyl halides as in ATRP, thioesters as in RAFT, alkoxyamines as in NMP, and potentially even organometallic species. Free radicals may be generated by a spontaneous thermal process (NMP), via a catalyzed reaction (ATRP), or reversibly via a degenerative exchange process with dormant species (RAFT).\textsuperscript{164,165,166} These processes are shown in Scheme 2.10.

The first reported controlled radical polymerization method was NMP, in which a stable nitroxide free radical acts as a reversible terminating agent to the propagating free radical (case 1 in Scheme 2.10).\textsuperscript{165,166} Conventional free-radical initiators\textsuperscript{167} and functionalized/dormant nitroxides that produce an initiating cumyl radical were used as a source of free radicals.\textsuperscript{124}

In ATRP, the propagating free radical is deactivated through a reversible oxidation/reduction reaction of the metal halide (case 2 in Scheme 2.10). Sawamoto\textsuperscript{168} and Matyjaszewski\textsuperscript{4,169} independently reported ATRP of methyl methacrylate and styrene, respectively in 1995. Rizzardo et al.\textsuperscript{170} reported RAFT in 1998. In RAFT, a chain transfer agent, such as a thiocarbonate, reacts with the propagating chain to produce a polymeric chain transfer agent (case 3 in Scheme 2.10).
2.6.1 Atom Transfer Radical Polymerizations

ATRP originates from a widely used reaction in organic synthesis known as atom transfer radical addition (ATRA).

As shown in Scheme 2.11, a transition metal, Mt\textsuperscript{n} abstracts a halogen atom from an organic halide (RX) to form an oxidized species, Mt\textsuperscript{n+1}X, and a carbon centered radical. This is followed by addition of a radical to an alkene to form an intermediate radical species. The reaction of Mt\textsuperscript{n+1}X and intermediate radical produces a final halogenated product and generates Mt\textsuperscript{n}, which further reacts with RX, starting the redox cycle again. ATRP as shown in Scheme 2.10 is a thermodynamic reaction in which an organic halide and a transition metal are in equilibrium with an organic halide and transition metal at higher oxidation state. The equilibrium is between active, and therefore propagating, polymer and dormant forms of the polymer.

Controlled radical polymerizations are based on two principles. First, initiation should be fast, providing a constant concentration of growing polymer chains.
Second, because of the persistent radical effect\textsuperscript{4,177,178}, the majority of these growing polymer chains are dormant species that preserve the ability to grow because a dynamic equilibrium between dormant species and growing radicals is established. By keeping the concentration of active species or propagating radicals sufficiently low throughout the polymerization, termination is suppressed.\textsuperscript{179} The rate of polymerization, $R_p$, (Eq. 2.1) is proportional to the concentrations of the monomer and the growing polymer radical while the rate of termination, $R_t$, (Eq. 2.2) is proportional to the square of the concentration of growing polymer radical. The low concentration of growing polymer radicals in the ATRP system therefore minimizes termination relative to propagation.\textsuperscript{4}

\begin{align*}
R_p &= k_p [M][R.] \\
R_t &= k_t [R.][R.] 
\end{align*}

ATRP fulfills these requirements by using a transition metal in combination with a suitable ligand. The catalyst complexes establishes a reversible equilibrium between growing radicals and dormant species\textsuperscript{179} (Scheme 2.12).

Scheme 2.12: Thermodynamic equilibrium in ATRP

Transition metal complexes of Ru, Cu, Fe, Ni, and other are used as the catalysts. A variety of monomers can be polymerized using ATRP, including styrenes, (meth)acrylates, acrylonitrile, (meth)acrylamides, methacrylic acid and some water-
soluble monomers such as 4-vinylpyridine. The initiators used in ATRP are halogen containing initiators (R-X), which are widely available commercially or are easy to synthesize and tailor to other groups to produce functional polymers$^{180}$.

ATRP of side-chain liquid crystalline monomers has been studied by Pugh’s group. Polymers derived from 11-(4’cyanophenyl-4”-phenoxy)undecyl acrylate have been synthesized with different architectures, including linear$^7$, three-arm star$^8$ six-arm star$^9$, comb with six branches$^{10}$ and hyperbranched$^5$.

![Scheme 2.13: Some of the inimers used in SCVPs to obtain hyperbranched polymers](image)

Several AB* monomers (inimers), e.g. 2-(2-bromopropionyloxy)ethyl acrylate (BPEA) were polymerized by ATRP, resulting in low molecular weight hyperbranched polymers with high polydispersities$^{181}$, (e.g. $M_n = 6500$ Da, PDI = 3.3). Scheme 2.13
shows some of the inimers that were polymerized by SCVP to obtain hyperbranched polymers. These hyperbranched polymers bear multiple halogen end groups, which can be modified by radical addition reactions or nucleophilic displacement reactions. These hyperbranched polymers have been used as macroinitiators for the preparation of multi-armed stars.\textsuperscript{180}

2.6.2 ATRP of Acrylic Monomers

A number of functional acrylates were studied in ATRP reactions, including those with hydrophilic, hydrophobic, alkyl, perfluoroalkyl, and siloxane esters. Water-soluble poly(meth)acrylates were produced by ATRP of 2-hydroxyethyl acrylate (HEA)\textsuperscript{182,183}, 2-(dimethylamino)ethyl methacrylate (DMAEMA),\textsuperscript{184} oligo(ethylene oxide) methacrylate\textsuperscript{184}, and sodium 4-vinyl-benzoate\textsuperscript{185}. Glycidyl acrylate\textsuperscript{186}, allyl,\textsuperscript{187} ter-butyl acrylate,\textsuperscript{188} and 11-(4’cyanophenyl-4”-phenoxy)undecyl acrylate\textsuperscript{7} have also been polymerized by ATRP.\textsuperscript{189}

2.6.3 ATRP and Architectures/Topology

ATRP is very well suited for the preparation of (co)polymers with controlled topologies (Figure 2.1), including star- and comb-like polymers, as well as branched, hyperbranched, dendritic, network and cyclic type structures.\textsuperscript{164}

Figure 2.1: Illustration of polymers with controlled topology\textsuperscript{164}

Star-like polymers can be prepared using four different approaches.\textsuperscript{164} One of these techniques is a core first approach, which employs a multifunctional initiator to grow
several arms simultaneously. ATRP is useful due to the availability of many polyols that can be subsequently converted to an initiating core with 3, 4, 6, 12 or more initiating sites\textsuperscript{190,191,192}. Pugh’s group synthesized linear\textsuperscript{7}, three-arm star\textsuperscript{8} and six-arm star\textsuperscript{9} side-chain liquid crystalline polymers based on 11-(4’-cyanophenyl-4”-phenoxy)undecyl acrylate with well-defined molecular weights and relatively narrow molecular weight distributions using ATRP.

Comb polymers can be prepared by three different techniques: grafting-from, -onto and -through. Grafting-from is similar to a core-first approach for stars, in that chains are grown from a polymer backbone prepared by radical polymerization or another method\textsuperscript{193,194,195,196,197,198}. In grafting-onto side chains are attached to a pre-formed polymer backbone\textsuperscript{199}. In grafting-through, vinyl terminated macromonomers are utilized as comonomers together with a low molecular weight monomer\textsuperscript{200,201,202,203,204,205,206,207,208}. Variations in grafting density enabled the production of combs of different shapes, as well as gradient brushes and tadpole or dumbbell structures\textsuperscript{207,173} Similar to conventional radical polymerization, branching occurs in polymers synthesized by ATRP as a result of transfer to polymer. ATRP of inimers can be used to prepare hyperbranched polymers\textsuperscript{209,210,211}. Hyperbranched structures can also be obtained by copolymerizing a monomer with a relatively small amount of divinyl monomer to relatively low conversion\textsuperscript{212}. Regular dendritic structures were prepared by ATRP\textsuperscript{213,214} in this case the degree of branching is controlled by the degree of polymerization. ATRP can significantly improve network uniformity over structures prepared by conventional radical polymerization\textsuperscript{215}. Microgel networks were formed by well-defined polymers with crosslinking pendant moieties; disulfide
linkages\textsuperscript{216} were introduced to prepare degradable gels. Additionally, it is possible to use crosslinkers that can be reversibly cleaved and therefore produce reversible gels.\textsuperscript{217} Anionic and/or cationic polymerizations are preferred over CRP/ATRP processes to produce cyclic polymers using complimentary reagents at very low concentrations. However, cyclization was reported when click chemistry was used in a reaction of azido and acetylene-terminated chains.\textsuperscript{218} This process was recently optimized to provide an efficient route to polystyrene macrocycles.\textsuperscript{219}

2.7 Statistics of SCVP of Inimers

The most common method proposed by Flory\textsuperscript{220} to obtain branched polymers is self-condensation polymerization of $AB_n$ (n $\geq$ 2) monomers. The second method is SCVP$^3$ using a vinyl monomer $AB^*$, in which A is a double bond and $B^*$ is an initiating group. As discussed in section 2.4 (Scheme 2.8), when $B^*$ initiates A to polymerize, a new propagating center $A^*$ is formed. Both $A^*$ and $B^*$ can reinitiate the polymerization of A with rate constants $k_A$ and $k_B$, respectively. Successive additions of the monomers produce branched polymers.\textsuperscript{221}

According to theoretical considerations, differences in the reactivity of the initiating and propagating groups, $A^*$ and $B^*$, respectively, strongly influence both the polydispersity and the degree of branching.\textsuperscript{6,222} In addition, in a process such as ATRP that is based on a dynamic equilibrium between active and dormant species, $A^*$ and $B^*$, may be deactivated at different rates. In this case, linear growth may occur several times before the more reactive site is deactivated, and the proportion of this type of moiety is enhanced. Thus, although $A^*$ and $B^*$ may have very similar intrinsic reactivities ($k_A \sim k_B$), the slow deactivation process may apparently consume one active group faster than
the other and produce an architecture with more of the other moiety.\textsuperscript{182} Hence, varying the reaction conditions in a SCVP of an inimer may lead to different molecular weight distributions and different hyperbranched architectures.\textsuperscript{6} The statistics of chain growth in SCVP were recently studied.\textsuperscript{222,6} The evolution of molecular weights and the expected degrees of branching in SCVP are different from those predicted by Flory\textsuperscript{220} for AB\textsubscript{2} polymerizations.

![Figure 2.2: Dependence of the molecular weight averages and polydispersity index on the conversion of A groups, x, for SCVP (AB*) and for polycondensation of AB\textsubscript{2} monomers\textsuperscript{222}](image)

Figure 2.2 plots the number and weight average degree of polymerization, \( P_n \) and \( P_w \), respectively and the polydispersity index, \( P_w/P_n \), of a polymeric system in which unreacted inimer is including in the calculations. For AB\textsuperscript{*}, \( P_n \) and \( P_w \) are independent of \( r \), but depend on conversion, \( x \). Figure 2.3 compares the degree of branching (DB) and fraction of branch points (FB) in AB\textsubscript{2} system and an AB\textsuperscript{*} with \( r = 1 \). The degree of branching and fraction of branch points are defined as follows\textsuperscript{6},

27
in which, $N$ is the total number of molecules present in the system.

For SCVP of an $AB^*$ inimer, the theoretically calculated molecular weight distribution is extremely broad, the polydispersity index (pdi) being equal to the number-average degree of polymerization: $P_w/P_n = P_n$. It is twice as broad as that for a polycondensation of $AB_2$ type monomers. Since, there are two different active centers in
SCVP, initiating center B*, and propagating center, A*, nonequal reactivities of the two centers (k_A ≠ k_B) have a strong effect on kinetics and molecular weight distribution. The pdi narrows to P_w/P_n = 2 for k_A << k_B (similar to common polycondensation of AB_2 monomers) but broadens for k_B >> k_A. For the limiting case r << 1, a linear polymer resembling a polycondensate is formed, whereas for r >> 1 a weakly branched vinyl polymer is expected. NMR experiments allow for the determination of the reactivity ratio, r.

The main drawback of hyperbranched polymers is their broad molecular weight distributions (MWDs). Hyperbranched polymers with narrower pdi were prepared by adding a small amount of multi-functional initiator, as theoretically predicted by Yan et al. A few reports about the effect of multi-functional initiator on molecular weight distribution and DB of hyperbranched polymers prepared by SCVP of AB* type monomers were published. In addition, the mechanism and kinetics of SCVP, molar mass, and polydispersity development with conversion, the degree of branching, influence of a core molecule as well as effect of different reaction rate constants were studied.

2.8 Characterization of the Hyperbranched Polymers prepared by SCVP

It is not possible to determine the DB of hyperbranched polymers prepared by SCVP technique directly via NMR analysis. ^1H-NMR spectra of the hyperbranched polymers are very similar to the corresponding inimer. The broader and overlapped peaks in the spectrum are difficult to resolve to get information about different structural units, including branch units. Therefore, we will also use indirect methods, such as,
viscosity and light scattering measurements to demonstrate the globular structure of the hyperbranched polymers.

2.9 Properties and Shape of Hyperbranched Polymers

In general, dendrimers are more soluble in common solvents than analogous linear polymers. The hydrodynamic radius of a polymer chain is defined as the radius of the spherical volume occupied by the chain in the solvent. Polymers have a variable hydrodynamic radius depending on the solvent. Since the hydrodynamic radii of hyperbranched polymers and dendrimers are smaller than those of their linear analogs with the same molar mass, we can use the errors in GPC determined molecular weight based on linear standards to study the extent of branching. The hydrodynamic radii are also susceptible to the polarity of functional groups at the periphery. This more compact nature of branched polymers compared to linear analogues at the same molecular weight also corresponds to the radius of gyration, \( R_g \), decreasing with increasing branching.

Although the physical properties of dendrimers have rarely been compared to exact linear analogs, many of their properties are unique. For example, they have low viscosity ([\( \eta \)]) passing through a maximum as function of generation number, and therefore molecular weight. The scaling relationship between molecular weight and radius of gyration (\( R_g = K M^v \)) depends on the conformation of the polymer chains in solution, with typical values of \( v = 0.33 \) for a hard sphere, \( v = 0.50 \) for a random coil in a theta solvent, \( v = 0.59 \) for a random coil in a good solvent, and \( v =1.0 \) for a polymer with an extended rod-like conformation. According to molecular dynamics simulation, \( v = 0.33 \) for dendrimers, regardless of solvent quality. Nevertheless, values of the scaling
parameter below the hard sphere limit were reported for an extremely branched, arborescent PSt in a linear deuterated PSt matrix ($\nu = 0.26$), as predicted by de Gennes for dendrimers in which all of the termini were located at the periphery of the molecule. Pugh’s group investigated the solution behavior of the linear, three-arm star, and comb poly[11-(4’-cyanophenyl-4”phenoxy)undecyl acrylate]s by GPC\textsubscript{PSt} (GPC using polystyrene standards) and light scattering measurements in order to correlate their size and shape with their molecular architectures. They demonstrated that the same polymer prepared by conventional radical polymerization was more branched than the linear polymers produced by ATRP. Their results were consistent with the extent of branching increasing from linear to three-arm star to comb topologies according to the synthetic design. For example, the error in the GPC\textsubscript{PSt}-determined molecular weights increased, the tendency to aggregate in solution decreased, and the root-mean-square radius of gyration ($<R_g^2>^{1/2}$) in CH$_2$Cl$_2$ decreased with increasing branching. The values of the contraction factor, $g = <R_g^2>_{br}/<R_g^2>_{lin}$ of the comb polymer was also lower than that of the three-arm star polymer in CH$_2$Cl$_2$.

The slopes of the log-log plots of $R_g$ vs molecular weight correspond to the scaling coefficients, $\nu$, relating $R_g$ to molecular weight ($R_g = K M^{\nu}$), and were essentially the same for all of the architectures (six-arm star, $\nu = 0.36$; comb, $\nu = 0.39$; linear, $\nu = 0.36$), as expected for linear and branched polymers based on the same chemical repeat unit with sufficiently long arms. However, these values were smaller than the lower limit of 0.50 for a random coil in a theta solvent (Gaussian limit) and approached the hard sphere limit of 0.33. As mentioned in the paper, this showed that the average segment density was greater than that for a Gaussian chain and approached
that for a bulk polymer, presumably due to both the long mesogenic side chains in every repeat unit and the strong intramolecular mesogen-mesogen interactions. Therefore, SCLCPs with the long mesogenic side chains behaved as more branched structures than the nominal star and comb structures.¹⁰

The glass transition temperature (T₉) is a function of backbone structure, molecular weight, the number of end-groups, and the number of crosslinks or branching points. For the dendrimers, the large number of end groups lowers the glass transition temperature, whereas it increases with increasing number of branch points and more polarity of end groups²⁴²,²⁴³. Stutz²⁴⁴ showed that the glass transition temperature based on these parameters became approximately constant at the fourth or the fifth generation without any significant change with further generations. Hawker and Chu⁶⁰ prepared poly(ether ketone)s with the same building block, but with different degrees of branching and terminal units such as fluoro, hydroxy, and benzophenone groups. They demonstrated that the thermal properties of the hyperbranched polymers with different degrees of branching were independent of macromolecular architectures, but depended strongly on the properties of the terminal groups. Kim and Webster²,²⁴ proposed that the glass transition of hyperbranched polymers is due to translational motion of the molecule rather than the segmental motion. According to the authors²,²⁴, the properties depend more on the chain length between the branching points rather than the molecular weights.

Pugh’s group investigated the thermal properties of linear⁷, three-arm star⁸ and comb¹⁰ poly[11-(4’-cyanophenyl-4”-phenoxy)undecyl acrylate]s synthesized by ATRP. The isotropization transitions of all of the polymers, including those with broad polydispersities, were narrow, indicating that the polymers had uniform topologies. The
transition temperatures of these polymers decreased with increasing branching at identical GPC_{PS}-determined molecular weights. The effect of the number of end groups and branch points at higher molecular weights were insignificant as the transition temperatures extrapolated at infinite molecular weight were essentially the same values (g 17 S_{C} 27 S_{A} 146 i) [g = glass; S_{C} = smectic C; S_{A} = smectic A]. Therefore, the differences in the thermotropic behavior of the polymers were also consistent with their designed architectures.

2.10 Potential Applications of Hyperbranched SCLCPs

SCLCPs have been considered for applications based on either electro-thermo-optical effects or separation effects, where the structural integrity, structural flexibility and/or high thermal stability of a polymer may be advantageous over the properties of LMMLCs. For example, liquid crystals are commercially available as the stationary phase for gas chromatography to separate solutes based on their molecular shape, with SCLCPs having much higher thermal stability and column efficiency than LMMLCs.\textsuperscript{12}

However, few applications based on electrical, thermal and/or optical effects have materialized, primarily because of the higher viscosities and slower switching rates of polymeric microphases. Therefore, a highly branched or cyclic architecture with a much lower viscosity might offer a superior polymer for applications that would combine the fluidity of a liquid crystalline phase with the ability of polymers to freeze an anisotropic arrangement below the glass transition.
2.11 Solution Viscosity and Rheological Properties of the Hyperbranched Side-Chain Liquid Crystalline Polyacrylates: Intrinsic Viscosity

The physical properties of a polymer solution depend on temperature, solvent quality and concentration and the nature of polymer itself. The effect of the polymer architecture on its solution properties can be studied by measuring the size and conformation of the polymer in solution. The hydrodynamic volume occupied by a polymer coil is represented by its intrinsic viscosity. Intrinsic viscosity is the volume per unit mass that the polymer occupies in a solution; it is inversely related to molecular density. Intrinsic viscosity can be determined by dilute solution viscosity measurements, which probe the interaction of molecular structure with the solvent. The branching information of a polymer can be obtained using mathematical equations derived from thermodynamic studies of polymer solution theory. In solution, each polymer coil contributes to the viscosity, and in a very dilute solution, the contribution is additive. The solution viscosity, \( \eta \), of a polymer solution increases above the solvent viscosity, \( \eta_s \), linearly with increasing polymer concentration, \( c \). Hence, the solution viscosity can be described by the Huggins and Kraemer Equations 2.3 and 2.4, respectively.

\[
\frac{(\eta - \eta_s)}{\eta_s c} = \eta_{\text{red}} = [\eta] + K_H [\eta]^2 c \
\]
(Equation 2.3)

\[
\ln \left( \frac{\eta}{\eta_s} \right) = \eta_{\text{inh}} = [\eta] + K_K [\eta]^2 c \
\]
(Equation 2.4)

Here, \( K_H \), \( K_K \), \( \eta_{\text{red}} \) and \( \eta_{\text{inh}} \) are the Huggins coefficient, Kraemer coefficient, reduced viscosity and inherent viscosity, respectively. Mathematically, the intrinsic viscosity, \([\eta]\), is defined as the limiting value of either the reduced viscosity, \( \eta_{\text{red}} \), or the inherent viscosity, \( \eta_{\text{inh}} \), as both the shear rate and concentration, \( c \), approach zero (Equation 2.5).
\[ [\eta] = \lim_{c \to 0} \eta_{inh} = \lim_{c \to 0} \eta_{rod} \]  

Equation 2.5

For polymers, the intrinsic viscosity depends on molecular weight, as expressed by Mark-Houwink-Sakurada equation \(^{247}\) (Equation 2.6).

\[ [\eta] = KM_w^\alpha \]  

Equation 2.6

in which, \( K \) and \( \alpha \) are the Mark-Houwink constant and exponent, respectively. These values depend on solvent quality, temperature, and the coil size of the polymer. The exponent \( \alpha \), varies with polymer shape and size, and is approximately equal to 1 for a rigid rod polymer, \(~0.5-0.7\) for a random coil, and \(~0.3\) for a hard sphere. The increase of molecular size with molecular weight is not rapid for a branched polymer as it is for the corresponding linear polymers. This results in a smaller value of \( \alpha \) for a branched polymer. Since branched polymers are more compact, with a lower hydrodynamic volume at a particular molecular weight, their intrinsic viscosities are lower than those of the corresponding linear polymers.

2.12 Melt Viscosity

For a semicrystalline, linear, flexible homopolymer at temperatures above its melting point, the temperature dependence of the melt viscosity, \( \eta_o(T) \), can be described by the Arrhenius equation (Equation 2.7).

\[ \eta_o(T) = k_o \exp\left(\frac{E}{RT}\right) \]  

Equation 2.7

in which, \( k_o \) is the pre-exponential factor, \( E \) is the activation energy for the shear flow, \( R \) is the universal gas constant, and \( T \) is the absolute temperature. An Arrhenius equation may be used to estimate \( \eta_o(T) \) at \( T > T_g + 100 \, ^\circ\text{C} \). For an amorphous, linear flexible
homopolymer at $T_g < T \leq T_g + 100 \, ^\circ\text{C}$, $\eta_o(T)$ can be estimated from the Williams-Landel-Ferry (WLF) equation\textsuperscript{246,248} (Equation 2.8).

$$\log \frac{\eta_o(T)}{\eta_o(T_r)} = -\frac{C_1(T - T_r)}{C_2 + T - T_r}$$

Equation 2.8

in which, $C_1$ and $C_2$ are constants for a given polymer structure and $T_r$ is an arbitrarily chosen reference temperature. The physical origin of this equation lies in the free volume theory.\textsuperscript{248,249,250} Values of $C_1$ and $C_2$ are available in the literature, for various linear flexible homopolymers or can be obtained by curve fitting if $\eta_o(T)$ at various temperatures is available.

When a frequency dependent shear stress is applied to the polymer, shear strain lags the applied stress with a phase angle, $\phi$; this is zero for an ideally elastic material and is $90^\circ$ for an ideally viscous material. The shear modulus is the ratio of shear stress to the shear strain, and it follows a complex relationship as: $G^* = G' + i G''$, in which $G'$ is the elastic or storage modulus and $G''$ is the viscous or loss modulus; and the complex viscosity, $\eta^*$ is defined as the ratio of the shear stress on shear rate.\textsuperscript{247}

Han, et al.\textsuperscript{251} have used log $G'$ vs log $G''$ plots obtained from oscillatory shear experiments to interpret the effect of molecular weight, molecular weight distribution, and long-chain branching on the rheological behavior of flexible homopolymers. For a flexible linear homopolymer, log $G'$ vs log $G''$ plots are virtually independent of temperature and are independent of molecular weight for flexible entangled polymers, but are dependent upon molecular weight for flexible unentangled homopolymers.\textsuperscript{251}

The presence of long-chain branching greatly influences the rheological behavior of flexible homopolymers. Bueche\textsuperscript{252} developed a molecular theory that relates the steady-
state shear viscosity, $\eta_{br}$, of a long-chain branched flexible homopolymer to that of the linear flexible homopolymer, $\eta_{l}$, as shown by Equation 2.9,

$$\frac{\eta_{br}}{\eta_{l}} = gE(g)$$

Equation 2.9

in which

$$E(g) = g^{5/2} \quad \text{when the chains are entangled}$$

$$1 \quad \text{when the chains are not entangled,}$$

$g$ is the ratio of the mean square radii of long-chain branched and linear polymers, and $E(g)$ is a factor that accounts for the change in interaction or entanglements between polymer molecules and depends on the amount of long chain branching. Bueche’s\textsuperscript{252} theory predicts that the viscosity of branched flexible homopolymers is lower than that of linear homopolymers of the same molecular weight. The reduction of the melt viscosity in the presence of long chain branching may be attributed to a reduction in relaxation times, and a reduction in chain entanglements or other interactions between polymer molecules in the bulk. The reduction in chain entanglements or other interactions between polymer molecules might be related to $E(g)$.\textsuperscript{251} For example, Petocolas and Watkins\textsuperscript{253} showed that the melt viscosity of a long-chain branched polyethylene is lower than that of linear polyethylene of the same molecular weight.\textsuperscript{251}
CHAPTER III
EXPERIMENTAL SECTION

3.1 Materials

Acryloyl chloride (Aldrich, 96%), allyl alcohol (Aldrich, 99%), ammonium chloride (Aldrich, EMD Chemicals, 99.5%), anisole (Aldrich, anhydrous, 99.7%), \( t \)-butyl acrylate (Aldrich, 98%), 11-bromoundecan-1-ol, (Alfa Aesar, 97%), CuBr (Aldrich, 99.999%), CuCl (Aldrich, 99.999%), 4-cyan-4'-hydroxybiphenyl (TCI-America, 95%), 2,2'-dipyridyl (Lancaster Synthesis), 1-dodecanol (Alfa Aesar, 98%), formaldehyde (Acros organics, 36% aqueous solution), formic acid (ACS reagent, 96%), hydrogen bromide (Sigma-Aldrich, 48% aqueous solution), hydrogen chloride (EMD, GR ACS, 12M), methacryloyl chloride (Aldrich, 97%), potassium bromide (Sigma-Aldrich, 99%), potassium carbonate (Riedel-De Haen, 99%), \( N,N,N',N' \)-pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%), potassium hydroxide (Fisher Chemicals, certified ACS), 1H, 1H, 2H, 2H-perfluoro-1-decanol (SynQuest), pentamethyldisiloxane (Gelest Inc.), platinum-divinyl tetramethyl-disiloxane complex (Gelest Inc.), DL-serine (Acros Organics, 99%), sodium nitrite (Sigma-Aldrich, 99.5%), sodium sulphate (EMD Chemicals, 98% ), sulfuric acid (EMD Chemicals, 95-98%), tris(2-aminoethyl)amine (TREN) (Strem Chemicals, 97%), tri(n-butyl) tin hydride (TCI, 95%) and tri(n-butyl) tin deutride (Alfa Aesar, 95%) were used as received. Triethylamine (EM Science, 98%)
was stirred over KOH, and distilled under N₂ and stored over KOH. Diethylene glycol monoethyl ether (Aldrich, 99%) was distilled from CaH₂ (Fluka, 95%) and stored over 4 Å molecular sieves. Azobisisobutyronitrile (AIBN) (Aldrich, 98.5%) was recrystallized in hexanes and stored in the refrigerator. p-Toluenesulfonic acid monohydrate (Mallinckrodt, organic reagent) was dried in a vacuum oven overnight at 30 °C. Benzene (Fisher Chemicals, Certified ACS) was washed with concentrated H₂SO₄ (EMD Chemicals, 95-98%) and water, and vacuum distilled from CaH₂ and stored over 4 Å molecular sieves. Reagent grade tetrahydrofuran (THF) was dried by distillation from purple sodium benzophenone ketyl under N₂. Methanol was stored over 4 Å molecular sieves before using as a reactant. All other reagents and solvents were commercially available and used as received.

3.2 Techniques

All reactions were performed under a N₂ atmosphere using a Schlenk line unless noted otherwise. Elemental analyses were performed on a PE 2400 Series II CHNS/O Analyzer. ¹H and ¹³C NMR spectra (δ, ppm) were recorded on either a Varian Mercury 300 (300 MHz and 75 MHz, respectively), an INOVA 400 (400 MHz and 100 MHz, respectively) or an INOVA 750 (750 MHz and 188 MHz, respectively) spectrometer. All spectra were recorded in CDCl₃ or a mixture of CDCl₃ and DMSO-d₆ unless mentioned otherwise; and the resonances were measured relative to the residual solvent resonances and referenced to tetramethylsilane (0.00 ppm). Number average (Mₙ) and weight average (Mₚ) molecular weights and polydispersities (pdi = Mₚ / Mₙ) were determined by GPC/PSI from calibration curves of log Mₙ vs. elution volume at 35 °C using THF as solvent (1.0 mL/min), a set of 50 Å, 100 Å, 500 Å, 10⁴ Å and linear (50-10⁴ Å) Styragel 5
μm columns, a Waters 486 tunable UV/Vis detector set at 254 nm, a Waters 410
differential refractometer, and Millenium Empower 2 software. Absolute molecular
weights were determined by GPC with a light scattering detector (GPC<sub>LS</sub>) at 35 °C using
CH<sub>2</sub>Cl<sub>2</sub> as solvent (1.0 mL/min), a set of 50 Å, 100 Å, 500 Å, 10<sup>4</sup> Å and linear (50-10<sup>4</sup> Å)
Styragel 5 μm, and either a Wyatt Technology DAWN-EOS 18-angle (20° - 153°) or
mini-DAWN (44°, 90°, 134°) light scattering detector equipped with a Ga-As laser (690
nm, 30 mW), with the concentration at each elution volume determined using a Optilab
903 differential refractometer (690 nm). The molecular weight data were calculated
using Astra 4.90.07 software (Wyatt Technology). The refractive index (RI) increments
(<i>dn/dc</i> = 0.120 mL/g in CH<sub>2</sub>Cl<sub>2</sub>) were measured online at room temperature at 690 nm by
Optilab 903 differential refractometer (690 nm) and used to determine the mass
concentrations at each elution volume and the physical constant K<sup>*</sup> for the light
scattering measurements. All samples (approximately 0.5 g/L) were dissolved overnight
and filtered through a 0.45 μm PTFE filter. Molecular weights were also determined by
GPC-RI-viscometry-right angle laser light scattering (GPC<sub>triple</sub>) from universal calibration
curves using the GPC<sub>LS</sub> system combined with a Viscotek 100 differential viscometer and
OmniSEC 4.3.1.246 software from Viscotek.

A Perkin-Elmer Pyris 1 differential scanning calorimeter was used to determine the
thermal transitions, which were read as the maximum or minimum of the endothermic
and exothermic peaks, respectively. Glass transition temperature was noted as the middle
of the change in heat capacity. All heating and cooling rates were 10 °C/min. The
transition temperatures were calibrated using indium and tin standards, and enthalpy
changes were calibrated using indium. All samples were dried in vacuo before
performing DSC experiments. A Leitz Laborlux 12 Pol S polarized optical microscope (magnification 200X) equipped with a Mettler FP82 hot stage and a Mettler FP90 central processor was used to analyze the thermal transitions and anisotropic textures. Thin samples were prepared by melting a minimum amount of compound between a clean glass slide and a cover slip. The breadth of the isotropization transitions was measured by cooling from the isotropic melt at 10 °C/min and recording the temperature at the first appearance of brightness till the last detection of isotropic range.

The mass spectra obtained from MALDI-TOF and tandem mass spectrometry were acquired by Prof. Chrys Wesdemiotis’ group using a Bruker REFLEXIII-TOF mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with a nitrogen laser (337 nm), a single-stage pulsed ion extraction ion source, a two-stage grid-less reflector, and the two dual microchannel plate detectors for detection in linear and reflectron mode. MS spectra were measured with reflectron mode, with the ion source and reflector lens potentials kept at 20 keV and 22.5 keV, respectively. The hyperbranched polymer, dithranol and lithium trifluoroacetate (LiTFA) were dissolved in THF at a concentration of 20 mg/mL, 10 mg/mL and 10 mg/mL, respectively. These solutions were mixed in the ratio of LiTFA: dithranol: hyperbranched polymer 1:10:2, and 0.5 µL of the mixture was applied on the MALDI sample target. The attenuation of the nitrogen laser was adjusted to get the maximum sensitivity without causing the fragmentation of fatty acid. The mass scale was calibrated by using 6 peaks of poly(methyl methacrylate) standard with molecular weight ~ 2000 Da. The sample preparation for tandem mass spectrometry was the same as for the MALDI-TOF mass spectrometry. The major peak obtained from
MALDI-TOF MS was chosen for fragmentation by varying the collisional energy (70-100 eV).

For the rheological measurements, disc shaped specimens were prepared after precipitation of the polymers from THF into methanol. The specimens were dried in vacuo 30 °C for two days. An Advanced Rheometrics Expansion System (ARES, Rheometric Scientific) with a parallel-plate (25 mm diameter plate) fixture, and a gap opening set at 0.6 mm, was employed to conduct oscillatory shear experiments in order to measure the dynamic storage and loss moduli \( (G' \text{ and } G'') \) of each polymer as a function of angular frequency \( (\omega) \) in the range of 0.5 to 100 rad/s. For each sample, the linear viscoelastic region was obtained for both isotropic (melt) and anisotropic (S_A liquid crystalline phase) regions. In the anisotropic phase of the sample, 0.5% strain was selected and for the isotropic region, it was kept at about 20% after confirmation of no edge fracture phenomenon by conducting a time-strain test at the corresponding temperature of measurements.

Two-dimensional \(^1\text{H}-^{13}\text{C} \) gradient Heteronuclear Single Quantum Correlation Spectroscopy (2D-gHSQC, from Varian pulse sequence library) data were acquired using a relaxation delay of 1 sec (d1) and an acquisition time of 0.11 sec with simultaneous \(^{13}\text{C} \) Globally-optimized Alternating-phase Rectangular Pulses (GARP)\(^{254} \) decoupling. Spectral widths of 6520 Hz in the \(^1\text{H} \) dimension and 36530 Hz in the \(^{13}\text{C} \) dimension were used. The \( \pi/2 \) pulse widths for \(^1\text{H} \) and \(^{13}\text{C} \) were 8.4 and 16 \( \mu \)sec, respectively. The acquired data consisted of 2 x 512 data points for \(^1\text{H} \) and 512 data points for \(^{13}\text{C} \) dimensions, with 24 transients for each increment. The \(^1\text{H}-^1\text{H} \) Correlation Spectroscopy (COSY) NMR experiments were carried out on a Varian Inova 750 MHz spectrometer at
30 °C using a H/C/N 5mm-PFG triple resonance probe equipped with Z-gradients. Data were collected using a relaxation delay of 1 sec (d1) and an acquisition time of 0.26 sec with spectral width of 7804 Hz in the $^1$H dimension. The $\pi/2$ pulse width for $^1$H was 8.4 μsec. The acquired data consisted of 2048 x 512 data points for the $^1$H dimensions, with 8 transients for each increment. Two-dimensional gradient $^1$H-$^1$C Heteronuclear Multiple Bond Correlation Spectroscopy (2D-gHMBC) data were acquired on a Varian Inova 750 MHz spectrometer at 110 °C (in d$_4$-o-dichlorobenzene) using a relaxation delay of 1 sec (d1) and an acquisition time of 0.14 sec for the $^1$H dimension. Spectral widths of 7804 Hz in the $^1$H dimension and 37736 Hz in the $^{13}$C dimension were used. The $\pi/2$ pulse widths for $^1$H and $^{13}$C were 8.4 and 16 μsec, respectively. The acquired data consisted of 2048 data points for $^1$H and 2048 data points for $^{13}$C dimensions, with 8 transients for each increment. Two dimensional $^1$H-$^1$H Total Correlation Spectroscopy (2D-TOCSY) NMR experiments were carried out on Varian Inova 750 MHz spectrometer at 110 °C (in d$_4$-o-dichlorobenzene). Data were collected using a relaxation delay of 1 sec (d1) and an acquisition time of 0.16 sec with spectral widths of 6356 Hz in the $^1$H dimensions. The $\pi/2$ pulse width for $^1$H was 8.4 μsec. The one dimensional (1D) $^2$H-NMR (on a Varian INOVA 400 MHz spectrometer) experiments were performed at 30 °C in CDCl$_3$/CHCl$_3$ solution mixture (20/80 w/w) using a pulse width of 8.4 μsec and a relaxation delay of 2 sec to collect 24576 scans using the sweep width of 719 Hz and an acquisition time of 1 sec. The $^2$H-$^{13}$C Insensitive Nuclei Enhanced by Polarization Transfer (INEPT) experiments were carried out on a Varian NMR 500 MHz spectrometer at 30 °C. A $\pi/2$ pulse width of 54 μsec for $^2$H and 12.2 μsec for $^{13}$C were used with the continuous $^1$H decoupling. A spectral window of 30487 Hz was used to collect 24576
scans with the d1 relaxation delay of 2 sec and 0.2 sec acquisition time using one bond 
\[ J^{2}H^{-13}C = 25 \text{ Hz}. \]

3.3 Synthesis of Acrylic Anhydride

Acrylic anhydride was synthesized in 70-80% yield as in the following example. Acryloyl chloride (2.7 g, 30 mmol) was added dropwise over 5 min to an ice-cooled solution of acrylic acid (2.0 g, 30 mmol) and triethylamine (2.8 g, 30 mmol) in THF (50 mL), and the solution was stirred at room temperature for 16 h. The NH\(_4\)\(^+\)Cl\(^-\) precipitate was collected in a fritted glass filter, and the solvent was then removed from the filtrate by rotary evaporation. The residue was dissolved in CH\(_2\)Cl\(_2\) (25 mL), washed twice with dil. aq. NaHCO\(_3\) (50 mL each) and once with satd. NaCl aq. (50 mL), and dried over anhyd. Na\(_2\)SO\(_4\). After filtration and removing the solvent by rotary evaporation, acrylic anhydride as a light yellow liquid (2.8 g, 80%) was obtained. It was used in the reactions without further purification. \(^1\)H NMR (CDCl\(_3\)): 6.04 (m, =CH\(\text{trans}\) to CO\(_2\)), 6.14 (m, =CH\(\text{gem}\) to CO\(_2\)), 6.50 (d, =CH\(\text{cis}\) to CO\(_2\)). \(^13\)C NMR (CDCl\(_3\)/DMSO-d\(_6\)): 127.4 (=CH), 134.7 (=CH\(_2\)), 161.2 (C=O).

3.4 Synthesis of Tris[2-(dimethylamino)ethyl]amine [Me\(_6\)TREN]\(^{255}\)

A solution of TREN (10 g, 70 mmol) in water (25 mL) was added dropwise over 1 h to an ice-cooled solution of formaldehyde (36% in water) (39 g, 0.47 mol) and formic acid (55 g, 1.2 mol). The solution was then refluxed gently for 20 h at 100 °C. After cooling to room temperature, water was removed by trap-to-trap distillation. Unreacted formic acid was removed by dissolving the residue in acetonitrile (20 mL) and passing through a plug of activated basic alumina. The solvent was removed by rotary evaporation and the product was then distilled at 90 °C at 3 mm of mercury to obtain a
colorless liquid (4.1 g, 26%).  $^1$H-NMR (CDCl$_3$):  2.22 (s, (CH$_3$)$_6$), 2.37 [dd, CH$_2$CH$_2$N(CH$_3$)$_2$], 2.60 [dd, CH$_2$N(CH$_3$)$_2$].  $^{13}$C-NMR (CDCl$_3$, 77.23 ppm): 46.1 (CH$_3$), 53.3 [CH$_2$N(CH$_2$)$_2$], 57.7 [CH$_2$N(CH$_3$)$_2$].

3.5 Synthesis of 2-Chloro-3-hydroxypropionic acid

2-Chloro-3-hydroxypropionic acid was synthesized in 45-58% yield as in the following example. In a 3-neck, 1000 mL round-bottom flask, sodium nitrite (68 g, 0.99 mol) was added in portions over 180 min to a solution of DL-serine (52 g, 0.50 mol), potassium chloride (130 g, 1.75 mol) and HCl (116 g of 36.5%-38% w/v aq. sol., 1.21 mol) in water (490 mL) at approximately -10 °C. After stirring at room temperature for 24 h, the light-greenish solution was saturated with NaCl and extracted five times with ethyl acetate (100 mL each). The combined organic extracts were washed five times with saturated aqueous NaCl (50 mL each), and dried over anhydrous Na$_2$SO$_4$. After filtration and removing the solvent by trap-to-trap distillation, the residue was recrystallized from CH$_2$Cl$_2$ to obtain 36 g (58%) of 2-chloro-3-hydroxypropionic acid as a white solid. $^1$H NMR (CDCl$_3$/DMSO-$d_6$): 4.08 (d, CH$_2$OH, $J$ = 6.0 Hz), 4.50 (t, CHCl, $J$ = 6.0 Hz), 6.40 (broad s, COOH and OH). $^{13}$C NMR (CDCl$_3$/DMSO-$d_6$): 57.8 (CCl), 64.3 (COH), 170.4 (C=O). Elemental Analysis (C$_3$H$_5$ClO$_3$): Calculated: C 28.94, H 4.04; Found: C 28.60, H 3.80.

3.6 Synthesis of 2-Bromo-3-hydroxypropionic acid

2-Bromo-3-hydroxypropionic acid was synthesized in 50-63% yield as in the following example. In a 3-neck, 1000 mL, round-bottom flask, sodium nitrite (12 g, 0.17 mol) was added in portions over 270 min to a solution of DL-serine (10 g, 0.10 mol), HBr (26 mL, 48% aq. w/w, 0.23 mol) and potassium bromide (40 g, 0.33 mol) in water (88
mL) at approximately -10 °C. After stirring at room temperature for 16 h, the light-greenish solution was saturated with NaCl and extracted five times with ethyl acetate (50 mL each). The combined organic extracts were washed five times with satd. aq. NaCl (50 mL each), and dried over anhyd. Na₂SO₄. After filtration and removing the solvent by trap-to-trap distillation, the residue was recrystallized from CH₂Cl₂ to obtain 10 g (63%) of 2-bromo-3-hydroxypropionic acid as a white solid. ¹H NMR (CDCl₃/DMSO-d₆): 3.89 (dd, CHHOH, J₁ = 11.9 Hz, J₂ = 5.5 Hz), 3.99 (dd, CHHOH, J₁ = 12.1 Hz, J₂ = 7.2 Hz), 4.30 (dd, CHBr, J₁ = 7.2 Hz, J₂ = 5.7 Hz), 7.19 (broad s, COOH and OH). ¹³C NMR (CDCl₃/DMSO-d₆): 45.6 (CBr), 64.0 (COH), 171.0 (C=O). Elemental Analysis (C₃H₅BrO₃): Calculated: C 21.32, H 2.98; Found C 20.95, H 2.90.

3.7 Synthesis of Methyl 2-chloro-3-hydroxypropionate

Methyl 2-chloro-3-hydroxypropionate was synthesized in 68-88% yield as in the following example. In a 250 mL RB flask, a mixture of 2-chloro-3-hydroxypropionic acid (20 g, 0.16 mol), and a catalytic amount of hydrochloric acid (9 drops) in methanol (200 mL, 5.0 mol) were stirred at 65 °C for 22 h. The unreacted excess methanol was removed by rotary evaporation. A brownish liquid residue was dissolved in CH₂Cl₂ (100 mL), and washed twice with dil. aq. NaHCO₃ (50 mL), and once with satd. aq. NaCl (50 mL), and then dried over anhyd. Na₂SO₄. The crude product was purified by silica gel chromatography using chloroform/diethyl ether (90/10) as the eluent with Rₚ = 0.51 to yield = 17.0 g (76%) of a colorless liquid. ¹H NMR (CDCl₃): 2.55 (broad s, OH), 3.82 (s, CH₃), 3.99 (m, CH₂OH), 4.41 (t, CHCl). ¹³C NMR (CDCl₃): 53.4 (CH₃), 57.0 (CCl), 64.2 (CH₂OH), 169.0 (CO₂CH₃). Elemental Analysis (C₄H₇ClO₃): Calculated: C 34.68, H 5.09; Found: C 34.33, H 4.99.
3.8 Synthesis of Methyl 2-bromo-3-hydroxypropionate

Methyl 2-bromo-3-hydroxypropionate was synthesized in 68-87% yield as in the following example. A solution of 2-bromo-3-hydroxypropionic acid (6.0 g, 35 mmol) and a catalytic amount of HBr (0.2 mL, 48% aq. w/w) in methanol (50 mL, 1.2 mol) was stirred at 65 °C for 21 h. The unreacted excess methanol was then removed by rotary evaporation. The brownish liquid residue was dissolved in CH₂Cl₂ (100 mL) and was washed twice with dil. aq. NaHCO₃ (50 mL), and once with satd. aq. NaCl (100 mL), and then dried over anhyd. Na₂SO₄. After filtration and removing the solvent by rotary evaporation, methyl 2-bromo-3-hydroxypropionate was obtained as a light yellow liquid. The crude product was purified by silica gel chromatography using CH₂Cl₂/diethyl ether (90/10) as the eluent with Rₚ = 0.31 to yield (5.7 g, 87%) of a colorless liquid. ¹H NMR (CDCl₃): 2.70 (broad s, OH), 3.81 (s, CH₃), 4.00 (m, CH₂OH), 4.35 (t, CHBr). ¹³C NMR (CDCl₃): 44.2 (CBr), 53.5 (CH₃), 63.8 (CH₂OH), 169.7 (CO₂CH₃). Elemental Analysis (C₄H₇BrO₃): Calculated: C 26.23, H 3.86; Found: 25.83, 4.10.

3.9 Synthesis of Dodecyl 2-chloro-3-hydroxypropionate

A solution of 2-chloro-3-hydroxypropionic acid (4.8 g, 30 mmol), dodecanol (6.0 g, 30 mmol) and p-TSA (25 mg, 0.26 mmol) in dry benzene (5 mL) in an RB (50 mL) with a Dean-Stark apparatus and condenser was stirred at 75-80 °C for 40 h. ¹H-NMR spectroscopy showed 85% conversion based on the unreacted dodecanol resonance (CH₂OH at 3.63 ppm). More 2-chloro-3-hydroxypropionic acid (1.0 g, 8.0 mmol) was added, and the reaction was continued at 75-80 °C for 20 h. ¹H-NMR spectroscopy showed almost complete conversion. After cooling to room temperature, CH₂Cl₂ (100 mL) was added and the organic phase was washed twice with dil. aq. NaHCO₃ (50 mL),
and once with satd. aq. NaCl (50 mL), and then dried over anhyd. Na₂SO₄. After filtration and removing the solvent by rotary evaporation, 7.76 g (78%) of a light yellow liquid was obtained. It was used for the next reaction without further purification. 

$^1$H-NMR (CDCl₃): 0.87 (t, CH₃), 1.26 [m, (CH₂)₉], 1.67 (m, CO₂CH₂CH₂), 2.66 (broad s, OH), 3.98 (m, CH₂OH), 4.20 (m, CO₂CH₂), 4.39 (t, CHCl). $^{13}$C-NMR (CDCl₃): 14.3 (CH₃), 22.9-32.1 [(CH₂)₉], 57.2 (CHCl), 64.4 (OCH₂CHCl), 66.8 (OCH₂CH₂), 168.7 [CO₂(CH₂)₁₁CH₃].

3.10 Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-decyl 2-chloro-3-hydroxypropionate

A solution of 2-chloro-3-hydroxypropionic acid (6.0 g, 50 mmol), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanol (18 g, 40 mmol) and a catalytic amount of hydrochloric acid (5 drops) were stirred at 65 °C for 36 h. Diethyl ether (300 mL) was added and the organic phase was washed twice with dil. aq. NaHCO₃ sol. (100 mL), and once with satd. aq. NaCl (100 mL), and then dried over anhyd. Na₂SO₄. The solution was filtered, solvent was removed by rotary evaporation and the unreacted alcohol was sublimed off at 70 °C under vacuum to obtain 15 g (67%) of a white solid. $^1$H-NMR (CDCl₃): 2.54 (m, CH₂CF₂), 3.20 (broad s, OH), 4.01 (m, CH₂OH), 4.42 (m, CHCl), 4.52 (m, CO₂CH₂CH₂).

3.11 Synthesis of 11-(4’-Cyanophenyl-4’’-phenoxy)undecyl 2-chloro-3-hydroxypropionate

A mixture of 2-chloro-3-hydroxypropionic acid (2.1 g, 20 mmol), 11-(4’-cyanophenyl-4’’-phenoxy)undecanol (5.2 g, 10 mmol) and a catalytic amount of hydrochloric acid (7 drops) were stirred at 65 °C for 42 h. $^1$H-NMR spectroscopy showed 80% conversion based on the unreacted alcohol resonance (CH₂OH at 3.72 ppm). After
cooling down to 25 °C, the product (R_f = 0.77) was purified by silica gel column chromatography using a solution of ether/chloroform (30/70 v/v) as the eluent. After removing the solvent by rotary evaporation, and drying in vacuo at 30 °C, 3.4 g (56%) of a white solid was obtained. \(^1\)H-NMR (CDCl\(_3\)): 1.31 [m, (CH\(_2\))\(_6\)], 1.48 (m, CH\(_2\)CH\(_2\)CH\(_2\)OAr), 1.69 (m, CH\(_2\)CH\(_2\)OAr), 1.82 (m, CH\(_2\)CH\(_2\)OCO), 2.40 (broad s, OH), 4.02 (m, CH\(_2\)OH & CH\(_2\)OAr), 4.21 (m, CO\(_2\)CH\(_2\)), 4.36 (m, CHCl), 7.00 (d, 2 aromatic H ortho to OCH\(_2\)), 7.53 (d, 2 aromatic H meta to OCH\(_2\)), 7.67 (m, 4 aromatic H ortho and meta to CN). \(^1\)3C-NMR (CDCl\(_3\)): 25.9-29.6 [(CH\(_2\))\(_6\)], 44.9 (CHCl), 64.1 [OCH\(_2\)(CH\(_2\))\(_{10}\)], 66.7 (HOCH\(_2\)), 68.4 (CH\(_2\)OAr), 110.3 (aromatic CCN), 115.3 (aromatic C ortho to O), 119.3 (CN), 127.3 (aromatic C meta to CN), 128.5 (aromatic C meta to O), 131.5 (aromatic C para to O), 132.8 (aromatic C ortho to CN), 145.5 (aromatic C para to CN), 160.0 (aromatic CO), 169.2 [CO\(_2\)(CH\(_2\))\(_{11}\)].

3.12 Synthesis of 11-(4’-Cyanophenyl-4’’-phenoxy)undecyl 2-bromo-3-hydroxypropionate

A mixture of 2-bromo-3-hydroxypropionic acid (5.8 g, 34 mmol), 11-(4’-cyanophenyl-4’’-phenoxy)undecanol\(^7\) (12.5 g, 34 mmol) and a catalytic amount of hydrobromic acid (6 drops) were stirred at 65 °C for 44 h. \(^1\)H-NMR spectroscopy showed 83% conversion based on the unreacted alcohol resonance (CH\(_2\)OH at 3.72 ppm). After cooling down to 25 °C, the product (R_f = 0.36) was purified by silica gel column chromatography using a solution of ether/dichloromethane (5/95, v/v) as the eluent. After removing the solvent by rotary evaporation, and drying in vacuo at 30 °C, (8.6 g, 46 %) of a white solid was obtained. \(^1\)H-NMR (CDCl\(_3\)): 1.32 [m, (CH\(_2\))\(_6\)], 1.49 (m, CH\(_2\)CH\(_2\)CH\(_2\)OAr), 1.69 (m, CH\(_2\)CH\(_2\)OAr), 1.82 (m, CH\(_2\)CH\(_2\)OCO), 2.38 (broad s, OH),

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4.02 (m, $CH_2OH$ & $CH_2OAr$), 4.21 (m, $CO_2CH_2$), 4.36 (s, $CHBr$), 7.00 (d, 2 aromatic $H$ ortho to OCH$_2$), 7.54 (d, 2 aromatic $H$ meta to OCH$_2$), 7.68 (m, 4 aromatic $H$ ortho and meta to CN). $^{13}$C-NMR (CDCl$_3$): 25.9-29.6 [(CH$_2$)$_9$], 44.9 (CHBr), 64.1 [OCH$_2$(CH$_2$)$_{10}$], 66.7 (HOCH$_2$), 68.4 (CH$_2$OAr), 110.3 (aromatic CCN), 115.3 (aromatic $C$ ortho to O), 119.3 (CN), 127.3 (aromatic $C$ meta to CN), 128.5 (aromatic $C$ meta to O), 131.5 (aromatic $C$ para to O), 132.8 (aromatic $C$ ortho to CN), 145.5 (aromatic $C$ para to CN), 160.0 (aromatic CO), 169.2 [CO$_2$(CH$_2$)$_{11}$].

3.13 Synthesis of $\{2$-(2’-Ethoxyethoxy)ethyl$\}$ 2-chloro-3-hydroxypropionate

A solution of 2-chloro-3-hydroxypropionic acid (5.0 g, 40 mmol) and a catalytic amount of $p$-TSA (30 mg, 0.17 mmol) in 2-(2’-ethoxyethoxy)ethanol (5.4 g, 40 mmol) was stirred at 60 °C in vacuo for 48 h. Diethyl ether (100 mL) was added and the organic phase was washed twice with dil. aq. NaHCO$_3$ (50 mL), and once with satd. aq. NaCl (50 mL), and then dried over anhyd. Na$_2$SO$_4$. After filtration, and removing the solvent by rotary evaporation, 4.8 g (47%) of a light yellow liquid was obtained. The product was used in the next reaction without further purification. $^1$H-NMR (CDCl$_3$): 1.22 (m, CH$_3$), 2.86 (broad s, OH), 3.60 (m, CH$_2$O, 6H), 3.75 (t, $CO_2$CH$_2$CH$_2$), 4.00 (d, HOCH$_2$), 4.41 (m, $CO_2$CH$_2$CHCl). $^{13}$C-NMR (CDCl$_3$): 15.2 (CH$_3$), 57.1 (CHCl), 64.5 (CO$_2$CH$_2$), 65.0 (HOCH$_2$), 66.9 (CH$_2$CH$_3$), 68.0 (CH$_2$OCH$_2$CH$_3$), 69.9 (CO$_2$CH$_2$CH$_2$OCH$_2$), 70.8 (CO$_2$CH$_2$CH$_2$O), 168.6 (CO$_2$).

3.14 Synthesis of $n$-(Pentamethyldisiloxyl)propyl alcohol by Hydrosilylation of Allyl alcohol with Pentamethyldisiloxane

A solution of pentamethyldilsiloxane (8.4 g, 56 mmol) and allyl alcohol (3.1 g, 54 mmol) and a catalytic amount of platinum-divinyl tetramethyl disiloxane complex (1
drop) was stirred at 25 °C for 18 h and the solution was passed through a plug of basic alumina. A light brown liquid, 10.3 g (89%) was obtained. This was used for the next reactions without any purification. ¹H-NMR (CDCl₃): 0.07 (m, C₂H₃, 15H), 0.53 (m, C₂H₂Si), 1.59 (m, C₂H₂CH₂Si), 3.60 (m, OCH₂). ¹³C-NMR (CDCl₃, 77.23 ppm): 0.45 [Si(CH₃)₃], 2.14 [Si(CH₃)₂], 14.3 (CH₂Si), 26.8 (CH₂CH₂Si), 65.8 (OCH₂).

3.15 Synthesis of [n-(Pentamethyldisiloxy)propyl] 2-chloro-3-hydroxypropionate

A solution of 2-chloro-3-hydroxypropionic acid (2.4 g, 0.02 mol), and a catalytic amount of p-TSA (36 mg, 0.20 mmol) in (pentamethyldisiloxy)propyl alcohol (4.0 g, 0.02 mol) was stirred at 60 °C for 48 h. Diethyl ether (100 mL) was added and the organic phase was washed twice with dil. aq. NaHCO₃ (50 mL), and once with satd. NaCl aq. soln. (50 mL), and then dried over anhyd. Na₂SO₄. The product (Rf = 0.78) was purified by silica gel column chromatography using a solution of diethyl ether/dichloromethane (10/90 v/v) as the eluent. After removing the solvent by rotary evaporation, and drying in vacuo at 30 °C, 2.19 g (51%) of a colorless liquid was obtained. ¹H-NMR (CDCl₃): 0.08 (m, C₂H₃, 15H), 0.54 (m, C₂H₂Si), 1.71 (m, C₂H₂CH₂Si), 2.36 (t, HOCH₂), 4.02 (m, HOCH₂), 4.19 (m, CO₂CH₂), 4.41 (t, CHCl). ¹³C-NMR (CDCl₃): 0.41 [Si(CH₃)₃], 2.12 [Si(CH₃)₂], 14.1 (CH₂Si), 22.6 (CH₂CH₂Si), 57.2 (CHCl), 64.3 (CO₂CH₂), 69.0 (CO₂CH₂), 170.9 (CO₂).

3.16 Synthesis of (2-Chloro-2-methoxycarbonyl)ethyl acrylate

(2-Chloro-2-methoxycarbonyl)ethyl acrylate was synthesized in 34-50% yield as in the following example. A solution of triethylamine (6.6 g, 65 mmol) in THF (25 mL) was added dropwise over 30 min to a solution of methyl 2-chloro-3-hydroxypropionate (5.0 g, 35 mmol) and acryloyl chloride (5.8 g, 63 mmol) in THF (5 mL) at 0 °C. After
stirring at 25 °C for 16 h, the milky white solution was poured into ice-cooled water (200 mL) and stirred for 6 h. The product was extracted with CH₂Cl₂ (5 times of each 50 mL). The combined organic phase was washed twice with dil. aq. NaHCO₃ (50 mL each) and once with satd. aq. NaCl (50 mL), and dried over anhyd. Na₂SO₄. After filtration and removing the solvent by rotary evaporation (2-chloro-2-methoxycarbonyl)ethyl acrylate was obtained as an yellow liquid. The product was obtained as a colorless liquid (3.4 g, 50%) by vacuum distillation at 3 mm of mercury at 94-96 °C. ^1H NMR (CDCl₃): 3.79 (s, CH₃), 4.52 (m, CO₂CH₂CHCl), 5.88 (dd, =CH trans to CO₂, J₁ = 10.4 Hz, J₂ = 1.20 Hz), 6.11 (dd, =CH gem to CO₂, J₁ = 10.6 Hz, J₂ = 10.6 Hz), 6.44 (dd, =CH cis to CO₂, J₁ = 17.3 Hz, J₂ = 1.20 Hz). ^13C NMR (CDCl₃): 53.5 (CH₃), 53.7 (CCl), 64.6 (CH₂O₂C), 127.6 (=CH₂), 132.3 (=CH), 165.4 (CO₂CH₃), 167.9 (CO₂CH₂). Elemental Analysis (C₇H₉ClO₄): Calculated: C 43.65, H 4.71; Found: C 43.48, H 4.73.

3.17 Synthesis of (2-Bromo-2-methoxycarbonyl)ethyl acrylate

(2-Bromo-2-methoxycarbonyl)ethyl acrylate was synthesized in 55-68% yield as in the following example. A solution of acrylic anhydride (0.80 g, 6.3 mmol) in THF (5 mL) was added dropwise over 10 min to a solution of methyl 2-bromo-3-hydroxypropionate (0.50 g, 2.7 mmol) and triethylamine (0.55 g, 5.4 mmol) in THF (25 mL) at 25 °C. After stirring 25 °C for 21 h, the solution was poured into ice-cooled water (25 mL) and stirred for 3 h. THF was removed by rotary evaporation and CH₂Cl₂ was added. After separating the two layers, the organic phase was washed twice with dil. aq. NaHCO₃ (25 mL each) and once with satd. aq. NaCl (25 mL), and dried over anhyd. Na₂SO₄. After filtration and removing the solvent by rotary evaporation, the resulting yellow liquid was vacuum distilled at 3 mm of mercury at 92-94 °C to yield (0.44 g,
68%) of a colorless liquid.  $^1$H NMR (CDCl$_3$): 3.83 (s, CH$_3$), 4.58 (m, CO$_2$CH$_2$CHBr), 5.92 (dd, =CH trans to CO$_2$, $J_1$ = 10.6 Hz, $J_2$ = 1.51 Hz), 6.14 (dd, =CH gem to CO$_2$, $J_1$ = 10.6 Hz, $J_2$ = 10.2 Hz), 6.43 (dd, =CH cis to CO$_2$, $J_1$ = 17.2 Hz, $J_2$ = 1.32 Hz).  $^{13}$C NMR (CDCl$_3$): 40.4 (CBr), 53.5 (CH$_3$), 64.31 (CH$_2$O$_2$C), 127.6 (=CH), 132.4 (=CH$_2$), 165.3 (CO$_2$CH$_3$), 168.3 (CO$_2$CH$_2$).  Elemental Analysis (C$_7$H$_9$BrO$_4$): Calculated: C 35.47, H 3.83; Found: 35.24, 3.75.

3.18 Synthesis of (2-Chloro-2-dodecan-1-oxycarbonyl)ethyl acrylate

A solution of acryloyl chloride (1.95 g, 21.5 mmol) in THF (5 mL) was added dropwise over 10 min to an ice-cooled solution of dodecyl 2-chloro-3-hydroxypropionate (4.20 g, 14.3 mmol) and triethylamine (2.17 g, 21.5 mmol) in dry THF (50 mL). The reaction mixture was removed from the ice bath and stirred at 25 ℃ for 21 h. The reaction mixture was poured into ice-cooled water (100 mL) and THF was removed by rotary evaporation. The aqueous solution was extracted five times with CH$_2$Cl$_2$ (50 mL each). The organic phase was washed twice with dil. aq. NaHCO$_3$ aq. (50 mL), and once with satd. aq. NaCl (50 mL), and then dried over anhyd. Na$_2$SO$_4$. After filtration, the solvent was removed by rotary evaporation. The product ($R_f$ = 0.47) was purified by silica gel column chromatography using a solution of ethyl acetate (1-5%/hexane as the eluant. A colorless liquid (2.9 g, 59%) was obtained after removing the solvent by rotary evaporation and drying in vacuo at 25 ℃. $^1$H-NMR (CDCl$_3$): 0.84 (t, CH$_3$), 1.26 [m, (CH$_2$)$_9$], 1.62 (m, CO$_2$CH$_2$CH$_2$), 4.18 (t, CO$_2$CH$_2$CH$_2$, $J$ = 6.75 Hz) 4.54 (m, CO$_2$CH$_2$CHCl), 5.86 (dd, =CH trans to CO$_2$, $J_1$ = 10.4 Hz, $J_2$ = 1.54 Hz), 6.10 (dd, =CH gem to CO$_2$, $J_1$ = 10.5 Hz, $J_2$ = 10.3 Hz), 6.45 (dd, =CH cis to CO$_2$, $J_1$ = 17.3 Hz, $J_2$ = 1.37 Hz). $^{13}$C-NMR (CDCl$_3$): 14.1 (CH$_3$), 22.4-31.8 [(CH$_2$)$_9$], 53.9 (CHCl), 64.7

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(OCH$_2$CH$_2$), 66.9 (OCH$_2$CHCl), 127.7 (=CH), 132.1 (=CH$_2$), 165.2 (CO$_2$CH$_2$CHCl), 167.6 [CO$_2$(CH$_2$)$_{11}$CH$_3$]. Elemental Analysis (C$_{18}$H$_{31}$ClO$_4$): Calculated: C 62.32, H 9.01; Found: 62.19, 9.36.

3.19 Synthesis of \{2-Chloro-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecan-1-oxycarbonyl)}ethyl acrylate

A solution of triethylamine (1.8 g, 20 mmol) in THF (5 mL) was added dropwise over 40 min to an ice-cooled solution of (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decyl)-2-chloro-3-hydroxy propionate (5.0 g, 10 mmol) and acryloyl chloride (1.5 g, 20 mol) in THF (80 mL), and the resulting mixture was stirred at 25 °C for 12 h. The reaction mixture was then poured into ice-cooled water (100 mL) and stirred overnight. CH$_2$Cl$_2$ (100 mL) was added and the water phase was neutralized with NaHCO$_3$. The two layers were separated and the aqueous phase was extracted five times with CH$_2$Cl$_2$ (50 mL each). The combined organic phase was washed twice with dil. aq. NaHCO$_3$ (50 mL each), and once with sat. aq. NaCl (50 mL each), and then dried over anhyd. Na$_2$SO$_4$. The product (R$_f$ = 0.61-0.74) was purified by silica gel column chromatography using CHCl$_3$ as an eluent. A white solid (2.37 g, 43%) was obtained after removing the solvent by rotary evaporation and drying in vacuo at 25 °C. $^1$H-NMR (CDCl$_3$): 2.52 (m, CH$_2$CF$_2$), 4.55 (m, CO$_2$CH$_2$CHCl & CO$_2$CH$_2$CH$_2$), 5.89 (dd, =CH trans to CO$_2$, $J_1$ = 10.4 Hz, $J_2$ = 1.03 Hz), 6.12 (dd, =CH gem to CO$_2$, $J_1$ = 10.6 Hz, $J_2$ = 10.4 Hz), 6.41 (dd, =CH cis to CO$_2$, $J_1$ = 17.3 Hz, $J_2$ = 1.03 Hz). $^{13}$C-NMR (CDCl$_3$): 30.5 (CH$_2$CF$_2$), 53.4 (CHCl), 58.4 (OCH$_2$CH$_2$), 64.4 (OCH$_2$CHCl), 105.0-122.0 [(CF$_2$)$_7$CF$_3$], 127.5 (=CH), 132.3 (=CH$_2$), 165.4 (CO$_2$CH$_2$CHCl), 167.2 (CO$_2$CH$_2$CH$_2$).
Elemental Analysis (C_{16}H_{10}ClF_{17}O_{4}): Calculated: C 30.76, H 1.71; Found C 30.84, H 1.55.

3.20 Synthesis of \{2-Chloro-2-[11''-(4''-cyanophenyl-4'''-phenoxy)undecan-1-oxycarbonyl]ethyl acrylate\}

A solution of acryloyl chloride (1.8 g, 20 mmol) in THF (5 mL) was added dropwise over 4 min to an ice-cooled solution of \{11-(4'-cyanophenyl-4''-phenoxy)undecyl\} 2-chloro-3-hydroxypropionate (6.0 g, 13 mmol) and triethylamine (1.9 g, 20 mmol) in THF (200 mL). After 17 h, the reaction mixture was poured into ice-cooled water (200 mL) and stirred for 21 h. The white precipitate was filtered off and dried in vacuo at 25 °C. The residue (R_f = 0.70) was purified by silica gel chromatography using a solution of ether/chloroform (5/95, v/v) as an eluent to yield 3.41 g (51%) of a white solid, which was recrystallized in ethanol (200 mL) to yield 3.3 g (50%) as a white powder. \(^1\)H-NMR (CDCl\(_3\)): 1.31 [m, (CH\(_2\))\(_6\)], 1.48 (m, CH\(_2\)CH\(_2\)CH\(_2\)OAr), 1.69 (m, CH\(_2\)CH\(_2\)OAr), 1.82 (m, CH\(_2\)CH\(_2\)OCO), 4.01 (t, CH\(_2\)OAr, J = 6.62 Hz), 4.20 (t, CH\(_2\)O\(_2\)C, J = 6.62 Hz), 4.54 (m, CO\(_2\)CH\(_2\)CHCl), 5.90 (dd, =CH trans to CO\(_2\), J = 10.6 Hz, J = 1.51 Hz), 6.15 (dd, =CH gem to CO\(_2\), J = 10.6 Hz, J = 10.2 Hz), 6.46 (dd, =CH cis to CO\(_2\), J = 17.4 Hz, J = 1.51 Hz), 6.99 (d, 2 aromatic H ortho to OCH\(_2\), J = 8.70 Hz), 7.53 (d, 2 aromatic H meta to OCH\(_2\), J = 8.70 Hz), 7.67 (m, 4 aromatic H ortho and meta to CN). \(^{13}\)C-NMR (CDCl\(_3\)): 25.9-29.7 [(CH\(_2\))\(_6\)], 53.9 (CHCl), 64.7 [OCH\(_2\)(CH\(_2\))\(_{10}\)], 66.8 (OCH\(_2\)CHCl), 68.4 (CH\(_2\)OAr), 110.2 (aromatic CCN), 115.3 (aromatic C ortho to O), 119.3 (CN), 127.3 (aromatic C meta to CN), 127.6 (=CH), 128.5 (aromatic C meta to O), 131.4 (aromatic C para to O), 132.3 (=CH\(_2\)), 132.8 (aromatic C ortho to CN), 145.5 (aromatic C para to CN), 160.0 (aromatic CO), 165.4
(CO₂CH₂CHCl), 167.4 [CO₂(CH₂)₁₁]. Elemental Analysis (C₃₀H₃₆ClNO₅): Calculated: C 68.49, H 6.90, N 2.66; Found: C 68.24, H 6.88, N 2.93.

3.21 Synthesis of {2-Bromo-2-[11’-(4”-cyanophenyl-4’’-phenoxy)undecan-1-oxycarbonyl]}ethyl acrylate

Solutions of triethylamine (1.4 g, 14 mmol) in THF (5 mL) and acrylic anhydride (1.8 g, 14 mmol) in THF (5 mL) were added separately but simultaneously dropwise over 15 min to an ice-cooled solution of {11-(4’-cyanophenyl-4’’-phenoxy)undecyl} 2-bromo-3-hydroxypropionate (4.8 g, 9.3 mmol) in THF (100 mL). After stirring at 25 °C for 24 h, the reaction mixture was poured into ice-cooled water (100 mL) and stirred for 21 h. The resulting precipitate was collected in a fritted glass filter and dried in vacuo 25 °C. The crude product (Rᶠ = 0.59) was purified by silica gel chromatography using dichloromethane as the eluent to yield (2.8 g, 51%) of a white solid, which was recrystallized from ethanol (200 mL) to yield (2.7 g, 48%) of a white powder. ¹H-NMR (CDCl₃): 1.31 [m, (CH₂)₆], 1.48 (m, CH₂CH₂CH₂OAr), 1.67 (m, CH₂CH₂OAr), 1.82 (m, CH₂CH₂OOCO), 4.02 (t, CH₂OAr, J = 6.43 Hz), 4.22 (m, CH₂O₂C), 4.42-4.64 (m, CO₂CH₂CHBr), 5.90 (dd, =CH trans to CO₂, J₁ = 10.3 Hz, J₂ = 1.51 Hz), 6.14 (dd, =CH gem to CO₂, J₁ = 10.2 Hz, J₂ = 10.2 Hz), 6.45 (dd, =CH cis to CO₂, J₁ = 17.4 Hz, J₂ = 1.41 Hz), 7.00 (d, 2 aromatic H ortho to OCH₂, J = 8.70 Hz), 7.52 (d, 2 aromatic H meta to OCH₂, J = 9.08 Hz), 7.67 (m, 4 aromatic H ortho and meta to -CN). ¹³C-NMR (CDCl₃): 25.9-29.7 [(CH₂)₆], 47.3 (CHBr), 64.7 [OCH₂(CH₂)₁₀], 66.8 (OCH₂CHCl), 68.4 (CH₂OAr), 110.2 (aromatic CCN), 115.3 (aromatic C ortho to O), 119.3 (CN), 127.3 (aromatic C meta to CN), 127.6 (=CH), 128.5 (aromatic C meta to O), 131.4 (aromatic C para to O), 132.3 (=CH₂), 132.8 (aromatic C ortho to CN), 145.5 (aromatic C para to
CN), 160.0 (aromatic CO), 165.4 (CO\textsubscript{2}CH\textsubscript{2}CHCl), 167.4 [CO\textsubscript{2}(CH\textsubscript{2})\textsubscript{11}]. Elemental Analysis (C\textsubscript{30}H\textsubscript{36}BrNO\textsubscript{5}): Calculated: C 63.16, H 6.36, N 2.46; Found: C 62.66, H 6.45, N 2.14.

3.22 Synthesis of \{2-Chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]\}ethyl methacrylate

A solution of methacryloyl chloride (0.67 g, 6.4 mmol) in THF (5 mL) was added dropwise over 7 min to an ice-cooled solution of \{11-(4’-cyanophenyl-4’’-phenoxy)undecyl\} 2-chloro-3-hydroxypropionate (2.0 g, 0.42 mmol) and triethylamine (0.65 g, 6.4 mmol) in THF (100 mL). After stirring at 25 °C for 16 h, the reaction mixture was poured into ice cooled water (200 mL) and stirred for 21 h. The white precipitate was collected on a fritted glass filter and dried in vacuo at 25 °C. The crude product (R\textsubscript{f} = 0.79) was purified by silica gel chromatography using a solution of ether/chloroform (5/95, v/v) as the eluent to yield 1.63 g (71%) of a white powder, which was recrystallized from ethanol (200 mL) to yield (1.58 g, 69%) of a white powder. ¹\textsuperscript{H}-NMR (CDCl\textsubscript{3}): 1.30 (m, [(CH\textsubscript{2})\textsubscript{6}]), 1.48 (m, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OAr), 1.66 (m, CH\textsubscript{2}CH\textsubscript{2}OAr), 1.82 (m, CH\textsubscript{2}CH\textsubscript{2}OCO), 1.95 (s, CH\textsubscript{3}), 4.01 (t, CH\textsubscript{2}OAr, J = 6.62 Hz), 4.21 (t, CH\textsubscript{2}O\textsubscript{2}C, J = 6.62 Hz), 4.54 (m, CO\textsubscript{2}CH\textsubscript{2}CHCl), 5.63 (s, =CH trans to CO\textsubscript{2}), 6.13 (s, =CH cis to CO\textsubscript{2}), 7.00 (d, 2 aromatic H ortho to OCH\textsubscript{2}, J = 8.70 Hz), 7.53 (d, 2 aromatic H meta to OCH\textsubscript{2}, J = 8.70 Hz) 7.67 (m, 4 aromatic H ortho and meta to CN). ¹³\textsuperscript{C}-NMR (CDCl\textsubscript{3}): 18.4 (CH\textsubscript{3}), 25.9-29.7 [(CH\textsubscript{2})\textsubscript{9}], 54.0 (CHCl), 64.9 [OCH\textsubscript{2}(CH\textsubscript{2})\textsubscript{10}], 66.8 (OCH\textsubscript{2}CHCl), 68.3 (CH\textsubscript{2}OAr), 110.2 (aromatic CCN), 115.3 (aromatic C ortho to O), 119.3 (CN), 126.9 (aromatic C meta to CN), 127.2 (=CH), 128.5 (aromatic C meta to O), 131.4 (aromatic C para to O), 132.4 (=CH\textsubscript{2}), 132.7 (aromatic C ortho to CN), 145.5 (aromatic C para to
CN), 160.0 (aromatic CO), 166.6 (CO$_2$CH$_2$CHCl), 167.5 [CO$_2$(CH)$_2$]$_{11}$. Elemental Analysis (C$_{31}$H$_{38}$ClNO$_5$): Calculated: C 68.94, H 7.09, N 2.59; Found: C 68.49, H 7.20, N 2.42.

3.23 Synthesis of {2-Chloro-2-(2’-ethoxyethoxy)ethan-1-oxycarbonyl}ethyl acrylate

A solution of acryloyl chloride (0.84 g, 9.3 mmol) in THF (5 mL) was added dropwise over 10 min to an ice-cooled solution of {2-(2’-ethoxyethoxy)ethyl} 2-chloro-3-hydroxypropionate (1.5 g, 6.2 mmol) and NEt$_3$ (0.96 g, 9.5 mmol) in THF (80 mL). After stirring at 25 °C for 18 h, [NEt$_3$H]$^+$Cl$^-$ was filtered off and the solution was concentrated by rotary evaporation. The concentrated solution was then passed through a plug of basic activated alumina. The product (R$_f$ = 0.36) was purified by silica gel column chromatography using solution of ethyl acetate/hexanes (40/60, v/v) as the eluent to yield (1.23 g, 67%) of a colorless liquid. $^1$H-NMR (CDCl$_3$): 1.18 (t, CH$_3$), 3.65 (m, OCH$_2$, 6H), 4.34 (t, CO$_2$CH$_2$), 4.53 (m, CO$_2$CH$_2$CHCl), 5.87 (dd, =CH$_{trans}$ to CO$_2$, J1 = 10.7 Hz, J2 = 1.50 Hz), 6.11 (dd, =CH$_{gem}$ to CO$_2$, J1 = 10.3 Hz, J2 = 10.3 Hz), 6.43 (dd, =CH$_{cis}$ to CO$_2$, J1 = 17.0 Hz, J2 = 1.50 Hz). $^{13}$C-NMR (CDCl$_3$): 15.3 (CH$_3$), 53.8 (CHCl), 64.6 (CO$_2$CH$_2$CH$_2$), 65.6 (CO$_2$CH$_2$CHCl), 66.8 (OCH$_2$CH$_3$), 68.8 (CH$_2$OCH$_2$CH$_3$), 69.9 (CO$_2$CH$_2$CH$_2$OCH$_2$CH$_2$), 70.8 (CO$_2$CH$_2$CH$_2$O), 127.6 (=CH$_2$), 132.21 (=CH), 165.3 (CO$_2$CH$_2$CH$_3$), 167.3 (CO$_2$CH$_2$CHCl). Elemental Analysis (C$_{12}$H$_{19}$ClO$_6$): Calculated: C 48.90, H 6.50; Found: C 48.59, H 6.42.

3.24 Synthesis of {2-Chloro-2-[n-(pentamethyldisiloxyl)propyl]ethan-1-oxycarbonyl}ethyl acrylate

A solution of acryloyl chloride (0.65 g, 7.2 mmol) in THF (5 mL) was added dropwise over 8 min to an ice-cooled solution of [n-(pentamethyldisiloxyl)propyl] 2-
chloro-3-hydroxypropionate (1.5 g, 4.8 mmol) and triethylamine (0.73 g, 7.2 mmol) in dry THF (100 mL), and the reaction mixture was stirred at 25 °C for 21 h. The precipitate [NEt₃H]⁺Cl⁻ was filtered off and the solution was concentrated by rotary evaporation. After passing through a plug of basic activated alumina, the product (R_f = 0.74) was purified by silica gel column chromatography using dichloromethane as the eluant to yield (1.1 g, 62%) as a colorless liquid. ¹H-NMR (CDCl₃): 0.06 [m, (CH₃)₃], 0.52 (m, CH₂Si), 1.68 (m, CH₂CH₂Si), 4.17 (t, CO₂CH₂CH₂, J = 7.00 Hz), 4.54 (m, CO₂CH₂CHCl), 5.89 (dd, =CH trans to CO₂, J₁ = 10.6 Hz, J₂ = 1.14 Hz), 6.1 (dd, =CH gem to CO₂, J₁ = 10.6 Hz, J₂ = 10.2 Hz), 6.45 (dd, =CH cis to CO₂, J₁ = 17.4 Hz, J₂ = 1.50 Hz). ¹³C-NMR (CDCl₃): 0.4 [Si(CH₃)₃], 2.1 [Si(CH₃)₂], 14.1 (CH₂Si), 22.7 (CH₂CH₂Si), 53.6 (CHCl), 64.7 (CO₂CH₂CH₂), 69.1 (CO₂CH₂CHCl), 127.7 (=CH₂), 132.2 (=CH), 165.4 [CO₂(CH₂)₆Si], 167.4 (CO₂CH₂CHCl). Elemental Analysis (C₁₄H₂₇ClO₅Si₂): Calculated: C 45.82, H 7.42; Found: C 45.69, H 7.42.

3.25 Synthesis of [11-(4’-Cyanophenyl-4’’-phenoxy)undecyl] acrylate⁷

A solution of triethylamine (0.42 g, 4.2 mmol) in THF (10 mL) was added dropwise over 5 min to an ice-cooled solution of 11-(4’-cyanophenyl-4’’-phenoxy)undecanol (0.91 g, 2.5 mmol) in THF (200 mL), which was followed by dropwise addition (over 5 min) of a solution of acryloyl chloride (0.33 g, 3.6 mmol) in THF (10 mL). After 18 h, the reaction mixture was poured into ice-cooled water (200 mL) and stirred overnight to evaporate THF. The product was collected on a fritted glass filter and was recrystallized from ethanol/toluene (50 mL/3 mL) to yield (0.87 g, 84%) a white solid. ¹H-NMR (CDCl₃): 1.31 [m, (CH₃)₆], 1.48 (m, CH₂CH₂CH₂OAr), 1.67 (m, CH₂CH₂OAr), 1.82 (m, CH₂CH₂OCO), 4.00 (t, CH₂OAr), 4.15 (t, CH₂O₂C), 5.81 (dd,
3.26 ATRP of (2-Chloro-2-methoxycarbonyl)ethyl acrylate and (2-Chloro-2-methoxycarbonyl)ethyl acrylate

In a typical example, a solution of (2-chloro-2-methoxycarbonyl)ethyl acrylate (0.30 g, 1.6 mmol) in water (0.30 g) was added to a mixture of Cu(I)Cl (3.1 mg, 0.03 mmol) and Me₆TREN (6.7 mg, 0.030 mmol) in a N₂ filled Schlenk tube and the mixture was degassed by three cycles (10-30-20-10 min) of freeze-pump-thaw and backfilling with N₂; the polymerization solution was stirred at 50 °C for 46 h. The polymerization was quenched by immersing the tube into liquid N₂. It was followed by a thaw and the tube was opened to ambient atmosphere. The solution was diluted with THF (5 mL) and precipitated into satd. aq. NH₄Cl (25 mL). The precipitate was reprecipitated from THF (5 mL) once into methanol (25 mL). The product was dried in vacuo at 25 °C to yield (0.12 g, 40%) of a light yellow waxy solid. GPCₚₛₜ (THF): Mₙ = 1.76 x 10⁴ Da, pdi = 1.52.

3.27 ATRP of {2-Chloro-2-[11'--(4''-cyanophenyl-4'''-phenoxy)undecan-1-oxy carbonyl]}ethyl acrylate and {2-Bromo-2-[11'--(4''-cyanophenyl-4'''-phenoxy)undecan-1-oxy carbonyl]}ethyl acrylate

In a typical example, {2-chloro-2-[11'--(4''-cyanophenyl-4'''-phenoxy)undecan-1-oxy carbonyl]}ethyl acrylate followed by a solution of acetonitrile/water (0.50 mL/0.10 mL) were added to a mixture of Cu(I)Cl (1.0 mg, 0.01 mmol) and Me₆TREN (2.1 mg, 0.010 mmol) in N₂ filled Schlenk tube. The mixture was degassed by three cycles (10-30-20 min) of freeze-pump-thaw and the polymerization solution was stirred at 90 °C for
120 h. The polymerization was quenched by immersing the tube into liquid N₂. It was followed by a thaw and the tube was opened to ambient atmosphere. The solution was diluted with THF (5 mL) and precipitated into satd. aq. NH₄Cl (25 mL). The precipitate was reprecipitated from THF (5 mL) twice into methanol (25 mL). The product was dried in vacuo to yield 0.12 g (66%) of a white solid. GPC_{PSt} (THF): Mₙ = 3.26 x 10⁴ Da, pdi = 1.90.

3.28 ATRP of {2-Chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxycarbonyl]ethyl methacrylate

{2-Chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxycarbonyl]ethyl methacrylate followed by anisole (0.60 mL) were added to a mixture of Cu(I)Br (1.90 mg, 0.013 mmol) and PMDETA (3.00 μL, 0.014 mmol) in N₂ filled Schlenk tube. The mixture was degassed by three cycles (10-30-20 min) of freeze-pump-thaw and the polymerization solution was stirred at 120 °C for 100 h. The polymerization was quenched by immersing the tube into liquid N₂. It was followed by a thaw and the tube was opened to ambient atmosphere. The solution was diluted with THF (5 mL) and precipitated thrice into methanol (25 mL). The product was dried in vacuo to yield (0.42 g, 70%) of a tan solid. GPC_{PSt} (THF): Mₙ = 17.5 x 10³ Da, pdi = 2.82.

3.29 ATRP of {2-Chloro-2-(2’-ethoxyethoxy)ethan-1-oxycarbonyl}ethyl acrylate

{2-Chloro-2-(2’-ethoxyethoxy)ethan-1-oxycarbonyl}ethyl acrylate (0.10 g, 0.34 mmol) followed by acetonitrile/water (0.15 g/0.15 g) were added to a mixture of Cu(I)Br (2.4 mg, 0.016 mmol) and PMDETA (3.5 μL, 0.017 mmol) in N₂ filled schlenk tube. The mixture was degassed by three cycles (10-30-20 min) of freeze-pump-thaw and the polymerization solution was stirred at 20 °C for 4 h. The polymerization was quenched
by immersing the tube into liquid N$_2$. It was followed by a thaw and the tube was opened to ambient atmosphere. The solution was diluted with THF (5 mL) and passed through a plug of neutral alumina. After removing THF by rotary evaporation, the product was dried in vacuo to yield (0.024 g, 24%) of a viscous oil was obtained. GPC$_{Ps}$ (THF): $M_n = 3.4 \times 10^4$ Da, $pdi = 2.33$.

3.30 ATRP of {2-Chloro-2-$[n$-(pentamethyldisiloxyl)propyl]ethan-1-oxycarbonyl}ethyl acrylate

{2-Chloro-2-$[n$-(pentamethyldisiloxyl)propyl]ethan-1-oxycarbonyl}ethyl acrylate (0.30 g, 0.82 mmol) followed by anisole (0.5 mL) were added to a mixture of Cu(I)Br (6.0 mg, 0.042 mmol) and PMDETA (8.5 $\mu$L, 0.041 mmol) in N$_2$ filled Schlenk tube. The mixture was degassed by three cycles (10-30-20 min) of freeze-pump-thaw and the polymerization solution was stirred at 120 °C for 96 h. The polymerization was quenched by immersing the tube into liquid N$_2$. It was followed by a thaw and the tube was opened to ambient atmosphere. The solution was diluted with THF (5 mL) and passed through a plug of neutral alumina. After removing THF by rotary evaporation, the product was dried in vacuo to yield (0.074 g, 24%) of a viscous oil was obtained. GPC$_{Ps}$ (THF): $M_n = 2.9 \times 10^3$ Da, $pdi = 1.44$.

3.31 Copolymerization of (2-Bromo-2-methoxycarbonyl)ethyl acrylate and ter-Butyl acrylate

A solution of (2-bromo-2-methoxycarbonyl) ethyl acrylate (0.37 g, 1.56 mmol) and ter-butyl acrylate (2.00 g, 15.6 mmol) were added to a mixture of Cu(I)Br (0.04 g, 0.31 mmol) and 2,2'-dipyridyl (0.15 g, 0.94 mmol) in a N$_2$ filled Schlenk tube. The mixture was degassed by three cycles (10-30-20 min) of freeze-pump-thaw and the polymerization solution was stirred at 90 °C for 4 h. The polymerization was quenched
by immersing the tube into liquid N₂. It was followed by a thaw and the tube was opened to ambient atmosphere. The reaction mixture was diluted with THF (5 mL) and precipitated thrice into methanol/water mixture (60 mL/30 mL) to yield (1.08 g, 46%) of a white paste. GPC₃₆ (THF): $M_n = 15.3 \times 10^3$ Da, $\text{pdi} = 8.84$.

3.32 Deprotection of the tert-Butyl group using Formic acid

Hyperbranched poly(ter-butyl acrylate) [0.5 g, GPC₃₆ (THF): $M_n = 15.3 \times 10^3$ Da, $\text{pdi} = 8.84$] was dissolved in excess of formic acid (10 mL, 0.25 mol) and stirred at 30 °C for 24 h. The solution was concentrated and then diluted with methanol (5 mL) and precipitated into hexanes (20 mL). The collected polymer was reprecipitated twice from methanol (5 mL) into hexanes (20 mL) to yield (0.18 g, 67%) of a tan solid. GPC₃₆ (DMF): $M_n = 22.5 \times 10^4$ Da, $\text{pdi} = 10.5$.

3.33 Copolymerization of {2-Chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxycarbonyl]}ethyl acrylate and 11-(4’-Cyanophenyl-4’’-phenoxy)undecyl acrylate

A mixture of {2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxycarbonyl]}ethyl acrylate (0.020 g, 0.040 mmol) and 11-(4’-cyanophenyl-4’’-phenoxy)undecyl acrylate (0.30 g, 0.72 mmol) followed by anisole (0.6 mL) were added to a mixture of Cu(I)Cl (4.1 mg, 0.040 mmol) and PMDETA (6.2 mg, 0.040 mmol) in N₂ filled Schlenk tube. The mixture was degassed by three cycles (10-30-20 min) of freeze-pump-thaw and the polymerization solution was stirred at 130 °C for 18 h. The polymerization was quenched by immersing the tube into liquid N₂. It was followed by a thaw and the tube was opened to ambient atmosphere. The solution was diluted with THF (5 mL) and precipitated into satd. NH₄Cl aq. (25 mL). The precipitate was
reprecipitated from THF (5 mL) twice into methanol (25 mL) and dried in vacuo to yield (0.10 g, 30%) of a tan solid. GPC<sub>PS</sub> (THF): M<sub>n</sub> = 1.03 x 10<sup>4</sup> Da, pdi = 1.22.

3.34 Reduction of Cl End groups of Hyperbranched Polymers using tri(n-Butyl)tin hydride/deutride

In a typical example, anisole (5 mL) was added to a mixture of Cu(I)Br (4.4 mg, 0.037 mmol) and Me<sub>6</sub>TREN (7.2 mg, 0.037 mmol) followed by the addition of the hyperbranched polymer (0.16 g, GPC<sub>PS</sub> M<sub>n</sub> = 13.0 x 10<sup>3</sup> Da, pdi = 1.40) in a N<sub>2</sub> filled schlenk tube. The solution was stirred until the entire polymer dissolved for 2 h, tri(n-butyl) tin hydride (0.11 g, 0.38 mmol) was then added, and the tube was degassed after three freeze-pump-thaw (10-30-20 min) cycles. After stirring at 120 °C for 5 h the reaction was quenched by immersing into liquid N<sub>2</sub>. After thawing, the reaction was brought to ambient atmosphere. The solution was diluted with THF (5 mL), passed through a plug of basic activated alumina and precipitated into methanol (50 mL). The precipitate was reprecipitated twice from THF (5 mL) into methanol (50 mL) to yield (0.13 g, 86%) a light brown/white solid. <sup>13</sup>C NMR spectroscopy showed no residual CCl resonance at 57.4 ppm. GPC<sub>PS</sub> (THF): M<sub>n</sub> = 9.90 x 10<sup>3</sup> Da, pdi = 1.35.

3.35 Synthesis of Linear Poly{[11-(4’-cyanophenyl-4”-phenoxy)undecyl] acrylate}

In a typical example, [11-(4’-cyanophenyl-4”-phenoxy)undecyl]acrylate (1.30 g, 3.10 mmol) followed by anisole (2.6 mL) was added to a mixture of Cu(I)Br (1.80 mg, 0.013 mmol) and PMDETA (2.5 μL, 0.013 mmol) in a N<sub>2</sub> filled Schlenk tube. After stirring for 15 min, [11-(4’-cyanophenyl-4”-phenoxy)undecyl]-2-bromopropionate<sup>7</sup> (6.40 mg, 0.013 mmol) was added to the solution. The solution was degassed after five freeze-pump-thaw (10-30-20 min) cycles and stirred at 110 °C for 75 h. The polymerization was
quenched by immersing the Schlenk tube into liquid N\textsubscript{2}. After thawing, the solution was
diluted with THF (5 mL) and it was passed through a plug of neutral alumina and
precipitated into methanol (125 mL). The collected precipitate was reprecipitated twice
from THF (5 mL) into methanol (125 mL) to yield (0.59 g, 45\%) of a white solid.

\text{GPC_{PSt}} (THF): M\text{\textsubscript{n}} = 2.05 \times 10^{4} \text{ Da}, \text{pdi} = 1.34.

3.36 Synthesis of Three-arm Star Poly\{[11-(4’-cyanophenyl-4’’-phenoxy)undecyl] acrylate\}

In a typical example, 11-(4’-cyanophenyl-4’’-phenoxy)undecylacrylate (1.00 g,
2.38 mmol) followed by anisole (2.00 mL) were added to a mixture of Cu(I)Br (2.60 mg,
0.018 mmol) and PMDETA (3.8 \mu L, 0.018 mmol) in a N\textsubscript{2} filled Schlenk tube and stirred
for 15 min. 2,4,6-Tris[4’-methyl-(2’’-bromopropionate)phenoxyethyl]mesitylene\textsuperscript{8} (6.40
mg, 0.007 mmol) was added to the solution. The solution was degassed after five freeze-
pump-thaw (10-30-20 min) cycles and stirred at 110 °C for 88 h. The polymerization was
quenched by immersing the Schlenk tube into liquid N\textsubscript{2}. After thawing, the solution was
diluted with THF (5 mL) and it was passed through a plug of neutral alumina and
precipitated into methanol (100 mL). The collected precipitate was reprecipitated twice
from THF (5 mL) into methanol (100 mL) to yield (0.65 g, 65\%) of a white solid.

\text{GPC_{PSt}} (THF): M\text{\textsubscript{n}} = 3.38 \times 10^{4} \text{ Da}, \text{pdi} = 1.47.

3.37 Synthesis of Six-arm Star Poly\{[11-(4’-cyanophenyl-4’’-phenoxy)undecyl]
acrylate\}

In a typical example, [11-(4’-cyanophenyl-4’’-phenoxy)undecyl]acrylate (2.40 g,
5.72 mmol) followed by anisole (5.00 mL) were added to a mixture of Cu(I)Br (8.20 mg,
0.057 mmol) and PMDETA (12 \mu L, 0.057 mmol) in a N\textsubscript{2} filled Schlenk tube and stirred
for 15 min. 1,2,3,4,5,6-hexa[4’-methyl-(2’’-bromopropionate)phenoxyethyl]benzene\textsuperscript{9}
(0.016 g, 0.010 mmol) was added to the solution. The solution was degassed after five freeze-pump-thaw (10-30-20 min) cycles and stirred at 110 °C for 18 h. The polymerization was quenched by immersing the Schlenk tube into liquid N₂. After thawing, the solution was diluted with THF (5 mL) and it was passed through a plug of neutral alumina and precipitated into methanol (100 mL). The collected precipitate was reprecipitated twice from THF (5 mL) into methanol (100 mL) to yield (1.20 g, 50 %) of a white solid. GPCₚₛₜ (THF): \( M_n = 3.18 \times 10^4 \) Da, pdi = 1.21.

3.38 Synthesis of Comb Poly{11-(4’-cyanophenyl-4”'-phenoxy)undecyl acrylate}

In a typical example, 11-(4’-cyanophenyl-4”'-phenoxy)undecyl acrylate (0.84 g, 2.00 mmol) was added to a mixture of Cu(I)Br (9.90 mg, 0.069 mmol) and PMDETA (14 \( \mu L \), 0.069 mmol) in a N₂ filled Schlenk tube and stirred for 15 min. The macroinitiator\(^{10} \) (0.19 g, 0.013 mmol) was added to the solution. The solution was degassed after five freeze-pump-thaw (10-30-20 min) cycles and stirred at 110 °C for 1 h. The polymerization was quenched by immersing the Schlenk tube into liquid N₂. After thawing, the solution was diluted with THF (5 mL) and it was passed through a plug of neutral alumina and precipitated into methanol (100 mL). The collected precipitate was reprecipitated twice from THF (5 mL) into methanol (100 mL) to yield (0.75 g, 89%) of a white solid. GPCₚₛₜ (THF): \( M_n = 3.73 \times 10^4 \) Da, pdi = 1.34.

3.39 Reduction of the Br End Group of Linear Poly{11-(4’-cyanophenyl-4”'-phenoxy)undecyl acrylate} of Various Architectures (Example: Linear Poly{[11-(4’-cyanophenyl-4”'-phenoxy)undecyl] acrylate})

AIBN (0.15 g, 0.023 mmol) and HSnBu₃ (0.008 g, 0.028 mmol) were added to a solution of linear poly{11-(4’-cyanophenyl-4”'-phenoxy)undecyl acrylate}(0.56 g, GPCₚₛₜ in THF, \( M_n = 2.50 \times 10^4 \), pdi = 1.15) in benzene (5 mL) in a N₂ filled Schlenk
tube. The contents were degassed after three freeze-pump-thaw (10-30-20 min) cycles and stirred at 60 °C for 3 h. The reaction was quenched by immersing the tube into liquid N₂. It was followed by a thaw and the tube was opened to ambient atmosphere. After thawing, the solution was diluted with THF (5 mL) and it was passed through a plug of neutral alumina and precipitated into methanol (100 mL). The collected precipitate was reprecipitated twice from THF (5 mL) into methanol (100 mL) to yield (0.49 g, 87%) of a white solid. GPC_{PSE} (THF): Mₙ = 1.82 x 10⁴ Da, pdi = 1.16.
4.1 Synthesis of Halohydrins

Our hyperbranched polyacrylates are synthesized by SCVP$^3$ of inimers that are based on a halohydrin derived from serine. This halohydrin is the key intermediate. Halohydrins are typically synthesized by either direct hydrohalogenation of the corresponding olefin, or by first converting the olefin to an epoxide, followed by reaction with HX (HCl or HBr). Ring-opening of glycidic esters with HCl and HBr generates the wrong regioisomer$^{256}$, with –OH alpha to the ester. Hydrobromination of methacrylates produces a mixture of regioisomers$^{257}$ Hydrobromination of acrylates also produces primarily the wrong regioisomer in low yield due to the formation of a large amount of dibromide as side product$^{257,258}$, although the products were initially assumed to be 2-bromo-3-hyroxypropionate$^{257,258}$, the amount of dibromide can be reduced by adding AgNO$_3$ to precipitate AgBr out of the reaction mixture$^{259}$. We have found that a much cleaner reaction is to convert the amine group of serine and its ester to a halogen atom by diazotization in the presence of KX (Br or Cl) as shown in Scheme 4.1.$^{260,261}$ The short alkyl esters of serine are either commercially available as HCl salts or are easily synthesized by acid-catalyzed esterification using the desired alcohol as solvent.
This diazotization route produces chloro or bromohydrin with a COOH substituent. The chlorine or bromine atom provides the initiating site in the inimer. The carboxylic acid group was reacted with different alcohols to obtain the desired ester functionality for the polyacrylate. We generally dissolved serine in acidic water and added sodium nitrite in small fractions at sub-zero temperatures. After reacting overnight at room temperature, we salted out the product and extracted it with ethyl acetate. After recrystallizing from CH₂Cl₂, we obtained the halohydrin as white crystals. For example, 2-chloro-3-hydroxypropionic acid (chlorohydrin) was synthesized from acidic aqueous solution (HCl) of (DL)-2-amino-3-hydroxy-propionic acid (DL-serine) (R = H) in the presence of KCl in ~60% yield. The products were characterized by ¹H and ¹³C-NMR spectroscopy and elemental analysis. Figures 4.1 and 4.2 present the ¹H and ¹³C-NMR spectra of 2-bromo-3-hydroxypropionic acid in CDCl₃/DMSO-d₆ at room temperature. In Figure 4.1, the broad resonance at 7.19 ppm is assigned to COOH. This might be due to fast exchange of COOH and OH protons of bromo-3-hydroxypropionic acid and therefore appears between the two resonances. Each of the CH₂OH protons appears as a doublet of doublets since the two protons are chemically inequivalent due to the asymmetric center (CHBr). Even though, the proton of OH was not significantly visible.
into $^1$H spectrum, into $^{13}$C-NMR spectrum as shown in Figure 4.2, the methylene carbon
($\text{CH}_2\text{OH}$) attached to OH group appears clearly, along with \text{COOH} and \text{CHBr}. The
product was analytically pure according to elemental analysis.

Figure 4.1: $^1$H-NMR (300 MHz) spectrum of 2-bromo-3-hydroxypropionic acid
synthesized by diazotization route

Figure 4.2: $^{13}$C-NMR (75 MHz) spectrum of 2-bromo-3-hydroxypropionic acid
synthesized by diazotization route
Figure 4.3: \(^1\)H-NMR (300 MHz) spectrum of 2-chloro-3-hydroxypropionic acid synthesized by diazotization route

Figure 4.4: \(^{13}\)C-NMR (75 MHz) spectrum of 2-chloro-3-hydroxypropionic acid synthesized by diazotization route
Figures 4.3 and Figure 4.4 show the $^1$H and $^{13}$C-NMR spectra of 2-chloro-3-hydroxypropionic acid in CDCl$_3$/DMSO-d$_6$ at room temperature. In Figure 4.3, the broad resonance at 6.40 ppm is assigned to COOH and OH of the 2-chloro-3-hydroxypropionic acid. Similar to the bromohydrin, the resonance appears at a position between those typical of COOH and OH due to fast exchange. Figure 4.4 demonstrates that the CHCl and CH$_2$OH resonance appear clearly, along with COOH. The product was analytically pure according to elemental analysis.

4.2 Synthesis of Halohydrin-based Esters

Scheme 4.2 shows the synthesis of esters of the 2-chloro-3-hydroxypropionic acid. The ester substituents can be synthesized from any alcohol, including aliphatic or non-aliphatic, linear or branched, mesogenic or non-mesogenic, chiral or achiral, and hydrocarbon or non-hydrocarbon, such as those with fluorocarbon, oligo(oxyethylene), and siloxane substituents. The carboxylic acid group in the halohydrin can be reacted with an alcohol under acid catalyzed conditions (aq. HCl or p-TsOH) in-vacuo or under N$_2$ to obtain the ester. The temperature of the reaction was maintained at 60 °C, since higher temperatures promote the self-condensation oligomerization of the halohydrin. Lower boiling esters, e.g. the methyl esters, were distilled to obtain pure product; silica gel chromatography was used to purify the other esters.

\[
\begin{align*}
\text{Cl} & \quad \text{ROH} \quad \text{cat. HCl, 60-65°C} \\
\text{HO} & \quad \text{Cl} \\
\text{OH} & \quad \text{Cl} \\
\text{O} & \quad \text{O} \\
\text{HO} & \quad \text{OR} \\
\end{align*}
\]

$\text{R} = \text{methyl, dodecyl, mesogenic, etc.}$

Scheme 4.2: Synthesis of esters of the chlorohydrin (2-chloro-3-hydroxypropionic acid)
The reaction conditions and yields are reported in the following Table 4.1 for the different esters.

Table 4.1: Synthesis and purification of various halohydrin-esters

<table>
<thead>
<tr>
<th>Ester substituent</th>
<th>X</th>
<th>Temp (°C)</th>
<th>Rxn Time (h)</th>
<th>Yield (%)</th>
<th>Purification conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>Cl</td>
<td>60-65</td>
<td>22</td>
<td>68-88</td>
<td>Et₂O/CHCl₃ (10/90), Rₓ = 0.51</td>
</tr>
<tr>
<td>Me</td>
<td>Br</td>
<td>60-65</td>
<td>21</td>
<td>68-87</td>
<td>Et₂O/CH₂Cl₂ (10/90), Rₓ = 0.31</td>
</tr>
<tr>
<td>(CH₂)₆H</td>
<td>Cl</td>
<td>75-80</td>
<td>40</td>
<td>78</td>
<td>Sublimation at 70 °C</td>
</tr>
<tr>
<td>(CH₂)₃(CF₂)₈F</td>
<td>Cl</td>
<td>60-65</td>
<td>36</td>
<td>67</td>
<td>---</td>
</tr>
<tr>
<td>(CH₂)₃Si(CH₃)₂OSi(CH₃)₃</td>
<td>Cl</td>
<td>60-65</td>
<td>48</td>
<td>51</td>
<td>Et₂O/CH₂Cl₂ (10/90), Rₓ = 0.78</td>
</tr>
<tr>
<td>(CH₂)₁₀OՓФCN</td>
<td>Cl</td>
<td>60-65</td>
<td>42</td>
<td>56</td>
<td>Et₂O/CH₂Cl₂ (30/70), Rₓ = 0.77</td>
</tr>
<tr>
<td>(CH₂)₁₁OՓФCN</td>
<td>Br</td>
<td>60-65</td>
<td>42</td>
<td>46</td>
<td>Et₂O/CH₂Cl₂ (5/95), Rₓ = 0.36</td>
</tr>
</tbody>
</table>

Scheme 4.3: Synthesis of \([n-(pentamethyldisiloxyl)propyl] 2\text{-chloro-3-hydroxypropionate}\)

The siloxane-based ester of the chlorohydrin was synthesized in high yield by hydrosilylation of allyl alcohol with pentamethyldisiloxane in the presence of platinum-divinyl tetraethyl-disiloxane at room temperature as shown in Scheme 4.3. The mesogenic ester was synthesized by esterification of 2-chloro-3-hydroxypropionic acid with 11-(4’-cyanophenyl-4’’-phenoxy)undecanol.7
4.1 Synthesis of Halohydrin-based Inimers

The acrylate and methacrylate inimers with different ester substituents were synthesized by reacting 2-chloro-3-hydroxypropionates with either acryloyl chloride, acrylic anhydride or methacryloyl chloride in the presence of NEt₃ in dry THF. This reaction introduces a polymerizable site for the inimers. When acryloyl chloride was used for the reaction with the bromohydrin-ester, a mixture of chlorine- and bromine-containing inimers were obtained, with the chlorohydrin-ester being the major product. This was confirmed by ¹³C-NMR spectroscopy and mass spectrometry. For example, Figure 4.5 shows the ¹³C-NMR spectrum of the product obtained by reaction of the bromine-containing mesogenic alcohol and acryloyl chloride. A mixture of 2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxycarbonyl]ethyl acrylate and 2-bromo-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxycarbonyl]ethyl acrylate was obtained as is evident from the CBr resonance at 41 ppm, and the CCl resonance at 54 ppm. The inimers with bromine initiating sites were synthesized by using acrylic anhydride to avoid halogen exchange.

Scheme 4.4: Synthesis of halohydrin-based inimers

The acrylate and methacrylate inimers with different ester substituents were synthesized by reacting 2-chloro-3-hydroxypropionates with either acryloyl chloride, acrylic anhydride or methacryloyl chloride in the presence of NEt₃ in dry THF. This reaction introduces a polymerizable site for the inimers. When acryloyl chloride was used for the reaction with the bromohydrin-ester, a mixture of chlorine- and bromine-containing inimers were obtained, with the chlorohydrin-ester being the major product. This was confirmed by ¹³C-NMR spectroscopy and mass spectrometry. For example, Figure 4.5 shows the ¹³C-NMR spectrum of the product obtained by reaction of the bromine-containing mesogenic alcohol and acryloyl chloride. A mixture of 2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxycarbonyl]ethyl acrylate and 2-bromo-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxycarbonyl]ethyl acrylate was obtained as is evident from the CBr resonance at 41 ppm, and the CCl resonance at 54 ppm. The inimers with bromine initiating sites were synthesized by using acrylic anhydride to avoid halogen exchange.
Figure 4.5: Expanded $^{13}$C-NMR spectrum of mesogenic inimer (Br)

Figure 4.6: Chemical structures of inimers with different ester substituents
Figure 4.6 shows the variety of inimers that we have synthesized. We synthesized inimers with acrylate and methacrylate monomeric sites and Cl and Br initiating sites.

<table>
<thead>
<tr>
<th>Inimers</th>
<th>X</th>
<th>Rxn Time (h)</th>
<th>Yield (%)</th>
<th>Purification conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>Cl</td>
<td>16</td>
<td>34-50</td>
<td>Vac. dist., 94-96 °C</td>
</tr>
<tr>
<td>Methyl</td>
<td>Br</td>
<td>21</td>
<td>55-68</td>
<td>Vac. dist., 92-94 °C</td>
</tr>
<tr>
<td>Dodecyl</td>
<td>Cl</td>
<td>21</td>
<td>59</td>
<td>EA /Hexanes (5/95), R\textsubscript{f} = 0.47</td>
</tr>
<tr>
<td>Perfluoro</td>
<td>Cl</td>
<td>12</td>
<td>43</td>
<td>CHCl\textsubscript{3}, R\textsubscript{f} = 0.61-0.74</td>
</tr>
<tr>
<td>Oligo(oxyethylene)</td>
<td>Cl</td>
<td>18</td>
<td>67</td>
<td>EA /Hexanes (40/60), R\textsubscript{f} = 0.36</td>
</tr>
<tr>
<td>Siloxane</td>
<td>Cl</td>
<td>21</td>
<td>62</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}, R\textsubscript{f} = 0.74</td>
</tr>
<tr>
<td>Mesogenic</td>
<td>Cl</td>
<td>17</td>
<td>51</td>
<td>Et\textsubscript{2}O /CHCl\textsubscript{3} (30/70), R\textsubscript{f} = 0.70</td>
</tr>
<tr>
<td>Mesogenic</td>
<td>Br</td>
<td>24</td>
<td>51</td>
<td>CH\textsubscript{2}Cl\textsubscript{2} (5/95), R\textsubscript{f} = 0.59</td>
</tr>
<tr>
<td>(Meth)mesogenic</td>
<td>Cl</td>
<td>16</td>
<td>71</td>
<td>Et\textsubscript{2}O /CH\textsubscript{2}Cl\textsubscript{2} (5/95), R\textsubscript{f} = 0.79</td>
</tr>
</tbody>
</table>

Table 4.2 lists the reaction conditions and yields for the synthesis of these inimers. The final yields of the acrylate inimers, especially the methyl acrylate inimer, were low due to the formation of a side product. The yield of the (meth) mesogenic acrylate inimer was higher than the mesogenic acrylate inimer since there was no side product. I did not positively identify this side product or characterized it thoroughly. While purifying the methyl acrylate inimer, this impurity was distilled off at 50-55 °C at 3 mm of mercury. The \textsuperscript{1}H-NMR spectrum of the impurity was similar to the pure methyl acrylate inimer except the vinylic region, where only two singlets at $\sim$ 5.8 ppm and 6.1 ppm were observed.
Figure 4.7: $^1$H-NMR spectra of inimers with different ester substituents
Figure 4.7 shows the $^1$H-NMR spectra of the different inimers. The $OCH_2$ and $CHCl$ resonances (d and e) for the chlorine-containing inimers are overlapped. For the bromine-containing inimers, the $OCH_2$ and $CHBr$ resonances (d and e) are partially resolved. The $OCH_2$ protons are non equivalent since they are alpha to a chiral carbon, $CBr$, and therefore appear as a doublet of doublets. For methyl inimer (Br), a resonance for one of the protons of $OCH_2$ appears at ~ 4.6 ppm, and another resonance overlaps with the $CHBr$ resonance at ~4.7 ppm. In chloro-containing inimers, the resonances from the two non-equivalent protons overlap with the $CHCl$ resonance. These inimers were also characterized by $^{13}$C-NMR spectroscopy and were analytically pure according to elemental analysis.
5.1 ATRP of Inimers with Different Ester Substituents

Although numerous dendrimers\textsuperscript{262} and hyperbranched polyacrylates\textsuperscript{263} have been synthesized with the mesogens attached only at their periphery, or within the main chain of the polymer\textsuperscript{264}, none have been synthesized with the mesogens attached as a side chain throughout the branched structure. In addition, although linear poly(meth)acrylates with a large variety of ester side chains have been synthesized, hyperbranched polyacrylates have not been synthesized by homopolymerization of an inimer with a free side chain. The hyperbranched poly(acrylate)s and poly(methacrylate)s that have been synthesized by homopolymerization of an inimer are not analogs of any particular linear poly(meth)acrylate.

In contrast, the first hyperbranched polystyrene\textsuperscript{210} produced by SCVP\textsuperscript{3} of an inimer by a radical mechanism produced a hyperbranched polymer that is fairly analogous to linear polystyrene (but with an extra –CH\textsubscript{2}O-) (Example 1 of Scheme 5.1).
Scheme 5.1: Hyperbranched Polystyrenes

Subsequently synthesized\textsuperscript{211} “hyperbranched polystyrenes”, such as the second example in Scheme 5.1, incorporated the aromatic ring within the main chain of the polymer and are therefore more analogous to polymers produced by step polymerizations; in addition, all free aromatic groups that are not incorporated into branches are functionalized with an initiator fragment. Similarly, all of the hyperbranched poly(meth)acrylates\textsuperscript{265} synthesized to date by SCVP incorporate the alkyl ester into the polymer backbone upon branching (Scheme 5.2), and leave an alkyl ester side chain functionalized with an initiator fragment at incomplete branching. These polymers are therefore not analogs of linear poly(meth)acrylates, whose properties could be compared to determine architectural effects. They are also not analogs of the branched poly(meth)acrylates produced in
conventional radical polymerizations in which branching occurs by chain transfer at a site along the polymer backbone, rather than at the ester side chains.

Scheme 5.2: “Hyperbranched” poly(meth)acrylates reported in the literature

versus

Scheme 5.3: Our approach to hyperbranched poly(meth)acrylates

We have synthesized the first true hyperbranched analogs (Scheme 5.3) of linear poly(meth)acrylates by SCVP of an inimer based on halohydrin (bromohydrin/chlorohydrin) intermediates with different ester substituents.

During ATRP, these inimers react with the more basic ligands, such as PMDETA, if the ligands are not complexed with the catalyst prior to adding the inimer and thereby starting the polymerization. If the ligand and catalyst are mixed first, only polymerization takes place and no side reaction is observed by $^1$H-NMR spectroscopy as summarized in Scheme 5.4.
Scheme 5.4: Reaction of the (2-chloro-2-methoxycarbonyl)ethyl acrylate with the ligand used in ATRP

Figure 5.1: $^1$H-NMR spectra (300 MHz) of the (2-chloro-2-methoxycarbonyl)ethyl acrylate with PMDETA at 25 °C after 2.5 h (inimer/CuCl/PMDETA 100/1/1)

For example, the top $^1$H-NMR spectrum in Figure 5.1 demonstrate that a mixture of (2-chloro-2-methoxycarbonyl)ethyl acrylate and PMDETA at room temperature without the catalyst produces new resonances at 7.6 ppm and 5.8 ppm. In addition, there are new resonances in the vinylic region compared to the polymer prepared by mixing the catalyst and ligand before adding the inimer (bottom spectrum, Figure 5.1). CuCl and PMDETA
were mixed for 15 min before adding the inimer. For all of the polymerizations, inimer was added to the mixture of catalyst and ligand.

Hyperbranched polymers were obtained by ATRP of inimers with different ester substituents, including methyl, dodecyl, mesogenic, perfluoro, oligo(oxyethylene) and siloxane, under a variety of reaction conditions. The polymerization conditions and results are summarized in Table 5.1.

Table 5.1: Polymerization conditions and results of inimer polymerization

<table>
<thead>
<tr>
<th>R</th>
<th>R’</th>
<th>X</th>
<th>Solvent System (ini./solv.)</th>
<th>Catalyst/ligand</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>GPC&lt;sub&gt;PS&lt;/sub&gt;*</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (Da) x10&lt;sup&gt;3&lt;/sup&gt;</th>
<th>Pdi</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>methyl</td>
<td>Cl</td>
<td>water (1/1 w/w)</td>
<td>CuCl/Me&lt;sub&gt;6&lt;/sub&gt;TREN (50/1/1)</td>
<td>50</td>
<td>44</td>
<td>40</td>
<td>11.6</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>dodecyl</td>
<td>Cl</td>
<td>anisole (1/1 w/v)</td>
<td>CuBr/PMDETA (50/1/1.2)</td>
<td>130</td>
<td>18</td>
<td>30</td>
<td>9.70</td>
<td>2.13</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>perfluoro&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Cl</td>
<td>toluene (1/1 w/v)</td>
<td>CuC/2,2’-bipyridyl (43/1/1.5)</td>
<td>90</td>
<td>6</td>
<td>22</td>
<td>49.8</td>
<td>2.39</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>siloxane</td>
<td>Cl</td>
<td>anisole (3/5 w/w)</td>
<td>CuBr/PMDETA (20/1/1)</td>
<td>120</td>
<td>96</td>
<td>28</td>
<td>2.01</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>oligo (oxyethylene)</td>
<td>Cl</td>
<td>ACN&lt;sup&gt;a&lt;/sup&gt;/water (2/3/3 w/w/w)</td>
<td>CuBr/PMDETA (20/1/1)</td>
<td>25</td>
<td>6</td>
<td>32</td>
<td>33.5</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>mesogenic</td>
<td>Cl</td>
<td>ACN&lt;sup&gt;a&lt;/sup&gt;/water (2/1/5 w/v/v)</td>
<td>CuC/Me&lt;sub&gt;6&lt;/sub&gt;TREN (30/1/1.2)</td>
<td>90</td>
<td>120</td>
<td>66</td>
<td>17.2</td>
<td>1.90</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>mesogenic</td>
<td>Br</td>
<td>anisole (2/1/5 w/w/v)</td>
<td>CuBr/PMDETA (80/1/1)</td>
<td>120</td>
<td>5</td>
<td>NA</td>
<td>34.5</td>
<td>1.30</td>
<td></td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>mesogenic</td>
<td>Cl</td>
<td>anisole (1/1 w/w)</td>
<td>CuBr/PMDETA (80/1/1)</td>
<td>120</td>
<td>100</td>
<td>70</td>
<td>7.66</td>
<td>2.56</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>mesogenic&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Cl</td>
<td>anisole (1/1 w/w)</td>
<td>CuBr/PMDETA (1/1/1)</td>
<td>130</td>
<td>18</td>
<td>30</td>
<td>8.44</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>methyl&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Br</td>
<td>Bulk (0/1/1/1)</td>
<td>CuC/2,2’-bipyridyl (5/3)</td>
<td>90</td>
<td>4</td>
<td>45</td>
<td>15.3</td>
<td>8.84</td>
<td></td>
</tr>
</tbody>
</table>

* in THF, molecular weight calculated excluding inimer or removing the unreacted inimer.

<sup>a</sup> ACN: acetonitrile

<sup>ab</sup> GPC experiment was performed in o-dichlorobenzene at 110 °C

<sup>c</sup> hyperbranched polymer obtained from copolymerization of the inimer and the corresponding monomer [2-chloro-2-[11’-(4''-cyanophenyl-4’’-phenoxy)undecan-1- oxy carbonyl]]ethyl acrylate + [11-(4’-cyanophenyl-4’’-phenoxy)undecyl] acrylate; Inimer/CuBr/PMDETA/monomer: 1/1/1/18; monomer/solvent: 50/50 w/w

<sup>d</sup> (2-bromo-2-methoxycarbonyl)ethyl acrylate + ter-butyl monomer; Inimer/CuBr/PMDETA/monomer: 5/1/3/50
The polymerization conditions were optimized for ATRP of different inimers. Not all inimers were polymerized at the same ATRP conditions. The molecular weight distributions obtained from GPC_{PSi} in THF of some of these polymers were broad demonstrating formation of the branched polymer with undefined structure. More polar solvents produced polymers with broader molecular weight distribution and required lower polymerization temperatures. Hyperbranched \{2-chloro-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluoro decan-1-oxycarbonyl)\}ethyl acrylate were obtained at milder ATRP conditions as reaction conditions similar to other inimers resulted in cross-linked polymer. The effect of the ester substituents on the polymerization was not obtained due to difficulty of polymerization of the inimers with different ester substituents at particular ATRP conditions.

Scheme 5.5: Synthesis of hyperbranched poly(acrylic acid) by SCVCP of the (2-bromo-2-methoxycarbonyl)ethyl acrylate and \( t \)-butyl acrylate
It is also possible to obtain hyperbranched polymers by copolymerizing an inimer with an acrylate monomer. This is more economical than homopolymerization of the inimer. As shown in Scheme 5.5, we synthesized a hyperbranched copolymer of acrylic acid by self-condensing vinyl copolymerization (SCVCP). The methyl inimer (Br) was copolymerized with ter-butyl acrylate using ATRP, and then deprotecting the ter-butyl group using formic acid to obtain hyperbranched polyacrylic acid. A hyperbranched mesogenic copolymer was also synthesized using similar reaction conditions and the results are listed in Table 5.1.

![Figure 5.2: GPC<sub>PSt</sub> chromatograms of the ATRP of the {2-chloro-2-[11’-(4”-cyanophenyl-4”'-phenoxy)undecan-1- oxy carbonyl]ethyl acrylate at various conversions synthesized at 120 °C in anisole (Inimer/CuBr/PMDETA: 80/1/1)](image)

85
Figure 5.2 shows the GPC traces of aliquots taken from the polymerization of \(2\text{-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]}\)ethyl acrylate at various conversions. The values of the molecular weights and polydispersity, excluding the unreacted inimer from the calculations, but include all other peaks. It clearly shows the formation of oligomers, and increasing molecular weight with increasing conversion. At the early stages of the polymerization, smaller oligomers are prominent, whereas higher molecular weight polymers were obtained at higher conversion. Growth of the polymer chain occurs by addition of both inimer and oligomers and results in polymers with broad polydispersities; this is a combined step-chain growth mechanism. The results obtained by GPC were consistent with the statistical nature of SCVP of the inimer. A peak at lower elution volume to the inimer-peak is clearly visible and is present even at higher conversion but with relatively low concentration. This may be attributed to a cyclic-dimer formation, which was also presumably observed by Matyjasweski and co-workers\(^{266}\). However, a linear dimer should also elute at a slightly lower elution volume relative to the inimer.

The molecular weight distributions of hyperbranched polymer synthesized by SCVP increase with increasing conversion and become very broad at moderate to higher conversions. For SCVP, the molecular weight distribution is equal to the number average degree of polymerization \(1/(1-x)^{222}\), in which \(x = \text{conversion}\). Matyjasweski and co-workers\(^{266}\) synthesized hyperbranched polymers by SCVP of \(2\text{-[(2-bromopropionyl)oxy]}\)ethyl acrylate and studied its polymerization kinetics. They observed that the molecular weight of the polymer increased with conversion similar to the predicted values, but appeared to reach a limit\(^{266}\), which they attributed to side
reactions at high conversion. They suggested that the side reaction was intramolecular cyclization by reaction of an A* or B* with the terminal vinyl group. The values of pdi from their experiments also increased with increasing conversion, but did not increase to the predicted high values (theoretical pdi = ∞ at x = 100%). However, these radical polymerizations must be limited to incomplete but almost 99% conversion to avoid cross-linking.

Figure 5.3: Plot of GPC_PSt molecular weight (Da) of the poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxycarbonyl]}ethyl acrylate) (including inimer and excluding inimer) vs conversion synthesized at 120 °C in anisole (Inimer/CuBr/PMDETA: 80/1/1)

Figure 5.3 plots the number average molecular weight of the hyperbranched SCLCP as a function of conversion, using the GPC traces from Figure 5.2. The molecular weights were calculated both with and without inimer peak included in the calculation. As expected, the molecular weights that include the inimer in the calculation are very low.

The number average molecular weights of these hyperbranched polymers increase with increasing conversion and can be qualitatively compared with theoretical
predictions\textsuperscript{222} of SCVP of an inimer. Since the molecular weight obtained by GPC\textsubscript{PS} is a relative molecular weight, and the absolute molecular weights of the oligomers present in the hyperbranched system are difficult to obtain, we qualitatively compared the experimentally obtained molecular weight with the theoretical molecular weight. If the calculated molecular weights of the polymer includes the inimer; $M_n$ is theoretically independent of the reactivity ratio\textsuperscript{222}, and $M_n = M_o \times (1-x)$; $M_o$ is the molecular weight of the inimer repeat unit.

Figure 5.4: Comparison of the theoretical and experimental GPC\textsubscript{PS} (including inimer) number average molecular weights (Da) of the poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]ethyl acrylate) at various conversions synthesized at 120 °C in anisole (Inimer/CuBr/PMDETA: 80/1/1)

As shown in Figure 5.4, the experimental number average molecular weights of the hyperbranched SCLCP calculated with the inimer included, agree with the theoretical values, except at higher conversions.
Figure 5.5: Conversion of the double bonds (A) present in the polymerization system of the poly(2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl])ethyl acrylate) at various intervals of time synthesized at 120 °C in anisole (Inimer/CuBr/PMDETA: 80/1/1): first order semi-logarithmic plot

Figure 5.5 plots 1st order kinetics from the polymerization of {2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]}ethyl acrylate. The conversion of the double bonds (all vinylic protons) was calculated by ¹H-NMR spectroscopy with respect to resonances of all OCH₂ and CHCl between 3.8- 4.6 ppm. SCVP of an inimer produces polymers with a one terminal double bond. The conversion of double bonds (A at time, t, and A = A₀ at time, t = 0) refers to all of the double bonds present in the polymerization system. Although, the data points are scattered, the relationship is fairly linear, this indicates that the number of the growing chains in the polymerization system was constant.
5.2 NMR Characterization of the Hyperbranched Polymers

Figure 5.6: $^1$H-NMR spectra (300 MHz) of the polymers synthesized using ATRP of the (2-chloro-2-methoxycarbonyl)ethyl acrylate (inimer/CuCl/ligand:50/1/1) at various polymerization conditions

Since the hyperbranched polymer derived from the methyl inimer should have the simplest spectra, we investigated it in detail by NMR spectroscopy. Figure 5.6 shows the $^1$H-NMR spectra (300 MHz) of the poly(methyl acrylate)s synthesized at various polymerization conditions by ATRP of the (2-chloro-2-methoxycarbonyl)ethyl acrylate. All of these polymerizations were performed in a Schlenk tube under vacuum, by adding inimer to premixed catalyst/ligand. The resonances at 1.2-3.0 ppm due to polymer
backbone are quite different for the polymerization conditions, indicating that different branched structures are generated under different conditions. The resonance at 2.8 ppm, as shown in the box, is prominent in the polymer produced in bulk using either PMDETA or Me₆TREN as the ligand and CuCl as the catalyst. When a more polar solvent such as methanol or water was used, this resonance is barely detectable.

Figure 5.7: ¹H-NMR spectra (300 MHz) of (2-chloro-2-methoxycarbonyl)ethyl acrylate and its polymer synthesized at 50 °C in water (inimer/water: 1/1 w/w) for 46 h (inimer/CuCl/Me₆TREN: 50/1/1)

Although the ¹H-NMR spectrum of the methyl inimer is relatively clear, the overlapping CHCl and OCH₂ resonances of polymer complicate its interpretation. As shown in Figure 5.7, the OCH₂ and CHCl resonances are overlapped in 300 MHz spectra of both the inimer and the polymer produced in water for 46 h at 50 °C. Although these resonances are more resolved using a higher magnetic field for the NMR experiments, the
polymer backbone resonances are also overlapped and their separation is insufficient to
differentiate the different chemical units (Figure 5.7).

Figure 5.8: $^{13}$C-NMR (75 MHz) spectrum of the hyperbranched poly[(2-chloro-2-
methoxycarbonyl)ethyl acrylate] synthesized from ATRP of methyl inimer at 50 °C in
water (inimer/water: 1/1 w/w) for 46 h (inimer/CuCl/Me$_6$TREN: 50/1/1)

Scheme 5.6: Structural units in the hyperbranched polymer

Scheme 5.6 shows the five different structural units present in the hyperbranched
polymer; R as the pendant ester substituent (e.g. methyl, mesogenic, dodecyl, perfluoro,
etc.). There is only one branch point, \( ab \). Any direct evidence of its presence by NMR spectroscopy or other means would confirm that branching occurs in the polymerizations. There is a vinyl end group, \( Ab \) per branched polymer. The other end groups are \( A*B^* \), in which both the monomeric and initiating sites are active. Structural units \( A*b \) or \( aB^* \), have one site that has reacted and one that is inactive. All of these structural units must be identified in the NMR spectrum and their resonances must be resolved to quantify the reactivity ratio and the degree of branching.

Figure 5.8 shows the corresponding \( ^{13}\text{C-NMR} \) spectrum of the hyperbranched poly(methyl acrylate). The resonance assigned as \( a \) is the methylene carbon, \( \text{CH}_2 \) of the backbone, and \( b \) & \( e \) are the methine carbons, \( \text{CH} \) of the backbone. The resonances, \( c, f \) & \( g \) are \( \text{CHCl} \) and \( \text{OCH}_3 \), respectively, \( d \) is \( \text{OCH}_2 \), and \( h \) & \( i \) are the carbonyl carbons, \( \text{COO} \). Expansion of the different resonances shows that there seem to be two distinct resonances for \( \text{CHCl} \) (\( c \) & \( f \)) and two overlapped resonances for \( \text{OCH}_2 \) (\( d \)), which indicates that different chemical units are present in the polymer. In Figure 5.8, we clearly observed two distinct resonances, \( c \) and \( f \). The two \( \text{CHCl} \) resonances may be attributed to \( aB^* \) and \( A*b \) or \( A*B^* \). Since 2D-NMR experiments are required to confirm the relationship of different bonds, we performed several 2D-NMR experiments for both the hyperbranched poly(methyl acrylate) and SCLCP.
Figure 5.9: Expanded region of the $^1$H-$^{13}$C HSQC-NMR (750 MHz at 30 °C in CDCl$_3$) spectrum of the hyperbranched poly(methyl acrylate) synthesized from (2-chloro-2-methoxycarbonyl)ethyl acrylate at 50 °C in water (inimer/water: 1/1, w/w) for 46 h (inimer/CuCl/Me$_6$TREN : 50/1/1)

HSQC is a phase sensitive experiment that provides information about the carbons/and hydrogens that are directly bonded. Figure 5.9, presents an expanded region of the HSQC spectrum of the same hyperbranched poly(methyl acrylate) used for Figures 5.7 and 5.8. The F2 scale is the $^1$H dimension and F1 is the $^{13}$C dimension. The contours, a and b are of opposite phases as evidenced by the different colors, and correspond to either methylene (CH$_2$) or methine (CH) groups. Similarly, contours c, f and d are of opposite phases, and are therefore of different types of groups. For example, Figures 5.8 and 5.9 demonstrate that contour a is a methylene carbon (CH$_2$) at ~35 ppm.
attached to a hydrogen of the backbone resonating at ~1.7 ppm. Although Figure 5.8 indicates that there are two CHCl resonances, it is not clear in Figure 5.9 if they are two. However, two contours (d) appear for OCH$_2$. Since the two contours (d) appear at the same position on the $^{13}$C axis but at different positions on the $^1$H axis, they are not likely to be due to OCH$_2$ groups from different structural units. The overlapping of the two CHCl peaks (c & f) also suggests that they are not due to CHCl or OCH$_2$ groups from different structural units. The splitting of d into two different contours is therefore most likely due to the chemical inequivalence of the two diastereotopic CH$_2$ protons since the methylene group is alpha to an asymmetric carbon.

If CHCl from aB$^*$ initiating site adds to a monomeric site A, it generates a branch point of structural unit ab (Scheme 5.6) and which would correspond to a methine proton alpha to OCH$_2$ and CH$_2$ in the $^1$H-NMR. This should be visible as a cross-peak of OCH$_2$ and CH, in a $^1$H-$^1$H COSY NMR spectrum since neighboring protons that are attached vicinally to two carbon atoms can be observed as contours. Since OCH$_2$ is bonded to CHCl in A*B* and aB$^*$ structural units, d and f would have a cross-peak in the spectrum. Similarly, since CH$_2$ and CHCl are bonded in A*B*, A*b, a and c would have a cross-peak.
Figure 5.10: Expanded region of the $^1$H-$^1$H COSY-NMR (750 MHz at 30 °C in CDCl$_3$) spectrum of the hyperbranched poly(methyl acrylate) synthesized from (2-chloro-2-methoxycarbonyl) ethyl acrylate at 50 °C in water (inimer/water: 1/1, w/w) for 46 h (inimer/CuCl/Me$_6$TREN : 50/1/1)

However, there are no crosspeaks for these combinations in the $^1$H-$^1$H COSY-NMR spectrum of the hyperbranched poly(methyl acrylate) shown in Figure 5.10 except for possibly d/f; both F1 and F2 axes are $^1$H frequencies. The only strong crosspeaks are due to the CH$_2$ and CH resonances (a and b).

Figure 5.11 shows a $^1$H-$^1$H TOCSY NMR spectrum of the same hyperbranched poly(methyl acrylate). TOCSY NMR detects protons that are separated by three or more bonds.
This experiment also did not show any crosspeaks between d and e or d and a for the structural unit ab and no other crosspeaks were observed except for a and b, and/or a and e, and d and f, similar to the COSY experiment.

Figure 5.12 shows an HMBC spectrum, of the same hyperbranched poly(methyl acrylate); F1 and F2 are the $^{13}$C and $^1$H frequencies, respectively. This experiment detects correlations between protons and carbons that are separated by two or three bonds. The assignments of the contours are summarized in Table 5.2 using the labeling system shown in Scheme 5.7 for the four non-vinyl structural units.
Figure 5.12: Expanded $^1$H-$^{13}$C HMBC-NMR (750 MHz) spectrum of the hyperbranched poly(methyl acrylate), synthesized from (2-chloro-2-methoxycarbonyl)ethyl acrylate at 50 °C in water (inimer/water: 1/1, w/w) for 46 h (inimer/CuCl/Me$_6$TREN : 50/1/1) (NMR experiment performed at 30 °C in CDCl$_3$)

Scheme 5.7: Non-vinylic structural units in the hyperbranched poly(methyl acrylate) and labels on different carbon and hydrogen atoms
Table 5.2: Crosspeaks between $^1$H and $^{13}$C resonances detected by HMBC NMR spectroscopy of hyperbranched poly(methyl acrylate) synthesized from (2-chloro-2-methoxycarbonyl)ethyl acrylate at 50 °C in water for 46 h (inimer/CuCl/Me₆TREN: 50/1/1) (inimer/water: 1/1 w/w) (NMR experiment performed at 30 °C in CDCl₃)

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</table>

*labeling system is defined in Scheme 5.7

The carbon and hydrogen atoms bonded to each other are labeled with the same letters, while the carbonyl carbons are labeled separately. For determination of branching structures by NMR spectroscopy, branching unit, ab (Scheme 5.6), should be observed. We used $^1$H, $^{13}$C and HSQC-NMR (Figure 5.9) spectroscopy to assign the resonances to specific methine, methylene and methyl carbons in the polymer.

Figure 5.12 and Table 5.2 demonstrate that there are two contours that correspond to 1.51 ppm on the $^1$H axis (CH₂; a or a’ in Scheme 5.7): one at 41.2 ppm (CH; b in Scheme 5.7), and one at 173.71 ppm (COOCH₂; i in Scheme 5.7). These crosspeaks therefore correspond to the aB* and/or ab structural units. However, there are no crosspeaks between a’ or e protons and d or h carbons which would be present for the ab structural unit. Similarly, there are two contours that correspond to 4.58 ppm on the $^1$H axis (CHCl; c or f in Scheme 5.7): one at 64.75 ppm (OCH₂; d in Scheme 5.7), and one
at 167.75 (CO₂CH₃; h in Scheme 5.7). These crosspeaks therefore correspond to the aB*, A*B* and/or A*b structural units. However, there are no crosspeaks between the c protons and i carbons for A*B* or A*b structural units. Therefore, the only structural units we have been able to detect by HMBC-NMR spectroscopy of the hyperbranched poly(methyl acrylate) is aB*; all of the remaining crosspeaks in Figure 5.12 and Table 5.2 are also consistent with the aB* structural unit.

Therefore, we have no conclusive results from NMR spectroscopy of the hyperbranched poly(methyl acrylate) to establish the presence of branching. This means that either branching is not detectable, or the polymerization occurs by only chain polymerization of the vinyl groups to produce a linear polymer, which is not consistent with the polydispersity of 1.52 (GPCₚₛₛ in THF) and 1.92 (GPCₗₛ in THF).

As mentioned in section 5.2 and the ¹H-NMR spectra in Figure 5.6 indicated that the different polymerization conditions of the methyl inimer produced polymers with different structural units. We therefore tried to investigate hyperbranched poly(methyl acrylate)s synthesized under varying polymerizing conditions, but found the reproducibility of the methyl inimer polymerizations to be poor under any particular conditions. In contrast, polymerization of the mesogenic inimer are reproducible, and we therefore continued our NMR investigations with hyperbranched poly({2-chloro-2-[(11'- (4''-cyanophenyl-4'''-phenoxy)undecan-1- oxy carbonyl)]ethyl acrylate}, although its chemical structure is more complicated than hyperbranched poly(methyl acrylate). We performed the same series of NMR experiments as with the poly(methyl acrylate), with similar results.
For example, Figure 5.13 shows a $^1$H-$^1$H TOCSY spectrum of the hyperbranched SCLCP, since TOCSY detects protons that are separated by three or more bonds, there is apparently a crosspeak between $OCH_2$ (d) and $CHCl$ (f), although there is no detectable crosspeak between $CH_2$ of the backbone (a) and $CHCl$ (c). In addition there was is no detectable crosspeak between $OCH_2$ (d) and $CH$ (e) of the polymer backbone. There are crosspeaks for $OCH_2$ (g and l) and aliphatic $CH_2$ of the side chains. The crosspeaks in 1.5 – 2.0 ppm are due to the $CH_2$ of the side chain, and no resonances are detectable for $CH$ (b) of the polymer backbone, although experiment was run at 110 °C to sharpen the resonances. Therefore, the TOCSY does not detect crosspeaks between a and b of the polymer backbone, nor between b and e of a branch point ab.

![Figure 5.13: Expanded region of the $^1$H-$^1$H TOCSY-NMR (750 MHz) spectrum of the hyperbranched poly(2-chloro-2-[11''-(4''-cyanophenyl-4'''-phenoxy)undecan-1- oxy carbonyl]ethyl acrylate) (at 110 °C in d$_4$-o-dichlorobenzene) synthesized from mesogenic inimer under ATRP condition (inimer/CuBr/PMDETA : 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C for 120 h, GPC$_{PST}$ (THF) $M_n = 1.3 \times 10^4$ Da, pdi = 1.38]
Similar to the hyperbranched poly(methyl acrylate), we were only able to conclusively identify the $aB^*$ structural units by HMBC-NMR spectroscopy.

Scheme 5.8: Structural units in the hyperbranched poly(2-chloro-2-[11'--(4''-cyanophenyl-4'''-phenoxy)undecan-1-oxy carbonyl]ethyl acrylate) before and after reduction of Cl end groups

Since the difficulty in detecting branching may be due to overlapped $^1H$ and/or $^{13}C$ resonances, we reduced the chlorine end groups to hopefully simplify the NMR spectra by removing the CHCl resonances from the OCH$_2$ region of the spectrum, due to an upfield shift of the resulting CH$_2$ resonances.
Scheme 5.9: Reduction of Cl end groups in the hyperbranched poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]ethyl acrylate} using tri(n-butyl) tin hydride under ATRP conditions (Cl/Cu(I)Br/Me₆TREN/ tri(n-butyl) tin hydride : 1/0.1/0.1/1.15) at 120 °C for 5 h in anisole (polymer/anisole : 1/30, w/w); GPC_PSt (THF) M_n = 1.3 x 10⁴ Da, pdi = 1.38 before reduction; GPC_PSt (THF) M_n = 1.0 x 10⁴ Da, pdi = 1.42 after reduction

Scheme 5.8 shows the four non-vinylic structural units of the hyperbranched polymer with and without chlorine end groups. The Cl end groups were reduced using tri-n-butyl tin hydride (or tri(n-butyl) tin deuteride) under ATRP conditions as shown in Scheme 5.9. The reactions using AIBN in benzene at 60 °C (Cl/AIBN/HSnBu₃ : 1/0.033/1.2 in benzene; polymer/benzene 1/13, w/v) for 3 h were unsuccessful in removing Cl end groups from the hyperbranched polymers. A more stringent reaction condition using ATRP at higher temperature was employed.

Figures 5.14 and 5.15 present ¹H and ¹³C-NMR spectra of the original polymer; the ¹H resonances of original polymer are overlapped. Figure 5.14 confirms that the OCH₂ resonance(s) at 4.5 ppm of the reduced polymer are now resolved, with the CHCl resonances replaced by overlapped CO₂CH₂CH₂CO₂ and CO₂CH₂CH₂H₂CO₂. Other resonances also seem to be resolved, in the 1.5-2.8 ppm region as shown in the box in Figure 5.14.
Figure 5.14: $^1$H-NMR spectra (750 MHz) (at 110 °C in $d_4$-o-dichlorobenzene) of the hyperbranched poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1- oxy carbonyl]}ethyl acrylate) (before and after reduction); polymer synthesized from mesogenic inimer under ATRP conditions (inimer/CuBr/PMDETA : 80/1/1) in anisole (inimer/ anisole : 1/1, w/w) at 120 °C for 120 h, GPC$_{PST}$ (THF) $M_n = 1.3 \times 10^4$ Da, pdi = 1.38 (before reduction); reduced hyperbranched SCLCP synthesized under ATRP conditions using tri-$n$-butyl tin hydride (Cl/Cu(I)Br/Me$_3$TREN/tri($n$-butyl) tin hydride : 1/0.1/0.1/1.15) at 120 °C for 5 h in anisole (polymer/anisole : 1/30, w/w); GPC$_{PST}$ (THF) $M_n = 1.0 \times 10^4$ Da, pdi = 1.42 (after reduction)

Figure 5.15 shows the $^{13}$C-NMR spectra of the hyperbranched SCLCP before and after reduction of the Cl end groups. After reduction, the resonance of the methylene carbon, $a$, at ~31 ppm is significantly more intense, and the $i$ and $h$ carbonyl resonances (160-180 ppm) are visibly different. Most importantly, the $c$ and $f$ resonances at 54.0 ppm for $\text{CHCl}$ are not observed in the reduced polymer, and are replaced with $\text{CH}_2$ resonances at 32.0 ppm.
Figure 5.15: $^{13}$C-NMR (300 MHz) (at 110 °C in $d_4$-$o$-dichlorobenzene) of the hyperbranched poly($\{2$-chboro-2-$[11'$-(4''-cyanophenyl-4'''-phenoxy)undecan-1-oxy carbonyl$]$ethyl acrylate$)$ (before and after reduction); polymer synthesized from mesogenic inimer under ATRP conditions (inimer/CuBr/PMD ETA : 80/1/1) in anisole (inimer/ anisole : 1/1, w/w) at 120 °C for 120 h, GPC$_{PsL}$ (THF) $M_n = 1.3 \times 10^4$ Da, pdi = 1.38 (before reduction); reduced hyperbranched SCLCP synthesized under ATRP conditions using tri($n$-butyl) tin hydride (Cl/Cu(I)Br/MegTREN/tri($n$-butyl) tin hydride : 1/0.1/0.1/1.15) at 120 °C for 5 h in anisole (polymer/anisole : 1/30, w/w); GPC$_{PsL}$ (THF) $M_n = 1.0 \times 10^4$ Da, pdi = 1.42 (after reduction)
We first examined the reduced hyperbranched SCLCP by $^1$H-$^1$H TOCSY NMR spectroscopy using the labeling system shown in Scheme 5.10 for the four non-vinylic structural units. The carbon and hydrogen atoms bonded to each other are labeled with the same letters while the carbonyl carbons are labeled separately. Labels are not shown for the mesogenic side chains since we are focused on identifying the backbone structural units. The $^1$H-$^1$H TOCSY NMR spectrometry of the original polymer was presented in Figure 5.13, and as discussed lacked any detectable crosspeaks for either the polymer backbone or the branch units.
Figure 5.16: Expanded regions of the $^1$H-$^1$H TOCSY-NMR (750 MHz) spectrum of the hyperbranched SCLCP, (at 110 °C in $d_4$-dichlorobenzene); original polymer synthesized from mesogenic inimer under ATRP condition (inimer/CuBr/PMDETA: 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C for 120 h, GPC$_{PSI}$ (THF) $M_n = 1.3 \times 10^4$ Da, pdi = 1.38; reduced hyperbranched SCLCP synthesized under ATRP conditions using tri(n-butyl) tin hydride (Cl/Cu(I)Br/M$_6$TREN/tri(n-butyl) tin hydride : 1/0.1/0.1/1.15) at 120 °C for 5 h in anisole (polymer/anisole : 1/30, w/w); GPC$_{PSI}$ (THF) $M_n = 1.0 \times 10^4$ Da, pdi = 1.42

Figure 5.16 presents expanded regions of the $^1$H-$^1$H TOCSY NMR spectrum of the reduced hyperbranched SCLCP. In this case, the crosspeak between d at 4.55 ppm and f at 2.85 ppm is clear, corresponding to aB* and/or A*B* structural units; the small cross-peak between the 2.30 ppm (b or c?) and 1.6 ppm (a?) resonance may also be due
to either of these structural units. There is also a crosspeak between d at 4.48 ppm and e at 2.77 ppm, which corresponds to the ab branch point and/or the A*b structural unit. The crosspeak between e at 2.77 ppm and 1.82 (a’?) resonances may also be due to these structural units.

Figure 5.17: Expanded regions of the $^1$H-$^{13}$C HSQC-NMR (750 MHz) spectrum of the hyperbranched SCLCP, (at 110 °C in d$_4$-o-dichlorobenzene); original polymer synthesized from mesogenic inimer under ATRP condition (inimer/CuBr/PMDETA: 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C for 120 h, GPC$_{PS}$ (THF) $M_n = 1.3 \times 10^4$ Da, pdi = 1.38; reduced hyperbranched SCLCP synthesized under ATRP conditions using tri(n-butyl) tin hydride (Cl/Cu(I)Br/M$_6$TREN/tri-n-butyl tin hydride : 1/0.1/0.1/1.15) at 120 °C for 5 h in anisole (polymer/anisole : 1/30, w/w); GPC$_{PS}$ (THF) $M_n 1.0 \times 10^4$ Da, pdi 1.42

In Figure 5.6, a resonance was observed at ~ 2.8 ppm for the hyperbranched poly(methyl acrylate) (as shown in the rectangular box) under different polymerizing
conditions, in addition to the CH and CH$_2$ backbone resonances at ~2.5 ppm. The resonance at 2.8 ppm should be for CH alpha to OCH$_2$ in the polymer. The TOCSY NMR spectrum of the reduced hyperbranched SCLCP also had a resonance at 2.77 ppm due to CH alpha to OCH$_2$.

We investigated the reduced hyperbranched SCLCP further using HSQC and HMBC-NMR experiments. Figure 5.17 shows the HSQC-NMR spectrum, with the $^1$H frequency on the F2 axis and the $^{13}$C frequency on the F1 axis. As mentioned earlier, HSQC is a phase sensitive experiment that detects directly bonded hydrogens on carbon. Figure 5.17 demonstrates that contours with the number of different colors, e and d are of opposite phases, and correspond to either methine or methylene groups, respectively. Similarly, contours e and f are of opposite phases and therefore different groups. According to the $^{13}$C-NMR spectrum in Figure 5.14, the resonance 33.10 ppm is due to a methylene (CH$_2$) and that at 42.02 ppm is due to a methine (CH), which is consistent with the crosspeaks with the contours, appearing at 2.85 ppm (CH$_2$) and 2.77 ppm (CH) $^1$H resonances, respectively. Contours due to a, c and b (Scheme 5.10) are not detectable in the HSQC spectrum, probably due to weak signals, also seen on the one-dimensional $^1$H and $^{13}$C-NMR spectra in Figures 5.14 (resonances shown in the box below 2.5 ppm) and 5.15, respectively.
Figure 5.18: Expanded region from the $^1$H-$^{13}$C HMBC-NMR (750 MHz) spectrum of the hyperbranched SCLCP, (at 110 °C in d$_4$-o-dichlorobenzene); original polymer synthesized from mesogenic inimer under ATRP condition (inimer/CuBr/PMDETA: 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C for 120 h, GPC$_{PS}$ (THF) $M_n = 1.3 \times 10^4$ Da, pdi = 1.38; reduced hyperbranched SCLCP synthesized under ATRP conditions using tri$(n$-butyl) tin hydride (Cl/Cu(I)Br/Me$_6$TREN/tri$(n$-butyl) tin hydride : 1/0.1/0.1/1.15) at 120 °C for 5 h in anisole (polymer/anisole : 1/30, w/w); GPC$_{PS}$ (THF) $M_n = 1.0 \times 10^4$ Da, pdi = 1.42
Table 5.3: Crosspeaks between \(^1\)H and \(^{13}\)C resonances detected by HMBC NMR (750 MHz) spectroscopy of the reduced hyperbranched SCLCP (at 110 °C in \(d_2\)-o-dichlorobenzene); original polymer synthesized from mesogenic inimer under ATRP condition (inimer/CuBr/PMDETA: 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C for 120 h, GPC\(_{\text{PSt}}\) (THF) \(M_n = 1.3 \times 10^4\) Da, pdi = 1.38; reduced hyperbranched SCLCP synthesized under ATRP conditions using tri-\(n\)-butyl tin hydride (Cl/Cu(I)Br/M\(_6\)TREN/tri-\(n\)-butyl tin hydride : 1/0.1/0.1/1.15) at 120 °C for 5 h in anisole (polymer/anisole : 1/30, w/w); GPC\(_{\text{PSt}}\) (THF) \(M_n = 1.0 \times 10^4\) Da, pdi = 1.42

| \(^1\)H (ppm) | \(^{13}\)C (ppm) | \(^{13}\)C (ppm) | 
|----------------|----------------|----------------|----------------|
| CH\(_2\) | a / a’ / c / f | 33.10 | * | * | * |
| CH | b / e | 42.02 |  |
| OCH\(_2\) | D | 59.00 | * | * |
| COOR | H | 168.80 | * | * | * | * |
| COOCH\(_2\) | I | 170.80 | * | * |
|  |  | 173.10 |  |  |

In Table 5.3 \(^1\)H and \(^{13}\)C chemical shifts are shown on the horizontal and vertical axes, respectively. The positions of the contours in the HMBC spectrum were assigned and listed in Table 5.3. For an example, if a contour at 2.85 ppm on F2 axis (CH\(_2\) on \(^1\)H chemical shift) is selected, it is related to contours at 59.00 ppm and 168.80 ppm on F1 axis (OCH\(_2\) and COOR on \(^{13}\)C chemical shift); these values were entered in Table 5.3 as f, d and h (as shown in the Scheme 5.10). Similarly, a contour at 2.77 ppm on F2 axis (CH on \(^1\)H chemical shift) is selected, it is related to contours at 33.10, 59.00 ppm, 168.80 ppm and 170.80 ppm on F1 axis (CH\(_2\), OCH\(_2\), COOR and COOCH\(_2\) on \(^{13}\)C chemical shift); these values were entered in Table 5.3 as e, a’, d, h and i (as shown in the Scheme 5.10). This relationship shows the presence of branching unit, ab, in the polymer. From Table 5.3, structure aB* or A*B* can easily be determined as the proton.
labeled as f is related to the carbon atoms, d and h; the protons, d is related to carbon atoms, i, h and f. Since, no contours were observed upfield of 2.7 ppm on $^1$H chemical shifts, other structural units were not observed.

Figure 5.18 and Table 5.3 demonstrate that there are three contours that correspond to 4.48 ppm on the $^1$H axis (OCH$_2$; d in Scheme 5.10): one at 33.10 ppm (CH$_2$; a' in Scheme 5.10), one at 168.80 ppm (COOR; h in Scheme 5.10), and one at 170.80 ppm (COOCH$_2$; i in Scheme 5.10). These crosspeaks therefore correspond to the A*b and/or ab structural units. However, there are no crosspeaks between d and a' protons and e carbons which would be present for the ab structural unit, probably due to the very weak intensity of the CH carbon signal. Similarly, there are three contours that correspond to 4.55 ppm on the $^1$H axis (OCH$_2$; d in Scheme 5.7): one at 33.10 ppm (CH$_2$; f, in Scheme 5.10), one at 170.80 ppm (COOCH$_2$; i. in Scheme 5.10), and one at 173.10 ppm (COOCH$_2$; i in Scheme 5.10). These crosspeaks therefore correspond to the aB*, A*B* structural units. Since no crosspeaks for c and b $^1$H resonances were obtained in the HMBC spectrum, structural units ab and A*b, and aB* and A*B were not separately identified. Combining the results obtained by $^1$H-$^1$H TOCSY, HSQC and HMBC NMR experiments, structural units ab and A*b are identified.

As mentioned earlier, in addition to the reduction of hyperbranched SCLCP using tri(n-butyl) tin hydride, tri(n-butyl) tin deutride was also used to replace all Cl atoms with deuterium. By performing $^2$D-NMR experiment, it was expected that CH$_2$CHD and OCH$_2$CH might be detected by $^2$D NMR.
As shown in Figure 5.19, only a broad resonance at 2.70 ppm was observed demonstrating the incorporation of $^2$D into the polymer.

Another experiment $^{13}$C-$^2$D INEPT was performed in an attempt to identify the directly attached but only the resonance of the solvent, CHCl$_3$/CDCl$_3$, was observed. Hence, no additional information about the structural units was obtained by this experiment.

In addition to hyperbranched poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]}ethyl acrylate), poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]}ethyl methacrylate) was also synthesized and characterized by NMR spectroscopy. This polymer has two kinds of
methine protons in contrast to four methine protons of poly(2-chloro-2-[1’-4’-cyanophenyl-4’’-phenoxy]undecan-1-oxy carbonyl)ethyl acrylate). The Cl end group was reduced to an H atom in an experiment similar to that used for the hyperbranched poly(2-chloro-2-[1’-4’-cyanophenyl-4’’-phenoxy]undecan-1-oxy carbonyl)ethyl acrylate).

Scheme 5.11: Comparison of the non-vinylic structural units in the hyperbranched poly(2-chloro-2-[1’-4’-cyanophenyl-4’’-phenoxy]undecan-1-oxy carbonyl)ethyl acrylate) and poly(2-chloro-2-[1’-4’-cyanophenyl-4’’-phenoxy]undecan-1-oxy carbonyl)ethyl methacrylate)
Scheme 5.11 shows various structural units in the hyperbranched poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]}ethyl acrylate) and poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]}ethyl methacrylate). It was assumed that by decreasing the number of methine protons and introducing a methyl groups in the polymer backbone, we might obtain some detectable and separate resonances for structural units, $ab$ and $A^*b$ or $A^*B^*$ and $aB^*$.

Figure 5.20: $^1$H-NMR spectra (300 MHz) (at 30 °C in CDCl$_3$) of the hyperbranched poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]} ethyl methacrylate) (before and after reduction); polymer synthesized from (meth)mesogenic inimer under ATRP conditions (inimer/CuBr/PMDETA : 84/1/1) in anisole (inimer/anisole : 1/1 w/w) at 120 °C for 100 h, GPC$_{PSI}$ $M_n = 1.85 \times 10^4$ Da, pdi = 2.68 (before reduction); reduced hyperbranched polymer synthesized under ATRP conditions using tri(n-butyl) tin hydride (Cl/Cu(I)Br/Me$_6$TREN/tri(n-butyl) tin hydride): 1/0.1/0.1/1.15; synthesized at 120 °C for 5 h in anisole (polymer/anisole : 1/20, w/w)
Figure 5.20 shows $^1$H-NMR spectra of poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]}ethyl methacrylate) before and after reduction of end groups. A broad resonance at 2.5 ppm can be assigned to either methine protons of $A^*b$ or $ab$ or methylene protons at the $\beta$ position$^{267}$ to $C(CH_3)Cl$ of $A^*b$ or $A^*B*$. Since this resonance still remained after reduction of Cl into H, it may be due to the methine proton of $A^*b$ or $ab$. With reference to the linear poly(methyl acrylate), it is observed that methylene protons of the backbone appear upfield of 2.0 ppm and the resonances downfield to 2.0 ppm can possibly be excluded.

More detailed analysis by 2D-NMR spectroscopy similar to experiments used on hyperbranched poly(methyl acrylate) and hyperbranched poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]}ethyl acrylate) for both before and after the reduction of the end groups, were performed. These experiments were unsuccessful and are not reported here. Major problems associated with the poor signals from the backbone methylene and methine groups and separation of the overlapped resonances (upfield of 2.0 ppm in Figure 5.20) in hyperbranched SCLCP can also be attributed to poly(mesogenic methacrylate).
5.3 Comparison of the Solution Properties of the Hyperbranched SCLCPs and Their Architectural Analogs

Scheme 5.12: Chemical structures of the poly(meosgenic acrylate)s of different architectures (linear\textsuperscript{7}, three-arm star\textsuperscript{8}, six-arm star\textsuperscript{9}, comb\textsuperscript{10}) except hyperbranched
Scheme 5.12 shows the chemical structures of the poly(2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]ethyl acrylate)s of different architectures, which will be discussed along with the hyperbranched poly(2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]ethyl acrylate). The absolute molecular weights obtained from GPC_{LS} of the branched polymers (three-arm^8, six-arm^9, comb^10) are different than relative molecular weights obtained from GPC_{PSt}.^153 The molecular weight data obtained from GPC_{PSt} is a relative molecular weight and is a measure of hydrodynamic volume of the polymer in the eluent. The hydrodynamic volume of the polymer is the volume occupied by a polymer chain in a particular solvent. Since branched polymers are more compact, the hydrodynamic volume of a branched polymer is lower than that of less branched polymers. Therefore, the errors in the GPC_{PSt}-determined molecular weights increased as branching increased.

![Comparison of the number average molecular weights (M_n) obtained from GPC_{PSt} and GPC_{LS} in CH_2Cl_2 at 30 °C of the hyperbranched poly(2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl])ethyl acrylate)s synthesized under ATRP condition (inimer/CuBr/PMDETA : 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C](image-url)
Figure 5.22: Comparison of the number average molecular weights (M<sub>n</sub>) obtained from GPC<sub>PSi</sub> and GPC<sub>LS</sub> in THF at 30 °C of the hyperbranched poly({2-chloro-2-[11'-(4''-cyanophenyl-4'''-phenoxy)undecan-1-oxy carbonyl]})ethyl acrylate)s synthesized under ATRP condition (inimer/CuBr/PMDETA : 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C

Table 5.4: Errors in the number average molecular weights of SCLCPs of different architectures in CH<sub>2</sub>Cl<sub>2</sub>-linear regression analysis

<table>
<thead>
<tr>
<th>Architectures</th>
<th>Intercept, c</th>
<th>Slope, m</th>
<th>&lt;sup&gt;a&lt;/sup&gt;r&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear&lt;sup&gt;7&lt;/sup&gt;</td>
<td>3.40</td>
<td>0.79</td>
<td>0.99</td>
</tr>
<tr>
<td>Three-arm&lt;sup&gt;8&lt;/sup&gt;</td>
<td>4.31</td>
<td>1.17</td>
<td>0.90</td>
</tr>
<tr>
<td>Six-arm&lt;sup&gt;9&lt;/sup&gt;</td>
<td>-9.95</td>
<td>3.52</td>
<td>0.88</td>
</tr>
<tr>
<td>Comb&lt;sup&gt;10&lt;/sup&gt;</td>
<td>5.89</td>
<td>1.50</td>
<td>0.94</td>
</tr>
<tr>
<td>Hyperbranched</td>
<td>31.65</td>
<td>4.27</td>
<td>0.90</td>
</tr>
</tbody>
</table>

<sup>a</sup>r<sup>2</sup> = square of linear correlation coefficient
Figure 5.21 plots the absolute $M_n$ (GPC$_{LS}$) of the hyperbranched SCLCP in CH$_2$Cl$_2$ vs the GPC molecular weight relative linear polystyrene $M_n$ (GPC$_{PS}$). The relationship is fairly linear with $r^2 = 0.90$, and a slope, $m$ of 4.27 and intercept, $c$, of -31.67. Similarly, Figure 5.22 plots the molecular weight values in THF. The linear relationship is with $r^2 = 0.99$, and a slope, $m$ of 2.77 and intercept, $c$, of -7.72. Table 5.4 summarizes the values of the slopes, intercepts and $r^2$ for the plots in Figure 5.23 of the hyperbranched SCLCP along with its architectural analogs. Although the six-arm star and comb polymers both have six branches$^{153}$, the errors in the GPC$_{PS}$-determined molecular weights are higher for the six-arm polymer than the comb polymers. This may be because the six-arm star polymers have a single branch point with six branches, whereas the comb polymers have five branch points which led to the six-arm star polymer being more compact structure. Table 5.4 and the corresponding plots in Figure 5.23 demonstrate that the slope, $m$ increases as linear $<$ three-arm star $<$ comb $<$ six-arm star $<$ hyperbranched polymer. Therefore, errors in the GPC$_{PS}$-determined molecular weights are consistent with the “hyperbranched” SCLCPs being more branched than any of the architectures we have synthesized previously. In addition, the hyperbranched SCLCP obtained from SCVP is not well-defined and has a random, non-uniform branching.
Figure 5.23: Comparison of the number average molecular weights GPC_{PSi} and GPC_{LS} (in CH₂Cl₂ at 30 °C) of the hyperbranched poly(2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl])ethyl acrylate)s synthesized under ATRP condition (inimer/CuBr/PMDETA : 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C

The molecular dependence of the root-mean squared radius of gyration \(<R_g^2>^{1/2}\) can be studied using GPC_{LS}.⁸,²⁶⁸ Since each elution slice of the GPC chromatogram corresponds to a single size polymer or a fraction of very narrow polydispersity²⁶⁹, a polymer with broad molecular weight distribution provides several single size polymers for calculating molecular weight dependence of its radius of gyration. The hyperbranched polymers synthesized by SCVP have higher polydispersities than the other architectures prepared by ATRP, and can therefore be used directly to calculate the root-mean squared radius of gyration. In contrast, blends of the other architectures¹⁵³ were prepared to study their size over a broad molecular weight range using GPC_{LS}. 

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Figure 5.24: Radius of gyration vs molecular weight $G_{PC_{LS}}$ (in CH$_2$Cl$_2$ at 30 °C) of the hyperbranched poly({2-chloro-2-[11'- (4''''-cyanophenyl-4''''-phenoxy)undecan-1-oxy carbonyl]})ethyl acrylate)s synthesized under ATRP condition (inimer/CuBr/PMDETA : 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C for 94 h.

Figure 5.25: Radius of gyration vs molecular weight ($G_{PC_{LS}}$) of the poly{[11-(4'-cyanophenyl-4''-phenoxy)undecyl] acrylate} of different architectures in CH$_2$Cl$_2$; line for the hyperbranched polymer corresponds to data in Figure 5.24.
Table 5.5: Dependence of the K and ν the SCLCP of different architectures on their molecular weights in CH₂Cl₂ at 30 °C

<table>
<thead>
<tr>
<th>Architectures</th>
<th>K</th>
<th>Scaling coefficient, ν</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear^7</td>
<td>18.6 x 10⁻²</td>
<td>0.36</td>
</tr>
<tr>
<td>Three-arm^8</td>
<td>15.1 x 10⁻²</td>
<td>0.36</td>
</tr>
<tr>
<td>Six-arm^9</td>
<td>12.6 x 10⁻²</td>
<td>0.37</td>
</tr>
<tr>
<td>Comb¹⁰</td>
<td>8.51 x 10⁻²</td>
<td>0.39</td>
</tr>
<tr>
<td>Hyperbranched*</td>
<td>8.93 x 10⁻²</td>
<td>0.38</td>
</tr>
</tbody>
</table>

* Polymerized at 120 °C in anisole for 94 h, (inimer/CuBr/PMDETA: 80/1/1)

Figure 5.25 compares the line of best fit from Figure 5.24 for the hyperbranched SCLCP to these of the other architectures. Table 5.5 lists the values of ν and K for these polymers. The values of K decreases with increasing branching (linear^7 > three-arm^8 > six-arm^9 > comb¹⁰ ~ hyperbranched). Since the scaling coefficient is approximately the same for all of the architectures, this corresponds to the radius of gyration at a particular molecular weight value decreasing in the same direction. Although radius of gyration of the hyperbranched polymers will vary with the polymerization conditions since the degree of branching will vary, this particular hyperbranched polymer is evidently more branched than the other architectures the group has synthesized thus far.
Figure 5.26: Comparison of the values of the contraction factor vs molecular weight (GPC$_{LS}$) of the hyperbranched poly({2-chloro-2-[[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]})ethyl acrylate)s with other architectures in CH$_2$Cl$_2$; hyperbranched SCLCP synthesized under ATRP condition (inimer/CuBr/PMDETA : 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C for 94 h.

Figure 5.26 plots the values of the contraction factor \( g = \frac{<R_g^2>_{br}}{<R_g^2>_{lin}}^{1/2} \) vs molecular weight at each slice of the GPC chromatogram \( (M_i) \) using the lines from Figure 5.25. At the plateau values at \( M_i = 10^6 \), the contraction factor, of the six-arm star \( (g = 0.56) \) and comb polymers \( (g = 0.58) \) are essentially the same.\(^9\) The contraction factors decrease with increasing branching: three-arm\(^8\) star > six-arm\(^9\) star ~ comb\(^10\) > hyperbranched polymers. The values of the contraction factor also demonstrate that as branching increases the compactness of the polymer in solution increases. Again, the values of the contraction factors for the hyperbranched polymers should vary depending on the degree of branching, Figure 5.26 demonstrates that this hyperbranched SCLCP is more compact.
Figure 5.27: Intrinsic viscosity vs weight average molecular weight ($M_w$) (GPC$_{LS}$) of the hyperbranched poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]}ethyl acrylate) with other architectures in CH$_2$Cl$_2$ at 30 °C; hyperbranched SCLCP synthesized under ATRP condition (inimer/CuBr/PMDETA : 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C for 120 h.

Figure 5.27 plots the intrinsic viscosity as a function of the weight average molecular weight for the SCLCP with different architectures which I have synthesized. None of these values have been reported previously. The intrinsic viscosity and especially the exponent, $a$, in Mark-Houwink-Sakurada relationship are a measure of macromolecular dimensions of a polymer chain in solution. In general, a polymer chain becomes more compact in solution with increasing branching, and the value of the exponent, $a$, decreases.
Table 5.6: Parameters of the Mark-Houwink-Sakurada equation ($[\eta] = KM_\eta^a$) in CH$_2$Cl$_2$ at 25 °C for hyperbranched poly(2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]ethyl acrylate) and poly{[11-(4’-cyanophenyl-4’’-phenoxy)undecyl] acrylate} of different architectures

<table>
<thead>
<tr>
<th>Architectures</th>
<th>$K$</th>
<th>Exponent, $a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear$^7$</td>
<td>0.327 x 10$^{-3}$</td>
<td>0.59</td>
</tr>
<tr>
<td>Three-arm$^8$</td>
<td>1.12 x 10$^{-3}$</td>
<td>0.48</td>
</tr>
<tr>
<td>Six-arm$^9$</td>
<td>2.07 x 10$^{-3}$</td>
<td>0.40</td>
</tr>
<tr>
<td>Comb$^{10}$</td>
<td>5.56 x 10$^{-3}$</td>
<td>0.32</td>
</tr>
<tr>
<td>Hyperbranched$^a$</td>
<td>5.57 x 10$^{-3}$</td>
<td>0.28</td>
</tr>
<tr>
<td>Hyperbranched$^b$</td>
<td>3.37 x 10$^{-3}$</td>
<td>0.31</td>
</tr>
</tbody>
</table>

$^a$ synthesized at 90 °C in acetonitrile/water for 6 h  
$^b$ synthesized at 120 °C in anisole for 120 h (shown in Figure 5.27)

Table 5.6 lists the values of the $K$ and the exponent, $a$, parameters. Both the intrinsic viscosity and the exponent values of the branched polymers are lower than those of the linear polymer, and decrease with increasing branching: linear $>$ three-arm $>$ six-arm $>$ comb $>$ hyperbranched. The exponent value and the intrinsic viscosity at a particular molecular weight are slightly lower for the six-arm star than the comb polymer. The six-arm star with one branch point is apparently more compact in solution than comb polymers with five branch points and six branches. In general, the intrinsic viscosity experiments are also consistent with the hyperbranched SCLCP being more branched than the other architectures.
5.4 Comparison of the Thermal Properties of the Hyperbranched Poly(2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1-oxy carbonyl]ethyl acrylate) and Their Architectural Analogs

Before performing the DSC experiments, the hyperbranched SCLCPs were precipitated and fractionated to remove unreacted inimers, oligomers and copper complexes.

Table 5.7 and Figure 5.28 demonstrate that all of the hyperbranched polymers exhibit narrow isotropization transitions with full widths at half of the maximum peak intensity, fwhm = 2.03–6.1°C, similar to the well-defined linear, three-arm, six-arm and comb...
architectures prepared by ATRP. These transitions are evidently narrower than expected based on ill-defined and random branching from SCVP, due to fractionation and removal of the lower molecular weight oligomers. However, these polymers were synthesized under a variety of polymerization conditions, as listed in the footnotes of Table 5.7.

Table 5.7: Thermotropic behavior of hyperbranched poly(2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1- oxy carbonyl]ethyl acrylate) synthesized by ATRP

<table>
<thead>
<tr>
<th>GPC_Pst</th>
<th>GPC_LS</th>
<th>Transition temperature (°C)</th>
<th>fwhm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP_n</td>
<td>Pdi</td>
<td>DP_n</td>
<td>Pdi</td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>10(^a)</td>
<td>1.48</td>
<td>10</td>
<td>1.81</td>
</tr>
<tr>
<td>16(^b)</td>
<td>2.56</td>
<td>17</td>
<td>2.56</td>
</tr>
<tr>
<td>23(^c)</td>
<td>1.56</td>
<td>86</td>
<td>1.38</td>
</tr>
<tr>
<td>29(^d)</td>
<td>3.46</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>30(^d)</td>
<td>2.97</td>
<td>145</td>
<td>1.44</td>
</tr>
<tr>
<td>31(^d)</td>
<td>2.76</td>
<td>146</td>
<td>1.38</td>
</tr>
<tr>
<td>38(^d)</td>
<td>3.37</td>
<td>90</td>
<td>2.11</td>
</tr>
</tbody>
</table>

\(^a\) Inimer/CuCl/Me₆TREN : 55/1/1 at 90 °C (inimer/acetonitrile/water : 1 /2.5/ 0.5, w/w/w)
\(^b\) Inimer/CuCl/Me₆TREN : 44/1/1 at 90 °C (inimer/acetonitrile/water : 1 /2.5/ 0.5, w/w/w)
\(^c\) Inimer/CuCl/Me₆TREN : 8/1/1 at 90 °C (inimer/acetonitrile/water : 1 /2.5/ 0.5, w/w/w)
\(^d\) (inimer/CuBr/PMDETA : 80/1/1) in anisole (inimer/ anisole : 1/1, w/w) at 120 °C (DP_n = M_n /526), as a mesogenic inimer (526 Da) corresponds to a repeat unit in the polymer

In contrast to the other architectures prepared by ATRP of {11-(4’-cyanophenyl-4’’-phenoxy)undecyl} acrylate, the hyperbranched SCLCPs have many more halogen end groups, which in this case are chlorine instead of bromine. The number of end groups in the hyperbranched SCLCP equals the number of repeat units, while the number of end
groups in the six-arm star SCLCP is six. Therefore, the isotropization transitions of the hyperbranched polymers are narrower in spite of them having a large number of end groups. In addition, the breadth of the transitions decreases as the molecular weight of the polymers increases, in spite of the relative number of end groups remaining constant.

Figure 5.29: Glass $T_g$ (°C) and isotropization $T_i$ (°C) transitions of the hyperbranched poly(2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1’-oxy carbonyl]ethyl acrylate) as a function of the degree of polymerization (DP$_n$ and pdi were determined by GPC$_{PST}$ in THF)

Figure 5.29 plots the transition temperature vs the GPC$_{PST}$-determined number average degrees of polymerization, and demonstrates that both the glass transition and isotropization temperatures increase with increasing degree of polymerization, until they reach a constant values at 20 °C and 102 °C, respectively. Figure 5.30 plots the transition temperatures vs inverse degree of polymerization in order to establish the infinite molecular weight transitions of $T_i = 111$ °C and $T_g = 19.7$ °C.
Figure 5.30: Glass $T_g$ (°C) and isotropization $T_i$ (°C) transitions of the hyperbranched poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1- oxy carbonyl]}ethyl acrylate) as a function of the inverse degree of polymerization ($DP_n$ and pdi were determined by GPC$_{PSt}$ in THF)

Figure 5.31: Glass $T_g$ (°C) and isotropization $T_i$ (°C) transitions of the hyperbranched poly({2-chloro-2-[11’-(4’’-cyanophenyl-4’’’-phenoxy)undecan-1- oxy carbonyl]}ethyl acrylate) as a function of the degree of polymerization ($DP_n$ and Pdi were determined by GPC$_{LS}$ in CH$_2$Cl$_2$)
Figure 5.32: Glass $T_g$ (°C) and isotropization $T_i$ (°C) transitions of the hyperbranched poly({2-chloro-2-[11’-(4''-cyanophenyl-4'''-phenoxy)undecan-1-oxy carbonyl]}ethyl acrylate) as a function of the inverse degree of polymerization (DP$_n$ and pdi were determined by GPC$_{LS}$ in CH$_2$Cl$_2$)

Figures 5.31 and 5.32 plot the transition temperatures vs the GPC$_{LS}$-determined DP$_n$ and 1/DP$_n$, respectively and demonstrate that $T_i = 104$ °C and $T_g = 17.3$ °C at infinite absolute molecular weight.

Table 5.8: Infinite molecular weight transition temperatures of poly{[11-(4’-cyanophenyl-4''-phenoxy)undecyl] acrylate} of different architectures and the hyperbranched poly({2-chloro-2-[11’-(4''-cyanophenyl-4'''-phenoxy)undecan-1-oxy carbonyl]}ethyl acrylate) synthesized by ATRP

<table>
<thead>
<tr>
<th>Architectures</th>
<th>GPC$_{PS}$ in THF</th>
<th>GPC$_{LS}$ in CH$_2$Cl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g$-$s_C$</td>
<td>$s_C$-$s_A$</td>
</tr>
<tr>
<td>Linear$^8$</td>
<td>16</td>
<td>25</td>
</tr>
<tr>
<td>Three-arm$^9$</td>
<td>16</td>
<td>24</td>
</tr>
<tr>
<td>Six-arm$^{10}$</td>
<td>18</td>
<td>28</td>
</tr>
<tr>
<td>Comb$^{11}$</td>
<td>19</td>
<td>29</td>
</tr>
<tr>
<td>Hyperbranched</td>
<td>20</td>
<td>NA</td>
</tr>
</tbody>
</table>
Table 5.8 summarizes that the infinite molecular weight transition temperatures, $T_i$, for all of our SCLCP architectures. It demonstrates that the isotropization temperature of the hyperbranched polymer is significantly lower than the other architectures as reported\textsuperscript{171}, although the glass transition temperatures are essentially equal.

Figure 5.33: Normalized differential scanning calorimetry traces (10 °C/min) of hyperbranched poly(mesogenic acrylate) before reduction of Cl end groups and after reduction of Cl end groups into H groups (DP$_n$ and pdi were determined by GPC$_{LS}$ in CH$_2$Cl$_2$); poly(mesogenic acrylate)s were synthesized by ATRP (inimer/CuBr/PMDETA : 80/1/1) in anisole (inimer/anisole : 1/1, w/w) at 120 °C; poly(mesogenic acrylate)s were synthesized under ATRP conditions using tri-$n$-butyl tin hydride (Cl/Cu(I)Br/Mc$_6$TREN/tri($n$-butyl) tin hydride : 1/0.1/0.1/1.15) at 120 °C in anisole (polymer/anisole : 1/20, w/w); for poly(mesogenic acrylate) DP$_n = M_n /526$, as a mesogenic inimer (526 Da) corresponds to a repeat unit in the polymer; for poly(mesogenic acrylate) DP$_n = M_n /490.55$, as a mesogenic inimer (526-35.45 Da) corresponds to a repeat unit in the polymer.
Figure 5.33 compares the DSC traces of the hyperbranched polymers with Cl end groups and with end groups reduced to –H. The isotropization temperatures increase after reduction, while the glass transition temperature remains the same. Surprisingly, the breadths of the transitions broaden after the Cl end groups are reduced to H. There may be some secondary interaction between the Cl end groups and the mesogenic groups that make the transition sharp similar to the other architectures, even though the architecture is not well-defined.

5.5 Comparison of the Rheological Properties of the Hyperbranched SCLCPs and Their Architectural Analogs in the Isotropic/Melt Phase

Before characterizing the dynamic rheological characterization of the polymers, we must first determine their linear viscoelastic region (LVE) over which the dynamic rheological parameters are independent of the applied strains. We therefore performed strain sweep tests for all of the architectures as a function of molecular weights and temperatures. The halogen end groups of the polymers were reduced to hydrogen atoms to avoid cross-linking, especially of the hyperbranched polymer at higher temperatures under mechanical stress. This also reduced the effect of the end groups on the rheological properties of the polymers. Table 5.9 lists the molecular weight characteristics of the polymers studied.

The LVE region is very wide for all of the architectures. Figure 5.34 plots G’ and G” vs % strain for one of the linear polymers in the isotropic melt. G’ and G” of these linear polymers remained constant throughout the test, and are independent of strain until at least 10% strain. Figure 5.35 plots G’ and G” vs % strain for one of the comb polymers in the isotropic melt. Both G’ and G” of this comb polymer are independent of
strain until at least 50% strain. Table 5.9 lists the % strain chosen to use in the LVE region for each of the polymers for all of the architectures at various molecular weights. In general both G’ and G” were independent of strain till at least 10% strain. However, some of the rheological tested had to be performed at higher strain (20% or 30%) to obtain acceptable torque values (>0.2 gm-cm).

Figure 5.34: Strain dependence of G’ and G” of linear poly{[11-(4’-cyanophenyl-4’’-phenoxy)undecyl] acrylate} (Mₙ = 12.3 x 10⁴ Da, pdi = 1.77, GPC₁₅) at 10 Hz at 150 °C in the isotropic melt

Figure 5.35: Strain dependence of G’ and G” of comb poly{[11-(4’-cyanophenyl-4’’-phenoxy)undecyl] acrylate} (Mₙ = 5.48 x 10⁴ Da, pdi = 1.65, GPC₁₅) at 10 Hz at 150 °C in the isotropic melt
Table 5.9: Molecular weights* of the poly\{11-(4’-cyanophenyl-4’’-phenoxy)undecyl\} acrylate\}s of different architectures for rheological experiments and their % strain in the LVE region used at 150 °C and 160 °C

<table>
<thead>
<tr>
<th>Architecture</th>
<th>GPC(_{LS})</th>
<th>% Strain (LVE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(M_n \times 10^4) (Da)</td>
<td>pdi</td>
</tr>
<tr>
<td>Linear</td>
<td>1.32</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>1.82</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>2.77</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>9.63</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>12.3</td>
<td>1.77</td>
</tr>
<tr>
<td>Three-arm</td>
<td>3.77</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>4.83</td>
<td>1.80</td>
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<tr>
<td></td>
<td>6.36</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>13.1</td>
<td>1.43</td>
</tr>
<tr>
<td>Six-arm</td>
<td>2.81</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>1.24</td>
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<td>4.66</td>
<td>1.74</td>
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<td></td>
<td>14.5</td>
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<tr>
<td>Comb</td>
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<td>1.21</td>
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<tr>
<td></td>
<td>5.48</td>
<td>1.65</td>
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<tr>
<td></td>
<td>8.52</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>1.58</td>
</tr>
<tr>
<td>Hyperbranched</td>
<td>1.88</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>2.67</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>3.14</td>
<td>1.30</td>
</tr>
</tbody>
</table>

*molecular weights were determined by GPC\(_{LS}\) in CH\(_2\)Cl\(_2\); halogen end groups were reduced.
Time-strain test on a randomly chosen polymer was also performed to determine if any edge fracture of the polymer occurred at higher strain (%). G’ and G” values were constant even at 100% strain for a time interval of 50 seconds. For example, Figure 5.36 plots G’ and G’’ vs time for one of the linear polymers in the isotropic melt at 150 °C, and demonstrates that the values of G’ and G” at 100% strain did not decrease over the 50 sec time period tested.

Figure 5.36: Time dependence of G’ and G” of linear poly{[11-(4’-cyanophenyl-4”-phenoxy)undecyl] acrylate} (M<sub>n</sub> = 2.77 x 10<sup>4</sup> Da, pdi = 1.32, GPC<sub>LS</sub>) at 100% strain at frequency 10 Hz at 150 °C

Figure 5.37: Frequency sweep plot for a linear poly{[11-(4’-cyanophenyl-4”-phenoxy)undecyl] acrylate} (M<sub>n</sub> = 12.3 x 10<sup>5</sup> Da, pdi = 1.77, GPC<sub>LS</sub>) at 150 °C at 10% strain
Figure 5.37 plots $G'$, $G''$ and $\eta^*$ as functions of frequency of one the linear polymers in the isotropic melt at 150 °C. This polymer behaved as a Newtonian fluid with $\eta^*$ constant as a function of frequency, showing no dependence on shear rate. This value of $\eta^*$ is therefore the zero shear rate melt viscosity of this polymer. In the isotropic melt, for all of the architectures of various molecular weights, $\eta^*$ was independent of shear rate.

Figure 5.38: Zero-shear melt viscosity vs number average molecular weight (GPC_{LS}) of the linear, three-arm, six-arm and comb poly{[11-(4’-cyanophenyl-4”'-phenoxy)undecyl]acrylate}s at 150 °C and 160 °C

The zero shear rate melt viscosities were obtained for all of the polymers in Table 5.9 of various molecular weights from dynamic frequency sweep experiments at 150 °C and 160 °C using a 25 mm diameter plate. Figure 5.38 presents the log-log plots of the zero-shear melt viscosity as a function of molecular weight for all of the architectures.
except the hyperbranched polymers. The relationship was fairly linear for all of them at both temperatures. The torque values were within the noise level for the data obtained for the hyperbranched polymer; possibly we had too little material to work with using parallel plates with a 25 mm diameter. The rheological properties of the hyperbranched polymers will be carried out by Prof. Patrick Mathers’ group (Syracuse University) using an instrument for smaller quantities of polymers.

Table 5.10: The exponent, $\nu$, constant K, and correlation coefficient, $r^2$ (from the best fit regression analysis) values from the equation, $\eta^* = KM^\nu$ of the poly{[11-(4'-cyanophenyl-4''-phenoxy)undecyl] acrylate)} of different architectures at 150 °C and 160 °C.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>$\nu$ (150 °C)</th>
<th>$K$ (150 °C)</th>
<th>$r^2$ (150 °C)</th>
<th>$\nu$ (160 °C)</th>
<th>$K$ (160 °C)</th>
<th>$r^2$ (160 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>1.20</td>
<td>5.19 X 10$^{-6}$</td>
<td>0.97</td>
<td>1.22</td>
<td>3.09 X 10$^{-6}$</td>
<td>0.97</td>
</tr>
<tr>
<td>Three-arm</td>
<td>0.99</td>
<td>4.48 X 10$^{-5}$</td>
<td>1.0</td>
<td>0.96</td>
<td>4.17 X 10$^{-5}$</td>
<td>1.0</td>
</tr>
<tr>
<td>Six-arm</td>
<td>0.82</td>
<td>2.34 X 10$^{-4}$</td>
<td>1.0</td>
<td>0.81</td>
<td>1.84 X 10$^{-4}$</td>
<td>1.0</td>
</tr>
<tr>
<td>Comb</td>
<td>0.89</td>
<td>1.08 X 10$^{-4}$</td>
<td>0.99</td>
<td>0.87</td>
<td>9.82 X 10$^{-5}$</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 5.10 lists the values of the exponent, $\nu$, constant K and $r^2$ from the equation, $\eta^* = KM^\nu$, obtained from Figure 5.38 for the non-hyperbranched polymers. The values $\nu$ decreased and the values K increased with increasing branching, i.e. linear > three-arm star > six-arm star ~ comb. Figure 5.39 presents log-log plots of the zero-shear melt viscosity of the non-hyperbranched polymers as a function of their vs GPC$_{LS}$-determined number average molecular weight at 150 °C and 160 °C.
Figure 5.39: Zero-shear melt viscosity vs number average molecular weight (GPC\textsubscript{LS}) of the poly{[11-(4’-cyanophenyl-4''-phenoxy)undecyl] acrylate}s of various architectures in log scale.

In contrast to conventional linear flexible polymers which exhibit a sharp increase in the slope of such plots from 1.0 to 3.4, a critical molecular weight corresponding to the entanglement molecular weight, the log of the melt viscosity of these SCLCPs increase at a constant slope with increasing log molecular weight over the molecular weight range studied. This indicated that these polymers are not entangled. However, as mentioned
previously the slopes of the plots (ν) decrease with increasing branching. Since these SCLCPs exhibit Newtonian behavior in the isotropic melt, plots of the melt viscosity vs inverse temperature follow an Arrhenius relation. Figure 5.40 presents the Arrhenius plots of the zero shear melt viscosity against 1/T(K), in which the melt viscosity is on a logarithmic scale and 1/T(K) is on a linear scale. The relationships are fairly linear, although only two data points are included for the linear polymer since its isotropization transition at approximately 140 °C precluded melt viscosity data for polymers of similar molecular weights.

Figure 5.40: Zero-shear melt viscosity vs 1/T(K) of the poly{[11-(4’-cyanophenyl-4’’-phenoxy)undecyl] acrylate} of various architectures of similar molecular weights (GPCLS in CH$_2$Cl$_2$) (linear, $M_n = 1.23 \times 10^5$ Da, pdi = 1.77; three-arm star, $M_n = 1.31 \times 10^5$ Da, pdi = 1.43; six-arm star, $M_n = 1.45 \times 10^5$ Da, pdi = 1.25; comb, $M_n = 1.05 \times 10^5$ Da, pdi = 1.58)

Figure 5.40 demonstrates that the linear polymer has the highest flow activation energy (Ea) required for its deformation although there is no clear trend with the extent of branching.
As described by Bueche$^{252}$, the zero-shear melt viscosity of unentangled polymers with long-chain branches depends on its mean square radius of gyration. As discussed in section 5.3, the radius of gyration of these SCLCPs decreases with increasing branching: linear < three-arm star < six-arm star ~ comb < hyperbranched. The zero-shear melt viscosity follows the reverse trend, as did the intrinsic viscosity in CH$_2$Cl$_2$: linear > three-arm star > six-arm star ~ comb. Since there are apparently no chain entanglements in the polymer samples used in these experiments the decrease in the intrinsic and the isotropic melt viscosities with increasing branching should correspond to a reduction in the relaxation time of the chains with increasing branching.

5.6 Comparison of the Rheological Properties of the Hyperbranched SCLCPs and their Architectural Analogs in Smectic A Mesophase

![Figure 5.41](image)

Figure 5.41: Strain dependence of $G'$ and $G''$ of linear poly{[11-(4’-cyanophenyl-4’’-phenoxy)undecyl] acrylate} ($M_n = 12.3 \times 10^4$ Da, pdi = 1.77, GPC$_{LS}$) and comb poly{[11-(4’-cyanophenyl-4’’-phenoxy)undecyl] acrylate} ($M_n = 5.48 \times 10^4$ Da, pdi = 1.65, GPC$_{LS}$) at 10 Hz at 100 °C in smectic A phase
We also established the linear viscoelastic region (LVE) of these polymers in the anisotropic smectic A mesophase before performing dynamic frequency sweep experiments. In contrast to the isotropic melt, the LVE region is very narrow for all of the architectures, and covers only 0.1 to 1.0 % strain.

For example, Figure 5.41 shows that G’ and G” of the linear and comb polymers remain constant below 1% strain, and then start to decrease. In addition, the relative magnitude of G’ and G” are reversed compared to the isotropic melt. In the smectic A mesophase, the elastic component of the modulus, G’, dominates, whereas the viscous component, G”, dominates in the isotropic melt.

Figure 5.42 plot G’ vs G” of the non-hyperbranched SCLCPs of various architectures at different molecular weights. All of the data points were obtained from dynamic frequency sweep experiments in the frequency range 1-100 Hz. Although, G’ and G” seem to depend somewhat on molecular weights, at least for the linear polymer, there is no clear trend. These data points are essentially separate for different molecular weights which demonstrate that are dependent on the molecular weights.
Figure 5.42: Storage vs loss modulus of poly[\{11-(4’-cyanophenyl-4’’-phenoxy)undecyl\} acrylate] of various architectures at different $M_n$ (GPC$_{LS}$ in CH$_2$Cl$_2$) 100 °C in the smectic A mesophase
Figure 5.43: Storage vs loss modulus of poly{[11-(4'-cyanophenyl-4’’-phenoxy)undecyl] acrylate} of various architectures at three different temperatures in the smectic A mesophase (M_n and pdi values calculated by GPC_L_S in CH_2Cl_2)

Figure 5.43 plots G’ vs G” of the non-hyperbranched SCLCPs of similar molecular weights at three different temperatures. The data points at all of the temperatures fall
essentially on the same curves, which demonstrate that $G'$ and $G''$ are independent of the
temperatures. These results demonstrate that $G'$ and $G''$ of these SCLCPs of various
architectures are dependent on the molecular weights but are independent of the
temperatures in the smectic A phase. This behavior is similar to that of conventional
linear flexible homopolymers that are unentangled.251

Figure 5.44: Complex viscosity vs frequency of poly{[11-(4’-cyanophenyl-4’’-
phenoxy)undecyl] acrylate}s of various architectures of similar molecular weights
(GPC$_{LS}$ in CH$_2$Cl$_2$) (Linear, $M_n = 1.23 \times 10^5$ Da, pdi = 1.77; Three-arm star, $M_n = 1.31 \times$
$10^5$ Da, pdi = 1.43; Six-arm star, $M_n = 1.45 \times 10^5$ Da, pdi = 1.25; Comb, $M_n = 1.05 \times 10^5$
Da, pdi = 1.58) at 100 °C

Figure 5.44 plots complex viscosity vs frequency for the non-hyperbranched
SCLCPs of similar molecular weights at 100 °C in the smectic A mesophase. The
complex viscosities of the branched polymers are lower than that of the linear polymer
except at higher frequencies. This is consistent with the intrinsic and isotropic melt
viscosities decreasing with increasing branching, although the effect of branching is not
as significant on the complex viscosity.
CHAPTER VI
CONCLUSION AND FUTURE DIRECTIONS

We successfully synthesized hyperbranched polyacrylates that are true analogs of linear polyacrylates. This was achieved by synthesizing a new class of inimer from a key halohydrin-based intermediate material, which was obtained from serine by a diazotization synthetic route. Polymerization of these inimers resulted in hyperbranched poly(meth)acrylates using the self-condensing vinyl polymerization (SCVP) by an atom transfer radical polymerization (ATRP) mechanism. These hyperbranched polyacrylates contain an ester group attached to every other carbon atom along the polymer backbone, with a non-initiator-containing alkyl ester attached as a free side chain. Because of flexibility of the synthetic-design, a variety of inimers and polymers with different ester substituents can be obtained. We have synthesized and characterized polyacrylates with alkyl, perfluoro, siloxane, oligo(oxyethylene) and mesogenic ester substituents. Polymerization of these inimers provided polymers with broader molecular weight distributions, consistent with the random and ill-defined branched structures. The kinetics of the growth of the polymerization was studied and compared with theoretical calculations, which followed the statistical nature of polymerization of an inimer by SCVP. The chemical structures of the hyperbranched poly(methyl acrylate) and SCLCP
were characterized in detail by $^1$H, $^{13}$C and 2D nuclear magnetic resonance (NMR) spectroscopy, which confirmed the presence of branching in the hyperbranched SCLCPs. This was achieved after reducing the halogen end-groups.

Comparative studies of the error analysis of the molecular weights obtained by GPC_{PSI} and GPC_{LS}, and solution properties, e.g. radius of gyration and intrinsic viscosity, demonstrated that hyperbranched SCLCP is more compact in structure and radius of gyration and the intrinsic viscosity decreased with increase in branching.

The thermal properties of the hyperbranched SCLCP were studied by DSC and POM. Similar to the architectures, the hyperbranched SCLCP showed smectic A mesophase. The glass transition and isotropization temperatures of the hyperbranched SCLCPs were lower than those of the polymers of other architectures. However, narrower isotropization transitions were observed similar to the well-defined linear, three-arm, six-arm and comb SCLCPs. Broader isotropization transitions were observed for hyperbranched SCLCPs with halogen end groups reduced to H groups. For the studies of rheological properties, linear, three-arm, six-arm and comb SCLCPs were synthesized and the end groups (Br) were reduced to H groups. Due to inconsistent results and smaller quantities of the hyperbranched SCLCPs, they were not included in this study. The linear, three-arm, six-arm and comb SCLCPs behaved like a Newtonian fluid in the isotropic melt. At a particular molecular weight, the melt viscosity of the polymer decreased with increase in branching. A higher flow activation energy value was obtained for the linear SCLCP compared to those of other branched architectures. In the smectic A mesophase, Hans’ plot ($G'$ vs $G''$) showed that $G'$, $G''$ are independent of temperature and dependent on the molecular weights of the polymers. This behavior of
SCLCPs of various architectures was similar to that of unentangled flexible linear homopolymers. The complex viscosity in smectic A phase at similar molecular weights of SCLCPs also decreased with increasing branching.

Further investigations of chemical structures of the hyperbranched polymers to obtain quantitative information of degree of branching by solid-state NMR spectroscopy could be performed. Electro-rheological properties of the hyperbranched side-chain liquid crystalline polyacrylates could be studied and compared to those of linear, three-arm star, six-arm star and comb polyacrylates.
REFERENCES


79. van Benthem, R.A.T.M.; Meijerink, N.; Geladé, E.; de Koster, C.G.; Muscat, D.;
Froehling, P.E.; Hendriks, P.H.M.; Vermeulen, C.J.A.A.; Zwartkruis, T.J.G
Macromolecules 2001, 34, 3559.


153. Kasko, A. Controlled Synthesis of Mesogenic Star Polymers and their Miscibility


254 Shaka, A. J.; Barker, P. B.; Freeman, R. J. Magn. Reson. 1985, 64, 547.

255. Johnson, M.R.; Ng, C.; Claire, C.M.S.; Fraser, C.L. Macromolecules, 2000, 33, 8629.


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