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Dielectric relaxations in side-chain liquid crystalline polymers

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Case Western Reserve University, 1993
DIELECTRIC RELAXATIONS IN
SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS

by

ZHENGZHONG ZHONG

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

Thesis Advisor: Professor Donald E. Schuele
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May 1993
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GRADUATE STUDIES

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date  2/11/93

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DIELECTRIC RELAXATIONS IN SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS

Abstract

by

ZHENGZHONG ZHONG

Side-chain liquid crystalline polymers represent a novel class of mesogenic materials which exhibit electro- and magneto-optical properties that are similar to those observed for the low-molecular-weight liquid crystals, whilst also having the good film-forming qualities that are characteristic of the high molar mass polymers. From the rotational dynamic theory, four relaxation modes which are dielectrically active arise from combinations of certain time-correlation functions for the angular motions of the dipolar groups in the local (nematic) potential. The practical dielectric relaxation spectroscopy over a wide frequency range shows two typical relaxation processes of the mesogenic side chain when the environmental temperature is above the polymer's glass transition ($T_g$), each of which can be a certain combination of some of the basic four modes, dependent upon the macroscopic alignment states.

Influences of the molecular weight and the spacer length on the dielectric relaxation have been investigated for a smectic polyvinylether
containing cyanobiphenyl side group. Both homogeneous and homeotropic alignments were achieved with an 8-Tesla magnetic field by slowly cooling the sample down from the isotropic phase to room temperature. The low-frequency $\delta$ loss peaks are suppressed in the homogeneous state and enhanced in the homeotropic state while high-frequency $\alpha$ loss peaks are enhanced in the homogeneous and almost absent in the homeotropic. The Arrhenius plot of each process shows a rapid decrease in the relaxation rate as the temperature approaches $T_g$, which may somehow reflect the glassy behavior of the polymer backbone and has been analyzed by Williams-Landel-Ferry (WLF) and Vogel-Fulcher-Tammann-Hesse (VFTH) equations.

The dielectric results of a nematic polymethacrylates containing a constitutional isomeric methoxy-methylstilbene mesogen (4-6-PMA and 4′-6-PMA) show that while 4-6-PMA has two typical relaxation processes, 4′-6-PMA essentially has one relaxation process. The temperature-dependent relaxation times, obtained through Havriliak-Negami data fitting, show “kinks” near calorimetric nematic–isotropic transition and a non-Arrhenius characteristic towards the glass transition as well. The experimental relaxation processes are well described by the four basic modes derived from the rotational dynamic theory in liquid crystals.
This thesis is dedicated to my grandmother,

Yu Shu-qing.
Acknowledgements

I wish to express my appreciation to Don Schuele for taking me on as a graduate student, working pleasantly in this laboratory with state-of-the-art research facilities. His physical insight and instrumentation knowledge have been inspiring me to explore the nature of material closely, precisely, and conveniently. I am also indebted to my co-advisor Bill Gordon for the graduate study support. Due to his commitments as the department chairman, many critical discussions regarding polymers and relaxations were scheduled on Saturdays, which have been proved to be indispensable for this research.

During the early stage of lab work, Rob Akins gave me tremendous help, not only in the lab topic but also in the American realities for a foreign student. Without his invaluable advice, I would not have avoided many possible mistakes and up-and-downs. Bing-Chang Xu meanwhile pushed me hard towards more publications according to his hybrid cultural background in the States over twelve years.

The thesis work was conducted within NSF Materials Research Group at Case Western Reserve University. The liquid crystal samples were kindly provided by Virgil Percec’s group and were magnetically aligned in Chuck Rosenblatt’s lab, where I have been enjoying the friendship with everybody, particularly with my fellow classmates, Greg DiLisi and Min-Hua Lu. The fruitful conversations with Dong-feng Gu, Alex Jamieson’s wonderful graduate student, have greatly benefited this research.
The loving understanding shown by my wife, Ruochen, for the five-year painstaking work is also acknowledged — without it this thesis would never have seen the light of day. *In the depth of winter ... we force the spring.*
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Chapter 1

Introduction

*Liquid crystal* is a term that is now commonly used to describe materials that exhibit partially ordered fluid phases that are intermediate between the three dimensionally ordered crystalline state and the disordered or isotropic fluid state. Phases with positional and/or orientational long-range order in one or two dimensions are termed *mesophases*. As a consequence of the molecular order, liquid crystal phases are anisotropic, i.e., their properties are a function of direction [1-7]. Although the technical applications of low molecular weight liquid crystals (LCs) and *liquid crystalline polymers* (LCPs) are relatively recent developments, liquid crystalline behavior has been known since 1888 when Reinitzer [8] observed that cholesterol benzoate melted to form a turbid melt that eventually cleared at a higher temperature. The term liquid crystal was coined by Lehmann [9] to describe these materials. The first reference to a polymeric mesophase was in 1937 when Bawden and Pirie [10] observed that above a critical concentration, a solution of tobacco
mosaic virus formed two phases, one of which was birefringent. A liquid crystalline phase for a solution of a synthetic polymer, poly(γ-benzyl-L-glutamate), was reported by Elliot and Ambrose [11] in 1950.

Modern-day interest in the LCPs had its origin with the molecular theories of Onsager [12] and Flory [13]. They predicted that rod-like molecules would spontaneously order above a critical concentration that depended on the aspect ratio of the molecule. These theories were later expanded to include other effects such as polydispersity and partial rigidity [13]. For example, a succession of para-oriented ring structure is widely used to prepare LCPs. Liquid crystalline phases do not depend on intermolecular associations, but occur as a result of intermolecular repulsions. That is, units of two molecules cannot occupy the same space. For rod-like molecules, or chains with rigid segments, there is a limit to the number of molecules that can arrange randomly in solution or the melt. When this critical concentration is exceeded, either a crystalline or an ordered, liquid crystalline phase forms. The rigid unit responsible for the liquid crystalline behavior is referred to as the mesogen.

For many rigid polymers, the critical concentration is achieved in solution, and these materials are classified as being lyotropic. Liquid crystalline phases are not observed in the bulk for lyotropic LCPs, primarily because the melting points of these materials are generally so high that they degrade before melt. The melting point can be depressed by introducing a degree of flexibility into the polymer chain, such as with structures that provide a kink or swivel to the chain or with flexible spacer groups that separate the rigid chain segments. In this case, the
critical concentration for forming a liquid crystalline phase is high, usually requiring bulk polymer, and anisotropic melts are obtained. These materials are thermotropic.

LCPs are high-molecular-mass materials that exhibit mesomorphism. Traditionally two major classes of LCP have identified: the so-called main chain and side chain types, see Fig. 1 - 1, page 4. More recently other various kinds of LCPs have appeared, which are combined LCPs that are hybrid between main-chain and side-chain LCPs, and the rigid rod types described by Watanabe et al. [5,14] Side-chain LCPs are polymers that have linked a conventional low molecular mass liquid crystal as side chains to a polymer backbone through a flexible spacer (usually a methylenic group \(-\text{CH}_2\text{-}\)) to form a “comb-like” structure [15-21]. This structure combines polymer advantages (good film-forming and other mechanical properties) with electro-, magneto-optical properties in low molecular mass LCs. They are of considerable interest scientifically as hybrid-nature materials and technologically as potential media for a variety of applications in physical optics and display technology [22].

Pioneered by Ringsdorf and Finkelmann [23-25] in Mainz and by Shibaev and Platé [26] in Moscow, such new comb-like polymers were designed and synthesized in the late 1970s. Systematic investigations of the synthesis, characterization and applications of side-chain LCP began only after Ringsdorf and coworkers proposed that a flexible spacer should be inserted between the polymeric main chain and the mesogenic side groups to decouple the motion of the main chain and side groups in the liquid crystalline state. Although numerous, previous investigations
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<th>Disc-like mesogenic group</th>
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Fig. 1 - 1  Example Liquid Crystalline Polymer Architectures.
concerning the synthesis of polymers with low-molecular-mass liquid crystalline compounds attached to their backbone did not lead to a synthetic method which could systematically produce side-chain LCPs, since most involved polymers with the mesogen attached to the backbone [27-31].

Based on the spacer model, a large number of side-chain liquid crystalline polymers and copolymers were synthesized. Different smectic, chiral smectic, nematic and cholesteric mesophases (see Fig. 1 - 2, page 6) are exhibited by these polymers based on different mesogenic groups and polymer backbones. Attainment of a thermotropic liquid crystalline mesophase from a flexible backbone containing mesogenic side groups requires reconciliation of the main chain’s tendency to form a statistical random coil conformation and the side groups’ tendency to arrange anisotropically. This is shown schematically in Fig. 1 - 3, page 7. The principle that the motions of both main chain and the side groups are coupled when the mesogenic groups are directly attached to the flexible backbone is well accepted. In this case, the conformation of the main chain is disturbed when the side groups adopt an anisotropic arrangement.

In order to balance the competition between the backbone’s random-coil conformation and the side groups alignment, Ringsdorf and coworkers predicted that the motion of the polymer main chain must be decoupled from that of the anisotropically oriented mesogenic side groups in the fluid state [23,24,25]. As demonstrated schematically in Fig. 1 - 3, page 7, decoupling should be achieved when a flexible spacer is inserted between
Fig. 1 - 2  Schematic representation of the different types of mesophases. Smectic with ordered (a) and unordered (a') arrangement of the molecules in layers; (b) nematic; (c) cholesteric; and (d) discotic.
Fig. 1 - 3  Schematic structure of liquid crystalline polymers showing the necessity of decoupling the mesogenic groups and polymer main chain through flexible spacers.
the polymer backbone and the mesogenic side chain. The side groups should be able to self-orient into anisotropic mesophase even when the main chain adopts a random-coil statistical conformation. The spacer concept therefore assumes that the main chain should do little to hinder the orientation of the mesogenic side chain; that is, for a given mesogen and spacer, the nature of the polymer backbone should theoretically not affect the type of mesophase formed and its thermal stability. However, the polymer backbone does in fact affect the mesomorphic behavior of side-chain LCPs [21]. Although a spacer helps to decouple the mesogenic groups from the main chain, and the decoupling becomes more effective with increasing spacer length, the decoupling is nevertheless incomplete. At least part of the spacer is anisotropically oriented with the mesogen [21].

Apart from their intrinsic scientific interest as hybrid materials, much interest has stemmed from the possible application of side-chain LCPs as media for digital or holographic optical information storage. For instance, thermo-recording of information as light-scattering spots on a transparent (homeotropically aligned) background has been described by Shibaev and coworkers [32,33] and by Coles and Simon [34] and is an extension to polymer liquid crystals of the laser-addressing method of thermo-recording introduced several years ago by Kahn [35] for low polar mass smectics. Ringsdorf and coworkers [36] have shown that digital and holographic storage of information is obtained using an LCP having azo groups in the side chain about which cis–trans isomerization occurs when a homeotropically aligned (see § 3.7 for definition) sample is subjected to
plane-polarized laser light. Other methods of optical storage are feasible, involving dichroic dye, photochromic or electrochromic moieties. Using such methods it seems possible that practical optical memories having density up to \(6 \times 10^7\) bit cm\(^{-2}\) may be realized using side-chain LCPs as has been discussed by Kaempf [37].

All applications of side-chain LCPs, including optical information storage, optical elements such as Fresnel zone plates [36] or nonlinear optical processing [38], require that the material be aligned macroscopically (homeotropic, planar or homogeneous, twisted-nematic). Alignment may be achieved using directing magnetic or electric fields (see § 3.7, Chapter 3), or by surface forces, in conjunction with thermal treatments. In the case of electric-field-induced alignment, the response of the material is dependent on the dielectric anisotropy, \(\varepsilon_{an}\), of the liquid crystal. This frequency-dependent quantity may be positive or negative as a result of dielectric relaxation of the principal permittivities \(\varepsilon'_{\omega}(\omega)\) and \(\varepsilon''(\omega)\). Thus homeotropic or planar alignment may be achieved for LCPs by choice of the frequency of the directing electric field, as was shown by Araki and Attard [39-41]. Thus the behavior of LCPs in directing electric fields has its origin in the anisotropic motions of the dipolar groups in the mesophase, which give rise to the dielectric relaxation properties. Such motions are conveniently studied by dielectric relaxation spectroscopy in the range \(10^{-3}\) to \(10^7\) Hz, as was demonstrated by Kresse et al. [42,43], by Zentel and et al. [44,45], by Haase et al. [46,47] for acrylate and methacrylate LCPs and by Williams et al. [48] for siloxane polymers. Following these researches, studies were made of samples aligned by
magnetic fields (acrylate polymers [46,49], siloxane polymers [50]) and by electric fields (siloxane polymers [39,40,51-54]). Multiple relaxations were observed and were assigned to the motions of dipolar groups in the main chain (important for acrylate and methacrylate polymers) and in the mesogenic group in the side chain [41].

Relaxation is generally a molecular dynamic process in materials. The term relaxation is used to mean all irreversible process which bring a system back to equilibrium after it has been perturbed by some external force. For instance, if an electric field is applied to a fluid of polar materials a polarization will be induced, but this will disappear after the field is removed, because of the randomization of the molecular orientations produced by brownian motions [55], see § 2.1.

In this thesis, we will first introduce the dielectric relaxation theory of liquid crystals (Chapter 2). Four basic relaxation modes were derived from the so-called rotational diffusion theory, which can also be used to explain the dielectric relaxation processes in the side-chain LCPs. Chapter 3 introduces the general approach to the dielectric relaxation phenomena, analyzed by various relaxation functions, and the experimental methods, especially for preparation of LCP samples (see § 3.6). Chapters 4 and 5 deal with a smectic liquid crystalline polyvinyl ethers containing cyanobiphenyl side groups. The constitutional isomeric effect in a nematic polymethacrylate side-chain LCPs was investigated in Chapter 6. Finally, we will jump to the another class of LCP, polymer dispersed liquid crystals (PDLCs). Although they can be theoretically thought to correspond to the case when the spacer length in the side-chain
LCPs goes to infinity, PDLCs have quite different properties and application aspects.

REFERENCES


[44] Zentel, R., Strobl, G., and Ringsdorf, H., in *Recent Advances in*


Chapter 2

Dielectric Relaxation Theory in Liquid Crystals

2.1 INTRODUCTION

Liquid-crystalline materials possess a significant anisotropy of their molecular and bulk properties [1-4]. It is well known experimentally that dielectric relaxation spectra of liquid-crystalline phase of elongated molecules have rich structures, dependent on how the molecules are oriented with respect to the measuring electric field [5]. They usually consist of two well-separated domains for measurements parallel to the order director, and two less obviously separated domains for a perpendicular geometry. It is believed that dielectric relaxation in liquid crystals is associated with reorientation of permanent dipole moments. Theoretical models which explain the observed spectra have considered a number of different mechanisms of molecular rotational motions responsible for the relaxation [6-10]. All these theories are based on
assumptions about the character of the molecular reorientations involved. A common approach is to use a general expansion of the orientational probability distribution functions. The most renowned of them, a theory of rotational diffusion by Nordio et al. [7], was successfully applied to analyze the experimental data in what has been by all means the most complete experimental study of dielectric relaxation in classical thermotropic liquid crystals (LCs). The model predicts four basic modes which are dielectrically active in liquid crystals. Accordingly, observed dispersion regions can be associated with the following molecular reorientations: the low MHz region with the end-over-end reorientation of a molecule via either diffusion or jump processes; the microwave (GHz) domains, with diffusional reorientation about the long axis and/or the diffusional fluctuations of the direction of the long axis about the director. Although theory properly predicts a simple Debye relaxation for the low frequency domain, it does not explain the distribution of relaxation times (see § 3.4 of the next chapter for definition) observed at high frequencies.

Such a picture of dielectric relaxation is quite acceptable as long as one considers low molecular mass thermotropic LCs. However, very similar dielectric relaxation spectra are observed in thermotropic side-chain liquid crystalline polymer (LCPs), where steric hindrances prevent a simple reorientation of a side-chain mesogenic unit about its long or short axes. Reorientation of the unit, if any, is possible only as a result of highly cooperative motions involving both rotations and translations of the unit and its neighboring environment. Because of such a complexity of motions, the dielectric relaxation spectra of polymeric liquid crystals are
significantly broader and shifted to lower frequencies in comparison with the thermotropic LCs.

Araki and Williams et al. have undertaken theoretical studies of a possible description of dielectric relaxation in LCs, without prior specification of the character of motions involved in the process [11]. They then presented a generalized theory [12,13] within the framework of the linear response concept proposed by Kubo [14]. It has been shown that a qualitative interpretation of dielectric relaxation spectra of liquid crystalline phases with the point symmetry of elongated mesogenic molecules (or units), like nematics and smectics, is possible without specifying the character of the stochastic motions involved. In this chapter, we will first go over briefly the general time correlation function, and will then describe the generalized rotational diffusion theory on the dielectric relaxation in (polymeric) liquid crystals by Williams, et al. [11, 12], particularly in the qualitative interpretation for the side-chain LCPs [15]. The central task is to calculate the dipole autocorrelation functions for such anisotropic liquids.

2.2 Dipole Correlation Function in Dielectric Relaxation

The essential feature with regard to models for molecular motion is that they are most conveniently expressed in terms of time correlation functions [16,17]. The dielectric relaxation experiments which detect molecular motions may be made in the time domain or the frequency
domain, which are connected by a Fourier transformation. In § 3.2 of the next chapter, we will see that from the macroscopic point of view, the normalized complex dielectric permittivity $\varepsilon_n^*(\omega)$ in frequency domain is a Fourier transformation of the decay rate in time domain, see Eq. (3.13),

$$
\varepsilon_n^*(\omega) = \frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_\infty - \varepsilon_\infty} = \int_0^\infty \left[ -\frac{d\phi(t)}{dt} \right] dt = \frac{1}{\varepsilon_\infty} \left[ -\frac{d\phi(t)}{dt} \right] \exp(-i\omega t) dt
$$

(2.1)

where, the complex dielectric permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, $\varepsilon_\infty$ and $\varepsilon_\infty$ are the static and high-frequency limiting dielectric constants, respectively; $\phi(t)$ is the normalized decay function in response to the removal of a static electric field applied to the materials. The various dielectric relaxation functions for $\varepsilon_n^*(\omega)$ and $\phi(t)$ and their properties are summarized in § 3.4.

Cole et al. applied the Kubo formalism† [14] for dielectric relaxation to establish the relation between the complex dielectric permittivity and the time correlation function (18-21). From the microscopic point of view, the decay function $\phi(t)$ in Eq. (2.1) is the corresponding time correlation function of the dipole moments. Consider a unit macroscopic volume containing $N$ dipoles. We define $\vec{M}(t)$ as the dipole moment of this volume at time $t$ arising from the elementary dipoles $\vec{\mu}_i(t)$. $\vec{M}(t)$ is the vector sum of $\vec{\mu}_i(t)$ so the dipole correlation function may be written as

† Kubo formalism is a general type of fluctuation-dissipation theorem which states that the physical quantities such as complex susceptibility of magnetic or electric polarization and complex conductivity for electric conduction can be rigorously expressed in terms of time-fluctuation of dynamical variables associated with such irreversible processes.
\[
\phi(t) = \frac{\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle}{\langle \mathbf{M}(0) \cdot \mathbf{M}(0) \rangle} = \sum_{i=1}^{N} \sum_{i'=1}^{N} \langle \tilde{\mu}_i(0) \cdot \tilde{\mu}_{i'}(t) \rangle \bigg/ \sum_{i=1}^{N} \sum_{i'=1}^{N} \langle \tilde{\mu}_i(0) \cdot \tilde{\mu}_{i'}(0) \rangle \tag{2.2}
\]

The term \( \langle \tilde{\mu}_i(0) \cdot \tilde{\mu}_{i'}(0) \rangle \) express the equilibrium orientation correlation between dipoles \( i \) and \( i' \) in the medium, and the denominator in Eq. (2.2) may be written as \( N g_r \mu^2 \) for a phase containing only one type of dipole. Here \( g_r \) is the Kirkwood reduction factor, and \( g_r = 1 \) for no orientations between dipoles in the gas state. Eq. (2.2) on expansion gives [19,22]

\[
\phi(t) = \sum_{i=1}^{N} \langle \tilde{\mu}_i(0) \cdot \tilde{\mu}_i(t) \rangle + 2 \sum_{i=1}^{N} \sum_{i'=1, i' \neq i}^{N} \langle \tilde{\mu}_i(0) \cdot \tilde{\mu}_{i'}(t) \rangle \bigg/ \sum_{i=1}^{N} \mu_i^2 + 2 \sum_{i=2}^{N} \sum_{i'=2, i' \neq i}^{N} \langle \tilde{\mu}_i(0) \cdot \tilde{\mu}_{i'}(0) \rangle \tag{2.3}
\]

Actually, Eq. (2.3) is general for a medium containing more than one type of dipole, e.g., a mixture of polar molecules. For a medium in which all the dipoles are equivalent, all the \( \langle \tilde{\mu}_i(0) \cdot \tilde{\mu}_i(t) \rangle \)'s are equal and

\[
\sum_{i=1}^{N} \langle \tilde{\mu}_i(0) \cdot \tilde{\mu}_i(t) \rangle = N \langle \tilde{\mu}_i(0) \cdot \tilde{\mu}_i(t) \rangle.
\]

It is appropriate to express here what \( \langle \tilde{\mu}_i(0) \cdot \tilde{\mu}_i(t) \rangle \) means for the reorientation of a dipole in the liquid state. Consider a dipole \( i \) at \( t = 0 \) whose orientation may be represented as \( \tilde{\mu}_i(0) \). As time develops, the dipole reorients in space, so that at a later time \( t \) it would have an average direction in \( \langle \tilde{\mu}_i(t) \rangle_{\tilde{\mu}_i(0)} \), where this means the average direction at \( t \) given that its direction at \( t = 0 \) was in \( \tilde{\mu}_i(0) \). As time develops so the average
projection of the vector on the original direction decreases, so \( \langle \hat{\mu}_i(0) \cdot \hat{\mu}_i(t) \rangle \) decreases. The cross-correlation terms \( \langle \hat{\mu}_i(0) \cdot \hat{\mu}_i'(t) \rangle \) in Eq. (2.3) express the time-dependent orientation correlations between the dipole \( i \) and \( i' \). The cross-correlation term is evaluated as the weighted sum of the decay terms obtained for given initial relative orientations of \( i \) and \( i' \), where the weighting factors are the equilibrium probabilities of obtaining the given relative orientations. If we neglect the cross-correlation terms and the intramolecular motions assuming that a liquid crystalline molecule reorients as a rigid unit, we simply have an autocorrelation function

\[
\phi(t) = \frac{\langle \hat{\mu}_i(0) \cdot \hat{\mu}_i(t) \rangle}{\langle \hat{\mu}_i(0) \cdot \hat{\mu}_i(0) \rangle} \quad (2.4)
\]

### 2.3 Rotational Dynamic Theory in Liquid Crystals

In order to investigate how the stochastic rotational dynamics of molecules influences the dielectric spectra of liquid crystals, the Kubo linear response concept [14,23] can be applied as stated in the previous section. Because of the complexity of the local field problem, which has yet to be solved, we make a simplifying assumption by rewriting a relation between the complex dielectric permittivity \( \varepsilon_k^*(\omega) \) and the correlation function as [see Eqs. (2.1) and (2.4)],

\[
\varepsilon_k^*(\omega) - \varepsilon_k(\infty) = G_k \, L \omega \langle -\dot{y}_k(t) \rangle \quad (2.5)
\]

where the total local field factor \( G_k \) is assumed frequency independent;
\( \gamma_k(t) \ [ \propto \phi(t) ] \) is the unnormalized correlation function of the \( k \) component of the dipole moment; \( \varepsilon_\infty \) denotes the high frequency limit of the dielectric constant; and \( k = \parallel, \perp \) when the order director is parallel (homeotropic monodomain) or perpendicular (homogeneous or planar monodomain) to the electric field. Neglecting the frequency dependence of the local field, we inevitably lose some of the fine details of the cooperative motions leading to dielectric relaxation process. However in the present work we are primarily concerned with the general complexity of the dielectric spectra of liquid crystals, and we believe that for this purpose the assumption is justified. Hence, the following discussion will be restricted to the behavior of the dipole moment autocorrelation function [11,24].

Let the \( z \) axis of the molecular frame \{ \( x, y, z \) \} be the long axis of the molecule, and the \( Z \) axis of the laboratory frame \{ \( X, Y, Z \) \} be the director axis \( \vec{\eta} \) of a liquid-crystalline phase. The molecular motion is assumed to be the stochastic stationary Markov process [17] for which the Eulerian angles \( \Omega = ( \alpha, \beta, \gamma ) \) of the molecular frame with respect to form a three dimensional stochastic variable. Therefore, knowledge of the first conditional (orientational) probability distribution function and the stationary distribution function is necessary for calculation of the correlation function of interest. The conditional and stationary probability distribution function should be continuous almost everywhere (in mathematical sense), since employing the assumption of continuity, the orientational probability distribution function can be always expanded in terms of any orthogonal and complete set of functions. Assuming that the
probability distribution function, \( P(\Omega, t) \), fulfills the equation of evolution,

\[
\frac{\partial}{\partial t} P(\Omega, t) = \mathcal{R}_\Omega P(\Omega, t) \tag{2.6}
\]

where \( \mathcal{R}_\Omega \) is the evolution for \( P(\Omega, t) \), we expand \( P(\Omega, t) \) in terms of Wigner matrix elements \([17]\),

\[
P(\Omega, t) = \sum_{jm} b_{jm}(t) D_{jm}^l(\Omega) \tag{2.7}
\]

Since \( P(\Omega, t) \) should be the conditional probability distribution function, the initial condition has to be imposed,

\[
P(\Omega, 0) = \delta(\Omega - \Omega_0) \tag{2.8}
\]

\( \Omega_0 \) being the position of the molecule at the initial time. Because of the completeness of the set of Wigner functions one can write,

\[
\delta(\Omega - \Omega_0) = \sum_{KLM} \frac{2K+1}{8\pi^2} D_{LM}^K(\Omega) D_{LM}^{K*}(\Omega_0) \tag{2.9}
\]

Substitution of Eq. (2.9) into Eq. (2.8) and comparison with Eq. (2.7) for \( t = 0 \) yields

\[
b_{jm}(0) = \frac{2j+1}{8\pi^2} D_{jm}^{j*}(\Omega_0) \tag{2.10}
\]

where we benefited from the orthogonality of the Wigner functions. The \textit{conditional probability distribution} can now be written as,

\[
P(\Omega / \Omega_0) = \sum_{jm} \alpha_{jm}(t) \frac{2j+1}{8\pi^2} D_{jm}^{j*}(\Omega_0) D_{jm}^{j*}(\Omega) \tag{2.11}
\]
where $a'_{im}(t)$ are normalized correlation functions of $D'_{im}(\Omega)$,

$$a'_{im}(t) = \frac{\langle D'_{im}(\Omega_\alpha)D'_{im}(\Omega) \rangle}{\langle D'_{im}(\Omega_\alpha)D'_{im}(\Omega_\alpha) \rangle} \quad (2.12)$$

so $a'_{im}(0) = 1$. Sometimes $a'_{im}(t)$ can be expressed in an exponential format

$$a'_{im}(t) = \exp(\alpha'_{im}t), \quad b'_{im}(t) = b'_{im}(0)a'_{im}(t) = b'_{im}(0)\exp(\alpha'_{im}t).$$

Similarly, the one-particle stationary orientational probability distribution can be expanded,

$$P(\Omega_\alpha) = \sum_j \frac{2j + 1}{8\pi^2} \overline{P}_j D'_{io}(\Omega_\alpha) \quad (2.13)$$

where $\overline{P}_j = \langle P_j(\beta) \rangle$ is the $j$th orientational order parameter of the liquid crystalline phase and $P_j(\beta)$ is the Legendre polynomial of order $j$. Up to this point our considerations have been quite general. We limit now our attention to liquid crystalline phase with the point symmetry, which implies the same symmetry of $P(\Omega_\alpha)$ and, thus, subjects $j$ to even values.

We can now calculate the correlation functions of interest. Components of the dipole moment in the molecular frame can be conveniently expressed in terms of components of the first rank irreducible spherical tensor,

$$\mu^{(1,0)} = \mu_\parallel \quad \text{and} \quad \mu^{(1,\pm1)} = \mp \frac{1}{\sqrt{2}} (\mu_\pm \pm i\mu_\parallel). \quad (2.14)$$

The components of the dipole moment in the laboratory frame are then expressed by the components in the molecular frame in the following manner,
\[ \mu_z(\Omega) = \sum_k \mathbf{D}_{0k}^1(\Omega) \mu^{(1,k)} \]
\[ \mu_x(\Omega) = \sum_k [\mathbf{D}_{-1k}^1(\Omega) - \mathbf{D}_{1k}^1(\Omega)] \mu^{(1,k)} \]  

(2.15)

Autocorrelation functions of these components are defined as,
\[ \langle \mu_z^*(0) \mu_z(t) \rangle = \int \mu_z^*(\Omega_0) \mu_z(\Omega) P(\Omega/\Omega_0) P(\Omega_0) d\Omega d\Omega_0 \]
\[ \langle \mu_x^*(0) \mu_x(t) \rangle = \int \mu_x^*(\Omega_0) \mu_x(\Omega) P(\Omega/\Omega_0) P(\Omega_0) d\Omega d\Omega_0 \]

(2.16)

and can be explicitly calculated using the orthogonality relations and the formula for the triple integrals of the Wigner functions,
\[ \langle \mu_z^*(0) \mu_z(t) \rangle = \frac{1}{3} \left[ a_{00}^1(t)(1 + 2S) \mu_z^2 + [a_{01}^1(t) + a_{0-1}^1(t)](1 - S)(\mu_x^2 + \mu_z^2)/2 \right] \]

(2.17)

where \( S = \overline{P}_z = \langle P_z(\beta) \rangle \) is the nematic order parameter, ranging from -0.5 to 1. Thus, the correlation function can be written in the form, noting that \( \mu \) and \( \mu_z \) denote the longitudinal and transverse components of the molecular dipole moment, \( \mu_z \) and \( \mu_x \) respectively,

\[ \langle \mu_z^*(0) \mu_z(t) \rangle = \frac{1}{3} \left[ (1 + 2S) A_{00}(t) \mu_z^2 + (1 - S) A_{01}(t) \mu_z^2 \right] \]

(2.18)

Similar calculation yields the correlation function for the X-component,

\[ \langle \mu_x^*(0) \mu_x(t) \rangle = \frac{1}{3} \left[ (1 - S) A_{10}(t) \mu_x^2 + (1 + S/2) A_{11}(t) \mu_x^2 \right] \]

(2.19)

where,
\[ A_{00}(t) = a_{00}^0(t) \]
\[ A_{01}(t) = [a_{01}^0(t) + a_{00}^1(t)]/2 \]
\[ A_{10}(t) = [a_{10}^0(t) + a_{10}^1(t)]/2 \]
\[ A_{11}(t) = a_{11}^0(t) + a_{11}^1(t) + a_{11}^2(t) + a_{11}^3(t) \]  
(2.20)

and \( a_{im}^l(t) \) are the normalized correlation functions of \( D_{lm}^i(\Omega) \) [see Eq. (2.12)]. Respective substitutions of Eqs. (2.18) and (2.19) to Eq. (2.5) finally yields formulas for the complex dielectric permittivity of the liquid crystalline phase, being incorporated into the thermal fluctuation distribution \( \exp(-\vec{\mu} \cdot \vec{E}/k_BT) \),

\[ \varepsilon^*_\| (\omega) - \varepsilon^*_\| (\infty) = \frac{G_0}{3k_BT} \left[ (1 + 2S)\mu_0^2 F^i_\| (\omega) + (1 - S)\mu_0^2 F^i_\perp (\omega) \right] \]  
(2.21)

and

\[ \varepsilon^*_\perp (\omega) - \varepsilon^*_\perp (\infty) = \frac{G_0}{3k_BT} \left[ (1 - S)\mu_0^2 F^i_\| (\omega) + (1 + S/2)\mu_0^2 F^i_\perp (\omega) \right] \]  
(2.22)

where subscripts \( \| \) and \( \perp \) denote measurements with the electric field either parallel or perpendicular to the director axis, respectively. \( F(\omega) \)'s are Fourier transforms of linear combinations of the appropriate correlation functions of the Wigner matrices in Eq. (2.20). It has to be emphasized that these results are obtained without any assumption about the mechanism of reorientation, instead relying solely on the point symmetry of the phase.

It is also useful to calculate the dielectric relaxation spectrum from an unaligned or partially orientated liquid crystalline sample. To do so, according to Attard [25], we need a few assumptions: (i) a sample is in a
liquid crystalline state but it has a polydomain nature, (although a polydomain is a very crude approximation of a liquid crystalline phase, the local direction of the director persists over sufficiently long distances to justify the assumption for the present needs; (ii) the domains are orientationally disordered, so the sample is macroscopically unoriented; (iii) the orientational distribution of molecules within a domain is homogeneous and this distribution is not influenced by the disorder of the domains; and (iv) the macroscopic disorder of domains does not influence the molecular dynamics of a single molecule. We will not repeat the work by Attard [25] and Kozak [12] et al. here. In this model, the complex dielectric permittivity of the macroscopically disordered sample is given by

$$\varepsilon^*(\omega) - \varepsilon(\infty) = \frac{1}{3}(1 + 2S_d)[\varepsilon_{\parallel}^*(\omega) - \varepsilon_{\parallel}(\infty)] + \frac{2}{3}(1 - S_d)[\varepsilon_{\perp}^*(\omega) - \varepsilon_{\perp}(\infty)] \quad (2.23)$$

where $S_d = \langle D^2 \rangle_{\text{dir}}$ is the macroscopic director order parameter with respect to the measuring electric field (it should not be confused with the local nematic order parameter, $S$), and $\langle \rangle_{\text{dir}}$ denotes an average over the director distribution (orientational distribution of domains). $S_d$ ranges also from $-0.5$ (planar or homogeneous alignment) to $1$ (homeotropic alignment).

2.4 DISCUSSION

An explicit dependence of particular terms in Eqs. (2.21) and
(2.22) upon specific Euler angles enables direct qualitative interpretation of dielectric spectra of liquid crystals. Since the $D_m^l(\Omega)$ functions are the matrix elements of the rotation operator, see Eq. (2.6),

$$\mathcal{R}_\alpha = e^{-j_y\beta} e^{-j_z\alpha}$$  \hspace{1cm} (2.24)

where $J_x$ and $J_z$ are the x and z components of the angular momentum operator, it is easy now to link appropriate changes of Euler angles with a particular domain of relaxation, see Fig. 2-1 on page 28.

Let us consider the case when the probing electric field $\vec{E}$ is parallel to the nematic director $\vec{n}$, see Eq. (2.21). $F_{ny}^{l'}$, the Fourier transform of $A_n(t)$ in Eq. (2.20), is associated with the reorientations of the longitudinal component of the dipole moment $\mu_l$. Because of the amplitude of this process, this domain should be associated with large-scale reorientations of the long axis, i.e., "rotations" of the mesogenic unit about the short axis, as schematically indicated in Fig. 2-1(a). However, the quotation marks have been put down purposely, in order to signify that it does not need to be strictly a simple rotation about the short axis. Any significant change of the $\beta$ angle with respect to the laboratory frame should contribute to this relaxation domain. For example, in liquid crystalline side-chain polymers studied in this work, where polar mesogenic units are attached to the backbone chain by flexible spacers, pure rotation about the short axis is topologically restricted. There is however, a possibility of a large scale reorientation of the long axis of the mesogenic unit, but only together with the spacer [26]. Such a process may also involve a section of the backbone chain.
Fig. 2.1 Schematic representation of the four modes that relax the mean square dipole moment in liquid crystals, for the homeotropic cell: (a) $\mathcal{F}_{\parallel}^I$ and (b) $\mathcal{F}_{\perp}^I$; for the planar or homogeneous cell: (c) $\mathcal{F}_{\parallel}^I$ and (d) $\mathcal{F}_{\perp}^I$. 
The second domain observed in the parallel geometry by \( F_{\parallel} \) [\( \Lambda_{\parallel} \)] in Eq. (2.20) results from the molecular reorientation about the \( z \)-axis of the molecular frame (the long axis of molecule), which can easily be verified by the dependence of the appropriate \( a_{\parallel}^{\dagger} \) correlation functions on Euler angles, see Eq. (2.12) and Fig. 2-1(b). The dielectric relaxation signal from the reorientation of the transverse component (\( \mu_{t} \)) of the dipole moment is “visible” in this direction, only when the long axis of the molecule is tilted with respect to laboratory \( Z \)-axis, thus giving the additional relaxation domain. Since the rotation about the long axis is only slightly influenced by the presence of a liquid crystalline orienting potential (e.g., a nematic field) the dielectric relaxation time characteristic of this domain should be of the same order as in the isotropic phase of the material. Such correlation is indeed observed experimentally in thermotropic low molecular weight LCs [9]. Again, the term “rotation” is used above in a general sense and means a stochastic change of the appropriate angle. Such changes can be quite complicated processes in polymers with mesogenic units laterally attached to side-chain spacers [27, 28], where the reorientation of the mesogen unit about its long axis is strongly topologically constrained.

When the measuring electric field \( \vec{E} \) is perpendicular to the director axis \( Z \) or \( \vec{n} \) (the planar or homogeneous cell), Eq. (2.22) also predicts the appearance of two relaxation domains, see Fig. 2-1(c) and (d). The first one, described by \( F_{\perp}^{\dagger} \), results from changes of a projection of the longitudinal component of the dipole moment \( \mu_{l} \) on the direction of the probing field, and can be associated with a sort of stochastic precession
and/or fluctuations of the long molecular axis with respect to the director. Such motions are completely described by the $\beta$ and $\gamma$ Euler angles, see Fig. 2 - 1(c), page 28.

The last term in Eq. (2.22) can not be clearly identified with a particular rotation of the molecule since it depends on the full set of Euler angles, see Fig. 2 - 1(d). However, knowing that this contribution comes from the transverse component of the dipole moment, we notice that the relaxation must be dominated by molecular rotation about the long axis.

An important consequence of the result in Eq. (2.23) is the possibility of deducing the director order parameter from the dielectric relaxation data. Substituting explicitly the complex dielectric permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ in Eq. (2.23), we get

$$S_I = \frac{3[\varepsilon'(\omega) - \varepsilon(\infty)] - [(\varepsilon_0'(\omega) - \varepsilon_0(\infty)] + 2[\varepsilon_1'(\omega) - \varepsilon_1(\infty)]}{2[(\varepsilon_0'(\omega) - \varepsilon_0(\infty)] - [\varepsilon_1'(\omega) - \varepsilon_1(\infty)]}$$

(2.25)

for the dielectric permittivity, and

$$S_d = \frac{3\varepsilon''(\omega) - [\varepsilon_0''(\omega) + 2\varepsilon_1''(\omega)]}{2[\varepsilon_0''(\omega) - \varepsilon_1''(\omega)]}$$

(2.26)

for the dielectric loss factor. Thus, knowing the dielectric properties of the monodomain sample, we can study the degree of order of a polydomain sample as a function of different external factors, such as electric or magnetic fields, pressure, flow, heat, etc. In § 3.7, we will discuss and describe the field-induced alignment technique for LCPs.
If the frequency $\omega$ in Eqs. (2.21) and (2.22) is set to zero, we have the well-known results for the dielectric relaxation strength $\Delta \varepsilon \equiv \varepsilon_\infty - \varepsilon_0$ [9, 10],

$$\Delta \varepsilon_\parallel = \varepsilon_\parallel(0) - \varepsilon_\parallel(\infty) = \frac{G_i}{3k_BT} \left[(1 + 2S)\mu_i^2 + (1 - S)\mu_i^2\right] \quad (2.27)$$

and

$$\Delta \varepsilon_\perp = \varepsilon_\perp(0) - \varepsilon_\perp(\infty) = \frac{G_i}{3k_BT} \left[(1 - S)\mu_i^2 + (1 + S/2)\mu_i^2\right] \quad (2.28)$$

Eqs. (2.27) and (2.28) relate the dielectric strength for a specific relaxation process to the mean square effective dipole moments that have been relaxed in the process.

REFERENCES


(1973).


Chapter 3

Dielectric Relaxation Functions and Experimental Methods

3.1 INTRODUCTION

In general the chemical bonds between unlike atoms in polymer molecules possess permanent dipole moments. Many polymers have chemical structures such that the segmental moments can vectorially accumulate into molecular or segmental moments on many molecular configurations or conformations [1-3]. For instance, the mesogenic group in the side-chain liquid crystalline polymers (LCPs) essentially carry very large dipole moments compared with other moments in the polymer backbones. These polymers can therefore by virtue of these moments be polarized by an electric field. They are said to be dielectrically active, that is, they show polarization due to orientation of permanent dipoles. In some chemical structures the bond moments vectorially add to zero in all important conformations and the polymer is said to be dielectrically
inactive since no polarization due to permanent dipole orientation will be induced by field.

The measurement of the polarization induced in dielectrically active polymers has proven to be extremely useful method for probing polymer structures. The equilibrium polarization induced by a static electric field can give information concerning the equilibrium structure of the system including averaged conformational properties, which in turn depend on the accessible conformational states and their relative energies. Information can also be deduced concerning the strength and nature of interactions between chains. The time-dependent polarization in response to a changing field is especially interesting since the rate of dipole orientation is controlled by internal motions of the polymer chain or mesogenic groups in LCPs. Thus the response to time-dependent fields becomes a method for studying molecular dynamics in polymers [2].

Some advantages of the dielectric method are the following. Reasonably straightforward formulas have been derived from statistical mechanics and electrostatics that connect the magnitude of the induced equilibrium polarization with microscopic quantities such as the number and magnitude of dipole moments and the energetics of interaction between moments [4]. Thus it is often possible to deduce quantitative molecular information from dielectric measurements. Perhaps the most important advantage, however, is an experimental one. It is, relative to most other techniques, possible to vary conveniently the frequency of the perturbing field over wide ranges. It is thus possible to detect or follow molecular motions over a very wide range of time scales from slow to
extremely rapid by the same basic technique. It may require a number of experimental configurations to accomplish this. However, in some parts of the time scale a single apparatus may sometimes serve for measurements over a large number of decades of frequency. Since the molecular motions in a given polymer tend to have a very broad range of relaxation times at a fixed temperature and are thermally activated, often with large activation energies, the capability of broad frequency range of measurement is a very important consideration.

In what follows, we first give a brief account of the phenomenological approach for dielectric relaxations, and demonstrate various relaxation functions in both time and frequency domains, as well as the corresponding distribution functions of relaxation times. Then the methods available for experimental investigations are introduced. Finally the actual experimental set-up used in this research, as well as sample preparation and some field-induced alignment technique for LCs, are described.

3.2 PHENOMENOLOGICAL APPROACH

The application of a constant electric field $\vec{E}$ to a dielectric resolves into the development of an electric displacement $\vec{D}$ that increases with time until a constant value is reached if time is sufficient long, as a result of the establishment of the polarization $\vec{P} = \chi * \kappa_0 \vec{E}$ [5],

$$\vec{D}(t) = \kappa_0 \vec{E}(t) + \vec{P}(t) \quad (3.1)$$
where, $\kappa_{\infty}$ is the dielectric permittivity of free space, 8.854 pFm$^{-1}$; $\chi^* = \chi' - i\chi''$ is the complex susceptibility. After removal of the electric field, the electric displacement returns with time to zero. At sufficiently small electric displacements,

$$\vec{D}(t) = \varepsilon^* \kappa_{\infty} \vec{E}(t)$$  \hspace{1cm} (3.2)

that is, the system is linear and, consequently, it conforms to the superposition principle. The complex dielectric constant $\varepsilon^*$ is a time-dependent property, its value increasing from $\varepsilon_{\infty}$ for $t = 0$ (high-frequency limit) to $\varepsilon_0$ for $t \to \infty$ (static limit) [6]. The electric displacement can obviously be written as

$$\vec{D}(t) = [\varepsilon_{\infty} + (\varepsilon_0 - \varepsilon_{\infty})\Phi(t)]\kappa_0 \vec{E}(t)$$ \hspace{1cm} (3.3)

where $\Phi(t)$ is the normalized dielectric build-up function whose extreme values are

$$\Phi(t) = 1 - \phi(t) = 0 \hspace{1cm} \text{for} \hspace{0.5cm} t \leq 0$$

$$\Phi(t) = 1 - \phi(t) = 1 \hspace{1cm} \text{for} \hspace{0.5cm} t \to \infty$$ \hspace{1cm} (3.4)

where, $\phi(t)$, the normalized decay function of the polarization when a steady macroscopic electric field is removed from the medium, acquires the value 1 and 0 at $t = 0$ and $t \to \infty$, respectively. If an electric field is applied at $t = 0$, but it increases by an infinitesimal amount, $d\vec{E}$, at $t = \theta$ ($0 < \theta < t$), due to some retardation, the increase in electric displacement at $t$ will be

$$d\vec{D} = \varepsilon_{\infty}\kappa_{\infty}d\vec{E} + (\varepsilon_0 - \varepsilon_{\infty})\kappa_0\Phi(t - \theta)d\vec{E}.$$  \hspace{1cm} (3.5)
In linear systems, the total displacement at time $t$ caused by the electric field $\tilde{E}(\theta)$ is the result of the superposition of all the increments, $d\tilde{D}$,

$$
\tilde{D}(t) = \varepsilon_n \kappa_0 \tilde{E}(t) + (\varepsilon_n - \varepsilon_-) \kappa_0 \int_{\theta}^{t} d\tilde{E}(\theta) \Phi(t - \theta) d\theta
$$

(3.6)

By making the substitution $t - \theta = u$ and integrating by parts,

$$
\tilde{D}(t) = \varepsilon_n \kappa_0 \tilde{E}(t) + (\varepsilon_n - \varepsilon_-) \kappa_0 \int_{0}^{\infty} \tilde{E}(t-u) \frac{d\Phi(u)}{du} du
$$

(3.7)

By replacing $\Phi(u)$ by $\phi(u)$ from Eq. (3.4),

$$
\tilde{D}(t) = \varepsilon_n \kappa_0 \tilde{E}(t) + (\varepsilon_n - \varepsilon_-) \kappa_0 \int_{0}^{\infty} \tilde{E}(t-u)[-\frac{d\phi(u)}{du}] du
$$

(3.8)

If we apply Fourier transformation (or Laplace $L_{i\omega}$) to Eq. (3.8) and the convolution theorem, we obtain

$$
\tilde{D}(\omega) = \varepsilon_n \kappa_0 \tilde{E}(\omega) + (\varepsilon_n - \varepsilon_-) \kappa_0 \tilde{E}(\omega) L_{i\omega}[-\frac{d\phi(t)}{dt}]
$$

(3.9)

where, $L_{i\omega}[-\frac{d\phi(t)}{dt}] \equiv \int_{0}^{\infty} [-\frac{d\phi(t)}{dt}] \exp(-i\omega t) dt$. On the other hand,

$$
\tilde{D}(\omega) = \varepsilon^*(\omega) \kappa_0 \tilde{E}(\omega)
$$

(3.10)

Comparing Eqs. (3.9) and (3.10), we have

$$
\varepsilon^*(\omega) \equiv \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_- + (\varepsilon_n - \varepsilon_-) L_{i\omega}[-\frac{d\phi(t)}{dt}]
$$

(3.11)
and the corresponding susceptibility, by noting that \( \varepsilon^* (\omega) = \varepsilon_\infty + \chi^* (\omega) \),

\[
\chi^* (\omega) \equiv \chi' (\omega) - i \chi'' (\omega) = (\varepsilon_0 - \varepsilon_\infty) L \omega \int \left[ -\frac{d\phi(t)}{dt} \right] dt.
\]  (3.12)

Eq. (3.11) can be conveniently expressed as the normalized complex dielectric constant, \( \varepsilon^*_n (\omega) \)

\[
\varepsilon^*_n (\omega) \equiv \frac{\varepsilon^* (\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = L \omega \int \left[ -\frac{d\phi(t)}{dt} \right] \exp(-i \omega t) dt
\]  (3.13)

i.e., \( \varepsilon^*_n (\omega) \) is the Fourier transform of the decay rate \(-d\phi(t)/dt\) [7,8], and the dielectric strength \( \Delta \varepsilon \equiv \varepsilon_0 - \varepsilon_\infty \):

\[
\frac{\varepsilon' (\omega) - \varepsilon_\infty}{\Delta \varepsilon} = \int \left[ -\frac{d\phi(t)}{dt} \right] \cos (\omega t) dt
\]  (3.14)

\[
\frac{\varepsilon'' (\omega)}{\Delta \varepsilon} = \int \left[ -\frac{d\phi(t)}{dt} \right] \sin (\omega t) dt
\]  (3.15)

These equations may be inverted, giving

\[
-\frac{d\phi(t)}{dt} = \frac{2}{\pi} \int_0^\infty \frac{\varepsilon' (\omega) - \varepsilon_\infty}{\Delta \varepsilon} \cos (\omega t) d\omega = \frac{2}{\pi} \int_0^\infty \frac{\varepsilon'' (\omega)}{\Delta \varepsilon} \sin (\omega t) d\omega
\]  (3.16)

It is obvious that if one of the normalized components of the complex dielectric constant is known over the entire relaxation range, then the decay function \( \phi(t) \) can be determined. Actually, this function can be obtained by integration of Eq. (3.16) under the conditions of Eq. (3.4),

\[
\phi(t) = \frac{2}{\pi} \int_{\omega = -\infty}^{\infty} \frac{\varepsilon_0 - \varepsilon' (\omega)}{\Delta \varepsilon} \sin (\omega t) d(\ln \omega) = \frac{2}{\pi} \int_{\omega = -\infty}^{\infty} \frac{\varepsilon'' (\omega)}{\Delta \varepsilon} \cos (\omega t) d(\ln \omega)
\]  (3.17)
Since the decay function is unity at \( t = 0 \), the relaxation strength \( \Delta \varepsilon \) is directly related to the loss factor by means of the expression,

\[
\Delta \varepsilon = \frac{2}{\pi} \int_{\ln \omega}^{\infty} \varepsilon''(\omega) \, d(\ln \omega)
\]

(3.18)

In principle, it is assumed that the sample consists of capacitor \( C(\omega) \) and resistance \( R \ (= 1/G) \) in parallel, with an empty-cell capacitance \( C_0 \), see Fig. 3 - 1, and the impedance \( Z^* \) is given by

\[
\frac{1}{Z^*} = i\omega \varepsilon^* C_0 = i\omega C + G
\]

(3.19)

By comparing the real and imaginary parts on the two sides of Eq. (3.19), we have,

![Diagram of a dielectric in a parallel capacitor and its equivalent circuit in parallel.](image)

**Fig. 3 - 1**  A dielectric in a parallel capacitor and its equivalent circuit in parallel.
\[
\varepsilon'(\omega) = \frac{C(\omega)}{C_0} \quad (3.20)
\]

\[
\varepsilon''(\omega) = \frac{G(\omega)/\omega}{C_0} \quad (3.21)
\]

\(G(\omega)/\omega\) is called the dielectric loss. Both \(C(\omega)\) and \(G(\omega)/\omega\) are measurable, hence the complex permittivity \(\varepsilon^*\) can be easily obtained through Eqs. (3.20) and (3.21).

### 3.3 Kramers-Kronig Relaxations

As indicated in Eq. (3.16), both the real part \(\varepsilon'(\omega)\) and the imaginary part \(\varepsilon''(\omega)\) of the complex dielectric constant are not fully independent and they are related through the Kramers-Kronig (K–K) relations [9]. These relations are ultimately a consequence of the principle of causality — the fact that the dielectric response function \(\Phi(t)\) satisfies Eq. (3.4). The K–K relations state that the real and imaginary parts of the complex susceptibility \(\chi^*(\omega)\) are

\[
\chi'(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega' \chi''(\omega')}{\omega^2 - \omega'^2} d\omega' \quad (3.22)
\]

\[
\chi''(\omega) = -\frac{2}{\pi} \int_0^\infty \frac{\omega \chi'(\omega')}{\omega^2 - \omega'^2} d\omega' \quad (3.23)
\]

where the integrals denote the Cauchy principal values, i.e., they ignore the imaginary contributions arising from integration through the pole at
\( \omega' = \omega \). For the corresponding complex dielectric permittivity 
\( \varepsilon^*(\omega) = \varepsilon_\omega + \chi^*(\omega) \), the K–K relations [10] are

\[
\varepsilon'(\omega) - \varepsilon_\omega = \frac{2}{\pi} \int_0^\infty \frac{\omega''(\omega')}{\omega'^2 - \omega^2} d\omega' \tag{3.24}
\]

\[
\varepsilon''(\omega) = -\frac{2}{\pi} \int_0^\infty \frac{\omega[\varepsilon'(\omega') - \varepsilon_\omega]}{\omega'^2 - \omega^2} d\omega' \tag{3.25}
\]

We shall find the K–K relations have a fundamental significance for our approach to the interpretation of the dielectric behavior of polymeric materials. They are very useful in certain experimental situations where they may enable the values of one of the functions to be obtained from those of the other when for some reason the measurements of them are impeded.

One very immediate consequence of these relations is their evaluation for the case of zero frequency in Eq. (3.24),

\[
\Delta \varepsilon = \frac{2}{\pi} \int_0^\infty \frac{\varepsilon''(\omega')}{\omega'} d\omega' = \frac{2}{\pi} \int_{ln\omega_\omega}^{ln\omega_{\omega}} \varepsilon''(\omega') d(ln\omega) \tag{3.26}
\]

This is identical to Eq. (3.18), derived from the decay function expression. This relates the dielectric strength for a given polarization mechanism or a combination of mechanisms, to the area of the loss curve plotted against the logarithm to the natural base of frequency. This immediately shows that a mechanism leading to a strong polarization must inevitably give rise to correspondingly high losses somewhere in the frequency spectrum. Eq. (3.26) can also be used to check the availability
and consistency for various phenomenological relaxation functions as discussed in the following section.

### 3.4 Dielectric Relaxation Functions

**Debye Model — The Simple Relaxation Time Process**

In specifying the nature of $\phi(t)$ in Eq. (3.13), the simplest assumption to make is that the decay rate in change of polarization is proportional to its displacement from equilibrium and that the electronic and atomic polarizations respond instantaneously in the time scale of interest. Thus, a simple exponential retardation [see Fig. 3 - 3(b)] results from

$$\frac{d\phi}{dt} \propto -\frac{\phi}{\tau_D}$$

or

$$\phi(t) = \exp(-t/\tau_D) \quad (3.27)$$

in consistence with the normalized decay conditions in Eq. (3.4), where $\tau_D$ is the Debye relaxation time. Substitution of $\phi(t)$ in Eq. (3.27) into Eq. (3.13) results in

$$\frac{\varepsilon^*(\omega) - \varepsilon_-}{\varepsilon_0 - \varepsilon_-} = \frac{1}{1 + i\omega\tau_D} \quad (3.28)$$

from which the real and loss components are given by
\[
\frac{\varepsilon'(\omega) - \varepsilon_-}{\varepsilon_0 - \varepsilon_-} = \frac{1}{1 + \omega^2 \tau_D^2} \quad (3.29)
\]

\[
\frac{\varepsilon''(\omega)}{\varepsilon_0 - \varepsilon_-} = \frac{\omega \tau_D}{1 + \omega^2 \tau_D^2} \quad (3.30)
\]

Fig. 3 - 2(a) shows the real and imaginary parts of Eq. (3.28) against \(\omega \tau_D\); Fig. 3 - 2(b) plots the imaginary part versus the real part, which is often called a Cole-Cole plot. The Cole-Cole plots are, in general, extremely useful in checking the mutual consistency of the dielectric constant and loss measurements at a number of frequencies and are to be recommended whenever possible. The high-frequency limit \(\varepsilon_- (\omega >> 1/\tau_D)\) is sometimes called the “unrelaxed” dielectric constant, \(\varepsilon_s\); the eventual value at long time or low-frequency limit \(\varepsilon_0 (\omega << 1/\tau_D)\) is called the “relaxed” dielectric constant, \(\varepsilon_r\).

A close examination of Eqs. (3.29) and (3.30) or Fig. 3 - 2 suggests that whereas \(\varepsilon'\) is a continuously decreasing function of frequency \(\omega\), \(\varepsilon''\) approaches zero both for small and for large values of frequency, reaching a maximum at

\[
\omega \tau_D = 1 \quad (3.31)
\]

that is, the the relaxation time is equal to the reciprocal of the angular frequency at the maximum of the loss absorption. Eqs. (3.29) and (3.30) are known as the Debye equations since they were first derived and used by him in his molecular theory of “anomalous dispersion” of polar liquids [11]. However, they are now taken to mean any single relaxation time process of this form.
Fig. 3.2  The complex dielectric behaviors (a) and the corresponding circle arc Cole-Cole plot (b) for the Debye model.
Fig. 3.3  (a) Distribution function of relaxation times for the Debye model; (b) the Debye decay function.
Although very simple liquids follow the Debye equations, in most cases, and principally in polymers, the dispersion commonly occurs over a wider frequency range than the predicted by Eqs. (3.29) and (3.30). The most straightforward method of writing a more general relaxation function than the exponential retardation above is to assume that parts of the polarization relax through different paths but in each path the decay rate of relaxation is still proportional to the displacement from equilibrium, thus

\[ \phi(t) = \sum \exp(-t/\tau_n) \]  \hspace{1cm} (3.32)

which leads to, according to Eq. (3.13),

\[ \frac{\varepsilon^*(\omega) - \varepsilon_-}{\varepsilon_0 - \varepsilon_-} = \sum_{n} \frac{w_n}{1 + i\omega \tau_n} \]  \hspace{1cm} (3.33)

where \( w_n \) is a weight factor, \( \sum w_n = 1 \). As \( \tau_n \) changes continuously, the summation in Eq. (3.33) becomes an integration,

\[ \frac{\varepsilon^*(\omega) - \varepsilon_-}{\varepsilon_0 - \varepsilon_-} = \int_{0}^{\infty} \frac{F(\ln \tau)}{1 + i\omega \tau} d(\ln \tau) \]  \hspace{1cm} (3.34)

with \[ \int_{\tau=0}^{\infty} F(\ln \tau) d(\ln \tau) = 1 \]  \hspace{1cm} (3.35)

where \( F(\ln \tau) \) is the normalized distribution function of relaxation times. Eq. (3.34) is, in some cases, rewritten as
\[ \varepsilon_p^*(i\omega \tau_0) = \frac{\varepsilon^*(i\omega \tau_0) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + \frac{i\omega \tau}{1}} \int F(\tau/\tau_0) d[\ln(\tau/\tau_0)] \] (3.36)

then, according to Davidson and Cole [12],

\[ F(\tau/\tau_0) = \frac{1}{2\pi i} [\varepsilon_p^*(\frac{\tau_0}{\tau e^{i\pi}}) - \varepsilon_p^*(\frac{\tau_0}{\tau e^{-i\pi}})] \] (3.37)

The distribution function of relaxation times for the Debye model Eq. (3.28) is, by setting \( \tau_0 = \tau_D \), see Fig. 3-3(a), page 46, given by

\[ F(\tau/\tau_D) = \delta(\tau/\tau_D - 1) \] (3.38)

It has been emphasized [7] that if \( \phi(t) \) is not a single exponential decay in linear time, the numerical fitting of \( \phi(t) \) to a weighted sum of different exponential decays, as indicated in Eq. (3.33), does not necessarily mean that a distribution of relaxation times \( F(\tau/\tau_D) \) is really present. A decay function with a non-exponential form in linear time could give a good account of the dielectric behavior of complex molecules [see the Kohlrausch-Williams-Watts (KWW) function in this section on page 64].

**Cole-Cole Function**

The Cole-Cole (CC) function [13,14] is based on an empirical modification of the equation for the complex dielectric constant for the single relaxation time [Eq. (3.28)],

\[ \frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + (i\omega\tau_{CC})^\beta} \] (3.39)
The effect of the parameter $\beta$ is to broaden the loss curve compared to the Debye relaxation time ($\beta = 1$) for values $0 < \beta < 1$, see Fig. 3-4, page 50. The real and imaginary parts from Eq. (3.39) are

\[
\frac{\varepsilon' - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{1 + (\omega \tau_{\text{CC}})^{\beta} \cos(\beta \pi / 2)}{1 + 2(\omega \tau_{\text{CC}})^{\beta} \cos(\beta \pi / 2) + (\omega \tau_{\text{CC}})^{2\beta}} \tag{3.40}
\]

\[
\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{(\omega \tau_{\text{CC}})^{\beta} \sin(\beta \pi / 2)}{1 + 2(\omega \tau_{\text{CC}})^{\beta} \cos(\beta \pi / 2) + (\omega \tau_{\text{CC}})^{2\beta}} \tag{3.41}
\]

The parameters $\tau_{\text{CC}}$, $\beta$, and $\Delta \varepsilon$ are determined by the following procedure. The equations for $\varepsilon'$ and $\varepsilon''$ may be combined by eliminating $\omega \tau_{\text{CC}}$ between them to give

\[
(\varepsilon' - \frac{\varepsilon_0 + \varepsilon_{\infty}}{2})^2 + (\varepsilon'' + \frac{\varepsilon_0 - \varepsilon_{\infty}}{2} \cot \frac{\beta \pi}{2})^2 = \left[\frac{1}{2}(\varepsilon_0 - \varepsilon_{\infty}) \csc \frac{\beta \pi}{2}\right]^2 \tag{3.42}
\]

If $\varepsilon''$ is regarded as plotted against $\varepsilon'$ (Cole-Cole plot, Fig. 3-5), this equation is a circle with center at $(\varepsilon_0 + \varepsilon_{\infty})/2$, $\frac{1}{2}(\varepsilon_0 - \varepsilon_{\infty}) \cot(\beta \pi / 2)$ and radius $\frac{1}{2}(\varepsilon_0 - \varepsilon_{\infty}) \csc(\beta \pi / 2)$. Referring to Fig. 3-5(b), it may be seen that

\[
\sin \theta = \frac{1}{2}(\varepsilon_0 - \varepsilon_{\infty})/\frac{1}{2}(\varepsilon_0 - \varepsilon_{\infty}) \csc \frac{\beta \pi}{2}
\]

or

\[
\theta = \frac{\beta \pi}{2} \tag{3.43}
\]

Thus $\Delta \varepsilon \equiv \varepsilon_0 - \varepsilon_{\infty}$ is determined from the intercepts of the circle arc with the $\varepsilon'$ axis and $\beta$ from the angle $\theta$. The parameter $\tau_{\text{CC}}$ is usually determined from the maximum in the loss curve versus $\omega$. 
Fig. 3 - 4  Variations of the real part (a) and the imaginary part (b) of the Cole-Cole Eq. (3.39) for the different width parameter $\beta$. 
Fig. 3.5  The Cole-Cole plot for the different $\beta$ (a) and the determination of the angle $\theta$ (b).
Only asymptotical form of the decay function for the Cole-Cole relaxation can be obtained analytically, by recalling \(-d\phi(t)/dt = L^{-1}_{\omega}[\varepsilon'_s(\omega)]\) from Eq. (3.13),

\[
\phi(t) = \begin{cases} 
1 - \frac{1}{\Gamma(1+\beta)} \left( \frac{t}{\tau_{CC}} \right)^\beta & , \quad t \ll \tau_{CC} \\
\frac{1}{\Gamma(1-\beta)} \left( \frac{t}{\tau_{CC}} \right)^{-\beta} & , \quad t \gg \tau_{CC}
\end{cases}
\]  \hspace{1cm} (3.44)

and the decay rate is [15]

\[
\frac{d\phi(t)}{dt} = \begin{cases} 
\frac{1}{\tau_{CC} \Gamma(\beta)} \left( \frac{t}{\tau_{CC}} \right)^{\beta-1} & , \quad t \ll \tau_{CC} \\
\frac{\beta}{\tau_{CC} \Gamma(1-\beta)} \left( \frac{t}{\tau_{CC}} \right)^{-(1+\beta)} & , \quad t \gg \tau_{CC}
\end{cases}
\]  \hspace{1cm} (3.45)

where \(\Gamma\) is a gamma function.

\[\text{Fig. 3 - 6} \quad \text{The distribution for the Cole-Cole function.}\]
The distribution of relaxation times for the Cole-Cole function is, see Fig. 3 - 6,

\[ F(\tau / \tau_{cc}) = \frac{1}{2\pi} \frac{\sin(\beta \pi)}{\cosh[\beta \ln(\tau / \tau_{cc})] + \cos(\beta \pi)}. \quad (3.46) \]

**Cole-Davidson Function**

Cole and Davidson introduced the function, with \( 0 < \alpha \leq 1 \) \[16,12\]

\[ \frac{\varepsilon^*(\omega) - \varepsilon_-}{\varepsilon_0 - \varepsilon_-} = \frac{1}{(1 + i\omega \tau_{cd})^\alpha} \quad (3.47) \]

which leads to (see Fig. 3 - 7)

\[ \frac{\varepsilon'(\omega) - \varepsilon_-}{\varepsilon_0 - \varepsilon_-} = (\cos \varphi)^\alpha \cos \alpha \varphi \quad (3.48) \]

\[ \frac{\varepsilon''(\omega)}{\varepsilon_0 - \varepsilon_-} = (\cos \varphi)^\alpha \sin \alpha \varphi \quad (3.49) \]

where \( \tan \varphi = \omega \tau_{cd} \), \( \omega_{\text{max}} \tau_{cd} = \tan[\pi / (2(\alpha + 1))] \quad (3.50) \)

and to [see Fig. 3 - 9(a)]

\[ F(\tau / \tau_{cd}) = \begin{cases} \frac{\sin \alpha \pi}{\pi} \left(\frac{\tau}{\tau_{cd} - \tau}\right)^\alpha, & \tau < \tau_{cd} \\ 0, & \tau > \tau_{cd} \end{cases} \quad (3.51) \]

The low-frequency end of the plot is circular, but the plot is skewed at the high-frequency end, see Fig. 3 - 8 on page 55. The skewness increases with decreasing \( \alpha \). Many measurements on polymer solutions on
Fig. 3 - 7 The real (a) and imaginary (b) parts of the Cole-Davidson relaxation.
low-molecular-weight solvents often give results that are fit by the Cole-Davidson (CD) function. Eq. (3.50) means that the relaxation time $\tau_{CD}$ is not equal to the reciprocal frequency where the loss maximum happens and it is shifted towards a lower frequency position. Referring to Fig. 3-8 on page 55, the angle $\psi$ depends on the frequency

$$\tan \psi = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega) - \varepsilon_\infty} = \tan \alpha \varphi$$

so,

$$\psi = \alpha \varphi \quad (3.52)$$

At the high-frequency limit $\omega \rightarrow \infty$, from Eq. (3.50), $\tan \varphi \rightarrow \infty$,

$$\varphi_L = \frac{\pi}{2}$$
Fig. 3 - 9  (a) The distribution of relaxation times for the Cole-Davidson expression; (b) the corresponding decay function.
Hence,
\[ \psi_L = \alpha \varphi_L = \frac{\alpha \pi}{2} \quad (3.53) \]

Whereas the relaxation happens, from Eq. (3.50), \( \tan \varphi_R = \omega \tau_{CD} = 1 \), then
\[ \psi_R = \alpha \varphi_R = \frac{\alpha \pi}{4} = \frac{\psi_L}{2} \quad (3.54) \]

The decay function for the Cole-Davidson process is, see Fig. 3 - 9(b),
\[ \phi(t) = 1 - \frac{1}{\Gamma(\alpha)} \gamma(\alpha, t/\tau_{CD}) \quad (3.55) \]

where, \( \gamma(\alpha, t/\tau_{CD}) \) is the incomplete gamma function as defined in Gradshteyn & Ryzhik 8.350(1) [17],
\[ \gamma(\alpha, t/\tau_{CD}) = \int_0^{t/\tau_{CD}} r^{\alpha-1} \exp(-r)dr \]

As \( t \to \infty \), the above equation reduces to the gamma function \( \Gamma(\alpha) \).

**Fuoss-Kirkwood Function**

This representation [18] is also based on an empirical modification of the Debye Eq. (3.28),
\[ \frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_\infty - \varepsilon_\infty} = \frac{\beta}{1 + i(\omega \tau_{FK})^\beta}, \quad 0 < \beta \leq 1 \quad (3.56) \]

The corresponding real and imaginary parts are, see Fig. 3 - 10 on page 58,
\[ \frac{\varepsilon'(\omega) - \varepsilon_\infty}{\varepsilon_\infty - \varepsilon_\infty} = \frac{\beta}{1 + (\omega \tau_{FK})^\beta} \quad (3.57) \]
Fig. 3 - 10  The frequency-dependence of the Fuoss-Kirkwood function with different width parameter $\beta$. 
Fig. 3 - 11  (a) The Cole-Cole plot; (b) the distribution function for the Fuoss-Kirkwood Eq. (3.56).
\[
\frac{\varepsilon''(\omega)}{\epsilon_0 - \epsilon_{\infty}} = \frac{\beta}{2} \sec h[\beta \ln(\omega \tau_{FK})]
\]

(3.58)

which is equivalent to, by noting that \( \Delta \varepsilon = 2 \varepsilon'' / \beta \),

\[
\varepsilon''(\omega) = \epsilon'' \sec h[\beta \ln(\omega \tau_{FK})]
\]

(3.59)

The loss factor \( \varepsilon''(\omega) \) in the above equation is a symmetric function in the logarithm of the frequency domain [see Fig. 3 - 10(b)] and it has the maximum value \( \varepsilon'' \) at \( \omega \tau_{FK} = 1 \). The distribution function of relaxation times [Eq. (3.37)] for the Fuoss-Kirkwood expression is, see Fig. 3 - 11(b),

\[
F(\tau / \tau_{FK}) = \frac{(\beta / \pi) \cos(\beta \pi / 2) \cosh[\beta \ln(\tau / \tau_{FK})]}{\cos^2(\beta \pi / 2) + \sinh^2[\beta \ln(\tau / \tau_{FK})]}
\]

(3.60)

**Havriliak-Negami Function**

With Cole-Cole or Cole-Davidson relaxation functions mentioned above, the experimental data can often be represented with high accuracy. For polymeric materials however, the complex plot is more complicated; in most cases, the dielectric dispersion is neither Cole-Cole-like nor Cole-Davidson-like. Havriliak-Negami (HN) function [19,20] combines the Cole-Cole circular arc and Cole-Davidson skewed semicircle as follows,

\[
\frac{\varepsilon^*(\omega) - \varepsilon_{\infty}}{\epsilon_0 - \varepsilon_{\infty}} = \frac{1}{(1 + (i \omega \tau_{HN})^\beta)^\alpha}
\]

(3.61)

where, \( \beta \) is the broadening parameter, \( 0 < \beta \leq 1 \), the width of dispersion increases as \( \beta \) ranges from unity to zero; \( \alpha \) is the skewness parameter, \( 0 < \ldots
\]
\( \alpha \leq 1 \), and the skewness increases as \( \alpha \) ranges from unity to zero. When the parameter \( \alpha = 1 \) in Eq. (3.61) the Cole-Cole circular arc is obtained [Eq. (3.39)], while \( \beta = 1 \) the Cole-Davidson skewed semicircle is obtained [Eq. (3.47)] and when \( \alpha = \beta = 1 \), the Debye function is obtained [Eq. (3.28)].

In order to test the HN function, it is necessary to separate the real and imaginary parts, the resulting expressions are,

\[
\frac{\varepsilon'_{\omega} - \varepsilon_{\omega}}{\varepsilon_{\omega}} = r^{-\alpha/2} \cos \alpha \theta \\
(3.62)
\]

\[
\frac{\varepsilon''(\omega)}{\varepsilon_{\omega} - \varepsilon_{\omega}} = r^{-\alpha/2} \sin \alpha \theta \\
(3.63)
\]

with

\[
r = 1 + 2(\omega \tau_{HN})^\beta \cos \frac{\beta \pi}{2} + (\omega \tau_{HN})^{\beta} \\
(3.64)
\]

\[
\theta = \arctan \left[ \frac{(\omega \tau_{HN})^\beta \sin \frac{\beta \pi}{2}}{1 + (\omega \tau_{HN})^\beta \cos \frac{\beta \pi}{2}} \right] \\
(3.65)
\]

Fig. 3 - 12 on page 62 shows the case when \( \alpha = 0.5 \) and \( \beta = 0.8 \). \( \varepsilon_{\omega} \) and \( \varepsilon_{\omega} \) can be evaluated as the high and low frequency intercepts of the experimental quantities with the real axis in the Cole-Cole plot. The parameters \( \alpha \) and \( \beta \) are related through \( \psi_{L} \), which is the high frequency limiting angle that the experimental locus makes with the real axis, see Fig. 3 - 12(b). This relationship may be obtained by noting that

\[
\tan \psi = \frac{\varepsilon''(\omega)}{\varepsilon'_{\omega} - \varepsilon_{\omega}} = \tan \alpha \theta \\
(3.66)
\]
Fig. 3 - 12  (a) The dielectric constant and loss for the Havriliak-Negami function; (b) the corresponding Cole-Cole plot.
If the condition of \( \omega \tau_{HN} \to \infty \) is introduced into the above Eqs., we have

\[
\lim_{\omega \tau_{HN} \to \infty} \psi = \tan \psi_L = \tan(\beta \pi / 2) \\
\therefore \quad \psi_L = \alpha \beta \pi / 2
\]  

(3.67)

which is a useful connection between the graphical parameter \( \psi_L \) and the dispersion parameters \( \alpha \) and \( \beta \). The relaxation time is given by the definition \( \omega \tau_{HN} = 1 \), which upon substitution into Eqs. (3.62) – (3.65) followed by taking the ratio of the imaginary to the real parts, we have

\[
\tan \psi_R = \frac{\varepsilon''(\omega \tau_{HN} = 1)}{\varepsilon'(\omega \tau_{HN} = 1) - \varepsilon_-} = \tan(\alpha \beta \pi / 2) \\
\therefore \quad \psi_R = \alpha \beta \pi / 2 = \psi_L / 2
\]  

(3.68)

The angle bisector of the limiting angle \( \psi_L \) intersects the locus at the relaxation time. The parameter \( \beta \) is determined by noting that the absolute value of \( |\varepsilon'(\omega \tau_{HN} = 1) - \varepsilon_-| \) is given, after taking logarithms by

\[
\frac{1}{\psi_L} \log \frac{\varepsilon'(\omega \tau_{HN} = 1) - \varepsilon_-}{\varepsilon_0 - \varepsilon_-} = -\frac{1}{\beta \pi} \log[2 + 2 \cos(\beta \pi / 2)]
\]  

(3.69)

so that with graphical values of \( \psi_L \), \( |\varepsilon'(\omega \tau_{HN} = 1) - \varepsilon_-| \), and \( \varepsilon_0 - \varepsilon_- \), \( \beta \) can be looked up in suitably prepared tables. Finally, the normalized distribution function of relaxation times for the HN expression is,

\[
F(\tau / \tau_{HN}) = \begin{cases} 
\frac{1}{\pi} \sum_{k=0}^{\infty} \frac{(-1)^k (\alpha + \cdots + \alpha + k - 1) \tau^k}{k!} (\frac{\tau}{\tau_{HN}})^\beta(\alpha + k) \sin[\beta(\alpha + k)\pi], & \tau < \tau_{HN} \\
\frac{1}{\pi} \sum_{k=0}^{\infty} \frac{(-1)^k \alpha + \cdots + \alpha + k - 1} {k!} \tau^k (\frac{\tau}{\tau_{HN}})^{-\beta k} \sin(\beta k \pi), & \tau > \tau_{HN}
\end{cases}
\]  

(3.70)
and the corresponding decay function in asymptotical form,

\[
\phi(t) = \begin{cases} 
1 - \frac{t}{\Gamma(1+\alpha\beta)}(\tau_{HN})^{\alpha\beta} & , \quad t << \tau_{HN} \\
\frac{\alpha}{\Gamma(1-\beta)}(\frac{t}{\tau_{HN}})^{-\alpha} & , \quad t >> \tau_{HN}
\end{cases}
\]  
(3.71)

**Kohlrausch-Williams-Watts Function**

If we consider the empirical decay function in Eq. (3.13),

\[
\phi(t) = \exp[-(t/\tau_{KWW})^\beta] 
\]  
(3.72)

with \(0 < \beta \leq 1\), then Eq. (3.72) is called Kohlrausch-Williams-Watts (KWW) stretching exponential function [21-23], see Fig. 3-14(b). The resulting normalized complex permittivity is

\[
\frac{\varepsilon^*(\omega) - \varepsilon_-}{\varepsilon_0 - \varepsilon_-} = \sum_{n=1}^{\infty}(-1)^n \frac{\Gamma(n\beta+1)}{\Gamma(n+1)} \frac{1}{i\omega\tau_{KWW}^\beta(n)} \frac{1}{(n\beta+1)} \frac{\cos(n\beta\pi/2) - i\sin(n\beta\pi/2)}{(\omega\tau_{KWW}^\beta)^{n\beta}} 
\]  
(3.73)

Hence \(\varepsilon^*(\omega)\) may be obtained from the above equation for given values of \((\omega\tau_{KWW})\) and \(\beta\), see Fig. 3-13 on page 65. However as \(\beta \to 1\), the convergence of the series becomes very slow. The computations using Eq. (3.73) are only conveniently carried out in the following ranges,

\[
0 < \beta \leq 0.25, \quad -4 \leq \log(\omega\tau_{KWW}) \leq +4 \\
0.25 < \beta < 1, \quad -1 \leq \log(\omega\tau_{KWW}) \leq +4 
\]  
(3.74)

For small \((\omega\tau_{KWW})\) combined with large \(\beta\), the more convenient expression is,
Fig. 3 - 13 The complex dielectric constant for the KWW decay Eq. (3, 72) with different parameter $\beta$, (a) the real part; (b) the imaginary part.
Fig. 3-14  (a) The Cole-Cole plot and (b) the decay function for the KWW stretching exponential model.
\[
\frac{\varepsilon^*(\omega) - \varepsilon_-}{\varepsilon_\eta - \varepsilon_-} = \sum_{n=1}^{\infty} (-1)^{n-1} \left(\frac{\omega \tau_{KW}}{\pi \tau_{KW}}\right)^{n-1} \Gamma\left(\frac{n + \beta - 1}{\beta}\right) \left[\cos(n-1)\frac{\pi}{2} + i \sin(n-1)\frac{\pi}{2}\right]
\]

(3.75)

in the range \(0.25 < \beta < 1.0\), \(-4 \leq \log(\omega \tau_{KW}) < -1\). The distribution function of relaxation times for the KWW expression is

\[
F(\tau / \tau_{KW}) = \frac{1}{\pi} \sum_{n=1}^{\infty} (-1)^{n-1} \frac{\Gamma(n\beta + 1)}{\Gamma(n + 1)} \left(\frac{\tau}{\tau_{KW}}\right)^{n\beta} \sin(n\beta \pi)
\]

(3.76)

**Jonscher’s Many-Body Representation**

Jonscher examined a broad spectrum of the published experimental data for the dependence of the dielectric loss \(\varepsilon''\) on frequency, \(\omega\), and on temperature in a range of polymeric dielectrics, especially in the \(\log \varepsilon'' - \log \omega\) plots, and suggested that an empirical formula [9,24,25]

\[
\frac{\varepsilon''(\omega)}{\varepsilon_\eta - \varepsilon_-} = \frac{1}{(\omega \tau_1)^{m} + (\omega \tau_2)^{1-n}}
\]

(3.77)

fits the data in most cases, see Fig. 3 - 15 on page 68. Here \(\tau_1\) and \(\tau_2\) are temperature-dependent times which show simple activated behavior with well-defined activation energies. The exponents \(m\) and \(n\) are both positive and smaller than unity and in some case they decrease slightly with decreasing temperature. The loss peaks are strongly asymmetric in the \(\log \omega\) representation and their width at half-height may be as large as 6 decades. Some materials reveal clearly the presence of two superimposed loss mechanisms with different activation energies.
Fig. 3-15 The loss curve under the Jonscher's model.

On the basis of this combined evidence it is suggested that the interpretation of the loss peaks in terms of a distribution of relaxation times for Debye-like dipolar processes is not very plausible. An alternative theoretical interpretation is suggested, based on the concept of a single set of dipoles making sudden jumps between fixed orientation in space and causing a slow screening response in the surrounding medium. This gives the result that \( \varepsilon'' \) is proportional to the real part of the dielectric permittivity, \( \varepsilon' \), at least up to some upper limiting frequency. This leads directly to the second term in Eq. (3.77) as a consequence of Kramers-Kronig relations of Eqs. (3.24) and (3.25), without any need to invoke a distribution of dipolar relaxation times. The loss peak arises from an interplay of this mechanism, which determines the high-frequency
behavior, with another mechanism, which leads to vanishing loss at very low frequencies. The corresponding decay function in time domain can therefore be described as

$$
\phi(t) = \begin{cases} 
\left( \frac{t}{\tau_1} \right)^{-m} , & 0 < t << 1/\omega_p \\
\exp(-\omega_p t) , & t \sim 1/\omega_p \\
\left( \frac{t}{\tau_2} \right)^{-n} , & t >> 1/\omega_p
\end{cases}
$$

(3.78)

3.5 EXPERIMENTAL METHODS

Lumped Circuits (10^{-4}–10^{9} \text{ Hz})

As seen earlier [Eqs. (3.19)–(3.21), see page 40], the complex dielectric constant may be determined by measuring the complex impedance of the dielectric as a circuit element. This may be accomplished by employing calibrated purely capacitive and purely resistive circuit elements that are adjusted to the same impedance as the circuit element containing the dielectric sample. The comparison capacitor and resistor may be effectively connected either in series or in parallel. If effectively connected in parallel, the results yield the same as Eqs. (3.19)–(3.21),

$$
\varepsilon' = C_p / C_\text{e} \\
\varepsilon'' = 1/(\omega R_p C_\text{e}) \\
\tan \delta = \varepsilon'' / \varepsilon' = 1/(\omega R_p C_p)
$$

(3.79)

If the comparison circuit is effectively connected in series,
\[ Z^* = \frac{1}{i\omega C_i} + R_i = \frac{1}{i\omega C_i \varepsilon^*} \]

or

\[
\varepsilon' = \frac{C_i}{C_0} \cdot \frac{1}{1 + \frac{\omega^2 R_i^2 C_i^2}{C_0}} \\
\varepsilon'' = \frac{C_i}{C_0} \cdot \frac{\omega R_i C_i}{1 + \frac{\omega^2 R_i^2 C_i^2}{C_0}} \\
\tan \delta = \frac{\omega R_i C_i}{2} \\
(3.80)
\]

**Bridge Methods (Intermediate frequencies: 10^1–10^7 Hz)**

The most convenient method for measuring the sample impedance is to connect the comparison circuit element and the sample in an a.c. Wheatston bridge, i.e., an impedance bridge (see Fig. 3-16 on page 71). Using relatively conventional resistive and capacitive circuit elements in the bridge, a frequency range of approximately 10 Hz to 100 kHz may be covered with high sensitivity and precision. Special-purpose bridges of considerably less accuracy are available in the 1–10 MHz region.

In any real circuit element containing the sample dielectric, there will be additional distributed impedances due to the leads, etc. The effect of these may be more or less satisfactorically handled by either of two methods: (a) two-terminal measurements subtracting out lead impedance or (b) three-terminal guarded-circuit measurements.

Two-terminal measurements suffer the disadvantage of the fact that the lead capacitance \( C_{pl} \) is often not highly stable and can vary somewhat from run to run. This is especially important since it is not unusual in
Fig. 3 - 16 A typical impedance bridge. Some bridges regard the equivalent circuit of sample as (a) a series capacitor and resistor and (b) a parallel capacitor and resistor.

many configurations for the lead capacitance to be comparable to or even considerably greater than the sample capacitance.

In three-terminal guarded-circuit measurements, it is possible to largely eliminate the lead capacitance and confine the measurement to a fairly well-defined portion of the sample. For example, in a parallel-plate configuration, one of the plates can be divided into two electrodes: an inner circular one, and a surrounding ring (see Fig. 3 - 17 on page 72). If the sample leads are used for making the capacitance measurement and guard lead is kept isolated from but at the same potential as sample lead 1, then the capacitance measured will be well-defined geometrically by the area of the lower inner circle. Further, if lead 1 has a shield connected to the guard this lead will see no stray capacitance since the shield will be at the same potential.
The resistive-capacitive ratio arms in $Z_I$, $Z_2$ in Fig. 3 - 16, page 71 can be replaced by the inductances and the voltage applied by means of transformers as in Fig. 3 - 18, page 73. This arrangement has the important property that the voltage ratio and therefore the impedance ration $Z_2/Z_1$ at balance is determined almost entirely by the ratio of turns in the transformers $N_x/N_s$. This means that stray capacitances from the point H (high voltage, low impedance) to the guard or ground point G will not affect the balance condition. The same condition holds if the guard ring is connected to G. If the shield to the L electrode (low voltage, high impedance) is connected to G, the stray capacitance of the L lead will appear across the detector. It will therefore shunt the detector and reduce its sensitivity somewhat but not affect the balance condition. Hence, a completely guarded circuit not requiring special balancing provision can be achieved.
Fig. 3-18 A transformer arm ratio bridge.

Low-Frequency Methods (10^-4–10^2 Hz)

Both bridge and transient methods have been used for low-frequency measurements. The low-frequency limit of Schering transformer arm ratio bridges is approximately 10 Hz, due to the problems in coupling the generator to the bridge using transformers.

Transient methods are particularly useful at very low frequencies. As stated in Section 3.2, much the same information concerning the relaxation process can be obtained from the transient response to a suddenly applied static field (step function voltage with amplitude $V_0$), see Eq. (3.13) and Fig. 3-19 on page 73. The decay rate (discharge) is proportional to the discharging current $I(t)$ in response to a step applied voltage $V_0$.

$$-rac{d\phi(t)}{dt} = \frac{I(t)}{CV_0}$$

(3.81)
where, $C$ is the capacitance of the sample at the high-frequency limit and very close to the empty cell capacitance, $C_0$. Eqs. (3.14) & (3.15) can be consequently rewritten as

$$\frac{\varepsilon'(\omega) - \varepsilon_0}{\Delta\varepsilon} = C_0 V_0 \int_0^\infty I(t) \cos(\omega t) dt$$  \hspace{1cm} (3.82)$$

$$\frac{\varepsilon''(\omega)}{\varepsilon_0 - \varepsilon_\infty} = C_0 V_0 \int_0^\infty I(t) \sin(\omega t) dt$$  \hspace{1cm} (3.83)$$

Thus $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ may be determined from the discharging current data by numerical integration of Eqs. (3.82) and (3.83), a relatively straight-forward matter using a computer.
D. C. Conductivity Problem

The main interest of the present treatment is the dipolar relaxation. However, polymers in general also transport charge under the influence of an electric field. That is, they have a bulk resistivity, see Fig. 3 - 19. This resistivity will trend to behave as a resistance in parallel with the capacitance of the sample. Unlike the resistive component due to dipolar relaxation, the resistance (or conductivity) due to this source will tend to be independent of frequency. That is, if the current is due to bulk charge migration in a quasi-static field uninfluenced by electrode effects, this resistance is characterized by bulk resistivity, a material constant. Looking again at the parallel equivalent circuit formulation, Eq. (3.79), we see that the dielectric constant $\varepsilon'$ is uninfluenced by this resistive contribution. However, we see that it does contribute to the loss,

$$
\varepsilon''(\omega) = \frac{1}{\omega C_0} \left[ \frac{1}{R_p(\omega)} + \frac{1}{R_{dc}} \right] = \frac{1}{\omega C_0} \left[ G_p(\omega) + G_{dc} \right] \quad (3.84)
$$

From the above equation, we see that although the dipolar parallel resistance becomes infinite at low frequency, the loss due to d.c. conductance is frequently observed and can mask or obscure dipolar loss process. In fact, only in exceptionally low d.c. conductance polymers (i.e., perhaps exceptionally clean, low-ionic-impurity-containing low-dielectric-constant polymers) can dipolar loss processes be studied at frequencies below $\sim 1-10$ Hz. Otherwise the suitable data fitting has to be made to extract this d.c. component so that the dipolar relaxation information could be obtained, see the data fitting process in the following chapters.
High Frequency Methods

There are a number of methods to obtain dielectric data at very high frequency region [26], such as resonant circuits (10⁶–10⁸ Hz), distributed circuits in the microwave band including standing waves in transmission lines, cavity resonance [27], time domain reflectometry (TDR), etc. These techniques will not be discussed.

3.6 EXPERIMENTAL SETUP IN THIS LAB

There are a number of instruments involved in dielectric measurements in this lab. Fig. 3 - 20 on page 77 gives an overall experimental setup. Besides the apparatus described in Fig. 3 - 20, a TA DEA 2970 Dielectric Analyzer (0.01 Hz – 100 kHz) has been used. As follows, we will briefly describe the measurements with the CGA-83 transformer ratio-arm bridge.

CGA-83 Transformer Ratio Arm Bridge

Our primary bridge is a ratio-arm transformer bridge (CGA-83) developed by Carl Andeen in the 1970’s [28-30]. The bridge uses hand-wound, precision tapped transformers to develop 10 voltage steps per decade over 8 decades. Capacitance and loss references are connected to the appropriate taps on the transformers to balance the current through the unknown sample. The bridge achieves its remarkable precision (7 digits or 0.1 ppm at 10 pF) through unique proprietary circuits. The
Fig. 3 - 20  Schematic experimental setup in this lab.
resistive component current is generated by phase shifting the source by 90° and using standard capacitors. This enables the use of low-loss, fused-silica capacitors for both capacitance and loss references. These capacitors have such low loss that they are nearly ideal (resistors have a significant capacitance which, when used for the loss reference, limits the sensitivity of a bridge). In addition, the reference capacitors are kept stable by placing them in a temperature controlled enclosure inside the bridge. The bridge covers the frequency range from 10 Hz to 100 kHz in 4 steps per decade. The steps are at 1, 2, 3.125, and 5. The frequency range represents the approximate limit for transformer type bridges (see § 3.5).

The CGA-83 is a true three-terminal bridge, see Fig. 3 - 21. The high and low connections are isolated from ground and the samples may

![Schematic of a three-terminal measurement with CGA-83 transformer ratio-arm bridge.](image-url)

Fig. 3 - 21  Schematic of a three-terminal measurement with CGA-83 transformer ratio-arm bridge.
employ a guard ring for accuracy (see Fig. 3 - 17). In this configuration, any stray capacitance or loss to ground on the high side of the sample merely shunts the transformer. To the extent that the voltage output of the transformer is independent of current-loading, this has no effect. Similarly any stray or loss between the low side of the sample and ground shunts the detector, resulting in a slightly lower sensitivity. As an example of the strength of this approach note that one can easily measure below 1 fF with 50 Ω coaxial leads in a background of 1000 pF capacitance to ground.

Sample Cells

To confine polymer samples for dielectric measurements, a reusable three-terminal brass cell was first developed, see Fig. 3 - 22, consisting of two machined brass electrodes. One electrode is a simple brass disc. The other is a two-piece assembly with an inner electrode set into an outer guard electrode with OmegaTherm 200 epoxy [30].

For the LCP samples, we have an obligation to optically exam their mesogenic phases and macroscopic alignment states. So an ITO glass cell has been constructed, consisting of two parallel ITO (Indium-Tin-Oxide) glass plates, see Fig. 3 - 23 on page 81. The edge of the ITO plate was stripped using a solution of hydrochloric and nitric acids. The two plates, separated by 25 µm Kapton spacer, were adhered together with a high temperature epoxy (Theramic Epoxy 250) to form a parallel-plate capacitor with the empty cell capacitance $C_0$ between 5 and 10 pF. The LCP samples were inserted onto the cell through capillary action, being
Fig. 3 - 22 A three-terminal brass sample cell.

placed on a hot stage in a vacuum chamber and heated above the isotropic temperature. The casting time ranges from one hour to 10 hours, depending upon the individual sample viscosity. For the samples with extremely high viscosity, they were first applied to one ITO glass plate heated to well above the isotropic points. The top ITO plate was then pressed and squeezed onto the samples, followed by slowly cooling down to room temperature under a constant force. These sample cells were completed by sealing with a high temperature epoxy. To fully take advantage of the three-terminal measurements, a three-terminal ITO glass cell has also been made, see Fig. 3 - 24 on page 81.

Temperature Control

To measure the dielectric relaxations pertinent to the present studies, a wide range of temperatures is needed. Two systems are used to cover the required range. The low temperature side is covered by a
Fig. 3 - 23  An ITO glass cell for LCP samples.

Fig. 3 - 24  A three-terminal ITO cell.
cryostat, which is capable of temperatures from liquid Helium (4 K) to 350 K. In all of our studies we have limited the low to the liquid nitrogen temperature, near 80 K. To cover higher temperatures a small vacuum oven was constructed, which operates from 250 K (incorporated with a FTS Multi-Cooling system) to 475 K. The higher temperature limit is imposed by the teflon insulation in the coaxial cables and connectors.

The individual sample cells described above are set into a cell holder where the electrical contact is made by phosphor bronze leaf springs to which coax cables are attached. The cell holder bolts onto the bottom of the cold finger of the cryostat. The vacuum oven was designed with a small copper "dummy" cold finger which mechanically matches the cryostat mounting. The cell holder containing the sample cells can be placed in the cryostat for measurements to 325 K and then moved directly to the oven to continue measurements up to 475 K.

To measure the sample temperature, a platinum resistance thermometer (RTD) was placed into the cold finger on the cryostat. A similar RTD was placed in the dummy cold finger in the oven. The two RTDs were obtained from Lakeshore Cryotronics specially calibrated to be within 0.1 degree absolute accuracy. The RTD in the cryostat is optimized to operate from 75 K to 325 K and the one in the oven from 250 K to 475 K. The thermometers are measured on the the same instrument, which contains their calibration curves in ROM memory [30].

To maintain temperature stability both systems operate in vacuum. In addition the cryostat has two radiation shields and the oven has one.
We find that the temperature stabilizes to 5 mK within 1 hour in the cryostat and 20 minutes in the oven.

**Switching and Automation**

The system is capable of running four sample cells in the cell holder. Most of the time involved in dielectric measurements is used in establishing thermal equilibrium. If a run consists of going from 80 K to 450 K in 5 K steps, and it takes approximately half hour to change temperatures and reestablish thermal equilibrium, then a run can easily occupy 1 to 2 days. This necessitates automated data acquisition. All instruments have an IEEE-488 bus, which allows remote control and data retrieval by a computer. Measuring more than one sample in an automated set-up (see Fig. 3 - 20) requires that the bridge be remotely switched to each sample in turn. A Keithley model 705 scanner accomplish this. No difference in measured dielectric parameters is observable with or without the switches installed in the measurement setup [30].

### 3.7 FIELD-INDUCED ALIGNMENTS IN SIDE-CHAIN LCPs

For low-molecular-weight nematic liquid crystals subjected to external electric and magnetic fields, the total elastic deformation free energy is [31,32]
\[ F = \frac{1}{2} \int \left( K_{11} (\operatorname{div} \vec{n})^2 + K_{22} (\vec{n} \cdot \operatorname{curl} \vec{n})^2 + K_{33} (\vec{n} \times \operatorname{curl} \vec{n})^2 \right) dV \\
\quad \quad \quad - K_{24} \operatorname{div} (\vec{n} \times \operatorname{curl} \vec{n} + \vec{n} \operatorname{div} \vec{n}) dV \\
\quad \quad \quad - \frac{1}{2} \int \varepsilon_0 \chi_0 (\vec{E} \cdot \vec{n})^2 dV - \frac{1}{2} \int \frac{\chi_a}{\mu_0} (\vec{B} \cdot \vec{n})^2 dV + \frac{1}{2} \int W_0 \sin \varphi dS \tag{3.85} \]

where, \( \vec{n} \) is the nematic director; \( K_{11}, K_{22}, \) and \( K_{33} \) are respectively the basic splay, twist, and bend elastic constants, \( K_{24} \) is the surface elastic constant associated with the saddle-splay deformation; the dielectric anisotropy \( \varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp \), \( \varepsilon_\parallel \) and \( \varepsilon_\perp \) are the dielectric constants when the \( \vec{n} \) is respectively parallel and perpendicular to the electric field \( \vec{E} \); the magnetic anisotropy \( \chi_a = \chi_\parallel - \chi_\perp \), \( \chi_\parallel \) and \( \chi_\perp \) are the magnetic susceptibilities when the \( \vec{n} \) is parallel and perpendicular, respectively, to the magnetic field \( \vec{B} \); the molecular anchoring angle \( \varphi \) is between \( \vec{n} \) and the surface normal, and the anchoring strength \( W_0 \) are associated with the molecular anchoring interactions on the surface. Generally speaking, if the external field strength exceeds a threshold field, the induced reorientation takes places as a consequence of the given anisotropy of the dielectric or diamagnetic permittivity of the LC samples [33].

Let's first look at the electric interaction term \(- \frac{1}{2} \int \varepsilon_0 \chi_0 (\vec{E} \cdot \vec{n})^2 dV\) qualitatively, assuming that the rest of others in Eq. (3.85) are virtually kept unchanged. The minimization of the free energy \( F \) requires either \( \vec{n} \parallel \vec{E} \) or \( \vec{n} \perp \vec{E} \), depending upon the sign of \( \varepsilon_a \). Hence, for the sample with the positive dielectric anisotropy \( \varepsilon_a \) under a low-frequency electric field, it tends to be homeotropically aligned \((\vec{n} \parallel \vec{E})\); for the sample with the negative anisotropy \( \varepsilon_a \) under a high-frequency electric field, it tends to be
homogeneously or planarly aligned ($\vec{n} \perp \vec{E}$). This is the so-called two-frequency addressing technique [34,35]. Unfortunately, our efforts to align the side-chain LCs had little success, probably due to the high viscosity of the samples and the a.c. voltage source was not high of sufficient amplitude.

On the other hand, the magnetic interaction term $-\frac{1}{2} \int \frac{\chi_a}{\mu_0} (\vec{B} \cdot \vec{n})^2 dV$ can also be examined qualitatively assuming the other terms remain fixed in Eq. (3.85). The LC samples commonly demonstrate the diamagnetic property (both $\chi_a$ and $\chi_\perp$ are of small negative values) coming from some phenyl rings in the molecule, and we usually have a positive magnetic anisotropy $\chi_a$. It is obvious that when $\vec{n} \parallel \vec{B}$, the free energy can be minimized. Therefore, either homeotropic or planar alignment can be achieved under a magnetic field by placing the cell with the layer normal, respectively, parallel or perpendicular to the magnetic field [33].

In our experiments, the magnetic field induced alignments were made successful by slowly cooling down the samples in an 8-Tesla superconducting magnet (Cryomagnetics, Inc.) from the well above isotropic phase to the mesogenic phase at room temperature. The cooling rate of 5 K per hour was well controlled by a Lakeshore temperature controller together with a custom-built ramp circuit. The macroscopic alignment results were confirmed by a Nikon polarizing microscope.
REFERENCES


[35] Haws, C. M., Clark, M. G., and Attard, G. S., in *Side Chain
Chapter 4

Smectic Side-Chain Liquid Crystalline Polymer Containing Cyanobiphenyl Mesogenic Unit

4.1 INTRODUCTION

Many dielectric measurements have been conducted on various kinds of thermotropic side-chain liquid crystalline polymers (LCPs) [1-17]. At low temperature usually below the glass transition $T_g$, side-chain LCPs are either semi-crystalline or glassy, like most of conventional polymers in the solid state, whose locally-involved relaxation processes are often labeled as $\beta$, $\gamma$, etc. with decreasing temperature [18]. Above the solid-liquid transition temperatures, sometimes equal to $T_g$, they exhibit liquid crystalline mesophases, i.e., smectic, nematic, and isotropic, etc., in which there are usually two relaxation processes in the neighborhood of $T_g$, being labeled $\delta$ and $\alpha$. 

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To analyze the dielectric spectra in the mesogenic phases of the polymeric liquid crystals (LCs), the rotational diffusion modes in nematics [19-22] can be adapted, see Eqs (2.21) and (2.22) in chapter 2. Although the rotational diffusion models of relaxation were first developed for nematics, they are also a good approximation to the dielectric relaxations in smectic-A ($s_A$) phase. This follows from a molecular point of view since the long range spatial periodicity characteristic of $s_A$ phase plays no role in relaxing the dipole moments, although it will affect the internal field. Thus, on passing from the nematic to $s_A$ phase, broad continuity would be expected with only slight change in permittivity and relaxation rate [23]. This theoretical consideration is more valid when the side-chain polymer system is in the mesophase higher-temperature side closer to the isotropic temperature, or clearing point $T_c$. On the other hand, when the side-chain LCP samples are in the lower-temperature side closer to $T_g$, the molecular rotations of mesogenic group will be strongly correlated to the stiff polymer chain motion, resulting in the theoretical interpretations having to take into account the dipolar segments in both side chain and backbone [24]. Fortunately, in most cases, the relaxations due to the mesogenic group are more promising than those due to the backbone and just slow down rapidly as temperature approaches $T_g$ from the LC phase. So the mesogenic relaxation processes may reflect the glassy behaviors of the polymer chain, which will, to some extent, be helpful in understanding the debated glass transition in polymeric materials [25].

Cyano-biphenyl side-chain LCPs were first studied dielectrically by Kresse and coworkers, with the unaligned samples based on either
polyacrylate or polymethacrylate [1], and polysiloxanes [2], from which only one relaxation process was observed. Haws et al. did observe both δ and α processes in their unaligned GN/19 sample, however the main chain was a siloxane copolymer [13].

In this chapter, the dielectric measurements were conducted with two polyvinyl-ether based cyanobiphenyl side-chain LCP samples with methylenic (–CH$_2$–) spacer length of 7, one having degree of polymerization (DP) of about 7.3 and the other 30, which are both in $s_A$ phases at room temperature [15]. The samples were successfully aligned both homeotropically and planarly in an 8-Tesla superconducting magnetic field by carefully slowly cooling down from the isotropic temperature to room temperature. In the homeotropically (H–) aligned sample, the low-frequency δ peaks are enhanced dramatically compared with the unaligned while the high-frequency α peaks are completely absent. In contrast, the δ peaks are suppressed while α peaks are enhanced in the planar (P–, or homogeneous) alignment. The data has been fitted to semi-empirical relaxation line shapes (Fuoss-Kirkwood) using nonlinear least squares minimization to distinguish these two processes with a subtracted d.c. conductivity. The Arrhenius plot, frequency maxima of each process vs. reciprocal temperature, shows typical glassy behaviors as temperature approaches to $T_g$ from the mesophase region, which will be analyzed using Williams-Landel-Ferry (WLF) and Vogel-Fulcher-Tammann-Hesse (VFTH) equations. The longer chain sample (DP = 30), having an 8 K higher $T_g$ than the shorter chain (DP = 7.3), has basically the same relaxation processes as the shorter
one, except the relaxation frequencies are about $10^{0.8}$ Hz lower than those in the shorter chain.

4.2 EXPERIMENTAL

The side-chain LCP samples, Poly[7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether]s, were synthesized using living cationic polymerization by V. Percec and M. Lee in an attempt to elucidate the molecular design mechanism in the side-chain system [26]. The chemical structure is shown in Fig. 4-1, which contain a cyano-biphenyl-oxy mesogen attached via seven methylenic spacers (−CH$_2$−) to a vinyl-ether backbone. C7DP8, which was designed to have a DP of 8, has an average DP of 7.3 and C7DP30 has a DP of 30. At room temperature and 1 kHz frequency, the dielectric constant ($\varepsilon'$) is approximately 3.2 and the conductivity ($\sigma$, a.c. plus d.c.) is 6.2x10$^{-9}$ S/m for C7DP8; 2.8 and 1.7x10$^{-9}$ S/m respectively for C7DP30. Both samples are in $s_A$ phase at room temperature, and were measured without further chemical treatment.

Differential scanning calorimeter (DSC) measurements were taken with a Dupont 910 cell base with Dupont 990 thermal analyzer at a 10 K/min heating rate. The phase transitions of the samples are summarized in Table 4-1. The first DSC scanning with C7DP8 showed a semi-crystalline transition at 285 K, overlapping its glass transition at 282 K, which disappeared in subsequent scans. The glass transition of C7DP30 is 290 K, 8 K higher than C7DP8. The isotropic transition temperature ($T_i$)
\[ \begin{align*} &\text{CH} - \text{CH}_2 \quad \begin{array}{c} \text{O} \\ \text{O} \end{array} \quad \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \quad C=\text{N} \\ &\begin{array}{c} \text{n} \end{array} \end{align*} \]

Fig. 4 - 1  Chemical structure of the studied cyanobiphenyl side-chain liquid crystalline polymer (LCP).

Table 4-1. Phase transitions in the studied side-chain LCP samples from the repeated DSC scan at 10 K/min heating rate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{n}$ (DP)</th>
<th>phase transitions (K)</th>
<th>$10^{-3}M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7DP8</td>
<td>7.3</td>
<td>$g \quad 282 \quad s_A \quad 392 \quad i$</td>
<td>2.43</td>
</tr>
<tr>
<td>C7DP30</td>
<td>30</td>
<td>$g \quad 290 \quad s_A \quad 408 \quad i$</td>
<td>10.3</td>
</tr>
</tbody>
</table>
is 392 K for C7DP8 and 408 K for C7DP30.

The dielectric sample cell was constructed of two parallel ITO with the empty cell capacitance $C_0$ of approximate 7 pF, as described in § 3.6. In order to identify the relaxation processes in terms of local molecular dynamic modes and to determine its dielectric anisotropy, the side-chain LCP sample has to be macroscopically aligned in either the homeotropic or the planar orientation states. Both H– and P– alignments were achieved by using the magnetic-field-induced alignment technique as described in § 3.7.

The dielectric loss ($G/\omega$) and capacitance ($C$) were taken at 17 frequencies (10 Hz–100 kHz, in a linear log ratio) using a ratio arm transformer bridge [27] at 5 K interval temperature from 100 K to 400 K. For the aligned samples, the upper temperature was 370 K, well below the clearing points, to avoid possibly destroying the alignments, see § 3.6. The bridge’s oscillation voltage was chosen to be the lowest level ( = 0.1 volts/rms ) to avoid disturbing the LC’s macroscopic alignment and inducing the additional dipole moments. The relationship between the complex dielectric constant ($\varepsilon^*$) and the measured capacitance $C$ and loss $G/\omega$ is given by the following, see Eqs. ( 3. 20 ) and ( 3. 21 ),

\[ \varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \]
\[ \varepsilon'(\omega) = C(\omega)/C_0 \]
\[ \varepsilon''(\omega) = G(\omega)/\omega C_0 \]

( 4. 1 )
4.3 RESULTS

The dielectric spectrum of the studied LCP over the temperature range \( T < T_i \) shows totally four relaxation processes. Fig. 4 - 2 gives the dielectric loss factor \( \varepsilon' \) of the unaligned C7DP8 at 10 Hz, 1 kHz, and 100 kHz. There are two relaxations below calorimetric \( T_g \), labeled by \( \beta \) and \( \gamma \) with decreasing temperature. The \( s_A \) region \( T_g < T < T_i \) contains two typical processes in the side-chain LCP mesophase, labeled with \( \delta \) and \( \alpha \) with decreasing temperature. This labeling loss peaks does not follow traditional nomenclature for polymeric materials, but has been widely accepted by authors in the LCP field [23]. The isotropic temperature \( T_i \), having a thermodynamic nature in mesophase transitions, appears to be independent of probing frequency.

**Low-Temperature \( \beta \) and \( \gamma \) Relaxations**

\( \beta \) and \( \gamma \) relaxations occur below the glass transition of the side-chain LCP sample, where the polymer chain is essentially frozen. These two low-temperature relaxations are very similar to those in poly(vinyl methyl ether) [28] and usually involve only local motions of some segments either in the main chain or in the side chain [29]. Fig. 4 - 3, page 97 shows the \( \gamma \) peaks of the unaligned C7DP8 from 145 K to 165 K, which are stronger and broader than \( \beta \) peaks. The loss amplitude in the \( \gamma \) relaxation increases with increasing temperature and the relaxation frequency at a given temperature is much higher than that in the \( \beta \) relaxation. The broad \( \gamma \) process may combine a few different local motions, including some in the cyanobiphenyl group [30] in the side chain, and has an activation
Fig. 4 - 2  Dielectric loss factor $\varepsilon''$ overview for the unaligned C7DP8 at 10 Hz (---), 1 kHz (-----), and 100 kHz (---) as compared with its glass transition $T_g$ and isotropic temperature $T_i$ from DSC data. Four processes are labeled as $\delta$, $\alpha$, $\beta$, and $\gamma$ in decreasing temperature.
Fig. 4 - 3  Dielectric loss spectrum of the low-temperature \( \gamma \) process in the unaligned C7DP8 from 145 K to 165 K with 5 K increment.
energy of about 40 kJ/mole. The $\beta$ peaks are merged with the $\alpha$ process at higher frequencies ($>1$ kHz), where the main glass transition of the polymer appears.

**Two Major Relaxations — $\alpha$ & $\delta$**

In the $s_A$ region there are two major dielectric relaxation processes, a broad, high-frequency $\alpha$ peak and a narrow, low-frequency $\delta$ peak. The real part $\epsilon'$ and imaginary part $\epsilon''$ of the complex dielectric constant for the unaligned C7DP8 are shown in Fig. 4 - 4, page 99 from 310 K to 330 K, with the $\delta$ peaks being much stronger than the $\alpha$ peaks. Fig. 4 - 5 shows the corresponding spectra in H– and P–aligned samples. In the H–alignment, the $\delta$ peaks are enhanced dramatically compared with the unaligned while the $\alpha$ peaks are completely absent. In contrast, the $\delta$ peaks are suppressed while $\alpha$ peaks are increased in the P–alignment. The longer chain sample C7DP30 basically shows the similar relaxation phenomena except a slowdown in the relaxation rate at a given temperature as compared with C7DP8.

**Fuoss-Kirkwood Data Fitting**

In simple systems, dielectric spectra often contain a few relatively narrow peaks which are often well separated in temperature, and are readily interpreted. The samples in the present investigation, however, have spectra in which the individual peaks, though discernible, are broad and overlap to the point that dielectric information (peak areas, widths and relaxation frequencies) is corrupted by the tails of the adjacent peaks.
Fig. 4 - 4  δ and α processes of the unaligned C7DP8 in the smectic-$A$ ($s_A$) phase (+ 310 K, × 315 K, △ 320 K, ◇ 325 K, ○ 330 K). (a) real part $\varepsilon'$; (b) imaginary part $\varepsilon''$. 
Fig. 4 - 5  Dielectric loss spectra for the aligned C7DP8 from 310–330K (+ 310 K, × 315 K, Δ 320 K, ◊ 325 K, ○ 330 K). (a) homeotropic (H−); (b) planar (P−) or homogeneous. Note, (a) and (b) have different vertical-axis scale in order to see the α peaks in (b) more clearly.
A major goal is to obtain the activation energy for each process which requires the accurate determination of the relaxation frequency, \( \omega_R \) or \( f_R \) (recall from § 3.4, relaxation time \( \tau_R = 1/\omega_R \) ) at a given temperature [23,31].

The Fuoss-Kirkwood function is a symmetric empirical lineshape, see Eq. (3.56) and it has been used to fit the spectra to get the necessary information by means of nonlinear least-squared minimization method (Levenberg-Marquardt) [31]. The Fuoss-Kirkwood data fitting is often used in the dielectric relaxations in the side-chain LCP system [23,10,11]. In the temperature range from 295–350 K where the samples are in \( s_A \) phase, the dielectric loss spectra, \( G(\omega)/\omega \), are thought to consist of a low-frequency \( \delta \) peak, a high-frequency \( \alpha \) peak, and a d.c. conductance. The data is fitted with two Fuoss-Kirkwood functions plus a d.c. conductivity \( (\sigma_{dc}) \) term, according to Eq. (3.59),

\[
G(\omega)/\omega = (G_{dc}/\omega) + \sum_{\delta, \alpha} A_i \text{Sech} [\beta_i \ln (\omega/\omega_R)]
\]

Alternatively, with \( \omega = 2\pi f \) and Eq. (4.1), the normalized loss spectra are,

\[
\varepsilon''(\omega) = (\sigma_{dc} / 2\pi f \varepsilon_0) + \sum_{\delta, \alpha} \varepsilon_m^\alpha \text{Sech} [2.303\beta_i \log_{10}(f/f_R)]
\]

where, \( A \) and \( \varepsilon_m^\alpha \) are respectively loss amplitude and the amplitude of the imaginary part of the complex dielectric constant; \( \beta \) lies between 0 and 1 and is a width distribution parameter and equals to 1.14/(width of loss peak at half-height). The Fuoss-Kirkwood function reduces to a Debye-type when \( \beta = 1 \), see Fig. 3–11. The dielectric relaxation strength for
Fig. 4 - 6  The experimental loss factor $\varepsilon'' ( \ast )$ of the P-aligned C7DP8 at 315 K fitted into a d.c. conductivity, $\sigma_{dc} = 1.23 \times 10^{-10}$ S/m, and two Fuoss-Kirkwood lineshapes (dashed curves) according to Eq. (4.3). The solid curve represents a superposition of the three dashed curvatures.
Table 4 – 2. Results from Fuoss-Kirkwood data fitting for all the studied samples at 320 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Align.</th>
<th>$\sigma_{dc}$ (10$^{-10}$S/m)</th>
<th>log$f_R$</th>
<th>$\varepsilon''_m$</th>
<th>$\beta$</th>
<th>$\Delta\varepsilon'$</th>
<th>log$f_R$</th>
<th>$\varepsilon''_m$</th>
<th>$\beta$</th>
<th>$\Delta\varepsilon'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7DP8</td>
<td>U-</td>
<td>7.55</td>
<td>2.53</td>
<td>1.17</td>
<td>0.85</td>
<td>2.76</td>
<td>4.29</td>
<td>0.39</td>
<td>0.34</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>H-</td>
<td>7.94</td>
<td>2.64</td>
<td>3.19</td>
<td>0.82</td>
<td>7.75</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>P-</td>
<td>3.08</td>
<td>2.42</td>
<td>0.50</td>
<td>0.94</td>
<td>1.07</td>
<td>4.17</td>
<td>0.43</td>
<td>0.33</td>
<td>2.56</td>
</tr>
<tr>
<td>C7DP30</td>
<td>U-</td>
<td>0.40</td>
<td>1.79</td>
<td>1.16</td>
<td>0.78</td>
<td>2.98</td>
<td>3.51</td>
<td>0.28</td>
<td>0.34</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>H-</td>
<td>0.77</td>
<td>1.83</td>
<td>2.62</td>
<td>0.83</td>
<td>6.32</td>
<td>3.38</td>
<td>0.15</td>
<td>0.32</td>
<td>0.97</td>
</tr>
</tbody>
</table>
each process, $\Delta \varepsilon'$, the difference in the dielectric constants at low-end and high-end frequencies, is proportional to the amount of the effective dipole moments involved in the relaxation, and can be expressed in terms of two fitting parameters [23],

$$\Delta \varepsilon' \equiv \varepsilon'_n - \varepsilon'_\infty = 2\varepsilon''_m / \beta$$  \hspace{1cm} (4.4)

Fig. 4 - 6 demonstrates the fitting process in which the normalized loss factor $\varepsilon''$ of the P-aligned C7DP8 at 315 K has been fitted to a d.c. conductivity, $\sigma_{dc} = 1.23 \times 10^{-10}$ S/m, and two Fuoss-Kirkwood lineshapes representing the $\delta$ and $\alpha$ peaks [ see Eq. (4.3), $\delta$ peak: $\varepsilon''_m = 0.52$, $\beta = 0.92$, $\log f_R = 1.95$, $\Delta \varepsilon' = 0.92$; $\alpha$ peak: $\varepsilon''_m = 0.43$, $\beta = 0.35$, $\log f_R = 3.72$, $\Delta \varepsilon' = 2.24$ ]. This data fitting process has been employed to all the samples in the $s_A$ region from 300–350 K and Table 4-2 summarizes the results at 320 K as well as the calculated dielectric strengths, see Eq. (4.4). C7DP8 has a d.c. conductivity nearly one order of magnitude larger than C7DP30 probably due to the shorter chain length resulting in a relatively small viscosity and high mobility. The deviation in d.c. conductivities in different alignments for each sample may be due to the different mobilities of ions in various orientations.

4.4 Discussion

$\delta$ Relaxation

The individual dielectric relaxation domains in this chapter will be
assigned in terms of the rotational diffusion mode theory described in chapter 2 [20,21,23] according to the loss spectra in the different macroscopic orientations. The longitudinal component of the dipole moment in the side-chain mesogen, $\mu_l$, is approximately 5 Debye, which comes from its cyanobiphenyl end-group (−C≡N), and is much larger than the transverse component, $\mu_t$, approximately 2 Debye from the oxy-group (−O−). The fact that the $\delta$ peaks are much stronger than the $\alpha$ peaks (see Fig. 4.4 and Fig. 4.5) implies that the stronger dipole moments (mainly $\mu_l$) and/or large-scale relaxation are involved in this $\delta$ process. As mentioned above, the $\delta$ peak is enhanced in the H-alignment and is suppressed in the P-alignment at a certain temperature as compared with the unaligned sample, e.g., the dielectric relaxation strength $\Delta\varepsilon'$ is 7.75 in the H-aligned C7DP8 at 320K, 1.07 in the P-alignment, and 2.76 in the unaligned sample (see Table 4.2), which suggests an involvement by the longitudinal component $\mu_l$ since $\mu_l$ is almost along the easy-optical axis in the uniaxial LC. Because the width parameter $\beta$ is close to 1, the $\delta$ peak is mainly associated with only one single mode, hence it is a Debye-like process [23]. It follows that the low-frequency $\delta$ peak can be assigned to the “rotation” of the longitudinal dipole moment in the mesogenic group about its short axis. In smectic-A phase, it is possible for the side group to flip around the polymer backbone, hopping from one smectic layer to another. This is a large scale reorientation process for the long axis in the side-chain unit together with the attached spacer and some section of the backbone chain, although the pure rotation about the short axis is topologically restricted, see § 2.4 of Chapter 2.
The relaxation frequency in the $\delta$ process at a given temperature is almost independent of the alignment configuration, for instance about 316 Hz for C7DP8 at 320 K, in light of local-ordering in a LC system \cite{5,8}. However, the polymer chain length or molecular weight does affect the relaxation of the mesogen so that the longer chain length with its higher $T_g$ and higher viscosity produces a lower relaxation rate. On the average, the longer chain C7DP30 has a relaxation frequency about $10^{0.8}$ Hz lower than the shorter chain C7DP8 at the same temperature, which clearly indicates that the longer polymer backbone hinders the rotation of the mesogen about its short axis and also makes $\beta$ slightly smaller in amplitude than the shorter chain sample.

The amplitude in $\varepsilon''$ for the H-aligned sample decreases slowly with increasing temperature, see Fig. 4 - 5(a), which may result from the deviation of the LC director (the long axis of the molecule, or the easy-optical axis) from the layer normal due to the increasing thermal fluctuations with increasing temperature.

**$\alpha$ Relaxation**

The weak fast $\alpha$ relaxation peaks are observed in the unaligned samples (Fig. 4 - 4), while they are enhanced in the P-alignment and are almost absent in the H-alignment (see Fig. 4 - 5 and Table 4 - 2). The average width parameter $\beta$ is about 0.33 and roughly independent of the chain length, therefore, this process can be thought to involve both longitudinal and transverse dipole moments in the mesogenic group which combine into a few different rotational modes, see Eqs. (2.21) and
Since the amplitudes of the $\alpha$ peaks are much smaller than those of the $\delta$ peaks and almost uncoupled with the driving electric field in the H–aligned samples, the major contribution to the $\alpha$ process comes from the transverse dipole moments $\mu_t$ ($\mu_t < \mu_l$) rotating about their long axis. Being similar to the $\delta$ process, the relaxation frequency in the $\alpha$ process of each sample in the isothermal condition remains nearly unchanged, independent of the alignment and is slowed down by $10^{0.8}$ Hz from C7DP8 to C7DP30.

The dielectric strength $\Delta\varepsilon'$ of the $\alpha$ process of C7DP8 at 320 K changes from 2.25 for the unaligned to 2.56 for the P–aligned being virtually zero for the H–aligned; $\Delta\varepsilon'$ for C7DP30 changes from 0.93 with the H–aligned to 1.68 with the unaligned (see Table 4 - 2 page 103).

The case in Fig. 4 - 5(a) where the sample is H–aligned is exactly the one described by Eq. (2.21) and Fig. 2-1(a) & (b). Only the slower relaxation mode $\mathcal{F}_{\perp}^l$ ( ~ $\delta$ process ) is detected because: (1) the sample is in a quite ideal homeotropic state and the long axis of the molecule is tilted very slightly with respect to the electric field; (2) the transverse dipole moment is much smaller than the longitudinal so that the mode $\mathcal{F}_{\perp}^l$ ( ~ $\alpha$ process ) is dielectrically “invisible”. On the other hand, the case in Fig. 4 - 5(b) when the sample is in the planar alignment is more complicated, but qualitatively in agreement with descriptions of $\mathcal{F}_{\perp}^l$ and $\mathcal{F}_{\parallel}^l$ in Eq. (2.22) and Fig. 2-1(c) & (d). The dielectric relaxation processes in the unaligned sample are basically a combination of these four rotation diffusion modes, $\mathcal{F}_{\parallel}^l$, $\mathcal{F}_{\perp}^l$, $\mathcal{F}_{\parallel}^l$, and $\mathcal{F}_{\perp}^l$ in Fig. 2 – 1.
Glassy Behaviors

The loss-maxima frequencies vs. reciprocal temperature (Arrhenius plot) in the both \( \delta \) and \( \alpha \) processes display curved, non-Arrhenius behaviors and the relaxation frequencies decrease rapidly as the temperature approaches \( T_g \) in the mesophase region (see Fig. 4 - 7 for C7DP8), which demonstrates typical glassy behaviors in the polymeric materials. The activation energy for the \( \delta \) process at 320 K is around 153 kJ/mole for C7DP8, 218 kJ/mole for C7DP30. The \( \alpha \) process has a similar activation energy but deviates from the \( \delta \) process as \( T \) approaches \( T_g \). The activation energies in both \( \delta \) and \( \alpha \) processes increase rapidly as \( T \) approaches \( T_g \). Although this kind of glassy behavior is performed by the mesogenic group in the side-chain, which is connected to the polymer backbone via seven carbon spacers, it must represent some of the polymer’s structural motion to some extent. In other words, some information regarding the polymer backbone’s motion near \( T_g \) may be provided by monitoring the relaxations in the side chain. It is of fundamental interest to understand the debated glass transitions in the polymeric materials [25,32].

Two phenomenological equations, based on the free volume theory, WLF and VFTH equations [33,34] have been used to analyze the glassy behaviors in the \( \delta \)- and \( \alpha \)- relaxations.

WLF equation,

\[
\log_{10}\left[ \frac{f_R(T)}{f_R(T_0)} \right] = A \frac{(T - T_0)}{(B + T - T_0)} \quad (4.5)
\]
Fig. 4 - 7  Arrhenius plot for the δ and α processes in C7DP8 (+ unaligned, ○ H-aligned, ◇ P-aligned). Note, the α process is absent in the H-aligned sample.
Fig. 4 - 8  The $\delta$ and $\alpha$ processes of the P-aligned C7DP8 fitted by WLF and VFTH equations. $+$, relaxation frequencies; $\cdots\cdots$, WLF fitting; $\cdots\cdots$, VFTH fitting.
where, \( A \) and \( B \) can take the universal values, \( A = 8.66, B = 101.6 \), where 
\( T_0 = T_g + 50 \text{ K} \). This equation basically gives the relation between the 
relaxation frequency and the glass transition in most polymeric materials.

VFTH equation,

\[
f_R = f^0 \exp\left[-C/(T - T_\infty)\right]
\]  \( (4.6) \)

where, \( f^0 \) is very high usually between \( 10^{10} \text{ Hz} \) and \( 10^{12} \text{ Hz} \), may also be a 
polynomial function of temperature; \( T_\infty \) is sometimes called Vogel 
temperature with \( T_\infty < T_g \).

Fig. 4 - 8 demonstrates the \( \delta- \) and \( \alpha- \) processes in the P–aligned 
C7DP8 being fitted to either WLF or VF equations and Table 4 - 3 lists all 
the results for the studied samples. The WLF results can be verified by 
inspecting the consistency between \( f_R(T_0) \) and \( T_0 \), i.e., \( f_R(T_0) \) should be the 
relaxation frequency at temperature \( T_0 \). For example, \( \log f_R(310 \text{ K}) \) for the 
a process of the unaligned C7DP8 is, respectively, 3.34 from the WLF 
equation \( (4.5) \) and 3.35 from the direct loss peak finding. In C7DP8, the 
relaxation frequency average \( 10^{0.8} \text{ Hz} \) higher than C7DP30 roughly 
equals to 8 K difference in \( T_g \), which is consistent with the DSC 
measurement (see Table 4 - 1, page 93). Fig. 4 - 9 shows the \( \delta- \)relaxation 
frequency vs. “normalized temperature” \( (T - T_g)/T_g \) for both the shorter 
chain C7DP8 and the longer chain C7DP30. The WLF equation \( (4.5) \) fits 
them very well and both C7DP8 and C7DP30 have the similar glassy 
nature, independent of the polymer chain length. However, the WLF 
calculated glass transition \( T_g^{WLF} (= T_0 - 50 \text{ K}) \) is 12–22 K lower than the
Table 4 - 3. Results from WLF and Vogel-Fulcher equations for two major relaxation processes of all studied samples ( \( f \) and \( f^0 \) in Hz; \( T_0, C, \) and \( T_\infty \) in K).

| Sample  | Align. | \( \delta \) | \( \alpha \) | \( \log(f(T_0)) \) | \( T_0 \) | \( \log(f^0(T_0)) \) | \( T_0 \) | \( \log(\delta) \) | \( C \) | \( T_\infty \) | \( \log(\delta^0) \) | \( C \) | \( T_\infty \) |
|---------|--------|-------------|-------------|----------------|--------|----------------|--------|----------------|-----|--------|----------------|-----|--------|-----|
| C7DP8   | U-     | 2.45        | 3.34        | 3.10           |        |                |        | 9.11           | 1159| 243    | 6.99           | 240| 281    |
|         | H-     | 2.36        |             | --             | 10.4   | 1721           | 224    |                |      |        | --             | --  | --     |
|         | P-     | 2.37        | 3.53        | 3.14           | 9.54   | 1361           | 237    | 7.64           | 351 | 376    |                |     |         |
| C7DP30  | U-     | 2.78        | 3.60        | 3.22           | 6.83   | 586            | 270    | 5.05           | 84.7 | 297    |                |     |         |
|         | H-     | 2.22        | 2.68        | 3.10           | 8.99   | 1188           | 248    | 10.5           | 1620| 221    |                |     |         |
Fig. 4 - 9  δ-relaxation frequency vs. “normalized temperature” \((T-T_g)/T_g\). +, C7DP8 (\(T_g = 282 \text{ K}\)); □, C7DP30 (\(T_g = 290 \text{ K}\)); ------, WLF fitting.
calorimetric $T_g$ for C7DP8 and 10–30 K lower for C7DP30. On the other hand, the glass transition of poly(vinyl methyl ether) (PVME) $T_g^{PVME}$ [28], is at 245 K, about 37 K and 45 K lower than our polyvinyl-ether based C7DP8 and C7DP30, respectively. The $T_g^{WLP}$ is allocated in the range between $T_g^{PVME}$ and the side-chain LCP glass transition temperature $T_g^{SCLCP}$, which implies that the glassy behavior in the side-chain LCP system may result from the cooperative motion between the side-chain and the polymer backbone. The observed glassy behavior of the side-chain mesogen, therefore, also reflects the structural cooperative motion of the polymer main chain to some extent. In the VFTH [ Eq. (4.6) ] results, the frequency prefactor $f^0$ is far smaller than the universal value $10^{12}$ Hz and $f^0$ should have been treated as a polynomial function of temperature. The Vogel temperature $T_{\infty}$ is overall below the calorimetric $T_g$ for both $\delta$ and $\alpha$ processes in all the studied samples, except for the $\alpha$ process in the unaligned C7DP30, which has fewer data points.

**Dielectric Anisotropy**

The dielectric anisotropy, $\varepsilon_s$, is defined as the difference between dielectric constants when the director of the LC monodomain is parallel to the external electric field and when it is perpendicular to the field, i.e., the dielectric constant difference between the H–alignment and the P–alignment [35], see § 3.7,

$$\varepsilon_s \equiv \varepsilon'_\parallel - \varepsilon'_\perp \quad (4.7)$$

Fig. 4-10(a) plots the $\varepsilon'_\parallel$ & $\varepsilon'_\perp$ of C7DP8 vs. log frequency at 320 K with a crossover $f_c = 1.6$ kHz. The sample has a positive dielectric
Fig. 4 - 10  Dielectric anisotropy $\varepsilon_a$ in C7DP8, (a) $\varepsilon_{||}'$ & $\varepsilon_{\perp}'$ at 320 K with crossover frequency $f_c = 1.6$ kHz; (b) $f_c$ varying with temperature, nearly an exponential relation.
anisotropy, $\varepsilon_a > 0$ for $f < f_c$ and exhibits a negative anisotropy, $\varepsilon_a < 0$ for $f > f_c$. Fig. 4 - 10(b) shows the crossover frequency $f_c$ vs. temperature and $\log f_c$ is in a near linear increase with temperature. The sample favors H–alignment when a low-frequency a.c. electric field is applied while it favors P–alignment if a high-frequency field is applied. From this point of view, using two-frequency addressing technique [5,36], the sample can also be aligned into H– or P–states when it is cooled down from its isotropic temperature to room temperature under intensive a.c. electric fields. However, in our cyanobiphenyl samples, the positive anisotropy $\varepsilon_a (f < f_c)$ is much larger than the negative anisotropy $\varepsilon_a (f > f_c)$ and it is expected that the H–alignment could be obtained while the P–alignment would be very difficult to be achieved by a.c. electric fields.

**Director Order Parameter**

As we have seen in § 2.4, the director order parameter $S_d$, between −0.5 and 1.0, can be used to evaluate the degree of alignment of LCs, assuming that $S_d$ is 1 in the perfect H–alignment, −0.5 in the ideal P–alignment, 0 in the absolutely unaligned sample. Attard, Araki, and Williams[8] suggested that $S_d$ can be expressed as, see Eq. (2.26),

$$
\varepsilon''_U(\omega) = \frac{(1+2S_d)\varepsilon''_H(\omega)}{3} + \frac{2(1-S_d)\varepsilon''_P(\omega)}{3} \quad (4.8)
$$

where, subscripts U, H, and P stand for unknown or “unaligned”, H–alignment, and P–alignment, respectively.

Fig. 4 - 11 shows the spectra of the unaligned, H–aligned, and P–aligned C7DP8 at 310 K. The $S_d$ for the “unaligned” sample is −0.125
Fig. 4 - 11 $\varepsilon''$ spectra of C7DP8 at 310 K ($\times$ $\varepsilon''_V$, $+$ $\varepsilon''_H$, $\diamond$ $\varepsilon''_B$). The dashed curve is a result of Eq. (4.8) with $S_d = -0.125$. 
from fitting Eq. (4.8), which indicates that our "unaligned" C7DP8 shows some H-alignment and LC molecules tend to be perpendicular to the glass plates without any alignment efforts although such tendency is rather weak.

4.5 CONCLUSION

Two major relaxation processes in the polyvinyl-ether based cyanobiphenyl side-chain liquid-crystalline polymers have been confirmed and analyzed in terms of the rotational diffusion mode theory in comparisons of the unaligned, homeotropically and planarly aligned samples in smectic-A phase. The glassy behaviors of these two relaxations near $T_g$ investigated by WLF and VFTH equations may also have some correlations with the polymer backbone. The polymer chain length only affects the relaxation frequency and basically does not change the nature of the specific relaxation process. The strong positive dielectric anisotropy in such a system suggests that the samples can be homeotropically aligned in a presence of a low-frequency a.c. electric field.
REFERENCES


Chapter 5

Influence of the Spacer Length in a Side Chain Liquid Crystal Polymer

5.1 Introduction

It is well known that a flexible spacer plays important roles in side chain liquid crystal polymers (LCPs). Systematic investigations of the synthesis, characterization, and applications of side chain liquid crystal polymers began only after Finkelman and coworkers proposed that a flexible spacer should be inserted between the polymer main chain and the mesogenic side groups to decouple the motions of the main chain and side groups in the liquid crystalline state [1,2]. The numerous, previous investigations concerning the synthesis of polymers with low-molar-mass liquid crystals (LCs) attached to their backbones did not lead to a synthetic method which could systematically produce side-chain LCPs, since most involved polymers with mesogens attached directly to the backbone [3].
The spacer, usually a methylene chain (–CH₂–), may function in a way that the main chain could do little to hinder the orientation of the mesogenic side group. Although a spacer helps to decouple the mesogenic groups from the main chain and that decoupling becomes more effective with increasing spacer length, this kind of decoupling is nevertheless incomplete. In most cases, the glass transition temperature decreases with increasing spacer length in a similar manner to increasing the polymer backbone flexibility.

The methylene group does not carry a significant dipole [4] however, its flexibility allows internal reorientations between the backbone and the pendant LC mesogens, which often carry strong dipole moments and are dielectrically active. The spacer length influence on the molecular dynamics in a side-chain LCP system can thus be detected by dielectric relaxation spectroscopy, as we have seen in the previous chapter, measuring the relaxation processes of the LC side group attached to the backbone through different methylene spacers. Spacer length influence on the dielectric relaxation has been compared before [5-9], however most of studies were conducted on the polyacrylate or polymethylacrylate based side-chain LCP samples with even-number methylene spacer. In this chapter, dielectric measurements on three polyvinylether based cyano-biphenyl LCP samples, with the odd-number spacer lengths of 7, 9, and 11, are reported [10].
5.2 EXPERIMENTAL

Poly(ω-[(4-cyano-4’-biphenyl)oxy] alkyl vinyl ether)s, the same series of the side-chain LCPs discussed in Chapter 4, were synthesized by V. Percec and coworkers using a cationic polymerization method [11]. The results demonstrate that the transformation of the nematic mesophase of the monomer into a smectic mesophase after polymerization occurs at the level of monomeric structural unit [12,13]. The molecular structure is shown in Fig. 5 - 1, which contains a cyanobiphenyloxy mesogen attached via a flexible methylene spacer to a polyvinylether backbone. Molecular weight was determined by gel permeation chromatography (GPC) [12], with degree of polymerization (DP) around 30. Three samples with three different spacer lengths m, 7, 9, and 11, are denoted as C7DP30, C9DP30, and C11DP30, respectively. They are all in smectic-A ($s_A$) phase at room temperature, verified by a Nikon polarizing microscope with a custom-built oven. The sample preparation, DSC measurements, and the dielectric data acquisition are described in § 4.2.

\[
\begin{align*}
&\text{CH} - \text{CH}_2 \underbrace{\vdots}_{n} \\
&\text{O} \leftarrow \text{CH}_2 \underbrace{\vdots}_m \text{O} \leftarrow \text{C} = \text{N}
\end{align*}
\]

**Fig. 5 - 1** Molecular structure of the polyvinyl-ether based cyanobiphenyl side-chain LCP with the methylene spacer length m = 7, 9, and 11.
5.3 DSC Results

The DSC measurement for each sample was repeated at least three times. Some transitions, such as molecular crystalline and semi-crystalline, were absent from the thermal scan following the initial scan. Fig. 5 - 2 shows the second scan result for C7DP30, where the glass transition $T_g$ is 290 K and the $s_A$ transition is at 408 K. The phase transitions for the three studied samples are summarized in Table 5 - 1.

As expected, the glass transition $T_g$ decreases with increasing spacer length $m$, e.g., $T_g$ is 290 K for C7DP30 ($m = 7$) and 282 K for C9DP30 ($m = 9$). C11DP30 ($m = 11$) has a $T_g$ approximately the same as C9DP30, which may have resulted from the slight difference in the degree of polymerization $n = 32$ for C9DP30 and $n = 30.6$ for C11DP30, since the smaller molecular weight usually corresponds to a lower $T_g$. Each sample establishes a smectic-A mesophase, since these three samples have fairly long spacer lengths ($m = 7-11$), which decouple the side-chain motion from the polyvinyl-ether backbone. In contrast, the same cyanobiphenyl side-chain LCP samples with shorter spacer lengths ($m = 2$, 3, and 4) hardly demonstrate an $s_A$ mesogenic phase [14]. The isotropic temperature $T_i$ increases with increasing spacer length, i.e., $T_i = 408, 422$, and 435 K respectively for $m = 7, 9$, and 11. In short, given the approximately same DP, the longer spacer length enlarges the temperature range of the mesophase. C11DP30, the longest spacer length sample, has a more complicated phase diagram, having a $T_k = 295$ K. The longest spacer length may sufficiently decouple the interaction between the backbone and LC side chain to possibly result in some microphase separation [15-17].
Fig. 5 - 2  Differential scanning calorimetric (DSC) measurement for C7DP30 at a heating rate of about 10 K/min. This is a result of the second scan.
Table 5.1. Phase transitions in the studied side-chain LCP samples from DSC scan at 10 K/min heating rate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{n} (DP)$</th>
<th>$m$</th>
<th>Phase Transitions ($K$)$^a$</th>
<th>$10^{-3}M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7DP30</td>
<td>30</td>
<td>7</td>
<td>$g$ 290 $s_A$ 408 $i$</td>
<td>10.3</td>
</tr>
<tr>
<td>C9DP30</td>
<td>32</td>
<td>9</td>
<td>$g$ 282 $s_A$ 422 $i$</td>
<td>11.6</td>
</tr>
<tr>
<td>C11DP30</td>
<td>30.6</td>
<td>11</td>
<td>$g$ 282 $k$ 295 $s_A$ 435 $i$</td>
<td>11.97</td>
</tr>
</tbody>
</table>

$^a$ $g$, Glass; $k$, crystalline; $s_A$, smectic-A; $i$, isotropic.
5.4 Dielectric Constant & Conductivity

The dielectric constant $\varepsilon'(\omega) = C(\omega)/C_0$ and conductivity $\sigma(\omega) = \varepsilon_0 G(\omega)/C_0$ can be obtained from the dielectric measurement described in this paper. Table 5-2 lists the dielectric constant $\varepsilon'$ and conductivity $\sigma$ for each sample at 1 kHz measuring frequency and at room temperature ($=295$ K) as well as the corresponding empty cell capacitance $C_0$.

The dielectric constant increases with increasing spacer length, which can be attributed to the increase in the effective dipole moments. Here, the effective dipole moments mean those capable of being thermally activated to reorientate relatively freely. At a given temperature above $T_g$, the polymer chain together with the LC side group containing permanent dipoles tends to be thermally activated more easily for the lower $T_g$ material, which has a longer spacer length in this case. The conductivity (d.c. + a.c.) for each sample is of the order of $10^{-9}$ Sm$^{-1}$ at 1 kHz and room temperature. There seems no obvious correlation in the conductivities among the three samples. C7DP30 has a conductivity of $1.7\times10^{-9}$ Sm$^{-1}$, smaller than that of C9DP30 with $5.4\times10^{-9}$ Sm$^{-1}$. However, C11DP30 with the longest spacer length has the least conductivity of $1.1\times10^{-9}$ Sm$^{-1}$.

5.5 Dielectric Relaxation Spectrum Overview

The dielectric spectrum of the studied LCP system in the whole measured temperature range ($T < T_i$) shows four relaxation processes. Fig. 5-3 gives the dielectric loss spectra of the homeotropically ($H-$)
Table 5 - 2. Dielectric constants and conductivities for the unaligned samples at room temperature (≈295 K) and 1 kHz measuring frequency.

<table>
<thead>
<tr>
<th>Unaligned Sample</th>
<th>C₀ (pF)</th>
<th>ε'</th>
<th>σ ×10⁹ (Sm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7DP30</td>
<td>7</td>
<td>2.8</td>
<td>1.7</td>
</tr>
<tr>
<td>C9DP30</td>
<td>7</td>
<td>3.1</td>
<td>5.4</td>
</tr>
<tr>
<td>C11DP30</td>
<td>6</td>
<td>3.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Fig. 5 - 3  Dielectric loss spectra for the homeotropically (H-) aligned C7DP30 at 10 Hz (---), 1 kHz (--.--.--), and 100 kHz (--.--.--). The four processes are labeled as $\delta$, $\alpha$, $\beta$, and $\gamma$ in decreasing temperature.
aligned C7DP30 at 10 Hz, 1 kHz, and 100 kHz. There are two relaxations below the calorimetric \( T_g \), labeled by \( \beta \) and \( \gamma \) with decreasing temperature. The \( s_A \) region \( (T_g < T < T_i) \) contains two typical processes in the side-chain LCP mesophase, labeled by \( \delta \) and \( \alpha \) in decreasing temperature.

Both \( \beta \) and \( \gamma \) relaxations occur below the glass transition of the sample, where the polymer chain is essentially frozen. These two low-temperature relaxations are very similar to those in poly(vinyl methyl ether) [18] and usually involve only local motions of some segments either in the main chain or in the side chain [19]. Although they are almost independent of the alignment and the spacer length, there are slight deviations in the loss amplitude for different alignment configurations. The loss amplitude in the \( \gamma \) relaxation increases with increasing temperature and the relaxation frequency at a given temperature is much higher than that in the \( \beta \) relaxation. The broad \( \gamma \) process may combine a few different local motions, including some in the cyanobiphenyl group [20] in the side chain, and has an activation energy of about 40 kJ/mole. The \( \beta \) peaks are merged with the \( \alpha \) process at higher frequencies \( (> 1 \text{ kHz}) \), where the glass transition of the polymer appears. In this chapter, the discussion will be focused on the two major relaxation processes \( \alpha \) and \( \delta \).

5.6 \( \alpha \) and \( \delta \) Relaxations

In the \( s_A \) region, there are two major dielectric relaxation processes, a broad, high-frequency \( \alpha \) peak and a narrow, low-frequency \( \delta \) peak. Fig. 5 - 4 shows the dielectric loss for the unaligned \( (U^-) \) and planarly \( (P^-) \) aligned C9DP30 from 305–325 K, where the \( \delta \) peaks are suppressed.
Fig. 5-4  δ and α processes in C9DP30 from 305–325 K
(+, 305 K; □, 310 K; △, 315 K; ◇, 320 K; ○, 325 K).
(a) unaligned (U−); (b) planarly or homogeneously aligned (P−).
Fig. 5 - 5  \( \delta \) and \( \alpha \) processes in C7DP30 from 305–325 K
( +, 305 K; □, 310 K; Δ, 315 K; ◊, 320 K; ○, 325 K).
(a) unaligned (U-); (b) homeotropically aligned (H-).
compared with the unaligned and the $\alpha$ peaks are increased. In contrast, in Fig. 5 - 5 for C7DP30, the $\delta$ peaks are dramatically enhanced while $\alpha$ peaks are almost absent in the H-alignment. These are typical dielectric loss behaviors in a side-chain LCP system, see § 4-3 [21-23].

The Fuoss-Kirkwood function, see § 3.4 [24], has been used to fit the spectrum in order to extract the necessary information. In the temperature range from 295-330 K where the samples are in the $s_A$ phase, the dielectric loss spectrum $G(\omega)/\omega = \varepsilon'^{\prime\prime}C_\eta$, is thought to consist of a low-frequency $\delta$ peak, a high-frequency $\alpha$ peak, and a d.c. conductance,

$$
\varepsilon'^{\prime\prime}(\omega) = G(\omega)/\omega C_\eta
= (\sigma_{DC}/2\pi f_0) + \sum_{\delta, \alpha} \varepsilon_{m, i}^{\prime\prime} \text{Sech} [2.303\beta, \log_{10}(f / f_R)]
$$

(5.1)

where, angular frequency $\omega = 2\pi f$ and relaxation frequency $\omega_R = 2\pi f_R$; $\sigma_{DC}$ is a DC conductivity; $\varepsilon_{m}^{\prime\prime}$ is the amplitude of the imaginary part of the complex dielectric constant $\varepsilon^* = \varepsilon^{\prime} - i\varepsilon^{\prime\prime}$; $\beta$ lies between 0 and 1 and is a width distribution parameter and is equal to $1.14/(\text{width of loss peak at half-height})$. The Fuoss-Kirkwood function reduces to a Debye-type relaxation when $\beta = 1$, see Fig. 3 - 11. The dielectric relaxation strength for each process, $\Delta\varepsilon^{\prime}$, can be expressed as [4],

$$
\Delta\varepsilon^{\prime} \equiv \varepsilon^{\prime}_{0} - \varepsilon^{\prime}_{\infty} = 2\varepsilon_{m, i}^{\prime\prime} / \beta
$$

(5.2)

The results from Fuoss-Kirkwood data fitting [Eq. (5.1)] for all the studied samples at 315 K are listed in Table 5 - 3. The DC conductivity $\sigma_{DC}$ of the aligned sample seems larger than that of the unaligned, for
Table 5–3. Results from Fuoss-Kirkwood data fitting for all the studied samples at 315 K by using Eq. (5.1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Align.</th>
<th>$\sigma_{\text{DC}}$ (10^{12} \text{ Sm}^{-1})</th>
<th>$log f_R$</th>
<th>$\varepsilon'_m$</th>
<th>$\beta$</th>
<th>$\Delta \varepsilon'$</th>
<th>$log f_R$</th>
<th>$\varepsilon'_m$</th>
<th>$\beta$</th>
<th>$\Delta \varepsilon'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7DP30</td>
<td>U−</td>
<td>2.5</td>
<td>1.24</td>
<td>1.25</td>
<td>0.73</td>
<td>3.40</td>
<td>3.07</td>
<td>0.26</td>
<td>0.32</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>H−</td>
<td>6.0</td>
<td>1.31</td>
<td>2.67</td>
<td>0.80</td>
<td>6.72</td>
<td>3.02</td>
<td>0.13</td>
<td>0.31</td>
<td>0.87</td>
</tr>
<tr>
<td>C9DP30</td>
<td>U−</td>
<td>10.1</td>
<td>1.95</td>
<td>0.97</td>
<td>0.83</td>
<td>2.34</td>
<td>3.81</td>
<td>0.24</td>
<td>0.31</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>P−</td>
<td>18.3</td>
<td>2.11</td>
<td>0.34</td>
<td>0.92</td>
<td>0.75</td>
<td>3.92</td>
<td>0.34</td>
<td>0.30</td>
<td>2.22</td>
</tr>
<tr>
<td>C11DP30</td>
<td>U−</td>
<td>3.4</td>
<td>1.35</td>
<td>0.22</td>
<td>0.54</td>
<td>0.82</td>
<td>4.08</td>
<td>0.04</td>
<td>0.26</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>H−</td>
<td>10.0</td>
<td>1.39</td>
<td>0.20</td>
<td>0.51</td>
<td>0.80</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>P−</td>
<td>33.9</td>
<td>2.39</td>
<td>0.03</td>
<td>0.54</td>
<td>0.12</td>
<td>3.59</td>
<td>0.09</td>
<td>0.20</td>
<td>0.88</td>
</tr>
</tbody>
</table>
instance, $\sigma_{DC}$ is $10.1 \times 10^{-12}$ Sm$^{-1}$ for the unaligned C9DP30 while $18.3 \times 10^{-12}$ Sm$^{-1}$ for the P-aligned. Overall, the DC conductivity increases with increasing the spacer length, however, this is very dependent on the impurities in a particular sample. The relaxation frequency $f_R$ for an $\alpha$ or $\delta$ process is basically independent of the specific alignment configuration except it shifts slightly towards a higher frequency position in P–aligned samples.

The two major relaxation processes are also interpreted in terms of rotational diffusion theory [4,25,26], see Eqs. (2. 21) & (2. 22) and Fig. 2 - 1. The longitudinal component of the dipole moment in the uniaxial side chain mesogen $\mu_l$ is approximately 5 Debye [27], which comes from its cyanobiphenyl end-group (–C≡N), and is much larger than the transverse component $\mu_t$, approximately 2 Debye from the oxy-group (–O–). The low-frequency $\delta$ peak can be assigned to the rotation of the longitudinal dipole moment in the mesogenic group about its short axis. In the smectic-A phase, it is possible for the side group to flip around the polymer backbone, hopping from one smectic layer to another. The high-frequency and broad $\alpha$ process can be thought to involve both longitudinal and transverse dipole moments in the mesogenic group, combined into a few different rotational modes. Since the amplitude of the $\alpha$ peak is much smaller than that of the $\delta$-peak and is almost uncoupled from the driving electric field in the H-aligned samples, the major contribution to the $\alpha$ process comes from the transverse dipole moments ($\mu_t < \mu_l$) rotating about the mesogens' long axis. These relaxation processes can consequently be completely described by the four modes ($\mathcal{F}_n^\parallel$, $\mathcal{F}_n^\perp$, $\mathcal{F}_\perp^\parallel$, and $\mathcal{F}_\perp^\perp$) in Fig. 2 - 1.
It is worth pointing out here again that the above interpretation based on the rotational diffusion theory is in qualitative agreement with the processes in polymeric liquid crystals. The rotational diffusion theory was derived for dielectric results in nematic liquid crystals [25,26]. In side chain polymeric liquid crystal materials, steric hindrance prevents a simple reorientation of the side chain mesogenic unit about its long or short axes. Reorientations of the unit, if any, are possible only as a result of highly cooperative motions involving both rotation and translation of the unit and of the neighboring environment [28,29].

Generally speaking, at a given temperature, the longer spacer length can decouple the LC side group from the motion of the polymer backbone more efficiently so that the side group would reorient faster and the \( f_R \) would be higher. This is observed in C7DP30 and C9DP30, e.g., the peak relaxation frequency \( f_R \) in the \( \delta \) process for the unaligned C7DP30 is \( 10^{1.24} \) Hz at 315 K while the unaligned C9DP30 is \( 10^{1.95} \) Hz — a 0.71 decade difference in relaxation frequency (see Table 5 - 3). Unfortunately, it does not hold for C11DP30, the longest spacer length sample among those studied. The \( f_R \) of the \( \delta \) process in the unaligned C11DP30 is \( 10^{1.35} \) Hz, smaller than that \( 10^{1.95} \) Hz in the unaligned C9DP30, even though C11DP30 has the higher \( f_R \) in the \( \alpha \) process. This "abnormal" phenomenon cannot be simply attributed to the difference in DP (see Table 5 - 1, DP for C9DP30 is on average 32 and C11DP30 is 30.6), since such a small difference in molecular weight would not be expected to have this large effect on the corresponding relaxation. The width parameter \( \beta \) in the \( \delta \) peak of C11DP30 is around 0.54, much smaller than that of C7DP30 or
C9DP30, in other words, the δ process of C11DP30 is no longer Debye-like and must be combined with some other processes. As mentioned before, there might be an intramolecular microphase separation of the side group from the polymer backbone [3,15,30] in the longest spacer C11DP30. So, the microscopic structure in C11DP30 may include not only the conventional side chain liquid crystal polymer system but also a phase separated sub-system. As a result, the δ reorientational relaxation in such a nonhomogeneous structure could be slowed down in a complicated way compared with the pure side-chain LCP structure. The dielectric strength Δε′, calculated according to Eq. (5.2), decreases reasonably with increasing spacer length since Δε′ is proportional to the density of dipole moments within the sample and therefore the longer spacer sample has a lower dipole density.

Fig. 5 - 6 is the Arrhenius plot for the three unaligned samples, which clearly shows that in the α process the longer spacer length has the higher relaxation frequency at fixed temperature; however in the δ process the curve of the longest spacer C11DP30 lies between the curves of C7DP30 and C9DP30. On the average in the plotted temperature region, the activation energy of the δ process is approximately 217, 200, and 182 kJ/mole respectively for C7DP30, C9DP30, and C11DP30; the activation energy of the α process is estimated to be 179, 221, and 199 kJ/mole. Further investigations on C11DP30 with the longest spacer length are needed to verify the hypothesis of the microphase separation in such a smectic-A side chain liquid crystal polymer.
Fig. 5 - 6  Arrhenius plot for all the unaligned samples.  
Δ, C7DP30; ○, C9DP30; ◆, C11DP30. Solid line is for δ relaxation and dash line is for α relaxation.
REFERENCES


Chapter 6

Constitutional Isomeric Effect in a Nematic Polymethacrylate Containing Methoxy-methylstilbene Side Group

6.1 INTRODUCTION

Side-chain liquid crystalline polymers (LCP's) are polymers that have linked conventional low molecular mass liquid crystals (LC's) as side chains to a polymer backbone through a flexible spacer (usually a methylenic group \(-\text{CH}_2^-\)) \([1-6]\). As we have seen in the last chapter, the flexible spacer plays an important role in such a new class of liquid crystals. The nature of the mesomorphic phases exhibited by side-chain LCP's with degrees of polymerization higher than twelve are usually controlled by the spacer length and the nature of the mesogenic group. For the same spacer length and the degree of polymerization, the degree of decoupling the mesogenic side group from the polymer backbone seems to be strongly correlated to the nature of the polymer backbone \([7-9]\).
Percec and co-workers have suggested that side-chain liquid crystalline "copolymers" of the monomer pairs containing constitutional isomeric mesogenic units are useful both to depress side-chain crystallization of polymers containing long flexible spacers and to obtain qualitative information about the degree of decoupling [8]. In the synthesis and characterization of copolymethacrylate and copolyacrylate based on side groups with two isomeric methoxy-methylstilbenes [7], they found a suppression of side-chain crystalline and transformation of monotropic mesophases into enantiotropic mesophases by copolymerization of the parent polymers' monomer pairs containing constitutional isomeric mesogenic side groups. Copolymers of constitutional isomeric groups may represent a chemical sensor which provides at least qualitative information on the dynamics of the side-chain LCP's. Therefore, it is of interest to investigate comparatively the corresponding homopolymers with the same constitutional isomeric mesogen in the side group.

Silvestri and Koenig employed $^{13}$C nuclear magnetic resonance (NMR) spectroscopy to study the local molecular dynamics of polymethacrylate attached by 4-hydroxy-4'-methoxy-α-methylstilbene side chain through a methylenic spacer length of three (4'-3-PMA) [10]. Within the glassy state, the mobility of all spins increased continuously with temperature due to thermal motions. The mobility then increased discontinuously at the glass to mesogenic phase transition. They observed that the outer carbons in the spacer are nearly as rigid as the mesogen while the center spacer carbon is nearly two orders of magnitude more mobile. Gu and Jamieson, et al. attempted dynamic light scattering from a
nematic monodomain containing polymethacrylate with 4-methoxy-4'-hydroxy-α-methylstilbene side group linked by a spacer length of six (4-6-PMA) [11]. The addition of the side-chain LCP to a nematic LC (4'-n-pentyl-4-cyanobiphenyl, or 5CB) results in significant increases in the relaxation times from all three scattering geometries (splay, bend, and twist), which had been attributed to small decreases of the three elastic constants and larger increases of the three viscosities.

In this chapter, we will report and discuss the dielectric results of two liquid crystalline polymethacrylates containing a constitutional isomeric methoxy-methylstilbene side group (4-6-PMA and 4'-6-PMA) within the same side-chain LCP series mentioned above [12]. The dielectric relaxation spectroscopy with broad frequency band (10⁻¹ – 10⁷ Hz) shows that there are two typical relaxation processes in the nematic phase for 4-6-PMA and there is basically only one process for 4'-6-PMA. The results will be interpreted in terms of rotational diffusion theory in nematics [13-15] and Vogel-Fulcher-Tammann-Hesse (VFTTH) [16-18] glassy diagram.

6.2 EXPERIMENTAL

The two thermotropic liquid crystalline polymethacrylates with a constitutional isomeric mesogens in the side chain were synthesized by Percec and co-workers using radical polymerization of monomers, one containing 4-methoxy-4'-hydroxy-α-methylstilbene (4-6-PMA) [9] and another containing 4-hydroxy-4'-methoxy-α-methylstilbene (4'-6-PMA)
The molecular structure is shown in Scheme 6-1, which contains an isomeric methoxy-methylstilbene attached to a polymethacrylate backbone via a flexible methylenic spacer length of six. The isomerism was determined by the position of methyl unit (–CH₃) in the bridging group of methylstilbene.

Molecular weight was determined by gel permeation chromatography (GPC) [8]. Both samples are in a nematic state at a temperature slightly higher than room temperature, verified by a Nikon polarizing microscope with a custom-built hot stage. Differential scanning calorimetric (DSC) measurements were taken with a DuPont 910 cell base incorporating a DuPont 990 thermal analyzer at a 10 K/min heating rate. The mesogenic phase transitions were recorded at the maximum or minimum of their endothermic peaks while glass transition temperatures (Tg) were recorded at the midpoint of the step change in the heat capacity. Each sample was measured at least three times. Table 6-1 summarizes the number-average molecular weight (Mₙ), the width of molecular-weight distribution (Mₘ/Mₙ), the degree of polymerization (DP), and phase transitions from the repeated heating scans.

Four capacitance bridges were employed in the dielectric measurement in order to obtain the permittivity (ε') and loss factor (ε'') over a broad frequency range: TA DEA 2970 Dielectric Analyzer (0.1 Hz–100 kHz), HP 4284A Precision LCR Meter (20 Hz–1 MHz), HP 4275A Multi-frequency LCR Meter (20 kHz–10 MHz), and CGA-83 Ratio-arm Transformer Bridge (10 Hz–100 kHz).
Scheme 6.1 Molecular structure for the studied side-chain liquid crystalline polymethacrylate (LCP) containing either 4-methoxy-4'-hydroxy-α-methylstilbene (4-6-PMA) or 4-hydroxy-4'-methoxy-α-methylstilbene (4'-6-PMA). Only the trans conformational molecule of the mesogenic side chain is presented as drawn.
### Table 6 - 1  Phase Transitions of 4-6-PMA & 4'-6-PMA from the Repeated DSC Scan at 10 K/min Heating Rate (g – glassy, n – nematic, i – isotropic).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Name</th>
<th>$10^{-3}M_n$</th>
<th>$\bar{M}_w/\bar{M}_n$</th>
<th>DP (X)</th>
<th>Phase Transitions (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>4-6-PMA</td>
<td>11.63</td>
<td>1.36</td>
<td>29</td>
<td>g 302 n 387 i</td>
</tr>
<tr>
<td>II</td>
<td>4'-6-PMA</td>
<td>24.70</td>
<td>2.50</td>
<td>60</td>
<td>g 302 n 372 i</td>
</tr>
</tbody>
</table>
The low-frequency measurements were completed with DEA 2970 which employed parallel ceramic plates with gold-coated three-terminal sensors [19], separated by a 50 μm Kapton spacer. The sample was first applied to the center of the bottom sensor and heated to melt at about 450 K and held for ten minutes. The upper sensor was driven into the sample with a 150 N force to reach the final 50 μm separation. The DEA was programmed to measure dielectric permittivity (ε') and loss factor (ε'') isothermally at 2.5 K temperature increments from 300–430 K, over a frequency range from 0.1 Hz–100 kHz at four frequencies per decade with the excitation voltage being approximately 1 V.

For the measurements with the other bridges, the dielectric sample cell was constructed of two parallel ITO plates with the empty cell capacitance C₀ of approximately 10 pF, see § 3.6. The sample 4-6-PMA was inserted onto the cell through capillary action, being placed on a hot stage in a vacuum chamber and heated above the isotropic temperature. The sample 4′-6-PMA having a much higher viscosity was first applied to one ITO glass plate heated to well above its isotropic point, the top ITO plate was then pressed and squeezed onto the sample, followed by slowly cooling down to room temperature under a constant force. This sample cell was completed by sealing with a high temperature epoxy. Each sample cell was placed in a custom-built vacuum oven for data collection at elevated temperatures from 300–400 K. The temperature was controlled by a Lakeshore DRC 82C Controller with two platinum thermal sensors with temperature stability within 10 mK. The data acquisition steps were controlled by a HP-87 computer.
All the data has been converted to permittivity $\varepsilon'$ and loss factor $\varepsilon''$ (complex dielectric constant $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$) through the simple relations, $\varepsilon'(\omega) = C(\omega)/C_0$ and $\varepsilon''(\omega) = (G/\omega)/C_0$, where $C(\omega)$ is the loaded capacitance; $G(\omega)/\omega$ is the dielectric loss, equal to the product of dissipative factor $D(\omega)$ or tan$\delta(\omega)$ and capacitance $C(\omega)$. At the frequency 10 kHz and temperature 300 K, the dielectric constant $\varepsilon'$ and conductivity $\sigma$ ($=\varepsilon''\varepsilon_0\omega$) of the sample 4-6-PMA are typically measured to be 3.16 and 2.20$\times$10$^{-9}$ S/m, respectively, while 3.60 and 1.75$\times$10$^{-9}$ S/m for 4' -6-PMA.

6.3 RESULTS AND DISCUSSION

Fig. 6.-1 on page 150 shows the dielectric spectroscopy of the 4-6-PMA in the nematic phase at 350.14 K. Either the real part $\varepsilon'(\omega)$ or the imaginary part $\varepsilon''(\omega)$ of the complex dielectric constant $\varepsilon^*(\omega)$ provides complete information regarding all the processes as a result of the Kramers-Kronig relations. In the frequency range from 0.1 Hz to 10 MHz, the dielectric spectrum shows d.c. conductivity, two major relaxation processes of the mesogen in the side chain — labeled by the low-frequency $\delta$ and the high-frequency $\alpha$, and a not-so-clear $\zeta$ process at the high frequency end. This kind of loss peak labeling ($\delta$, $\alpha$ with decreasing temperature) is contrary to the traditional nomenclature for polymeric materials ($\alpha$, $\beta$, $\gamma$, ... with decreasing temperature), but has been widely accepted by authors in the LCP field [20-23]. The $\zeta$ process which exhibits no temperature dependence of the peak position might result from two
Fig. 6-1  Dielectric spectrum overview of the nematic side-chain LCP 4-6-PMA at 350.14 K, which consists of four components in the measured frequency range (0.1 Hz–10 MHz), a d.c. conductivity, two major relaxation processes (α & δ) of the mesogens in the side chain, and a ζ process at high frequency end. (a) permittivity ε'; (b) loss factor ε'' of the complex dielectric constant ε*. 
possibilities. One is the "localized" β relaxation, which is often observed with low intensity but appears to be at the extremely high frequency end when the temperature goes above $T_g$. The other is due to the surface resistivity of the ITO glass. The possibility of the β relaxation can be ruled out since the amplitudes of the amplitudes of the ζ process are higher than those of the δ– and α–processes at $T > 330$ K and, with temperature–independence of peak frequency, contain no molecular relaxation mechanism. By measuring the empty cell the effective surface resistance is approximately 50 Ω at 5 MHz and 350 K, and the loaded capacitance is approximately 40 pF. So, $f \sim (2\pi RC)^{-1} \sim 8.0 \times 10^7$ Hz, which is very close to the extrapolated frequency of ζ peaks. Thus the ζ process is thought to be due to the cell resistance and will not be included.\textsuperscript{\dag} In the following, we shall only focus on the two major relaxation processes α and δ of the mesogens of the side-chain LCP.

\textsuperscript{\dag} In practice, this a technical problem while involving high frequency measurements. See reference [24], the side-chain LCP sample is generally treated as a capacitor $C_p$ with a conductance $G_p$ in parallel. It is essential above $10^5$ Hz, and often convenient below, to model the leads (including the ITO electrodes in this paper) by introducing into the equivalent circuit an inductor $L_s$ and a resistor $R_s$ in series with the sample. The capacitance $C$ and conductance $G$ measured by the impedance analyzer in parallel mode are related to the equivalent circuit parameters by

$$\frac{G}{G^2 + \omega^2 C^2} = \frac{G_p}{G_p^2 + \omega^2 C_p^2} + R_s$$

$$\frac{C}{G^2 + \omega^2 C^2} = \frac{C_p}{G_p^2 + \omega^2 C_p^2} - L_s.$$
Fig. 6-2 Dielectric relaxation spectra obtained by DEA 2790 from 315–325 K, ×, 315.15 K; Δ, 317.65 K; ○, 320.15 K; ○, 322.65 K; +, 325.15 K. (a) 4-6-PMA; (b) 4'-6-PMA. Both samples endured the strictly same measuring procedures. Dashed curves are the least-square fitting according to Havrilaiak-Negami Equation (6. 4) plus a d.c. conductivity Equation (6. 1).
Havriliak-Nagami data fitting

Fig. 6 - 2 on page 152 shows the dielectric relaxation spectra (0.1 Hz–100 kHz) in the temperature range from 315–325 K. Fig. 6 - 2(a) for 4-6-PMA has both δ and α processes while Fig. 6 - 2(b) for 4*-6-PMA has only an α process. The data has been fitted with Havriliak-Nagami (HN) [24] empirical line shapes (see § 3.4) plus a d.c. conductivity using a least-square method. Usually, the d.c. conductance component obeys a power rule of frequency ω ( = 2πf ), here we simply treat it as a pure d.c. conductivity, i.e.,

\[ \varepsilon''_{dc} = \frac{\sigma_{dc}}{\varepsilon_0 \omega} \]  \hspace{1cm} (6.1)

The Havriliak-Nagami function is

\[ \frac{\varepsilon^*(\omega) - \varepsilon_*}{\varepsilon_0 - \varepsilon_*} = \frac{1}{[1 + (i\omega \tau)^{1-\gamma}]^\beta} \]  \hspace{1cm} (6.2)

where, \( \varepsilon_0 \) and \( \varepsilon_* \) are the limiting low- and high- frequency permittivities, respectively, \( \Delta \varepsilon \equiv \varepsilon_0 - \varepsilon_* \) is the dielectric relaxation strength, representing the effective dipole moment of the orienting unit; \( \tau \) is a relaxation time, \( \tau = (2\pi f_R)^{-1} \) while \( f_R \) is a relaxation frequency; parameter \( \gamma \left( 0 \leq \gamma < 1 \right) \) describes the symmetric width of relaxation time distribution, and the width increases as \( \gamma \) ranges from 0 to 1; parameter \( \beta \left( 0 < \beta \leq 1 \right) \) describes the skewness of the relaxation time distribution, and the skewness increases as \( \beta \) ranges from 1 to 0. When \( \beta = 1 \), a Cole-Cole [25] circular arc is obtained; when \( \gamma = 0 \), a Cole-Davidson [26] skewed
semicircle is obtained and when $\beta = 1$ and $\gamma = 0$, a Debye [27] relaxation
function is obtained, see Fig. 3 - 12 on page 62.

Equation (6.2) can be separated into the real and imaginary parts,

$$\varepsilon'(\omega) - \varepsilon_\infty = r^{-\beta/2} \Delta \varepsilon \cos \beta \theta \quad (6.3)$$

$$\varepsilon''(\omega) = r^{-\beta/2} \Delta \varepsilon \sin \beta \theta \quad (6.4)$$

with

$$r = [1 + (\omega \tau)^{1-\tau} \sin(\frac{\pi}{2} \gamma)]^2 + [(\omega \tau)^{1-\tau} \cos(\frac{\pi}{2} \gamma)]^2 \quad (6.5)$$

$$\theta = \arctan \left[ \frac{(\omega \tau)^{1-\tau} \cos(\frac{\pi}{2} \gamma)}{1 + (\omega \tau)^{1-\tau} \sin(\frac{\pi}{2} \gamma)} \right] \quad (6.6)$$

Fig. 6 - 2 also demonstrates the HN least-square fitting results
(dashed curves) according to Equation (6.4) in the temperature range
315–325 K. This data fitting has been applied to both isomeric samples
from nematic phase to isotropic phase (300–400 K) to obtain the necessary
information about each relaxation process, such as relaxation time $\tau$,
dielectric relaxation strength $\Delta \varepsilon$, etc.

Table 6 - 2 gives an example of the HN fitting results at 325.15 K.
The d.c. conductivity $\sigma_{dc}$ for 4-6-PMA is $1.6 \times 10^{-13}$ S/m and larger than
that of $4'\cdot6$-PMA, $4.0 \times 10^{-14}$ S/m. For 4-6-PMA, the data was fitted with
two HN loss factors according to Equation (6.4) by first extracting a d.c.
conductance [Equation (6.1)]. The relaxation strength $\Delta \varepsilon$ of the $\delta$
process is 0.27, smaller than that of the $\alpha$ process, 0.74. This difference
can be attributed to the smaller longitudinal dipole moment $\mu_l$ of the
Table 6 - 2  Results from Havriliak-Negami Data Fittings at 325.15 K after Extracting a d.c. Factor in Equation (6.1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>σ₀ (10⁻¹² S/m)</th>
<th>Δε</th>
<th>τ (sec)</th>
<th>γ</th>
<th>β</th>
<th>Δε</th>
<th>τ (sec)</th>
<th>γ</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-6-PMA</td>
<td>0.16</td>
<td>0.27</td>
<td>9.19×10⁻²</td>
<td>0.33</td>
<td>1.0</td>
<td>0.74</td>
<td>3.52×10⁻⁴</td>
<td>0.59</td>
<td>1.0</td>
</tr>
<tr>
<td>4'-6-PMA</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.84</td>
<td>7.87×10⁻³</td>
<td>0.64</td>
<td>0.79</td>
</tr>
</tbody>
</table>
mesogen in the side chain associated with the $\delta$ peak and the larger transverse component $\mu_t$ associated with the $\alpha$ peak.[14,20,23,28] The width parameter of the $\delta$ peak ($\gamma = 0.33$) is narrower than than that of the $\alpha$ peak ($\gamma = 0.59$). Both processes have the skewness parameter $\beta$ slightly larger than one, and we set $\beta = 1.0$ (see Table 6-2), which indicates the HN function has been reduced to a Cole-Cole expression. The data for 4′-6-PMA was fitted into one HN loss factor $\varepsilon^*(\omega)$ [Equation (6. 4)] plus a d.c. conductance [Equation (6. 1)] with the dielectric strength $\Delta \varepsilon$ of 1.84, $\gamma = 0.64$, and $\beta = 0.79$. The relaxation time of 4′-6-PMA, $\tau = 7.78 \times 10^{-3}$ sec, is between the two relaxation times of 4-6-PMA, $3.52 \times 10^{-4}$ sec ($\alpha$ peak) and $9.19 \times 10^{-2}$ sec ($\delta$ peak).

**Isomeric effect on two major relaxations – $\alpha$ and $\delta$**

The two major relaxation processes in mesogenic phase of a side-chain LCP are often interpreted in terms of rotational diffusion theory in nematics [13,14,29,20,23]. Generally speaking, they arise from the reorientations of the mesogens in the side chain. In a uniaxial liquid crystal system, the dipole moment of a mesogen can be divided into a longitudinal component $\mu_l$ (usually along the long axis of the molecule, sometimes equal to the easy optical axis) and a transverse component $\mu_t$ (usually perpendicular to the long axis of the molecule). The low-frequency $\delta$ peak can be assigned to the 180° rotation of the longitudinal dipole moment in the mesogenic group about its short axis. The high-frequency $\alpha$ peak can be thought to involve both longitudinal and transverse dipole moments in the mesogenic group, combined into a few
different rotational modes. The major contribution to the $\alpha$ process comes from the transverse dipole moment $\mu_t$ rotating about the mesogen’s long axis, see § 2.4 and Fig. 2 - 1 of Chapter 2 (13,14,15,30,31).

Kresse and co-workers made dielectric relaxation measurements on two isomorphic siloxane polymers with opposite direction of the ester bridging group in the phenyl-benzoate mesogenic side group (32). The ratio of the amplitudes of the two major relaxation processes in the mesogenic phase is strongly correlated to the isomerism, which can be simply attributed to the different ratios of longitudinal and transverse components of dipole moments.

The dipole moment in the constitutional isomeric mesogen of the side-chain LCP in this paper mainly comes from the two polar heads, consisting of the phenyl–O–CH$_3$ bond at two ends of methylstilbene molecule and each carrying about 1.28 Debye, as well as from the bridging group in the stilbene effectively carrying a longitudinal dipolar component. (33-35) The stilbenes generally form an interesting group of molecules because of their conformational properties (36-38). Assuming the mesogenic molecule is in trans conformation, the resulting effective transverse dipole moment $\mu_t$ is larger than the longitudinal $\mu_l$. This results in the dielectric relaxation strength $\Delta\varepsilon$ of the $\alpha$ process of 4-6-PMA, mainly associated with $\mu_t$, stronger than that of the $\delta$ process mainly associated with $\mu_l$ [ see Fig. 6 - 2(a) and Table 6 - 2 ]. The sample will exhibit a negative dielectric anisotropy $\varepsilon_\parallel = \varepsilon''_\parallel - \varepsilon''_\perp < 0$, where $\varepsilon''_\parallel$ and $\varepsilon''_\perp$ are the dielectric constants when the nematic director in a monodomain is parallel to and perpendicular to the measuring electric
field.

The isomeric effect on the $\delta$ and $\alpha$ processes is very obvious, i.e., 4-6-PMA shows both $\delta$ and $\alpha$ peaks [Fig. 6 - 2(a)] while $4'$-6-PMA shows only an $\alpha$ process [Fig. 6 - 2(b)]. Although both samples were measured under almost identical condition, a question can be raised about the macroscopic alignment states of the samples since the homeotropic alignment would cause an enhancement of the $\delta$ peaks and a suppression of the $\alpha$ peaks as compared with the unaligned state. On the other hand, the planar or homogeneous alignment would show just the opposite result [20,21,23,29]. In this sense, it seems that 4-6-PMA tends to be homeotropically aligned and $4'$-6-PMA tends to be planarly aligned in the measuring dielectric cells. To verify this, an experiment regarding macroscopic alignment by a magnetic field has been conducted on the sample $4'$-6-PMA, taking advantage of the diamagnetic anisotropy of "trans-methylstilbene". The sample was placed in an 8-Tesla superconducting magnet (Cryomagnetics, Inc.) with either homeotropically or planarly mounting configuration, cooling slowly from well above isotropic temperature to room temperature. The cooling rate of 5 K/hour was well controlled by a Lakeshore temperature controller together with a custom-built ramp circuit. For the homeotropic (H-) alignment, the sample cell was mounted with its layer normal parallel to the field; for the planar (P-, or homogeneous) alignment, the layer normal was perpendicular to the field. During each aligning process, the sample was monitored and recorded dielectrically by the CGA-83 bridge. The results are quite surprising as seen in Fig. 6 - 3, page 159 for the sample at 360 K after a d.c. conductivity of approximate
Fig. 6 - 3  Dielectric loss spectrum of the sample 4',6'-PMA at 360 K in an 8-Tesla magnetic field monitored by a CGA-83 bridge.  Δ, homeotropic (H-) configuration;  ○, planar (P-, or homogeneous) configuration;  ◌, the sample in a zero magnetic field. Note, a d.c. conductivity of approximate $7.5 \times 10^{-10}$ S/m has been extracted.
$7.5 \times 10^{-10} \text{ S/m}$ has been extracted. The strong magnetic field has little impact on the appearance of the relaxation process. The 4'-6-PMA with a planar cell has a spectrum similar to the unaligned sample while the sample with a homeotropic cell shows a slight rise of the $\delta$ peak. This $\delta$ appearance is still much weaker in comparison with 4-6-PMA even when 4'-6-PMA was subjected to an 8-Tesla magnet! This suggests that reorientational motions of the mesogen are hardly influenced by field alignment efforts and do not have a preferential direction. This is opposed to the trans conformation. While both samples have the same glass transition temperature (see Table 6 - 1 on page 147), the relaxation time of the 4'-6-PMA $\alpha$ process lies between those of the $\alpha$ and $\delta$ processes of 4-6-PMA at a given temperature (see Table 6 - 2 and Fig. 6 - 4). This might partly result from an intermediate moment of inertia of the 4'-6-PMA mesogen compared with those associated with the $\alpha$ and $\delta$ processes of 4-6-PMA. The "long" and "short" axes of the 4'-6-PMA seem to be no longer distinguishable and the two axes have similar characteristics. It may be therefore concluded that the mesogens of 4'-6-PMA are statistically no longer in a trans conformation as drawn in Scheme 6 - 1 on page 146 and they are probably in a cis conformation [32,38]. 4-6-PMA, tends to have a mesogen with trans-methylstilbene and hence, has two different preferential directions with effective dipole moments $\mu_t > \mu_l$ so that both $\alpha$ and $\delta$ processes are active; 4'-6-PMA, tends to have a mesogen with cis-methylstilbene, has no preferential axis so that all the rotational modes, in principle, can be combined into one and only one so-called "$\alpha$ process"

\[\text{This is essentially different from Kresse et al.'s work, in which no conformational isomerism was involved and their mesogens in the side chain were treated as rigid-rod-like.}\]
Fig. 6 - 4  Relaxation time versus temperature. (a) 4-6-PMA, \(\delta\), \(\alpha\) process and \(\alpha, \alpha\) process; (b) 4'-6-PMA, only one process \(\alpha)(\triangle)\) was observed. Dashed curves represent Vogel-Fulcher-Tammann-Hesse (VFTH) fittings according to Equation (6. 8) in the temperature region below \(T_{kink}\). \(T_g\) and \(T_{ni}\) are respectively glass transition and isotropic transition from DSC scan.
has been detected. This $\alpha$ process of 4′-6-PMA can virtually be thought of as a combination of two processes rather than a single $\alpha$ process in original sense of rotational modes. In short, in this case, a constitutional isomerism leads to a conformational isomeric configuration.

**Activation energy**

The relaxation times obtained from HN data fitting versus temperature are shown in Fig. 6-4. Overall, the relaxation time for each process decreases from approximately $10^{1.5}$ sec to $10^{-6.2}$ sec as temperature increases from the glass transition ($T_g = 302$ K) to 400 K. There is a kink near the nematic–isotropic transition $T_{ni}$. For 4-6-PMA, see Fig. 6-4(a), the kink temperature $T_{kink}$ for both $\alpha$ and $\delta$ processes is approximately 378K, about 9 K below its $T_{ni} = 372$ K. For 4′-6-PMA [see Fig. 6-4(b)], $T_{kink} = T_{ni} = 372$ K. When the temperature goes above $T_{kink}$, each process appears to have an Arrhenius characteristic, i.e., activation energy $E_A$ is independent of temperature. The Arrhenius expression is,

$$\tau = \tau'' \exp \left( \frac{E_A}{RT} \right)$$  \hspace{1cm} (6.7)

where, $\tau''$ is a high-temperature limited relaxation time; $R$ is the gas constant, 8.314 J/Kmol. The kink temperature $T_{kink}$ is practically the nematic–isotropic transition $T_{ni}$, even though it sometimes differs from the $T_{ni}$ obtained by DSC measurement. In the isotropic phase, where the nematic director field disappears, the activation energy $E_A$ is approximately 36 kJ/mol and 37 kJ/mol, respectively for the $\delta$ process and $\alpha$ process of 4-6-PMA; $E_A = 56$ kJ/mol for 4′-6-PMA. The $\delta$ and $\alpha$
processes of 4-6-PMA have a very close activation energy, which is typical of the isotropic phase behavior. The fact that 4'-6-PMA has a higher activation energy in the isotropic phase than any of two processes of 4-6-PMA and smaller than the sum of them reflects, to some extent, that the 4'-6-PMA relaxation process is a combination of the two processes.

When both samples are in the nematic phase, $T_g < T < T_{kink}$, the relaxation times are strongly dependent upon temperature, especially when the temperature approaches to $T_g$ (see Fig. 6 - 4), exhibiting a non-Arrhenius characteristic. The key concept for systematically synthesizing side-chain LCPs is an introduction of a flexible spacer between the liquid crystal mesogenic side group and the polymer backbone [39,40]. Although the spacer helps decouple the motion of the mesogenic group from the main chain and this decoupling becomes more effective with increasing spacer length, this kind of decoupling is nevertheless incomplete. Each relaxation process of the mesogens in nematic phase will still be influenced by the flexibility and motion of the polymer backbone, in particular, when the temperature approaches to the glass transition from the nematic phase the relaxation times will be rising much faster than that indicated by an Arrhenius behavior [Equation (6.7)]. Based on free-volume theory [41], this type of glassy behavior can be described by Vogel-Fulcher-Tammann-Hesse (VFTH) equation (17),

$$
\tau = \tau^0 \exp\left(\frac{B}{T - T^*}\right)
$$

(6.8)

where, $\tau^0$ is a short-limited relaxation time, in most cases, between $10^{-12}$
sec and $10^{-10}$ sec; B is an activation parameter; $T_\alpha$ is called Vogel temperature or the ideal glass temperature, usually a few 10-degrees below $T_g$. The dashed curves in Fig. 6 - 4 represent the VFTH fitting in the temperature range from $T_g$ to $T_{kink}$, and the VFTH fitting parameters for each process are listed in Table 6 - 3. The Vogel temperature $T_\alpha$ is 233.6 K and 227.8 K, respectively for the $\delta$ and $\alpha$ processes of 4-6-PMA while 269.6 K for 4'-6-PMA.

It is of interest that a general form of the effective activation energy for each process can be derived. From Arrhenius expression Equation ( 6. 7 ), one can have a generalized format for an activation energy,

$$E_A = R \frac{\partial \ln \tau}{\partial (1/T)} \quad (6. 9)$$

Because the samples are in nematic phase $T > T_g$, then $(T_\omega/T) < (T_g/T) < 1$, together with VFTH Equation (6. 8), we have,

$$\frac{\partial \ln \tau}{\partial (1/T)} = B \frac{\partial}{\partial (1/T)} \left( \frac{1}{T - T_\omega} \right) = \frac{B}{(1-T_\omega/T)^2} \quad (6. 10)$$

Finally,

$$E_A = \frac{R \cdot B}{(1-T_\omega/T)^2} \quad (6. 11)$$

It follows that the temperature dependence of an activation energy for any relaxation process can be expressed in terms of parameters B and Vogel temperature $T_\omega$ from VFTH Equation (6. 8). Fig. 6 - 5 on page 166 plots the activation energies versus temperature according to Equation (6. 11). The activation energy for the $\alpha$ process of 4'-6-PMA, $E_{A_{\alpha-PMA}}^{4'-6-PMA}$,
Table 6.3  Results from Vogel-Fulcher-Tammann-Hesse Eq. (6.8) for the Two Major Processes of 4,6-PMA and 4'-6-PMA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau^0$ ($10^{-10}$ sec)</th>
<th>$B$ (K)</th>
<th>$T_m$ (K)</th>
<th>$\alpha$ process</th>
<th>$\tau^0$ ($10^{-10}$ sec)</th>
<th>$B$ (K)</th>
<th>$T_m$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,6-PMA</td>
<td>0.191</td>
<td>2034</td>
<td>233.6</td>
<td>1.294</td>
<td>1435</td>
<td>227.3</td>
<td></td>
</tr>
<tr>
<td>4'-6-PMA</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.287</td>
<td>899.7</td>
<td>269.6</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 6.5  Activation energy from a general formula Equation (6.11) composed of FVTH parameters. 
⊙, δ process and ◦, α process of 4-6-PMA; 
Δ, α process of 4′-6-PMA.
lies between the α process $E^{4\rightarrow6}_{\alpha,\alpha}$ and the δ process $E^{4\rightarrow6}_{\alpha,\delta}$ of 4-6-PMA as long as the temperature is above 325 K. For 4-6-PMA, the trans–methylstilbene in the side chain can be treated as rigid-rod-like. It needs very large energy to overcome the nematic director field along the nematic direction (approximately along the long axis of the molecule) to be activated rotating about its short axis (δ process), while the rotation about its long axis associated with α process needs a relatively small activation energy. For $4'\cdot6$-PMA, the cis–methylstilbene in the side chain has an intermediate dipole moment coupling with a nematic field to form a localized potential that is roughly equivalent to an activation energy that the molecule overcomes to perform the relaxation process. It is therefore very natural that $E^{4\rightarrow6}_{\alpha,\alpha} < E^{4\rightarrow6}_{\alpha,\alpha} < E^{4\rightarrow6}_{\alpha,\delta}$ in the temperature range above 325 K. From this point of view, the argument about trans–4-6-PMA and cis–4'–6-PMA appears reasonable. However, $E^{4\rightarrow6}_{\alpha,\alpha}$ deviates in the region between $E^{4\rightarrow6}_{\alpha,\alpha}$ and $E^{4\rightarrow6}_{\alpha,\delta}$ when $T < 325$ K, and the $E^{4\rightarrow6}_{\alpha,\alpha}$ increases rapidly as the temperature approaches $T_g$ (see Fig. 6 - 5). The cause of this complex activation process of the side group mesogens, with the glassy state of the polymer, remains unclear.

In the neighborhood of the kink temperature $T \leq T_{kink}$, $E^{4\rightarrow6}_{\alpha,\alpha} = 82.5$ kJ/mol, $E^{4\rightarrow6}_{\alpha,\delta} = 127.2$ kJ/mol, and $E^{4\rightarrow6}_{\alpha,\alpha} = 87.2$ kJ/mol. The difference in activation energies at $T_{kink}$, $E^\alpha_{\alpha} - E^\alpha_{\delta}$, may be related to the corresponding enthalpy change in DSC scan. The total $E^\alpha_{\alpha} - E^\alpha_{\alpha}$ for 4-6-PMA ($\alpha + \delta = 137$ kJ/mol) is much larger than that for $4'\cdot6$-PMA ($\alpha = 31$ kJ/mol), which is qualitatively consistent with the DSC measurement [8,9].
6.4 CONCLUSION

From broad band frequency dielectric relaxation spectra, incorporated into Havriliak-Negami dielectric empirical line shapes, there are two typical relaxation processes (low-frequency δ and high-frequency α) in a nematic liquid crystalline polymethacrylate containing 4-methoxy-4′-hydroxy-α-methylstilbene mesogenic side group (4-6-PMA), while the corresponding polymethacrylate the containing constitutional isomeric mesogenic side chain (4′-6-PMA) hardly exhibits both δ and α processes even in a homeotropic cell subjected to an 8-Tesla magnetic field. A hypothesis of trans-4-6-PMA and cis-4′-6-PMA has been suggested in a light of the behavior of the relaxation time and activation energy for each individual process. A general formula for a temperature-dependent activation energy has been expressed in terms of Vogel-Fulcher-Tammann-Hesse parameters. The “kink” temperature in the relaxation time diagram is virtually at the nematic–isotropic transition point.
REFERENCES


(c) Maier, V. W. and Saupe, A, Z. Naturf. (a) 15, 287 (1960).


[27] Debye, P, Ann. Physik. 39, 789 (1921); Polar Molecules, Dover


Chapter 7

PMMA/E7 Polymer-Dispersed Liquid Crystal

7.1 INTRODUCTION

Recently, both basic and applied studies on polymer-dispersed liquid crystals (PDLCs) have been intensified since this new class of electro-optical materials may be tailored for a wide variety of applications, ranging from switching windows to active matrix projection displays and shutters for infrared cameras \[1,2\]. Usually, the PDLC films sandwiched between two conducting glass plates can be switched from a scattering state to a transparent state under certain AC electric field conditions. The complex electrical nature of the liquid crystal (LC) droplets in the PDLC materials arises because of the strong dipole moments of the LC along with interfacial charge layers between the droplets and the polymer matrix or between the electrodes and the PDLC samples as a result of the interactions with the applied electric field \[3\]. The dielectric relaxation
spectroscopy method can be used to detect these electric complications over a wide temperature and frequency range, which are also very sensitive to the DC conductivities due to conducting impurities and the interfacial charge layer effect. The existing theories on dielectric behavior in heterogeneous systems can be adapted to the PDLC system as a result of its phase separated nature [4,5].

In this chapter, we focus on the dielectric behaviors of 50 wt.% LC droplets (E7) in the polymer matrix (PMMA) in the temperature region in which the liquid crystal transforms from its nematic-like semicrystalline phase to its nematic liquid phase [6]. There are two distinct dielectric relaxation processes in the LC droplets, labeled \( \delta \) (low-frequency peak) and \( \alpha \) (high-frequency peak), in the temperature region below its nematic transition or melting point (220–250 K), which are similar to the two processes in pure E7, except the corresponding temperature for each process is about 5 K lower than that of pure E7. The additional measurements on the influence of the different concentration of E7 (10–70%) indicates that at a given temperature, the \( \delta \)-relaxation peak in the 50% mixture occurs at the “fastest” relaxation frequency, about 0.5 decade higher than the pure E7, although they all have similar non-Arrhenius behavior. The two processes disappear below 30% of E7, at which the PDLC sample is no longer phase separated as observed in an optical microscope. The Maxwell-Wagner (MW) effect, due to the interfacial charge buildup between the conducting LC droplets and the surrounding polymer matrix, has been observed in the low-frequency side (< 100 Hz) in the neighborhood of the nematic transition of the droplets.
This effect may screen the LC droplets from the external electric field and govern the driving frequency, as well as the driving voltage to switch the PDLC film. This result has confirmed Kelly and Seekola's work based on the same materials [3] but has been extended to below room temperature where the nematic transition of the droplets takes place. The excitation level influence on the dielectric loss of the 50% E7/PMMA at room temperature gives an interesting result: the MW frequency \( f_{MW} \), is independent of the level and its magnitude changes when the voltage increases from 1 to 20 V. The \( f_{MW} \), may be a crucial parameter to be related to the practical driving frequency for a PDLC material.

### 7.2 Experimental

#### Materials

The chemical structures of the constituent LC (E7) and polymer (PMMA) for the PDLC film are given in Fig. 7 - 1, page 175.

E7, a thermotropic nematic liquid crystal, was purchased from EM Industries, Inc., a distributor of BDH Ltd., Poole, England. E7 is a eutectic mixture of a number of cyanobiphenyls and cyanoterphenyls with a positive dielectric anisotropy, \( \varepsilon'_i = 18 \), \( \varepsilon'_\perp = 6 \), at 1 kHz frequency and room temperature. The conductivity of E7 is typically measured to be near \( 10^{-7} \) S/m for commercial grade stock and the phase transition points \( T_{kn} = 263 \) K, \( T_{ni} = 334 \) K, where \( k, n, \) and \( i \) stand for crystalline, nematic, and isotropic phases respectively.
PMMA:
\[
\begin{align*}
\text{CH}_3 &\quad \text{CH} - \text{CH}_2\!\uparrow_n
\end{align*}
\]
\[
\begin{align*}
\text{C} = \text{O} &\quad \text{O} \quad \text{CH}_3
\end{align*}
\]

e7:

51% 5CB  \quad \text{CH}_3 \!\uparrow \text{CH}_2\!\uparrow_4 \text{CH}_2\!\uparrow_4 \text{CH}_2\!\uparrow_4 \text{CH}_2\!\uparrow_4 \text{CH}_2\!\uparrow_4 \text{CH}_2\!\uparrow_4 \text{C} = \text{N}

25% 7CB  \quad \text{CH}_3 \!\uparrow \text{CH}_2\!\uparrow_6 \text{CH}_2\!\uparrow_6 \text{CH}_2\!\uparrow_6 \text{CH}_2\!\uparrow_6 \text{CH}_2\!\uparrow_6 \text{CH}_2\!\uparrow_6 \text{C} = \text{N}

16% 8OCB \quad \text{CH}_3 \!\uparrow \text{CH}_2\!\uparrow_7 \text{O} \quad \text{CH}_2\!\uparrow_7 \text{CH}_2\!\uparrow_7 \text{CH}_2\!\uparrow_7 \text{CH}_2\!\uparrow_7 \text{CH}_2\!\uparrow_7 \text{CH}_2\!\uparrow_7 \text{C} = \text{N}

8% 5CT \quad \text{CH}_3 \!\uparrow \text{CH}_2\!\uparrow_4 \text{C} = \text{N}

\text{Fig. 7 - 1} \quad \text{Chemical structures of the PDLC film: polymer matrix PMMA and nematic liquid crystal E7.}
We chose a low molecular wt \( M_w = 12,000 \) thermoplastic PMMA as a polymer matrix in the PDLC film. Electrically, PMMA is a very poor conductor when in the glassy state at the temperature below its \( T_g \) \((70–110 \, {^\circ}\text{C})\) with a conductivity of \(10^{-11} \, \text{S/m} \) at room temperature, and a dielectric constant of about 3.

**Preparation of PDLC Films**

The PDLC film was prepared by using the thermally induced phase separation (TIPS) [7]. A 50 wt.% E7 was dissolved with PMMA in chloroform solution and solvent cast. The sample, sandwiched between two ITO (Indium Tin Oxide, 200 \( \Omega/\square \)) glass plates, was heated to about 120 \( ^\circ \text{C} \) and then was fast cooled to room temperature to induce phase separation, with droplet size of 1.5–2 \( \mu \text{m} \) [8]. The sample thickness is 40 \( \mu \text{m} \) and the corresponding empty cell capacitance \( C_0 \), is about 100 pF. The other percentage samples were made in the same way.

**Differential Scanning Calorimetric Measurement**

In order to determine the glass transitions of E7 and the LC droplets in the PDLC sample, which are usually below room temperature for low molecular weight materials, DSC measurements were conducted from 120 to 459 K at a heating rate of 10 K/min using a Dupont 910 instrument. The PDLC sample was taken from the ITO glass cell. Each sample was measured at least three times.

**Dielectric Measurement**

The dielectric spectra were for the most part measured with a ratio-
arm transformer bridge ( CGA-83 ) with 17 frequencies in logarithm ratio from 10 Hz to 100 kHz at its least oscillation level ( = 0.1 V ). The oscillation level dependence measurements were taken with an HP-4284A LCR meter ( 1–20 V, 20 Hz–1 MHz ). The sample was mounted in a cryostat controlled by a Lakeshore temperature controller, which can stabilize temperature within 10 mK. The whole data acquisition system was completely controlled by an HP-87 computer through the IEEE 488 interface bus. The relation between the complex dielectric constant ( \( \varepsilon^* \) ) and the measured capacitance ( \( C \) ) and loss ( \( G/\omega \) ) is given by the following, with empty cell capacitance \( C_0 \):

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)
\]

\[
\varepsilon'(\omega) = C(\omega)/C_0
\]

\[
\varepsilon''(\omega) = [G(\omega)/\omega - G_{dc}/\omega]/C_0
\]

### 7.3 RESULTS AND DISCUSSION

**DSC Results**

The phase transitions for pure E7 and the PDLC sample are summarized in Table 7 - 1, page 178. E7 has a glass transition \( T_g \) at 209 K [9]. While there might be a semicrystalline phase between \( T_g \) and \( T_k \) ( 262 K ), the unknown transition happens at 255 K. The nematic transition or melting point \( T_{kn} \) and the isotropic transition \( T_{ni} \) are slightly different from that listed by the manufacturer.

The result of the 50%E7/PMMA sample (Fig. 7 - 2) shows that there
### Table 7 - 1. Phase Transitions from DSC measurement.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase Transitions (K)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$</td>
</tr>
<tr>
<td>E7</td>
<td>$g$ 209 $k'$ (255 unknown) 262 $k$ 264 $n$ 329 $i$</td>
</tr>
<tr>
<td>50%E7/PMMA</td>
<td>$g_{IPMMA}$ 248 $k$ 258 $n$ 313 $i$</td>
</tr>
</tbody>
</table>

<sup>a</sup> $g$, glass; $k'$, semicrystalline; $k$, crystalline; $n$, nematic; $i$, isotropic of E7 or its droplets in the PDLC sample. The $g_{IPMMA}$ is the low-temperature glass transition of the PMMA matrix in the PDLC sample.
Fig. 7 - 2  DSC result of the 50%E7/PMMA PDLC sample at a heating rate of 10 K/min. All the phase transition points are referred to LC droplets unless the specification is in a subscript.
still exists the crystalline (248 K), nematic (258 K), and isotropic (313 K) transitions of LC droplets; however, compared with pure E7, these phase transitions have shifted to lower temperature positions by 14, 6, and 16 K, respectively. Also, the crystalline and nematic transitions are strongly overlapped by a second-order transition, which may be associated with the β relaxation or low-temperature glass transition of PMMA in the PDLC sample. This β transition is about 22 K lower than that of pure PMMA (T_{gPMMA} = 270 K), considering DSC has a 1-Hz measuring frequency [10]. From this point of view, the 50% PDLC sample is well phase-separated.

**Dielectric Relaxation of the Pure E7 near its T_g**

The dielectric loss spectra (see Fig. 7-3) have been measured on three E7 samples with different macroscopically aligned configurations, i.e., unaligned, homeotropic, and planar or homogeneous, obtained by different surface treatments on the ITO glass plates. Special emphasis has been placed on the temperature range from 220 to 260 K since E7’s glass transition lies at the lower end, above which the sample is a nematic-like semicrystalline solid and is dielectrically active.

Two processes are observed, labeled δ (low frequency) and α (high frequency) as seen in the previous chapter, for each E7 sample in the region just above T_g, although their magnitudes change dramatically around 240 K. The δ peak is much larger than the α peak at a given temperature in these three different aligned samples. In the homeotropic sample, the low-frequency peak height is larger than and the high-
Fig. 7 - 3  Dielectric loss relaxation spectra of the pure E7 in the temperature range 228–240 K ( □, 228 K; △, 232 K; ◆, 236 K; ○, 240 K). (a) Homeotropic alignment; (b) planar or homogeneous alignment.
frequency peak lower than the corresponding homogeneous sample. Here, we assign these two processes in terms of the rotational diffusion theory in nematics [11], see § 2.4 and Fig. 2 - 1.

To be consistent with the traditional assignments, we designate the δ peak to the 180° rotation of the longitudinal components of the dipole moments in the LC about their short axis, and the α peak is thought to be coupled, to a few modes, with both longitudinal and transverse components of the dipole moments with major contribution being from the rotation of the transverse dipole moments about their long axis. It is not surprising that the δ-process is much stronger than the α-process because the cyano head (−C≡N) has a large dipole moment (≈ 5 Debye) in comparison with oxy group (−O−) in 8OCB, a 16% constituency of E7. The longitudinal component μ₁ is much bigger than the transverse μ₉, and so, the δ peak associated with μ₁ is quite large.

In this initial study, we show the loss-maxima versus reciprocal temperature only for the δ process, see Fig. 7 - 4, which has a non-Arrhenius behavior as the temperature approaches Tₙ. The activation energy for this process is about 100 kJ/mole for all three alignment configurations, which is in reasonable agreement with what Zeller found on similar LC mixture [9].

**Dielectric Relaxation in the PDLC Samples**

Fig. 7 - 5 shows ε' and ε'' of the 50%E7/PMMA sample at 1 kHz as the temperature increases from 160 to 330 K. There are four processes,
Fig. 7 - 4  Arrhenius diagram for the δ process of the pure E7 with the different alignment configurations: Δ, unaligned; ○, homeotropic; □, planar.
Fig. 7 - 5  Temperature dependence of the complex
dielectric constant at 1 kHz for the 50%E7/PMMA
film. (a) Real part $\varepsilon'$; (b) imaginary part $\varepsilon''$. The
four labeled peaks are illustrated in the text.
labeled by $\delta_{LC}$, $\alpha_{LC}$, $MW$, and $\beta_{PM}$, which respectively represent $\delta$ and $\alpha$ processes of the LC droplets, M-W process of the interfacial charge layer between the LC droplets and the polymer matrix, and a low-temperature $\beta$ relaxation of the polymer matrix. It will be seen from the following discussion that these assignments are reasonable.

The glassy transition behavior of the LC droplets in the PDLC sample has been observed in the dielectric relaxation spectra in the temperature range from 220 to 250 K (see Fig. 7 - 6, page 186), although it was not observable in our DSC measurement (see Fig. 7 - 2, page 179). The thermo-kinetic nature glass transition of the LC droplets seems to be lowered by about 5 K in the PDLC sample as compared with the corresponding relaxation process in the pure E7, for instance, the 1 kHz loss maximum of the PDLC peaks at 238 K while that of pure E7 is at 242 K. Being similar to E7, we assign these two processes to the $\delta$ and $\alpha$, respectively. The $\alpha$ peak sits on the shoulder of the $\delta$ peak. Compared to the 50% mixture and pure E7 in the Arrhenius plot of Fig. 7 - 7 the two curves have almost the same activation energy at a given temperature, but the relaxation frequency of the droplets is approximately 0.5 decade higher than that of pure E7, which reflects about a 5 K difference in temperature.

These two processes coalesce at about 250 K, where a strong, broad $\beta$ relaxation of PMMA and some other first-order transitions of the droplets, such as crystalline and nematic observed in the DSC, have appeared. The low-temperature $\beta$ relaxation of the PMMA in the PDLC sample occurs at about 22 K lower than that in pure PMMA, for example.
Fig. 7 - 6  Dielectric relaxation spectrum of the LC droplets in the 50%E7/PMMA PDLC film ( □, 220 K; △, 225 K; ○, 230 K; ○, 235 K ).
Fig. 7 - 7 Arrhenius diagram for the d process of the PDLC film with the different concentrations of E7: X, 40%; □, 50%; ◇, 60%; Δ, 70%; ○, 100%.
Also, the 10-Hz loss peak is at 285 K in the PDLC while 307 K in pure PMMA [10]. This is consistent with the DSC, assuming the DSC has an effective 1-Hz frequency. Here, we just treat this β relaxation as a background for the other more important processes. Kelly and Seekola did not observe this kind of relaxation behavior of the droplets in the solid state since their dielectric measurement was conducted with the sample in the liquid state above room temperature [3].

The additional experiment regarding the influence of different E7 concentration mixture (10–70%) in the PDLC samples shows the amplitude of the δ peak increases with increasing concentration of E7 and the peak vanishes below the 30% concentration, where no phase separation is observed. The activation energies of δ peaks, proportional to the tangential slope in the Arrhenius plot (see Fig. 7 - 7), are approximately the same, independent of concentration. However, at a certain temperature, the relaxation frequency deviates with the different percentage of E7, and our 50% sample has the highest relaxation frequency among all the samples, about 0.5 decade higher than that of E7. From the phase diagram of a PDLC prepared by TIPS [2], the 50% liquid crystal sample usually has the highest temperature dividing the two-phase region and the homogeneous region, which implies that the 50% sample has the maximum phase separation. It can also be interpreted that the 50% sample has the largest ratio of the LC droplets in the sample, or highest percentage of phase separation. From this point of view, the frequency shift relative to the pure liquid crystal may reflect the amount of the LC droplets in the PDLC sample, assuming that the droplet
size roughly remains same. Using this result in practice, the dielectric relaxation technique may alternatively provide a potential tool to electrically evaluate the degree of phase separation, besides the size of the droplets, in such a heterogeneous system.

**M·W Effect**

A MW effect [12] has been observed in the temperature range from 280 to 320 K (see Fig. 7 - 8 on page 190), which is attributed to the charge buildup at the interface between the LC droplets and polymer matrix, in the light of the fact that the droplets have a much higher conductivity than the polymer ($\sigma_{LC} = 1.4 \times 10^{-7}$ S/m, $\sigma_{PMMA} = 1.4 \times 10^{-10}$ S/m in the 60%E7/PMMA system [3]). This interfacial conducting process depends strongly upon temperature in the neighborhood of the nematic transition and occurs mainly in the low-frequency side ($f < 100$ Hz). The loss peak amplitude increases from 280 to 305 K and decreases rapidly from 305 to 320 K. This effect may play an crucial role in the electro-optic properties of the PDLC film, and may determine the driving frequency and voltage. For a low-frequency driving voltage, e.g., $f < 100$ Hz, the interfacial charge layers may screen the LC droplets from coupling with the external electric field. In other words, the electric field inside the LC droplets is so small that it cannot turn their nematic directors along the normal of the film layer to match the index of the polymer matrix. This is the main reason why there is a threshold frequency, at a given voltage and temperature, to switch the PDLC film from a scattering state to a transparent state.

In order to search for a correlation between the driving voltage and
Fig. 7 - 8  MW peaks in the 50%E7/PMMA film as temperature increases from 285 to 315 K with 5 K step ( +, 285 K; □, 290 K; △, 295 K; ○, 300 K; ○, 305 K; ●, 310 K; X, 315 K ).
Fig. 7 - 9  The changes in MW peak of the 50\%E7/PMMA with different oscillation levels at room temperature: □, 1 V; △, 10 V; ◊, 15 V; ◦, 20 V.
the MW effect, measurements were made on the 50% E7/PMMA at room
temperature with an HP bridge (20 Hz–1 MHz, 1–20 V/rms). The loss
spectrum at four different oscillation levels is shown in Fig. 7-9. The
driving voltage from 1 to 20 V changes the loss amplitude by a factor of
1.4 at the MW frequency ($f_{MW} = 101.5$ Hz) with the peak frequency
remaining unchanged. It appears that there might be a threshold voltage
of about 10 V for the amplitude change. That the MW loss peak decreases
in amplitude as the excitation level increases implies that the interfacial
charge layer can be “electrically” thinner and the internal field of the
droplets can be raised as the driving voltage is increased. From another
point of view, the interfacial layer can maximally shield electric field and
the droplets consume the least energy from the applied electric field when
the frequency sits at the MW loss maximum $f_{MW}$; the droplets can be
efficiently coupled with a certain a.c. field and consume a sufficient
energy to “turn themselves round” when $f >> f_{MW}$. However, it is worth
pointing out here that the change of loss with voltage can also be caused
by the different structural configuration in the nematic droplet (i.e.,
radial, axial, bipolar, etc. [13]) induced by the applied electric field and
then the droplet structure changes its interfacial layer with the polymer
matrix. Again, the increase or decrease in the dielectric loss with the
applied field may also depend on the nematic droplet configuration as well
as its initial polarization. In any event, the proper driving frequency for
switching at a given temperature should be chosen at higher than $f_{MW}$ to
avoid possible screening. There are at least three loss mechanisms in
terms of oscillation level, all of which may attribute to the M-W effects
associated with three different interfaces, i.e., polymer–electrode,
LC-polymer, and LC-electrode, with the LC-polymer interface playing the major role.

This MW effect mainly associated with the LC-polymer interface was also observed by Kelly and Seekola in their PMMA/60%E7 sample at room temperature, which peaks at about $10^{2.2}$ Hz [3]. The peak position of our 50%E7/PMMA is at $10^{1.5}$ Hz, considerably lower than theirs, which might result from two factors. One is the different frequency response of the interfacial charge layer for the different percentage of E7 in polymer matrix; another is that the measuring temperatures were not identical in the two experiments. Our above "screening" explanation for the LC droplet qualitatively agrees with the model prediction for the relative electric field inside the droplet as a function of the driving frequency for their PMMA/60%E7 sample [3].

7.4 CONCLUSION

The PDLC sample exhibits two relaxation processes in the liquid crystal droplets in the nematic-like semicrystalline solid, which have been attributed to the glassy behavior of the droplets. The mixture of liquid crystal with polymer matrix results in a faster relaxation in the liquid crystal droplets at a certain temperature as compared with that in pure liquid crystal. The dielectric relaxation method may provide a potential tool to monitor the phase separations in a PDLC film. The MW frequency $f_{MW}$, at room temperature is independent of the applied voltage and is an important parameter in determining the driving frequency for switching.
REFERENCES


Chapter 1


[44] Zentel, R., Strobl, G., and Ringsdorf, H., in Recent Advances in
Chapter 2


Chapter 3


Chapter 4


Chapter 5


Chapter 6


Akins, R. B., “Dielectric Properties of PMMA/E7 Polymer

Percec, V, “Dielectric Relaxations of a Smectic Side-Chain Liquid
Crystalline Polymer in Different Alignment States”, Mol. Cryst.


[32] Kresse, H., Ernst, S., Frücke, B., Kremer, F., and Vallerien, S. U.,


[35] Hedvig, P., Dielectric Spectroscopy of Polymers; John Wiley &


[37] Ogawa, K, Sano, T., Yoshimura, S., Takeuchi, Y., and Toriumi,


[39] Percec, V and Pugh, C., In Side Chain Liquid Crystal Polymers;
edited by C. B. McArdle, Chapman and Hall, New York, p 30
(1989).

Spacer Length on the Dielectric Relaxation of a Side-Chain

[41] McCrum, N. G., Read, B. E., and Williams, G, Anelastic
Dielectric Efforts in Polymeric Solids; Dover Publications, p169
Chapter 7


