Dielectric Relaxation Properties and Alignment Behavior of a Liquid-Crystalline Polymer Having Laterally Attached Mesogenic Groups

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ABSTRACT: The dielectric relaxation properties and electric-field-induced alignment behavior of a siloxane-chain liquid-crystalline polymer having laterally attached mesogenic groups in the side chain have been studied over a wide range of experimental conditions. It is shown that homeotropic or planarly aligned samples may be prepared, using the two-frequency addressing principle, for samples in the LC state well below the clearing temperature. The alignment behavior is followed by use of dielectric relaxation spectroscopy, which also gives information of the anisotropic reorientational dynamics of the dipolar groups in the LC state. It is shown that samples prepared as H-aligned or P-aligned slowly disalign when the directing field is removed. The dielectric relaxation spectra for samples of different macroscopic orientations are well-fitted by using a simple theory we have developed previously.

Introduction

Liquid-crystalline (LC) polymers having mesogenic groups in the side chain are of considerable interest scientifically as hybrid materials and technologically as media for a variety of applications in physical optics and computer technology. Such LC materials possess the good film-forming properties of polymers and have the anisotropic optical, electrical, and dielectric properties of the LC state. As films 1–100 μm in thickness, they show promise as media for high-density optical data storage, using the thermorecording[1-5] or photorecording[4,6-8] methods, for optical elements such as Fresnel zone plates or planar waveguides[4,6,9,10] or for nonlinear optical processing[4,9,10] such as the second harmonic generation of laser light.[4,10]

Most of the studies of LC side-chain polymers have been concerned with materials in which the mesogenic groups are attached longitudinally to the side-chain spacer group, as is indicated schematically in Figure 1a. However, there are a number of combinations for the incorporation of mesogenic groups into the side chain and main chain, and some of these have been reviewed recently by Percec and Pugh.[11] Of special interest are LC polymers in which (i) the mesogenic groups are contained in both the side chain and main chain,[11,12] as indicted in Figure 1b, and (ii) the mesogenic groups are attached laterally to the side-chain spacer group[13-15] (see Figure 1c).

All applications of LC side-chain polymers require the polymer film to be aligned macroscopically in the homeotropic (H), planar (P), or homogeneous orientations with respect to the plane of the film. Therefore, it has been important to establish quantitative, reproducible methods for aligning the LC polymer films using surface forces or electric or magnetic fields and to devise direct methods for monitoring the degree of alignment achieved. Dielectric relaxation spectroscopy has proved to be a useful method for estimating the nature and extent of the alignment obtained for LC polymer films aligned using magnetic fields[16-21] or electric fields.[22-31] It is shown that the ease of alignment varies markedly with chemical structure, the thermal/electrical or thermal/magnetic field treatments and that realignment is possible in some cases even in the absence of external fields or surface forces through the process of "template-induced" recrystallization.[32,33] These studies have shown that (i) H-aligned samples may be obtained by cooling a sample from the melt in the presence of a strong magnetic field or a strong low-frequency electric field or, in certain cases, by applying such fields to a material in its LC state at temperatures close to T_c: (ii) P-aligned samples may be obtained by cooling a sample from the melt in the presence of a strong magnetic field or a strong high-frequency electric field or, in certain cases, by applying such fields directly to a sample in its LC state. In practice, P-aligned samples may be difficult to obtain since inaccessibly high frequencies of the electric field may be required. The high viscosity of the LC state makes the field-induced alignment in the LC state difficult, and it may be necessary to work in the biphasic region, as we have discussed.[24] An important aim of current research is to obtain LC polymer materials that may be H- or P-aligned directly in the LC state using applied fields and that retain those alignments when the field is removed. In this connection it is appropriate to investigate the alignment behavior of LC polymers having novel structures. Bormuth and Haase[21] have studied the

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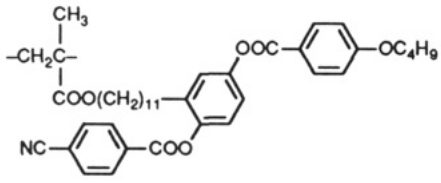
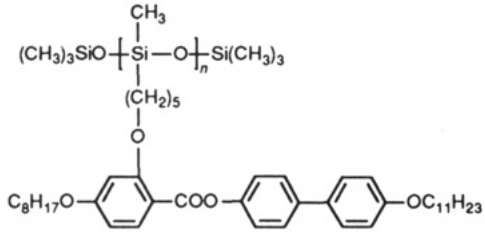
dielectric properties and alignment behavior of a carbon-chain polymer having the mesogenic group attached laterally to the spacer group as



I

and have shown that H-alignment was achieved by a magnetic field of 1.2 T supplemented by an electric field of 10 kV/cm at 100 Hz. Partial planar alignment was achieved by using a magnetic field supplemented by an electric field of 10 kV/cm at 200 kHz and by annealing for 24 h below the clearing temperature.

In the present work we describe studies we have made for a siloxane-chain polymer having a mesogenic group attached laterally to the spacer group and having the following structure:



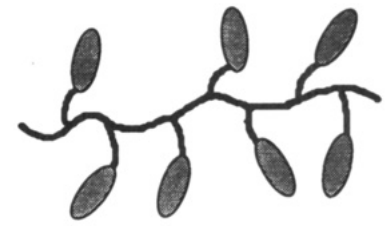
II; $n \sim 30$

Experimental Section

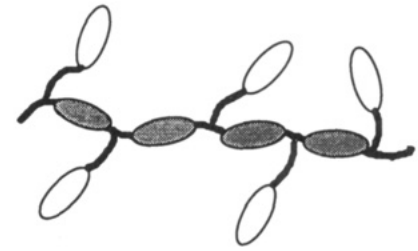
The nematic siloxane polymer II was synthesized by the method described previously.[34] The DSC scan (20 K min^{-1}) gave the apparent glass transition temperature $T_g = 9$ °C and the clearing temperature $T_c = 61$ °C. Disk samples, 100 μm thickness and 1 cm diameter, were prepared in a three-terminal dielectrics cell in which a PTFE spacer ensured dimensional stability. The dielectric measurements were made by using a Gen Rad 1689 precision RLC digibridge, which was computer-controlled as previously reported.[22,23] The sample temperatures were controlled to 0.05 °C by immersing the cell in a thermostated water bath. We are interested in the loss spectra of samples that have been subjected to different electrical/thermal treatments, and it is sufficient to record these spectra as G/ω where G is the equivalent parallel capacitance of the sample at the frequency $\omega = 2\pi f$ (Hz) and where $G/\omega = \epsilon'' C_0$, where C_0 is the geometrical capacitance of the electrodes and ϵ'' is the imaginary part of the complex dielectric permittivity.[35] The precision of the measurements of G/ω and C_0 is better than 1% at each frequency.

Results and Discussion

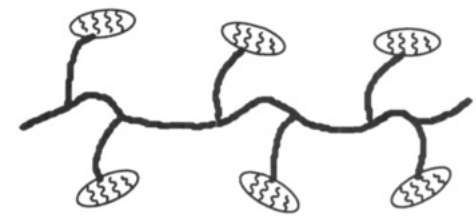
Figure 2 shows plots of the loss spectra for an unaligned sample at different temperatures in the LC state. The overall magnitudes of the loss peaks are far smaller than we observed for siloxane polymers containing cyano groups in the mesogenic head group.[22-29] The present loss peaks are broad and bimodal in the sense that a small high-frequency peak is observed in addition to the main peak. In order to establish the experimental conditions required to align the sample homeotropically or planarly, the sample was remelted and then cooled in the presence of a low-frequency (100-Hz) directing voltage (300 V). The sample thus prepared was H-aligned. Plots were made of the equivalent parallel capacitance $C_p(\omega)$ against log f for both the unaligned and H-aligned samples, and the crossover frequency, f_0, was determined at each sample temperature. Figure 3 shows the plot log f_0 vs temperature, and a variation of ~1.6 units of log f is observed for a change of 20 °C. According to the two-frequency addressing principle, if a strong electric field of frequency f_D is applied to a sample in its LC state, then for a "dielectrically



(a)



(b)



(c)

Figure 1. Three examples of LC polymers. (a) Mesogenic groups attached longitudinally in the side chain. (b) Mesogenic group in the main chain and mesogenic group attached longitudinally in the side chain.[11,12] (c) Mesogenic groups attached laterally in the side chain.

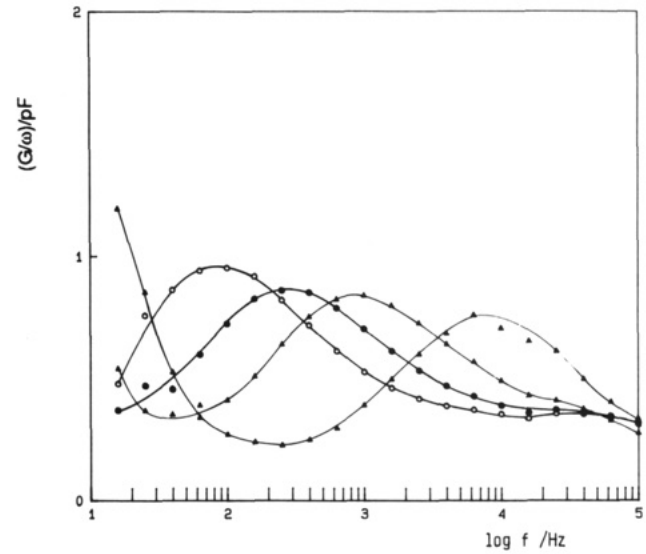


Figure 2. G/ω (pF) against log f (Hz) for unaligned polymers at different temperatures. ○, ●, △, and ▲ correspond to 42, 48, 59, and 62 °C, respectively.

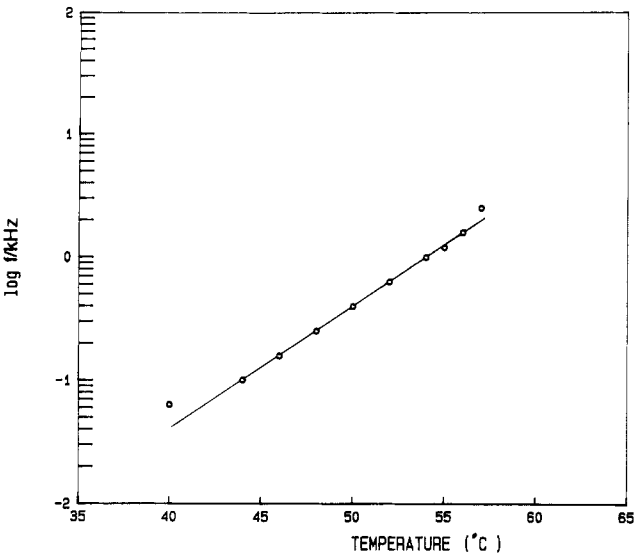


Figure 3. log f_0 (kHz) against sample temperature, where f_0 is the crossover frequency in kilohertz.

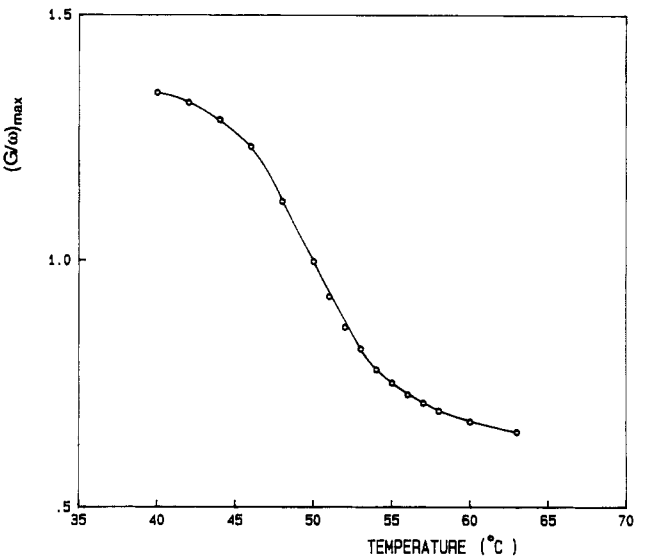


Figure 5. Height of dielectric loss peak, $(G/\omega)_{max}$, plotted aginst sample temperature for a sample that was initially H-aligned.

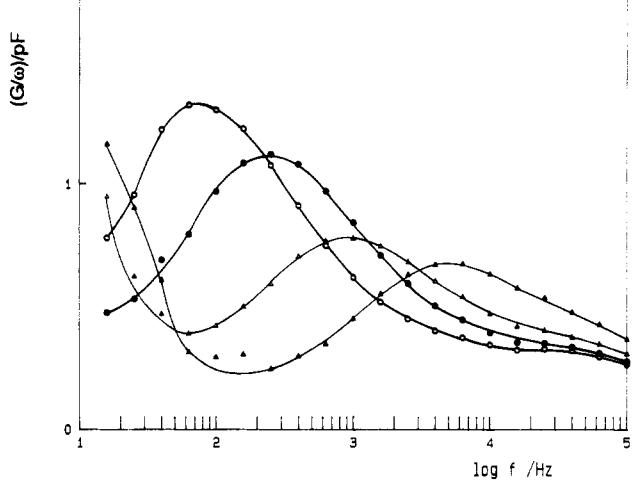


Figure 4. G/ω (pF) against log f (Hz) for a sample that was initially H-aligned and was studied at different temperatures starting at 42 °C. ○, ●, △, and ▲ correspond to 42, 48, 54, and 60 °C, respectively.

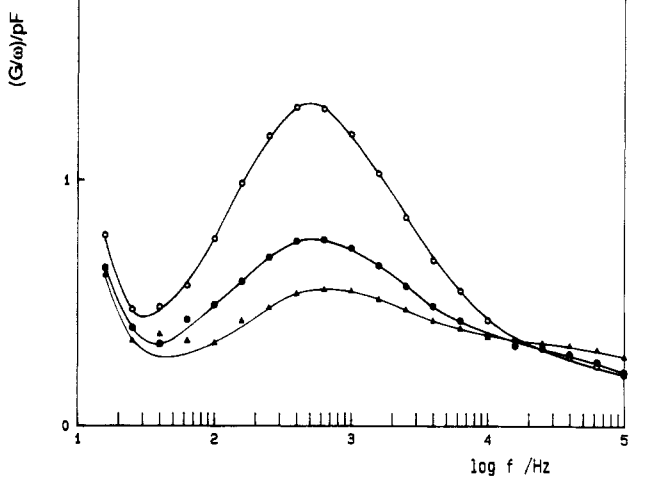


Figure 6. G/ω against log f (Hz) for H-aligned (○), unaligned (△), and a sample that was initially aligned homeotropically but measured 12 h following removal of the directing field (●). All measurements were made at 52 °C.

positive" material, if $f_D < f_0$, H-aligned is favored, whereas for $f_D > f_0$ P-alignment is favored. The time scale for field-induced realignment depends upon the viscosities and elastic constants of the LC phase,[30,36] and these are temperature dependent. The f_0–T locus in Figure 3 is convenient in relation to the practical aspects of applying strong ac fields, so, e.g., at 50 °C H-alignment and P-alignment should be attainable if $f_D \sim 100$ Hz and 10 kHz, respectively, which are readily accessible experimentally. It is important that f_D should be chosen so as to avoid the loss peak range, which would give dielectric heating, and the low-frequency conductivity tail, which would give dielectric heating and electrohydrodynamic instabilities. We found that the effective viscosity of the LC phase for II was sufficiently small to allow a sample to be aligned H ↔ P in the LC state, in contrast to our earlier observations for siloxane LC polymers having longitudinally attached mesogenic groups.[22-29] Figure 4 shows the loss spectra for a sample that was prepared H-aligned at 52 °C by using 300 V applied at 100 Hz for 1 h, followed by cooling at room temperature, which retained the sample alignment. The height of the loss peak at low temperatures is enhanced by alignment. However, as the sample temperature is increased stepwise, and held fixed for 20 min at each temperature to allow temperature equilibration and the spectrum to be measured, the height of the loss peak decreased markedly with increasing temperature, as is shown in Figure 5. Under these experimental conditions, the H-alignment is lost well below the clearing temperature (T_c = 61 °C). It was not clear if the variation shown in Figure 5 was an equilibrium property of this polymer or if it was a kinetic property in which alignment was being lost in time simultaneously with the experimental scans being made of frequency and temperature. If it had been an equilibrium property of the sample, Figure 5 would suggest a very wide transition range, in contradiction to the optical microscopy information and DSC data for the material. Therefore, a kinetic phenomenon of disalignment was suspected and was investigated by preparing samples of particular macroscopic alignment and then monitoring the dielectric spectra with elapsed time while holding the sample at the fixed temperature. The studies revealed that H-aligned or P-aligned samples lost their alignment when the directing

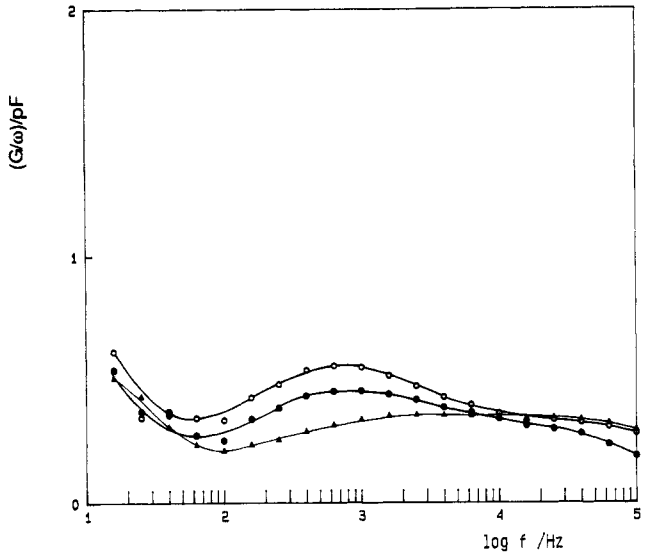


Figure 7. G/ω against log f (Hz) for P-aligned (△), unaligned (○) and a sample that was initially aligned planarly but measured 12 h following removal of the directing field (●). All measurements were made at 52 °C.

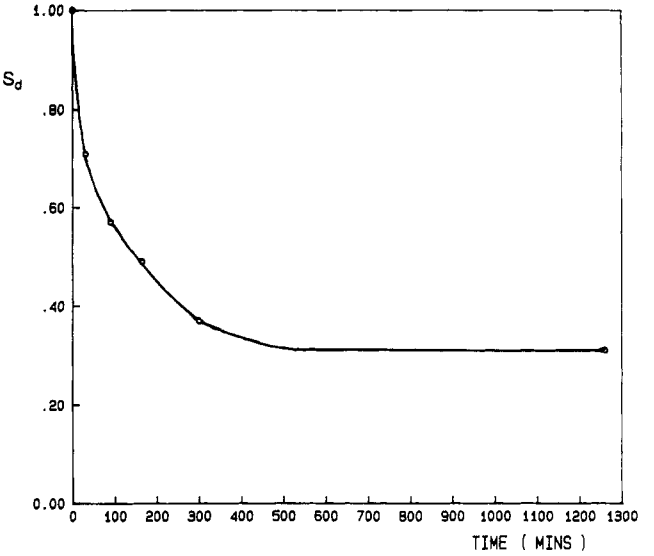


Figure 8. S_d against time (minutes) for a sample at 52 °C that was initially H-aligned but disaligned following the removal of the directing field.

field was removed. A fully H-aligned sample was prepared at 52 °C by using a directing voltage of 300 V at 100 Hz. After 12 h following the removal of this voltage the magnitude of the loss spectrum had decreased substantially toward that of the unaligned sample at this temperature, as is shown in Figure 6. Similarly, a fully P-aligned sample was prepared at 52 °C by using 300 V at 30 kHz, and, on removal of this voltage, the loss spectrum recovered toward that for the unaligned material, as is shown in Figure 7. We note that in both Figures 6 and 7 that the individual loss curves all cross at a common frequency (the isosbestic point), independent of the degree of macroscopic alignment of the sample, for a given sample temperature. According to a simple macroscopic theory, we have described earlier[25]

$$\epsilon_i''(\omega) = (1 + 2S_d)\epsilon_H''(\omega)/3 + 2(1 - S_d)\epsilon_P''(\omega)/3 \quad (1)$$

where S_d is the macroscopic director order parameter for the sample of intermediate alignment I, $\epsilon_i''(\omega)$ is the loss factor at frequency $\omega = 2\pi f$ and where i is I, H, and P. Rearranging eq 1 and converting to the loss representation used in the present work, we have

$$S_d = \frac{3(G/\omega)_I - [(G/\omega)_H + 2(G/\omega)_P]}{2[(G/\omega)_H - (G/\omega)_P]} \quad (2)$$

Thus, the measurement of values of G/ω for "unknown", homeotropic (H), and planarly aligned (P) samples at a chosen frequency for a given sample temperature allows S_d to be calculated. This may be repeated for the set of frequencies used in obtaining the dielectric spectra; hence, several S_d values may be determined and averaged. Figure 8 shows values of S_d determined in this way for a sample prepared initially at 52 °C as fully homeotropically aligned and held at this temperature following the withdrawal of the field. Given sufficient time, the H-alignment would be effectively lost for this polymer at this temperature. This behavior is in contrast with our earlier work with siloxane LC polymers[22-29] where it was found that *no* disalignment occurred for aligned samples for $T < T_c$, as monitored by the dielectric spectrum. However, it was found that those polymers could not be aligned by using electric fields applied to samples in their LC state. It was necessary to work in the biphasic region[24,25] or to cool from the melt with the field applied in order to cause the material to become aligned. Thus, it appears that a material that can be aligned to H- or P-aligned states in its LC state may also disalign when the field is removed. This is necessarily a bulk effect for this polymer (II) since disalignments H → U and P → U both occur similarly, indicating the absence of surface-induced disalignment processes. We note that Bormuth and Haase[21] found that they could align the carbon-chain LC polymer (I above) to obtain fully H-aligned material, but it was found to be impossible to obtain fully P-aligned material.

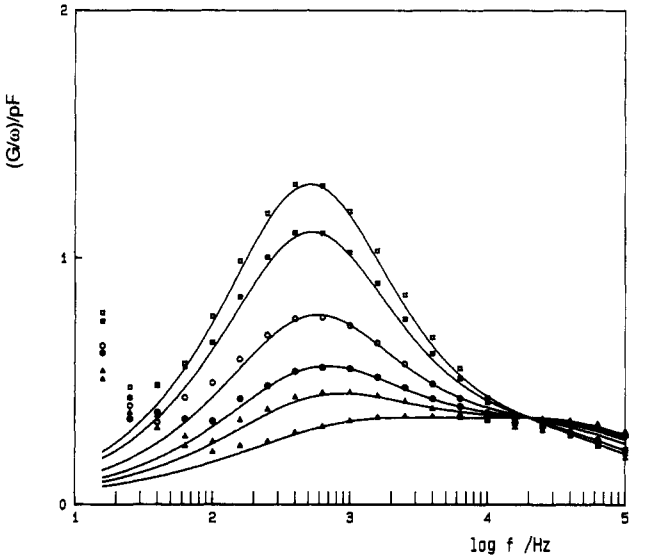


Figure 9. Loss spectra as for a sample that was prepared in different states of macroscopic alignment at 52 °C. The calculated curves are shown as continuous lines for S_d = 1.0, 0.71, 0.20, −0.12, −0.30, and −0.5, progressing from homeotropic (top curve) to planar (bottom curve).

Figure 9 shows the loss spectra for a sample that had been prepared in different states of macroscopic alignment at 52 °C. Note the isosbestic point and note that the P-aligned material shows clear evidence of two peaks. It is of interest to see if the family of loss curves shown in Figure 9 may be fitted using particular values for Sd and knowing the basic line shapes for H and P samples, in the manner we have described earlier.[25] According to theory, for the model case where the mesogenic groups have rigid dipole moments μ, which may be resolved into components μ_l and μ_t with respect to the principal axis, the principal

complex permittivities for a uniaxial material may be written as[25]

$$\epsilon_{\parallel}(\omega) = \epsilon_{\parallel}^{\infty} + \frac{G}{3kT}[\mu_l^2(1 + 2S)F_{\parallel}^{l}(\omega) + \mu_t^2(1 - S)F_{\parallel}^{t}(\omega)] \quad (3a)$$

$$\epsilon_{\perp}(\omega) = \epsilon_{\perp}^{\infty} + \frac{G}{3kT}[\mu_l^2(1 - S)F_{\perp}^{l}(\omega) + \mu_t^2(1 + S/2)F_{\perp}^{t}(\omega)] \quad (3b)$$

$\epsilon_{\parallel}^{\infty}$ and $\epsilon_{\perp}^{\infty}$ are the (real) limiting high-frequency permittivities, G is a constant, S is the local order parameter, and the $F_j^i(\omega)$ are given by $F_j^i(\omega) = 1 - i\omega f[F_j^i(t)]$ where the $F_j^i(t)$ are the time correlation functions for the angular motions of the mesogenic group with respect to the local director axis n and f indicates the Fourier transform. According to eq 3, four relaxation modes should occur, two for $\epsilon_{\parallel}(\omega)$ and two for $\epsilon_{\perp}(\omega)$, while for samples of intermediate alignment ($-0.5 \leq S_d \leq 1$), the loss spectrum should be a weighted sum of contributions from $\epsilon_{\parallel}(\omega)$ and $\epsilon_{\perp}(\omega)$ (according to eq 1). The loss specta for H- and P-aligned samples in Figure 9 show indications of multiple-relaxation processes. In order to use the phenomenological eq 1 to fit data for intermediate alignments using S_d as the single adjustable parameter, we choose to fit the loss curves for the H- and P-aligned samples using two component peaks, each having a Fuoss–Kirkwood line shape.[21,23,31] Figure 10 shows the loss curves fitted in this way. Also shown in the figure is the fit of the U-aligned loss curve using two F–K curves. The parameters used for these fits are given in Table I. Here the δ and α processes refer to the low- and high-frequency processes, respectively. The fits are seen to be good in all cases. This procedure gives the "calculated" loss spectra for H- and P-aligned samples, which can be used to calculate the loss curve for a sample of intermediate alignment using S_d as the single parameter. Figure 9 includes the curves calculated in this way for different degrees of macroscopic alignment. The values used for S_d are included in the caption to the figure. The agreement between the experimental and calculated curves is good in all cases and note the isosbestic frequency at $f = 17$ kHz. Therefore, eq 1 gives a satisfactory representation of the loss data, and our data provide support for the use of the concept of the macroscopic director order parameter, S_d, for uniaxial thermotropic liquid-crystalline polymers.

An advantage of fitting our data to analytical functions, i.e., two Fuoss–Kirkwood functions, is that we are able to obtain a reasonable estimate of the total integrated intensity $A = (\epsilon_0' - \epsilon_\infty')$ for a loss spectrum that is only measured over a limited range of frequency (i.e., the experimental loss spectrum is truncated at low and high frequencies). Using the present method of deconvolution of a loss spectrum, the relaxation strength, A_δ, is proportional to $(G/\omega)_{max}/\beta$ for the δ-process. The total relaxation strengths for the U and P samples are calculated as the sum of the terms $(G/\omega)_{max}/\beta$ for the component δ and α processes.[23,29] When the values of the parameters given in Table I were used, it was therefore possible to calculate A_δ, A_U, and A_P. It may be shown[23,29] that

$$\frac{A_\delta}{A_U} = \frac{1 + 2S}{1 + 2SS_d + (1 - SS_d)y} \quad (4a)$$

$$\frac{A_P}{A_U} = \frac{(1 - S) + (1 + S/2)y}{1 + 2SS_d + (1 - SS_d)y} \quad (4b)$$

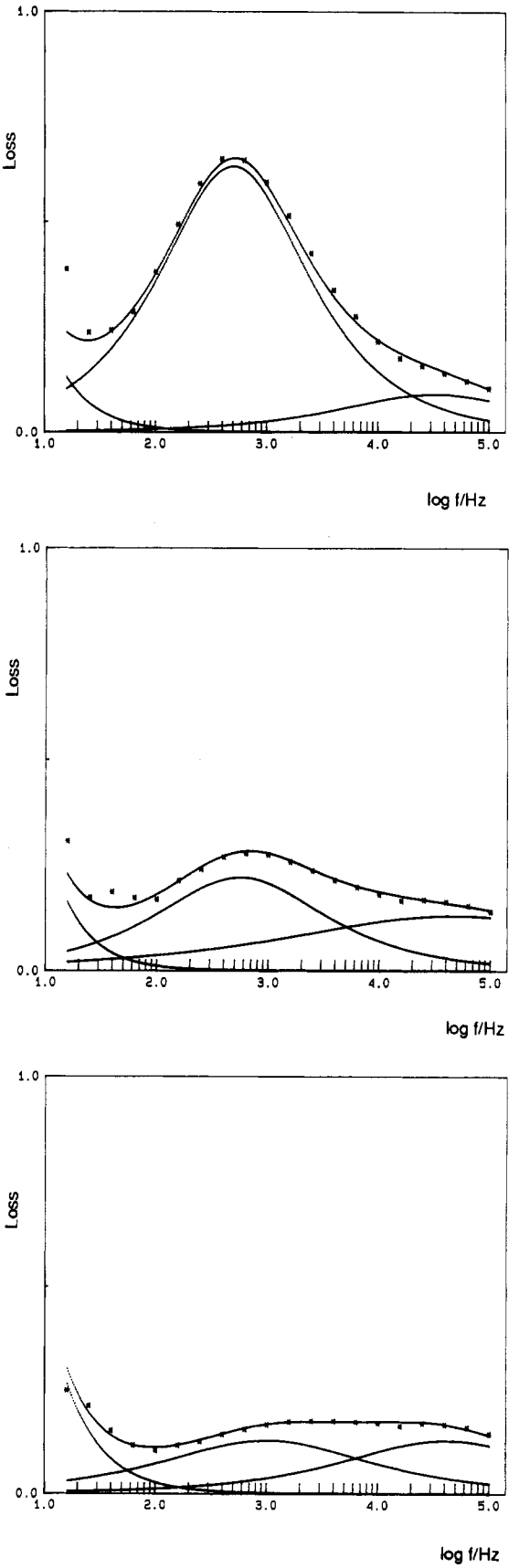


Figure 10. Fit of the observed loss spectra for H- and P-aligned and unaligned material at 52 °C using two Fuoss–Kirkwood curves; parameters are given in Table I. (a) Homeotropic. (b) Unaligned. (c) Planarly aligned.

where S is the value of the local order parameter and $y = (\mu_t/\mu_l)^2$ where μ_l and μ_t are the effective longitudinal and transverse components of μ, respectively. Equations 4a

Table I
Deconvolution of Data of Figure 10 for H, P, and "Unaligned" Samples at 52 °C, into Two Fuoss–Kirkwood Component Curves[a]

		peak position log f, Hz	rel peak ht	β
homeotropic	δ-process	2.70	1.00	0.72
	α-process	4.50	0.14	0.55
"unaligned"	δ-process	2.75	0.34	0.63
	α-process	4.65	0.21	0.32
planar	δ-process	2.99	0.21	0.51
	α-process	4.60	0.21	0.51

[a] The distribution parameter β = 1.14/(width of peak at half-height).

and 4b were solved for (S, S_d, y) by expressing $y = F(S,S_d)$ from eq 4a and $y = f(S,S_d)$ from eq 4b and plotting y against S for each function for different values of S_d. The set (S, S_d, y), which leads to a single contact point between the two functions is the required solution. For our calculations we take S_d = 1.0 for the H-aligned sample and S_d = −0.5 for the P-aligned sample and assume that S_d is close to, but not exactly equal to, zero for the U-aligned sample. The calculations were quite sensitive to the precision for the determined values of A_δ, A_U, and A_P. Taking the values of the fit parameters given in Table I, the solution obtained was (S, S_d, y) = (0.486, 0.26, 0.51). Increasing both A_δ/A_U and A_P/A_U by 10% gave (0.486, 0.05, 0.51) while decreasing each ratio by 10% gave (0.486, 0.52, 0.51). Clearly the solution having S_d = 0.05 is satisfactory. The value S = 0.486 is typical of that for a LC phase close to T_c; the value y = 0.51 shows that this is a dielectrically positive material at low frequencies.

The frequency of maximum loss factor for the δ-process was found to follow the Arrhenius equation with respect to temperature variation, with an apparent activation energy of 185 kJ mol^{-1}, which is to be compared with 240 kJ mol^{-1} obtained by Bormuth and Haase for polymer I and 160–180 kJ mol^{-1} in the temperature range closer to T_c for different siloxane-chain LC polymers having longitudinally attached mesogenic groups.[16-20,21-29] It seems unlikely that a process with such a large apparent activation energy could occur by small-step rotational diffusion in the local P_2-potential. The complexity of molecular packing of the backbone, alkyl spacer, and mesogenic head group is well-illustrated by Bormuth and Haase[21] (their Figure 6). Clearly there is a well-defined director axis in the aligned LC polymer in the steady ac directing field defined by the collective average orientation of the mesogenic head groups, with the alkyl spacer groups and polymer backbone having to take up arrangements that preserve the orientation of the head groups. In this condition the motion of the mesogenic groups is very extensive, giving rise to all the four dielectric relaxation modes. It is difficult to see how the bulky mesogenic groups may undergo 180° reorientations within the mean P_2-potential of the neighboring groups in the LC phase, since the volume swept out and the rearrangement required for the neighboring groups seem prohibitively large (see Figure 6, ref 21). Two possible mechanisms for the δ-species may be envisaged: (i) that the local region undergoes a wholly cooperative rearrangement that preserves the overall local director but allows individual groups to span the whole of the 4π solid angle and (ii) that the mesogenic groups undergo extensive angular fluctuations, leading to all the relaxation modes and allowing most of $\langle\mu^2\rangle$ for the mesogenic group to be relaxed. Again such motions would be highly cooperative, but the local director is readily preserved and 180° "flip–flop" motions would be excluded, thus avoiding the conceptual difficulties of a mesogenic group finding a pathway through the surrounding mesogenic groups, alkyl spacers, and backbone segments to achieve 180° reorientation of the dipole moment vector. It is not clear at this stage which, if either, of the mechanisms i and ii can be applied to our dielectric data.

Seiberle, Stille, and Strobl[37] studied the dielectric properties of H- and P-aligned samples of a siloxane LC side-chain polymer, a low molar mass LC material, and their mixtures. A well-defined δ-process was observed for all samples. The low molar mass material gave a δ-process whose loss peak resembled closely a single relaxation time process, while the polymer δ-loss peak resembled that for a Cole–Cole function with a distribution parameter $\alpha \simeq$ 0.08. The mixtures gave a δ-process whose relaxation frequency was intermediate between those for the individual components, and the loss peak showed no evidence for two-component processes. The δ-loss curve for the 1:1 mixture was very similar to that for the polymer. Seiberle and co-workers enquired if the δ-process of individual LC groups in the pure materials and their mixtures should be considered to be a single particle property or a result of a collective process. Since only one δ-process was observed for the mixtures, despite the fact that log f_m changes by ~3.5 on going from pure low molar mass material to pure polymer (see their Figure 10, ref 37), collectively might be indicated. However, they suggest that this is a wrong impression since other mixtures showed a splitting of the δ-process,[38,39] indicating, in those systems, a different δ-process for each component. They also suggest[37] that a collective relaxation process, "like the α-process, always exhibits marked deviations from single relaxation time behavior, showing a clear asymmetric broadening", which was not observed for their mixtures. Hence, they suggest that the δ-relaxation process of the different mesogenic groups in the mixture are too similar to be resolved by the measurement and that the elementary process corresponds to single particle motion, which they model using the theory of Martins, Meier, and Saupe.[40]

We note that the primary (α) relaxation in glass-forming liquids and polymers arises from the cooperative motions of molecules.[41,42] In those cases the loss peak is broad and asymmetric and may be approximated by Davidson–Cole or Kohlrausch–Williams–Watts functions. Furthermore, only one α-process is observed, normally, for mixtures of low molar mass liquids (e.g., alkyl halides) or for copolymers (e.g., styrene–chlorostyrene copolymers). The interpretation of a single loss peak for systems in which the dipolar groups are in different chemical environments is that the dipole moment correlation functions are the same, at least approximately, for each species in the mixture or in the copolymer. This may be expressed mathematically as[43,44]

$$\langle\mu_i(0)\cdot\mu_j(t)\rangle / \langle\mu_i(0)\cdot\mu_j(0)\rangle = \phi_{ij}(t) \cong \Phi(t)$$

for all i and j, and where i and j refer to particular chemical groupings. $\mu_j(t)$ is the dipole moment of group j at time t; $\mu_i(0)$ is the dipole moment of group i at t = 0. $\Phi(t)$ is an effective dipole moment correlation function for the α-process, and its form has been discussed for mixtures of glass-forming liquids[41] and for random copolymers.[42,45] The autocorrelation terms $\langle\mu_i(0)\cdot\mu_i(t)\rangle$ corresponds to motions of the group i and are, in that sense, single-particle motions. However, the dynamics of the motion of group i will involve the surrounding molecules, and thus the motion of group i will be cooperative with the surrounding molecules. If a mean field is assumed, then the motion of group i may be modeled as a single-particle motion in a continuum or in an effective local potential, as was

considered for liquid crystals by Martin et al.[40] and used by Seiberle et al.[37] It is important to stress, however, that motions of molecules in the liquid state are always cooperative motions involving the molecules surrounding any reference molecule or group. We should also comment further on the line shape for the dielectric loss curves for liquids. While many glass-forming liquids, e.g., glycerol and alkyl halides, exhibit broad asymmetric loss peaks of Davidson–Cole or Kohlrausch–Williams–Watts type, several alcohols exhibit near-single relaxation time behavior in the T_g region despite the fact that the motions are cooperative and involve the making and breaking of hydrogen bonds (see ref 41, pp 152–154). Perhaps the best example of cooperative motions leading to near-single relaxation time behavior is the case of liquid water, where computer simulation[46] shows that many molecules are involved in the reorientation of a reference molecule but the dipole moment correlation function is well-represented by a single-exponential decay function for times greater than that for local collisions.[46] Thus collective motions may lead to single relaxation time behavior or to broad, asymmetric loss peaks for glass-forming liquids and polymers.

For the present work and for our earlier work with side-chain LC polymers, we consider that the δ-process is due to the cooperative motions of a dipolar mesogenic group with its environment. Two mechanisms, i and ii above, are examples of cooperative motions that may lead to a total or partial relaxation, respectively, of the longitudinal component of the dipole moment of the mesogenic groups.

Finally, the disalignments H → U and P → U, on removal of the directing electric field, suggest that the directing electric fields, while causing the mesogenic groups to align collectively to form H- or P-alignment, also cause the spacer and backbone units to take up disfavored orientations, leading to a stress in the material. Removal of the directing electric field leaves an aligned material with internal stresses, which can be relieved by the spacer and backbone changing their conformations and in doing so tend to disalign the mesogenic groups and hence give a disalignment, in time, manifested as a change of the entire specimen, whether it be H-aligned or P-aligned initially.

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