Macromolecules **1995,** *28,* 6423–6431

Effect of Alkyl Chain Spacer Length on the Dynamics of Glass Transition in Side-Chain Liquid-Crystalline Polymers

K. L. Ngai*

Naval Research Laboratory, Washington, D.C. 20375-5320

S. Etienne

Laboratoire de Metallurgie Physique et Science des Materiaux, URA CNRS 155,
Ecole des Mines de Nancy, Parc de Saurupt, 54042 Nancy Cedex, France

Z. Z. Zhong and D. E. Schuele

Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079

Received March 10, 1995; Revised Manuscript Received June 16, 1995®

ABSTRACT: The influence of the flexible alkyl chain spacer on the molecular dynamics of glass transition in side-chain liquid-crystalline polymers (SCLCPs) and its dependence on the spacer length are considered in the framework of the coupling model. Short spacer length may enable the mesogenic groups in the side chain to enhance the degree of cooperativity of the segmental dynamics responsible for glass transition compared with that of the corresponding parent main-chain polymer without the side chains. However, when the spacer length becomes long, not only motions of the mesogenic group and the main chain are decoupled but also the preponderance of flexible methylene chains in the vicinity of the polymer backbone will diminish the degree of cooperativity of the segmental dynamics compared with that of the corresponding parent main-chain polymer without the side chain. The degree of cooperativity is quantified in the coupling model for SCLCPs by the steepness of the plot of a characteristic relaxation time, τ^*, of the segmental relaxation time spectrum against normalized reciprocal temperature, T_g/T, where T_g is operationally defined as the temperature at which $\tau^*(T_g)$ is equal to an arbitrarily chosen but fixed long time. Dielectric and mechanical relaxation data of several families of SCLCPs published in the past 10 years are used to test this prediction. The results from the analysis of these data are in accord with the predicted trends.

Introduction

There is sustained interest from both basic and applied research communities in thermotropic comblike liquid-crystalline polymers, consisting of a flexible polymeric backbone with mesogenic groups attached to it in the side chains, since they were first[1-3] synthesized in 1978. A flexible spacer which usually consists of an alkyl chain $(-CH_2-)_m$ is inserted in the side chain between the polymer main chain and the mesogenic group to minimize the mutual interaction between the mesogenic groups and the polymer chain. With the presence of the spacer the mesogens can reorient with minimal reordering of the polymer backbone. These materials having desirable mechanical properties of polymers and optical properties of thermotropic liquid crystals are useful in device applications. By now a variety of these side-chain liquid-crystalline polymers (SCLCPs) have been made, having therein acrylate, methacrylate, siloxane, vinyl ether, or phosphazene main chains.[4-8] Dielectric spectroscopy[9-21] and nuclear magnetic resonance spectroscopy[22,23] were primarily the tools used by many workers to probe the various molecular motions below and above the glass transition temperature. Recently, low-frequency dynamic mechanical spectroscopy was employed for the first time to investigate the glass transition in SCLCPs.[24] From these spectroscopic studies in a variety of SCLCPs, the nature of the molecular motions observed has been identified. The glass transition is of interest even from the device application point of view. This is because most of these SCLCPs are in the glassy liquid-crystalline state at ambient temperatures, and they must be heated up across the glass transition temperature to a temperature close to the liquid crystal–isotropic liquid transition region in order to obtain reasonably short optical response times to applied electric or magnetic aligning fields.

From a basic research point of view the SCLCPs having the interesting property of being able to freeze liquid-crystalline order into the glassy state ("glassy" liquid-crystalline state) offer a new class of materials to study the molecular dynamics of glass transition. Since the material is polymeric, the glass transition must be affected by the segmental motion of the backbone. An interesting aspect of the segmental motion of SCLCP that is worth looking into is the extent to which the presence of the alkyl spacer and the mesogenic group affects the dynamics. Since the spacer length is a variable, another interesting question to ask is the dependence of the dynamics on the spacer length. The synergism of applied and basic research often, as in the case of SCLCPs, leads to a spate of experimental data of the molecular dynamics of a variety of materials. The opportunity is here to extract new physics from these vast amounts of experimental data accumulated over the past 10 years. If new physics of the glass transition were to be gained from a study of the molecular dynamics of glass transition in SCLCPs, then this would not be the first time that has happened for the liquid-crystalline systems. Möller et al.[25] have already found the dynamics of glass transition in a columnar hexagonal ordered phase of a liquid-crystalline system formed by a chiral discotic mesogen is highly anisotropic and anomalous. The purpose of the present work is to take advantage of this opportunity provided by SCLCPs and starting from the experimental data come up with some conclusions of significance. How-

---

® Abstract published in *Advance ACS Abstracts,* August 1, 1995.

0024-9297/95/2228-6423$09.00/0

ever, to proceed in this manner, we need theoretical guidance of what to look for in the data, method to carry out the task, and how to interpret the final results. In this work we use the conceptual framework and the predictions of the *coupling theory*[26] as the means to unravel the intricate physics of glass transition dynamics contained in the data.

Dependence of Segmental Dynamics on Chemical Structure

The molecular motions of densely packed systems are necessarily cooperative in nature because there are dynamical constraints between the motions of the basic units that arise from their mutual interactions. How these dynamical constraints should be treated in an irreversible process (i.e., relaxation), in order to construct a theory that has predictions in agreement with experimental data, is a question that has remained unresolved. The coupling theory[26] is an attempt in this direction. In this theory, dynamical constraints have the effect of slowing down the averaged relaxation rate of the cooperative motions according to the time-dependent form of $(\omega_c t)^{-n}$, and n lying within the range $0 \leq n < 1$ is called the coupling parameter which quantifies the slowing down of the averaged relaxation rate of the mutually dynamically constrained motions. For a fuller description of the theoretical basis and applications of the coupling theory we refer the reader to recent reviews[26] and publications, some of which have appeared in this journal.[27-33]

The coupling parameter n is a monotonic increasing function of dynamical constraints. The correlation function of the relaxation has the Kohlrausch–Williams–Watts (KWW)[34,35] stretched-exponential form, $\exp[-(t/\tau^*)^{1-n}]$. This is usually true for segmental motions in many amorphous polymers that are not complicated by the presence of crystallinity,[36] diluent or another miscible polymer,[37] and long flexible side chains which cause internal blending.[38] These complicating factors when present will introduce heterogeneities which further broaden the dispersion of the segmental relaxation beyond that coming from the cooperative constraint dynamics in totally amorphous, undiluted, and unblended (whether externally or internally) homopolymer and as determined by the KWW stretched-exponential function in the time domain. The heterogeneities come from concentration fluctuations in the case of diluent blending with another polymer and internal blending with long flexible side chains. The broadening due to concentration fluctuation can be so severe in some cases[37-41] that it can completely obscure the KWW contribution. Under these circumstances the breadth of the experimentally observed dispersion bears no relation to the Kohlrausch exponent, $1 - n$, and the shape of the dispersion may even depart drastically from that of the family of KWW functions.[37-41] There is some similarity between the SCLCP of our present interest and the poly(*n*-alkyl methacrylates) which have flexible methylene side chains whose length can be varied. The side chain becomes very long in poly(*n*-lauryl methacrylate) (Pn-LMA), which is a member of the family of poly(*n*-alkyl methacrylates), with the structure of the alkyl group being $-(CH_2)_{11}CH_3$, and fluctuations of concentration of methylene chains in the vicinity of the methacrylate backbone are inevitable. Thus not only are local segmental motions of the methacrylate backbone intermolecularly and intramolecularly constrained but also they occur in different environments $\{i\}$ in which the local concentration of methylene chains fluctuates. The methylene chain is far more flexible and facile than the methacrylate backbone. As a consequence, methylene chains impose the least amount of dynamic constraints on other chains including the methacrylate backbones, and we may expect in Pn-LMA the coupling parameters n_i of segmental motions in environments i are, in general, smaller than that of poly(methyl methacrylate) (PMMA) which has $-CH_3$ as the alkyl group and no long methylene chain to speak about. Although we can anticipate that the coupling parameters n_i of local segmental motions in Pn-LMA should be small, this explanation cannot be verified directly by the experimental response function or loss spectrum (by dielectric and photon correlation spectroscopies) because of the additional heterogeneous broadening by concentration fluctuations.

However, all is not lost because the coupling theory has other predictions that, like the KWW correlation function, also depend on the coupling parameters n_i, but these predicted dependences on n_i are not obscured by the concentration fluctuations. An example of the other predictions is based on the T_g-scaled temperature dependence of a characteristic relaxation time such as the most probable relaxation time, $\tau_{max,P}$, of the local segmental relaxation time spectrum of a polymer, P. A T_g-scaled temperature dependence plot of $\tau_{max,P}$ is made by first making an arbitrary choice of a long time τ_g and an operationally defined *glass temperature* $T_{g,P}$ for each polymer such that $\tau_{max,P}(T_{g,P})$ is exactly the predetermined τ_g. With $T_{g,P}$ known the experimental data of $\tau_{max,P}(T)$ as a function of temperature for different polymers are replotted against the scaled reciprocal temperature variable $T_{g,P}/T$ or the scaled temperature difference variable $(T - T_{g,P})/T_{g,P}$. Each polymer has its own signature in this plot characterized by its slope and curvature. It is important to emphasize that the pattern of behavior obtained and the conclusion made do not depend on the choice of τ_g. In this manner and in the same plot the T_g-scaled temperature dependences of local segmental relaxation times of different polymers can be compared.[27,30,31,42] A fascinating question to ask is, what does such a comparison of these signatures of different polymers tell us about the difference in their molecular dynamics? The question is even more germane when the comparison is restricted to a subclass of polymers that can be related to each other by a systematic change in the chemical structure. One example of a subclass is the poly(*n*-alkyl methacrylates) where the change in the chemical structure is the length of the methylene chain in the side chain. The slope/curvature of the local segmental relaxation time in the $T_{g,P}$-scaled plot shows a monotonic decrease with increasing methylene chain length.[38,43] The correlation of the signature of local segmental motion with a systematic change in the chemical structure has been found in other subclasses. These include: (1) any component in a binary miscible blend on varying the composition,[37,44] (2) chemically cross-linked polymers with an increase in the density of cross-links,[32,33] (3) the polybutadienes with an increase in the 1,2 content in the microstructure,[45] and (4) diluted polymer with an increase in the diluent concentration.[46] SCLCPs have been made with variable length of the methylene chain in the spacer, starting with as short as $-(CH_2)_2-$. This analogy with the poly(*n*-alkyl methacrylates) naturally leads to the question of whether there is any systematic dependence of the slope/curvature of the segmental relaxation time of SCLCP in a $T_{g,P}$-scaled plot on the spacer length. An answer to this question will be given later in this work.

The history of the $T_{g,P}$-scaled plot and its use in the comparison of the molecular dynamics of various glass-forming liquids goes back a long way to Laughlin and Uhlmann[47] and Angell.[48,49] In the literature this plot is often referred to by others as the "fragility plot", although fragility is a misnomer for polymers and SCLCPs. This is because the chemical structures of these materials do not change with temperature and hence the terminology of "fragile" and "strong", which Angell[48,49] originally used to describe possible structural changes of *non*polymeric glass-forming materials with temperature, is improper for polymers and SCLCPs. An appropriate nomenclature for this kind of representation of data is the "cooperativity plot". To interpret the trends observed in the $T_{g,P}$-scaled plot, we have used the coupling theory. As has been explained in the earlier works,[27,30-33] a stronger $T_{g,P}$-scaled temperature dependence is due to an enhancement in the dynamic constraints opposing local segmental motion according to the coupling theory. In any of the examples of the study of local segmental relaxation with a systematic change in the chemical structure given in the previous paragraph, the direction of the corresponding change in dynamic constraints can be inferred without any ambiguity. Again, as an example, we cite the poly(*n*-alkyl methacrylates) which according to the reasoning given above should have the dynamic constraints decreased with increasing length of the side chains. Indeed in the $T_{g,P}$-scaled plot of the poly(*n*-alkyl metharylates) the steepness and curvature of the slope of the segmental relaxation time continuously decrease with increasing length of the side chains,[38,43] as anticipated by the coupling theory. There are other examples such as homopolymers[31,45] where the measured dispersions are consistent with correlation functions that have the Kohlrausch stretched-exponential form $exp[-(t/\tau)^{\beta}]$, and the stretch exponent, β, faithfully yields the coupling parameter, n, via the relation $\beta \equiv 1 - n$. In these examples, the experimentally obtained values of n indeed increase with the expected enhancement of dynamic constraints on varying the chemical structure and, at the same time, the steepness and curvature in the $T_{g,P}$-scaled plot also increase.

The consistency of the coupling theory demonstrated in the past for interpretating the change of molecular dynamics with chemical structure justifies our use of it once more to unravel the physics of molecular motions in SCLCPs. The situation here in SCLCPs bears some similarity to the poly(*n*-alkyl methacrylates) as far as the dependence on the spacer length is concerned. The spacer consisting of the methylene chain, $-(CH_2)_m-$, will mitigate the dynamic constraints of local segmental motion in SCLCP, and the effect increases with its length m. We expect from the coupling theory, even before making any attempt of examining the actual data, the local segmental relaxation time of SCLCP with identical polymer backbone and mesogenic group in a $T_{g,P}$-scaled plot will exhibit a decrease of the steepness and curvature with increasing spacer length, the same trend as observed in the poly(*n*-alkyl methacrylates). However, if the alkyl spacer is very short with length m equal to 2 or 3, the bulky and inflexible mesogenic group with possible steric constraints may now be appreciably coupled with the backbone to strengthen the dynamic constraints imposed on the local segmental motion. As a result the coupling parameter n_m of the local segmental motion in these short spacer SCLCPs may be even larger than the coupling parameter, n_{pP}, of the parent polymer which has neither the spacer nor the mesogenic group. Had it been possible to make the material with zero spacer length but having the mesogenic group still in the side chain, one can imagine in this ficticious material the coupling between the backbone and the bulky mesogenic group would be so strong that they move in concert to experience significantly enhanced intermolecular dynamic constraints impeding segmental motions. This extreme, but probably chemically unattainable, case should have a coupling parameter, $n_{m=0}$, significantly larger than n_{pP}.

When the alkyl spacer is introduced and as its length becomes longer, the motion of the polymer backbone is increasingly decoupled from that of the mesogenic group, as originally proposed by Finkelman and coworkers.[1-4] Not only will a more decoupled polymer backbone motion without involving the mesogen see less dynamic constraints but also the increasing presence of the flexible alkyl chains in its environment will reduce the coupling parameter n_m. If the alkyl chain is sufficiently long, fluctuations of the concentration of methylene molecules near the polymer backbone become inevitable. Concentration fluctuations engender a distribution of local environments for the backbone segments, a corresponding distribution of coupling parameters, $\{n_m\}$, and concomitant additional inhomogeneous broadening of the segmental relaxation spectrum, beyond that given by the Kohlrausch stretched-exponential $\exp[-(t/\tau^*)^{1-n_m}]$. Such a scenario has already been realized in miscible blends[37,44] and in poly(*n*-lauryl methacrylate).[38] This is likely the reason why the dielectrically measured α-relaxation spectra of SCLCPs with long alkyl spacer lengths are very broad.[9-21] Another source of broadening comes from the anisotropic mesogenic group which is coupled to the measuring field in several different modes. Hence, neither the distribution of coupling parameter n_m nor its most probable value $n_{m,\max}$ can be determined directly from the width and shape of the relaxation spectrum of a SCLCP with long alkyl spacer length. Thus, even though we expect the coupling parameter of a SCLCP with long spacer length to be smaller than that of another having short spacer length, this expectation cannot be verified by comparing their segmental relaxation spectrum. However, we shall use the other prediction of the coupling theory on the steepness/curvature of the $T_{g,m}$-scaled temperature dependence of the most probable relaxation time $\tau_{\max}$ is proportional to the corresponding most probable coupling parameter $n_{m,\max}$. If the expected dependence of the local segmental motion on spacer length is true, then the $T_{g,m}$-scaled temperature dependence of $\tau_{m,\max}$ of SCLCP belonging to the same family (i.e., same polymer backbone and mesogenic group) will have its steepness/curvature decreasing with increasing spacer length m. If we include the parent polymer in the comparison with SCLCP, then there is the possibility that $\tau_{m,\max}$ for short m, like 2 or 3, may have comparable or even larger steepness/curvature than that of τ_{pP}. However, it is certain that when m becomes large, the steepness/curvature of $\tau_{m,\max}$ will be smaller than that of τ_{pP}. Bringing in the parent polymer of the SCLCP and its local segmental relaxation dynamics to compare with those of the SCLCP enriches as well as bridges the discussion of glass transition in both the amorphous homopolymers and the SCLCPs.

We have basically assumed that $n_{m,\max}$ is temperature independent. The possibility that $n_{m,\max}$ were temperature dependent, increasing as the temperature is decreased toward T_g as found in dielectric relaxation of some glass-forming liquids, cannot be ruled out at this time. If $n_{m,\max}$ has a temperature dependence, then, according to both the coupling theory[50] and an alternative but compatible theory by Perez et al.[51] not only the magnitude of $n_{m,\max}$ but also the temperature dependence of $n_{m,\max}$ contribute in concert to the steepness/curvature.[52]

Analysis of SCLCP Experimental Data

a. Procedure. Having discussed the physics of local segmental motion in SCLCPs and how they are manifested in the experimental data, we proceed to verify these expectations by a thorough analysis of all available experimental data. Most data are taken from published literature,[9-21] but some new data are included also. The experimental undertakings that generate some of these new data[24,53] were motivated by predicted behaviors from the coupling theory, but in some SCLCPs with special spacer length there was previously no experimental measurement to either verify or falsify such predictions.

As discussed in the preceding section, the $T_{g,m}$-scaled plot of $\tau_{m,\max}$ for various m's together with the $T_{g,pP}$-scaled plot of τ_{pP} of the parent polymer (pP) is currently the best medium to bring out the change in molecular dynamics of local segmental motion with the spacer length of SCLCP. Albeit many different SCLCPs containing various mesogenic groups have been synthesized, the spacers are invariably the methylene chain and the monomer unit excepting the spacer, and the pendant mesogenic group can be identified principally as one of among four kinds: methylsiloxane, acrylate, methacrylate, and vinyl ether. The four parent polymers that have their monomer units corresponding closely in structure to methylsiloxane, acrylate, methacrylate, and vinyl ether are respectively poly(dimethylsiloxane) (PDMS), poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), and poly(vinyl methyl ether) (PVME). Consequently, we divide the SCLCPs into four groups according to their parentage and compare the local segmental dynamics of SCLCPs within each group. At the present time within each group we consider the change in dynamics with increasing spacer length. In so doing we are ignoring the possible dependence of the dynamics on the identity of the mesogenic group, given everything else being equal. There are not sufficient experimental data to warrant a study of the dependence on the mesogenic group, at this time. We reserve the right to examine such a dependence in the future.

Due to the Vogel–Fulcher temperature dependence of the local segmental relaxation time which varies rapidly with decreasing temperature near the glass transition, any difference that exists between the T_g-scaled temperature dependence of two materials will be magnified at longer times. Thus, any difference will be brought out more clearly by using data taken at longer times or lower frequencies in constructing the T_g-scaled plot. However, most dielectric data on the dynamics of glass transition were usually taken at frequencies higher than 1 Hz. The temperature dependence of $\tau_{m,\max}(T)$ are therefore determined only in a range above $(2\pi)^{-1}$ s, and its behavior at longer times or lower temperatures was obtained by an extrapolation using the empirical Vogel–Fulcher or the WLF equations to fit the temperature dependence of the measurements. To avoid large error that may arise in unduly large extrapolation down to long times, we choose 1 s to be the time for the definition of $T_{g,m}$, i.e., $\tau_{m,\max}(T_{g,m}) = 1$ s for all m. Similarly for the parent polymer, its $T_{g,pP}$ is also defined by $\tau_{pP}(T_{g,pP}) = 1$ s. In a few cases the dielectric data were taken by standard impedance bridges operating in the frequency range near and above a kilohertz. Again, to avoid error from extrapolation, we take under this circumstance the shorter relaxation time of $(2\pi \times 10^2)^{-1}$ s, corresponding to a frequency of 10^2 Hz for the definitions of $T_{g,m}$'s and $T_{g,pP}$ in these special cases. In these ways we are assured that in constructing the T_g-scaled plot the accuracy in the presentation of the data is retained and has not been compromised.

b. Results. Following the procedure outlined above, the $T_{g,m}$- and T_{pP}-scaled plots of $\tau_{m,\max}$ and τ_{pP} are made separately for each of the four parent polymers. The results will be discussed immediately below.

Poly(vinyl ether)-Based SCLCPs. The SCLCPs, poly{7-[(4-cyano-4′-biphenylyl)oxy]heptyl vinyl ether}s, have been studied by dielectric relaxation.[19] The chemical structure of these SCLCPs consists of a cyano–biphenylyl–oxy mesogen attached via a spacer ($-(CH_2)_7-$), a methylene chain with length $m = 7$, to a vinyl ether backbone. The dielectric relaxation times, $\tau_{m=7,\max}(T)$, of two samples having degrees of polymerization (DP) of about 7.3 and 30 and labeled respectively as C7DP8 and C7DP30 were plotted against $T_{g,m=7}/T$ where the glass temperatures were determined for each sample taken at its different macroscopically aligned configuration in the liquid crystal state, i.e., homeotropic (H), planar (P), or homogeneous and unaligned (U) orientations of side-chain mesogen with respect to the plane of the film. In all cases the condition $\tau_{m=7,\max} = 1$ s was used to find $T_{g,m=7}$. The results are shown in Figure 1 where we can see that the $T_{g,m=7}$-scaled data are practically independent of the alignment and the degree of polymerization. Actually we have plotted the δ-relaxation time instead of the α-relaxation time in Figure 1 because the former is very prominent and its use is to avoid the large errors inevitable in determining the α-relaxation time from the weak and broad absorption peak of the latter. Usually the α- and the δ-relaxations have parallel temperature dependences and hence similar T_g-scaled temperature dependences. Since these SCLCPs have poly(vinyl ether) as the backbone, naturally we identify PVME to be their parent polymer. Dielectric relaxation measurement of the local segmental motion in PVME had been made by Zetsche et al.[39] Their data for the relaxation time $\tau_{PVME}(T)$ is also $T_{g,PVME}$-scaled where again $T_{g,PVME}$ is determined by the condition $\tau_{PVME}(T_{g,PVME}) = 1\,s$. Comparing the SCLCPs with PVME in the T_g-scaled plot shows that there is a significant decrease of steepness/curvature when the side chain consisting of the spacer and the mesogenic group is introduced to the vinyl ether backbone of PVME to make our SCLCPs. The considerable length of the spacer, $m = 7$, not only causes segregation of the mesogen from the backbone but also makes the environment of the backbone rich in methylene chain molecules, which has the effect of mitigating the intermolecular dynamic constraints of the vinyl ether segmental motion like that present in PVME. As a consequence the coupling parameter n of local segmental motion in C7DP8 and C7DP30 is decreased in value from that of

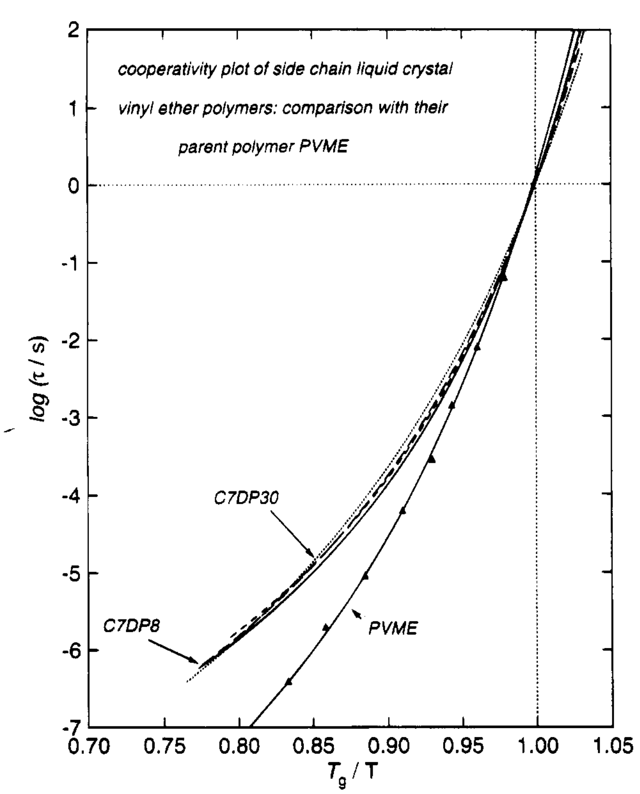

Figure 1. Comparison in a T_g-scaled temperature dependence plot of the δ-relaxation times of two cyanobiphenylyl SCLCPs attached via seven carbon spacers to a vinyl ether backbone with the α-relaxation time of the parent polymer, PVME.

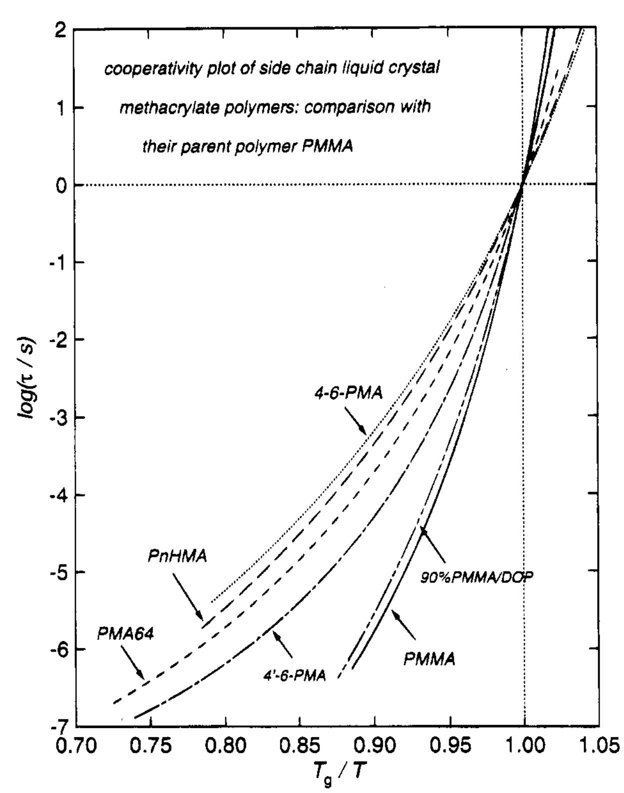

Figure 2. T_g-scaled temperature dependences of the α-relaxation times of three SCLCPs with different mesogenic groups attached via six carbon spacers to a methacrylate backbone. Comparisons are made with the α-relaxations of the parent polymer PMMA, 90% PMMA/10% DOP, and PnHMA.

PVME, and the steepness/curvature of the relaxation time is reduced according to the coupling theory. The data shown in Figure 1 are consistent with this expectation. SCLCPs based on poly(vinyl ether) having different spacer lengths are not available. For a study of the dependence of segmental dynamics on spacer length, we shall go to the other families based on polyacrylates and polysiloxanes.

Polymethacrylate-Based SCLCPs. SCLCPs based on polymethacrylate were first studied dielectrically by Kresse, Kostromin, and Shibaev.[10] Data were taken in a PMA-based sample, poly{1-[[[5-[(4′-cyano-4-biphenylyl)oxy]pentyl]oxy]carbonyl]-1-methylethylene}, that has a spacer length $m = 5$. These authors have represented the temperature dependence of the measured relaxation frequencies $f_{\max}$ over 3 decades by an Arrhenius equation with an activation enthalpy of 190 kJ/mol. The usefulness of this early data is limited by the narrow frequency range of measurement, although we hasten to say that they are consistent with more recent data obtained over a wider frequency range on other PMA-based SCLCPs by Vallerien et al.[14] and by Zhong et al.[18] The samples studied by these authors all have a spacer length of $m = 6$. The one (PMA 64) used by Vallerien et al. contains phenyl benzoate as the mesogen group, while the two others studied by Zhong et al. have a constitutional isomeric (methoxymethyl)stilbene side group (4–6-PMA and 4′–6-PMA). The dielectric α-relaxation time data for these three samples PMA 64, 4–6-PMA, and 4′–6-PMA are respectively scaled by the glass temperatures $T_{g,\mathrm{PMA64}}$, $T_{g,4-6\text{-}\mathrm{PMA}}$, and $T_{g,4'-6\text{-}\mathrm{PMA}}$ which are all defined as the temperature at which the local segmental relaxation time is 1 s. The results are shown in Figure 2. The parent polymer naturally is poly(methyl methacrylate) (PMMA), and its local segmental relaxation times have been determined by many authors.[54] We take the data from the recent work of Rizos et al.[55] which they have fit to the Vogel–Fulcher–Tammann–Hesse equation $\tau = \tau_0 \exp[B/(T - T_0)]$ where $\tau_0 = 3.2 \times 10^{-13}$ s, $B = 1480$ K, and $T_0 = 347$ K. This expression for τ is $T_{g,\mathrm{PMMA}}$-scaled and plotted in Figure 2 (solid curve). We have also included the recent data of local segmental motion in PMMA diluted with 10% DOP by Floudas and co-workers.[56] The slight decrease in steepness with the addition of a small amount of diluent is due to the reduction of intermolecular dynamic constraints or cooperativity of the polymer in the presence of the more mobile diluent molecules. Figure 2 clearly shows the steepness of any of the three SCLCPs with a spacer of length $m = 6$ is considerably smaller than that of PMMA and 90% PMMA/10% DOP. The decrease in steepness according to the coupling theory is caused by the presence of the spacers with long methylene chains which, for the same reason as in the case of DOP molecules in diluted PMMA, reduces the intermolecular constraints that impede local segmental motions of the methacrylate backbones. The effect of a long methylene chain on the local segmental motion of the methacrylate backbone can be demonstrated by examining the relaxation times of poly(n-hexyl methacrylate) (PnHMA) which has the alkyl group $-(CH_2)_5$-CH_3 attached to the methacrylate backbone.[57] These data, after having been $T_{g,\mathrm{PnHMA}}$-scaled and plotted in Figure 2, reveal the steepness of PnHMA is much reduced from that of PMMA and turns out to be comparable with those of the SCLCP with $m = 6$. The duplication by PnHMA of the same effect exhibited by the SCLCP having the same methylene chain length in a T_g-scaled plot leaves little doubt that there is a common physical origin of the effect in both the poly(alkyl methacrylates) and the side-chain liquid crystalline polymethacrylates.

On closer examination of Figure 2 we find that the steepness of 4′−6-PMA is noticeably greater than that of 4−6-PMA and PMA 64. We believe this is not an accident but due to the fact that the molecular motion responsible for glass transition in 4′−6-PMA is somewhat unique. The other two, 4−6-PMA and PMA 64, like many other SCLCPs show separate α and δ peaks in the dielectric loss spectrum. However, 4′−6-PMA exhibits only a single broad peak at all measurement temperatures with or without the presence of a strong magnetic field.[18] One interpretation of a single broad peak being observed is that the α and δ processes in 4′−6-PMA are coupled together to make the overall motion as observed dielectrically more extensive. A more extensive motion experiences increased dynamic constraints which show up as a steeper T_g-scaled temperature dependence.

SCLCP with a polymethacrylate backbone and a mesogenic group as 4′−6-PMA but having a shorter spacer length of $m = 3$ has been synthesized[58] and studied by ^{13}C NMR.[59] It would be nice to compare the signature of this sample, 4′−3-PMA, in the T_g-scaled plot with those of 4′−6-PMA and with the parent PMMA. Unfortunately, the sample 4′−3-PMA has a high dc conductivity contribution which overwhelms the dielectric loss peak to preempt any attempt to determine with accuracy the relaxation times longer than 10^{-3} s. The data collected are too limited to make a comparison with the others worthwhile.

Polyacrylate-Based SCLCPs. SCLCPs based on polyacrylate containing phenyl benzoate as the mesogen and having relatively short spacer length of $m = 2$ as well as longer spacer lengths of $m = 6$ and larger have been investigated dielectrically by Zentel et al.[9] and by Vallerien et al.[14] Another sample poly{1-[[[5-[(4′-cyano-4-biphenylyl)oxy]pentyl]oxy]carbonyl]ethylene} with a spacer of length $m = 5$ was measured by Kresse and co-workers.[10] The Vogel−Fulcher fits to the measured local segmental relaxation times of two samples with $m = 2$ and $m = 5$ are $T_{g,m}$-scaled and plotted in Figure 3. The sample with the shortest spacer length $m = 2$ (solid curve is the WLF fit to the experimental data) exhibits a very steep $T_{g,m=2}$-scaled temperature dependence. The comparison with samples having a longer spacer ($m = 5$, diamonds and dashed curve in Figure 3) is best made after we have incorporated into Figure 3 also the local segmental relaxation data of PMA (filled circles and dash-dotted curve), which is the parent polymer of all SCLCPs based on polyacrylate. The local segmental relaxation times data of PMA were obtained by photon correlation spectroscopy by Fytas and co-workers.[60] These authors had checked that their data were in good agreement with dielectric measurements[61] and hence are appropriate to use here for comparison with other dielectric data. Figure 3 shows the steepness of PMA (filled circles are the actual experimental data and the dashed-double dotted curve is the WLF fit to these data) falls in between those of the two samples with $m = 2$ and $m = 5$.

This result for $m = 5$ can be explained by the effect discussed in a section above that attaching the mesogenic group via a long spacer like $m \geq 5$ to the polyacrylate will cause a decrease in the intermolecular dynamic constraints on local segmental motion in the parent polymer, PMA. It follows as a consequence of the coupling theory that in a T_g-scaled plot of the relaxation times the steepness of SCLCP with long spacer lengths will be reduced from the value of the parent polymer.

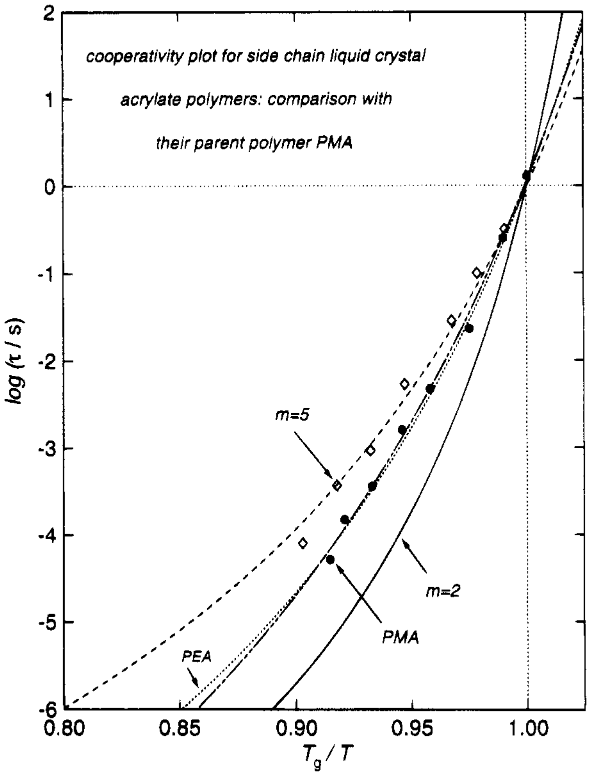

Figure 3. T_g-scaled temperature dependences of the α-relaxation times of two SCLCPs attached via respectively five and two carbon spacers to the acrylate backbone. Comparisons are made with the α-relaxation times of the parent polymer PMA and the closely related polymer PEA.

On the other hand, when $m = 2$, the spacer is short and the proximity of the mesogenic group to the backbone becomes the dominant factor and it has the opposite effect of increasing the dynamic constraints of local segmental motion in the parent polyacrylate polymer, PMA. In this comparison of dynamic constraints between the $m = 2$ SCLCP and PMA, it may help to consider the latter in this instance as a hypothetical side-chain liquid-crystalline polyacrylate polymer with spacer of length $m = 1$ that has its mesogenic group *removed*. Therefore, from this coupling theory, because of enhanced dynamic constraints contributed by the proximal mesogenic group near the backbone, the steepness of the $m = 2$ SCLCP will be larger than that of PMA, as experimentally observed.

Another way to think about the situation is to consider the SCLCP having $m = 2$ to originate from poly(ethyl acrylate) (PEA) by attaching the mesogenic group alone (without any spacer whatsoever) as an extension of the ethyl group $-CH_2CH_3$. According to the same reasoning as given in the paragraph above, the attached mesogenic group should increase the intermolecular cooperativity of segmental motion in PEA. Thus, in the T_g-scaled plot, the steepness of PEA should be smaller than that of the SCLCP with $m = 2$. In Figure 3 we have plotted also the $T_{g,\mathrm{PEA}}$-scaled relaxation times of PEA (dotted curve represents the WLF to the actual data) from photon correlation spectroscopy.[56] A comparison with the corresponding curve for our SCLCP with $m = 2$ indicates that the theoretically expected change is indeed observed experimentally.

Polysiloxane-Based SCLCPs. There has been a continued interest in SCLCPs based on polysiloxane. Many dielectric studies of molecular motions in these

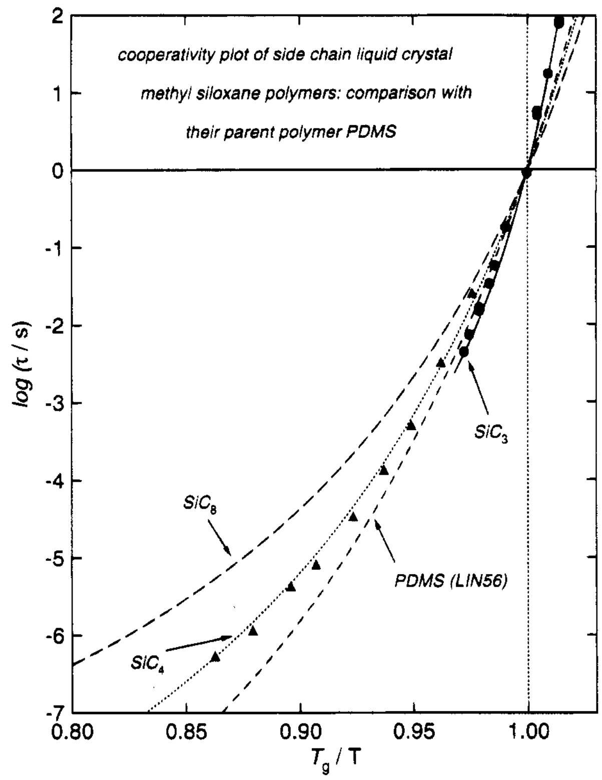

Figure 4. T_g-scaled temperature dependences of the α-relaxation times of three SCLCPs attached via respectively eight, four, and three carbon spacers to the methylsiloxane backbone. Comparisons are made with the α-relaxation time of the parent polymer PDMS.

materials were made.[13,15–17,22–25] The spacers in the samples used in these earlier studies have lengths $m \geq 4$. Among these sets of data we have chosen the one by Attard et al.[13] taken on a sample with $m = 8$ and another by Seiberle et al.[15] on a sample with $m = 4$. Other data sets are not further discussed here because the frequency range used in these works is either too narrow or too high. The $T_{g,m=8}$- and $T_{g,m=4}$-scaled plots of the α-relaxation times, τ_{max}, are constructed by using the fit to the data by the Vogel–Fulcher equation to find $T_{g,m=8}$ and $T_{g,m=4}$ by the condition $\tau_{max}(T_{g,m}) = 1$ s. The data of Attard have been obtained in the frequency range of $10^{5.5} > f_{max} > 10^{-4}$ Hz which requires no extrapolation to obtain $T_{g,m=8}$. However, the other set of data by Seiberle et al. requires extrapolation of about a decade in time in order to find $T_{g,m=4}$. The results are shown in Figure 4 in which we have incorporated the $T_{g,PDMS}$-scaled dielectric data of amorphous poly(dimethylsiloxanes) (PDMS) again with the choice of 1 s for the determination of $T_{g,PDMS}$ according to $\tau_{max}(T_{g,PDMS}) = 1$ s. The dielectric data are taken from the recent publication by Kirst et al.[62] in which they have measured the α-relaxation in a series of linear PDMS of various molecular weights in the frequency range of $10^{-1} < f < 10^{7}$ Hz. In spite of the fact that the glass transition temperature changes from 130 to 190 K with molecular weight ranging from 300 to 10 000, $T_{g,PDMS}$-scaled temperature dependences fall on one master curve,[63] as they should in order for the T_g-scaled plot to make physical sense.[64] In Figure 4 we have shown only the scaled data of the PDMS sample, with the average number of repeat units equal to 56. It is clear by inspection of Figure 4 that the steepness of the $m = 8$ sample is significantly smaller than that of its parent polymer which is PDMS. Again the reason for this decrease in steepness in the SCLCP having spacer composed of long methylene chains is the reduction of dynamic constraints. Nevertheless, as the spacer length is reduced to $m = 4$, the reduction is compensated by the increase of dynamic constraints contributed by the coupling of the mesogenic group to the backbone. As a consequence the steepness increases when going from the sample with $m = 8$ to the sample with $m = 4$ to approach that of PDMS, as shown in Figure 4. That the steepness of the $m = 4$ sample is sufficiently close to that of PDMS suggests the scenario that, had relaxation data for samples with $m \leq 3$ been available, the steepness of these SCLCPs may even exceed that of PDMS. Recently, such data absent in the published literature are made available by a low frequency ($1 < f < 10^{-4}$ Hz) mechanical relaxation measurement of a SCLCP-based on polysiloxane that has a spacer length of $m = 3$.[24] The mesogenic is either a biphenylyl or a cholesteryl group. The frequency range of mechanical measurement encompasses the 1 s time scale for the definition of $T_{g,m=3}$ which is determined without extrapolation. The mechanical segmental relaxation times are then $T_{g,m=3}$-scaled. The results are shown in Figure 4 (filled circles for the actual data and solid curve for the Vogel–Fulcher fit). It is gratifying to see not only that the steepness of the $m = 3$ sample is greater than that of the $m = 4$ sample but also that it becomes even larger than the parent polymer PDMS. These trends and relation to the parent polymer in the T_g-scaled plot now found in polysiloxane-based SCLCPs are in accord with those properties seen in the side-chain liquid-crystalline (SCLC) polyacrylates discussed in the previous section and depicted in Figure 3. The remarkable similarity in steepness and curvature of the SCLC polyacrylate (Figure 3) and the SCLC polysiloxane (Figure 4) with the same spacer length of $m = 4$ is worth pointing out. Moreover, in both families we have found the same overall trend of change in behavior with m, including an enhanced steepness beyond that of the parent polymer when m becomes sufficiently small. These rather general behaviors found in SCLCPs independent of the polymer backbone are indications that some physics of the glass transition have been captured in this present study.

Conclusion

The dependence of the molecular dynamics of the glass transition in SCLCPs on the length of the spacer, m, is the principal concern of this work. The conceptual basis of the coupling theory of molecular motion in densely packed systems is used as a tool to heuristically explore the cause of the dependence of molecular glass transition dynamics on m. A prediction of the coupling theory on a systematic dependence of the T_g-scaled temperature variation of the relaxation time on m makes it possible to check with experimental data what we have expected on theoretical grounds. Such a clear prediction has led us to examine exhaustively previously published data on glass transition (main-chain) dynamics in SCLCPs. In addition, some new data are generated for the purpose of a closer comparison between experimental and theoretical expectation. We find the experimental data indicate a systematic dependence of the intermolecular cooperativity of the main-chain local segmental motion on the spacer length.

For very short spacer length, the close proximity of the mesogenic group to the polymer backbone certainly will enhance the degree of intermolecular cooperativity (given by the coupling parameter n in the coupling theory) of the main-chain local segmental motion in the SCLCPs beyond that in the parent polymer. According to the coupling theory enhanced intermolecular cooperativity will be exemplified by a stronger T_g-scaled temperature dependence of the relaxation time than that of the parent polymer. This behavior is indeed observed for $m = 2$ in polyacrylate-based SCLCPs and for $m = 3$ in polysiloxane-based SCLCPs.

However, as the spacer length becomes long and the mesogenic group is further separated from the backbone and becomes unimportant in the consideration of relaxation dynamics on the main chain, the omnipresence of long flexible methylene chains near the backbone will take precedence to mitigate the dynamic constraints and decrease the degree of intermolecular cooperativity of local segmental motion of the main chain. Again, as a consequence of the coupling theory, decreasing intermolecular cooperativity leads to a continued weakening of the T_g-scaled temperature dependence. This trend is observed in both the polyacrylate- and polysiloxane-based SCLCPs where there is a sufficient amount of data for samples with various lengths to make the systematic change very clear.

The work presented here has been focused entirely on the dynamics of the main chain of SCLCPs and the dependence of their degree of cooperativity on spacer length. In closing let us ask the same questions on the local dynamics of the mesogen and, in particular, the hindered rotation (libration) around its long molecular axis. This librational process has been observed dielectrically as the β-relaxation. Such a local librational motion of the mesogen has no *inter*molecular cooperativity, although some *intra*molecular cooperativity remains. The intramolecular cooperativity will be different only when the spacer length is short because the mesogen can no longer be decoupled from the main chain. Following the coupling theory, the vanishing intermolecular cooperativity in the β-relaxation implies that the temperature dependence of the β-relaxation time, τ_β, will not be strongly dependent on the spacer length as in the case of the main-chain relaxation. In the literature there is only one set of published data of the β-relaxation of SCLCP in which the dynamics were measured for different spacer lengths.[65] The materials have acrylate backbones and methylene spacers of length m equal to 2, 6, 8, or 11. Experimentally it was found that the β-relaxation depends only slightly on the spacer length. Only in the polymer with spacer length equal to 2 the relaxation time is shifted slightly to lower frequencies, while other polymers having six or more methylenes show nearly the same β-relaxation, consistent with it being a local relaxational process that has no intermolecular cooperativity. The slight shift of τ_β to longer times observed in the polymer with $m = 2$ can be understood by the change of intramolecular cooperativity of the β-relaxation when the mesogen is no longer decoupled from the main chain as completely as in the other polymers with larger m's.

Finally, it has been established as an empirical fact that glass former having a strong T_g-scaled temperature dependence (or a large coupling parameter) is sensitive to physical aging. It would be interesting to study physical aging in SCLCPs with different values of m to look for the expected trend of decreasing effects of physical aging with increasing m.

Acknowledgment. We thank Ingo Alig and Frieder Kremer for a discussion on dielectric relaxation of side-chain liquid-crystalline polymers. K.L.N. is supported in part by ONR Contract N0001495WX20203. Z.Z.Z. acknowledges helpful discussions with Prof. W. L. Gordon and financial support from NSF/S&CT Advanced Liquid Crystalline Optical Materials (ALCOM) under Grant DMR 89-20147.

References and Notes

(1) Finkelmann, H.; Ringsdorf, H.; Wendorff, J. H. *Makromol. Chem.* **1978**, *179*, 277.

(2) Shibaev, V. P.; Platé, N. A. *Polym. Sci. U.S.S.R.* **1978**, *19*, 1065.

(3) Shibaev, V. P.; Platé, N. A.; Freidzon, Y. S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1655.

(4) Finkelmann, H.; Rehage, G. *Adv. Polym. Sci.* **1984**, *60/61*, 99.

(5) Shibaev, V. P.; Platé, N. A. *Adv. Polym. Sci.* **1984**, *60/61*, 173.

(6) Engel, M.; Hisgen, B.; Keller, R.; Kreuder, W.; Reck, B.; Ringsdorf, H.; Schmidt, H. W.; Tschirner, P. *Pure Appl. Chem.* **1985**, *57*, 1009.

(7) See articles in: *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Chapman & Hall: New York, 1989.

(8) Percec, V.; Lee, M. *Macromolecules* **1991**, *24*, 1017.

(9) Zentel, R.; Strobl, G. R.; Ringsdorf, H. *Macromolecules* **1985**, *18*, 960.

(10) Kresse, H.; Shibaev, V. P. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 63. Kresse, H.; Kostromin, S.; Shibaev, V. P. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 509.

(11) Haase, W.; Pranoto, H.; Bormuth, F. J. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 1229.

(12) Pareix, J. D.; Njeumo, R.; Legrand, L.; Le Barney, P.; Dubois, J. C. *Liq. Cryst.* **1987**, *2*, 167.

(13) Attard, G. S.; Moura-Ramos, J. J.; Williams, G. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1099.

(14) Vallerien, S. U.; Kremer, F.; Boeffel, C. *Liq. Cryst.* **1989**, *4*, 79.

(15) Seiberle, H.; Stille, W.; Strobl, G. *Macromolecules* **1990**, *23*, 2008.

(16) Kresse, H.; Ernst, S.; Kröcke, B.; Kremer, F.; Vallerin, S. U. *Liq. Cryst.* **1992**, *11*, 439.

(17) Borisova, T. I.; Burshtein, L. L.; Stepanova, T. P.; Nikonorova, N. A. *Int. J. Polym. Mater.* **1993**, *22*, 103.

(18) Zhong, Z. Z.; Schuele, D. E.; Smith, S. W.; Gordon, W. L. *Macromolecules* **1993**, *26*, 6403.

(19) Zhong, Z. Z.; Gordon, W. L.; Schuele, D. E.; Akins, R. B.; Percec, V. *Mol. Cryst. Liq. Cryst.* **1994**, *238*, 129.

(20) Zhong, Z. Z.; Schuele, D. E.; Gordon, W. L. *Liq. Cryst.* **1994**, *17*, 199.

(21) Akins, R. B.; Zhong, Z. Z.; Gordon, W. L.; Schuele, D. E. *Mol. Cryst. Liq. Cryst.*, in press.

(22) Pschorn, U.; Spiess, H. W.; Hisgen, B.; Ringsdorf, H. *Makromol. Chem.* **1986**, *187*, 2711.

(23) Oulyadi, H.; Lauprétre, F.; Sergot, P.; Monnerie, L.; Mauzac, M.; Richard, H. *Macromolecules* **1991**, *24*, 2800.

(24) Etienne, S.; David, L.; Mitov, M.; Sixou, P.; Ngai, K. L., *Macromolecules* **1995**, in press.

(25) Möller, M.; Wendorff, J. H.; Werth, M.; Spiess, H. W. *J. Non-Cryst. Solids* **1994**, *170*, 295.

(26) For a recent review, see: Ngai, K. L. In *Disorder Effects in Relaxational Processes*; Richert, R., Blumen, A., Eds.; Springer-Verlag: New York, 1994; p 89. Ngai, K. L.; Tsang, K. Y. *Makromol. Chem. Phys., Macromol. Symp.* **1995**, *90*, 95.

(27) Plazek, D. J.; Ngai, K. L. *Macromolecules* **1991**, *24*, 1222.

(28) Plazek, D. J.; Zheng, X. D.; Ngai, K. L. *Macromolecules* **1992**, *25*, 4920.

(29) Ngai, K. L.; Plazek, D. J.; Bero, C. *Macromolecules* **1993**, *26*, 1065.

(30) Böhmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. *J. Chem. Phys.* **1993**, *99*, 4201.

(31) Ngai, K. L.; Roland, C. M. *Macromolecules* **1993**, *26*, 6824.

(32) Ngai, K. L.; Roland, C. M. *Rubber Chem. Technol.* **1993**, *66*, 817.

(33) Roland, C. M. *Macromolecules* **1994**, *27*, 4242.

(34) Kohlrausch, R. *Ann. Phys. (Leipzig)* **1847**, *12*, 393.

(35) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.

(36) Roland, C. M.; Ngai, K. L. *Macromolecules* **1993**, *26*, 2688.

(37) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 2261; *J. Rheol.* **1992**, *36*, 1691.

(38) Fytas, G.; Rizos, A. K.; Alig, I.; Kremer, F.; Roovers, J. *Polymer* **1993**, *34*, 2263.

(39) Zetsche, A.; Kremer, F.; Jung, W.; Schulze, W. *Polymer* **1990**, *31*, 1883.

(40) Chung, G.-C.; Kornfield, J. A.; Smith, S. *Macromolecules* **1994**, *27*, 964.

(41) Floudas, G.; Placke, P.; Stepanek, P.; Brown, W.; Fytas, G.; Ngai, K. L. *Macromolecules* **1995**, in press.

(42) Angell, C. A.; Monnerie, L.; Torrell, L. *Proceedings of MRS Symposium on Aging of Polymers*; O'Reilly, J., Roe, R. J., Torkelson, J., Eds.; Materials Research Society: Pittsburgh, PA, 1991.

(43) Ngai, K. L.; Plazek, D. J. *Rubber Chem. Technol.*, in press.

(44) Alegria, A.; Colmenero, J.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1994**, *27*, 4486.

(45) Roland, C. M.; Ngai, K. L. *Macromolecules* **1992**, *24*, 5315.

(46) Rizos, A. K.; Johnsen, R. M.; Brown, W.; Ngai, K. L., *Macromolecules* **1995**, in press.

(47) Laughlin, W. T.; Uhlmann, D. R. *J. Chem. Phys.* **1972**, *76*, 2317.

(48) Angell, C. A. In *Relaxations in Complex Systems*; Ngai, K. L., Wright, G. B., Eds.; U.S. Government Printing House, Naval Research Laboratory: Washington, D.C.; 1985; p 3.

(49) Angell, C. A. *J. Non-Cryst. Solids* **1991**, *131–133*, 13.

(50) Ngai, K. L. *J. Non-Cryst. Solids* **1987**, *95* & *96*, 969.

(51) Perez, J.; Cavaillo, J. Y.; Etienne, S. *Rev. Phys. Appl.* **1988**, *23*, 125.

(52) David, L.; Sekkat, A.; Etienne, S. *J. Non-Cryst. Solids* **1994**, *172–174*, 214.

(53) Zhong, Z. Z.; Schuele, D. E.; Ngai, K. L., manuscript in preparation.

(54) McCrum, N. G.; Williams, G.; Read, B. E. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover: New York.

(55) Rizos, A. K.; Fytas, G.; Ma, R. J.; Wang, C. H.; Abetz, V.; Meyer, G. C. *Macromolecules*, in press.

(56) Floudas, G.; Rizos, A. K.; Brown, W.; Ngai, K. L. *Macromolecules* **1994**, *27*, 2719.

(57) Meier, G.; Kremer, F.; Fytas, G.; Rizos, A. *J. Chem. Phys.*, in press.

(58) Percec, V.; Tomazos, D.; Pugh, C. *Macromolecules* **1989**, *22*, 3259.

(59) Silvestri, R. L.; Koenig, J. L. *Macromolecules* **1992**, *25*, 2341.

(60) Fytas, G.; Patkowski, A.; Meier, G.; Dorfmöller *J. Chem. Phys.* **1984**, *80*, 2214.

(61) Williams, G. *Trans. Faraday Soc.* **1964**, *60*, 1548.

(62) Kirst, K. U.; Kremer, F.; Pakula, T.; Hollingshurst, J. *Colloid Polym. Sci.* **1994**, *272*, 1420.

(63) Ngai, K. L.; Roland, C. M., submitted to *Polymer*.

(64) Roland, C. M.; Ngai, K. L. *Macromolecules* **1992**, *25*, 5765.

(65) Schönfeld, A.; Kremer, F.; Hofmann, A.; Kuhnpast, K.; Springer, J.; Scherowsky, G. *Makromol. Chem.* **1993**, *194*, 1149.

MA950318P