Macromolecules

Volume 28, Number 25 December 4, 1995

Electrical and Optical Alignment Processes in Some Novel Liquid-Crystalline Side-Chain Polymers As Studied by Dielectric Relaxation Spectroscopy

S. R. Andrews,*[,†] G. Williams,[†] L. Läsker,[‡] and J. Stumpe[‡]

Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, U.K., and Department of Chemistry, Humboldt University, Haus 4, Erieseering 42, D-10319 Berlin, Germany

Received May 2, 1995; Revised Manuscript Received August 15, 1995[®]

ABSTRACT: Dielectric relaxation spectroscopy has been used in the present work to study the extent of the macroscopic alignment that is induced in some novel liquid-crystalline (LC) side-chain polymers containing either photoactive cyanoazobenzene groups or cyanoazobenzene groups interdispersed along the chain by nonactive cyanobiphenyl groups. The effects of an applied ac electric field on the cyanoazobenzene mesogenic side groups in a LC homopolymer (LC1) and a LC copolymer (LC2) have been studied. Also, the actions of polarized laser radiation (514 nm mode-lock pulse) on the copolymer via an isomerization mechanism of the cyanoazobenzene moieties have been examined. The changes with temperature through the liquid-crystalline phase to the clearing temperature in the loss part of the complex permittivity of the samples measured in the frequency plane give a good qualitative indication of the changes of alignment that are being induced by light or an electric field since the δ-relaxation process and other component processes may be used as indicators of macroscopic alignment.

Introduction

Since the works in 1978 of Ringsdorf, Finkelmann, and Wendorff at Mainz and Shibaev and Platé in Moscow first demonstrated that thermotropic liquid-crystalline polymers with acrylate or methacrylate backbones and having the liquid-crystal-forming mesogenic groups in the side chains could be synthesized, much has been done to understand their physical characteristics.[1-4] It was shown that such liquid-crystalline side-chain (LCSC) polymers could be aligned by electric or magnetic fields to form optically anisotropic polymer films which were of great interest, particularly with a view to applications in optical data storage, since they have a unique combination of the good film-forming properties of a polymer and liquid-crystalline properties. One study[5] showed that the $E \leftrightarrow Z$ (*trans–cis*) isomerization of azo units within mesogenic side groups of liquid-crystalline side-chain polymers could be induced by visible light and that some macroscopic modification of the alignment occurred. Further studies by Tredgold *et al.*[6] showed that optical birefringence could be induced in such liquid-crystalline side-chain polymers when polarized white light was used. Since then, many studies have been reported using polarized light to induce macroscopic alignment in liquid-crystalline side-chain polymers. Optical anisotropy has been produced in films of amorphous polymers[7,8] and in amorphous films of liquid-crystalline polymers[9,10] by photochemically induced alignment of isotropically distributed azobenzene side groups. These studies also showed that a cooperative motion may exist between the photoactive azobenzene groups and photoinactive mesogens within copolymers. Indeed, Natansohn *et al.*[11] showed by spectroscopic methods that this cooperative motion may occur in these types of LC copolymers.

Dielectric relaxation spectroscopy (DRS) has been used to study such physical changes in liquid-crystalline side-chain polymers,[12-19] and it is the aim of the present investigation to use DRS to study the changes in the complex permittivities of liquid-crystalline side-chain polymers that are induced by both an applied ac electrical field and polarized laser radiation. It should be possible to use DRS studies to monitor the resultant changes in the nature and extent of macroscopic alignment of the mesogenic groups within these polymers.

The side-chain polymers studied in the present investigation belong to a set of compounds having the

---

[†] University College of Swansea.

[‡] Humboldt University.

[®] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

0024-9297/95/2228-8463$09.00/0

Chart 1

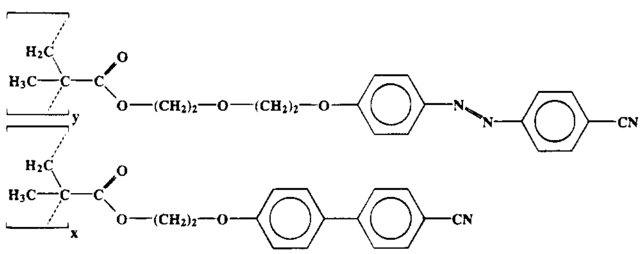

Table 1. Glass Transition and Clearing Temperatures of Side-Chain Liquid-Crystalline Polymers Synthesized with Different Ratios of Cyanobiphenyl (x) to Cyanoazobenzene (y) Moieties As Measured by Differential-Scanning Calorimetry (DSC)

polymer	y	x	T_g/°C	T_C/°C
LC1	1.0	0.0	57	115.1
LC2	0.8	0.2	67	89.5

same basic formula as given in Chart 1. The polymers (as random copolymers) were synthesized by Kostromin and Shibaev (University of Lomonossov, Moscow) with differing x and y proportions in the samples. The modification of the ratio of x to y components in the LCSC polymers means that their physical properties differ. These novel side chains have properties close to those of both amorphous and liquid-crystalline polymers, depending on composition. They show the typical features of liquid-crystalline side-chain polymers, *i.e.* a linear backbone containing the nonflexible rodlike mesogenic groups, the principles of which have been discussed and reviewed elsewhere.[4] However, because of the short alkyl spacer group between the cyanobiphenyl group and the backbone which results in a drastically restricted mobility of these side groups, the energetically preferred random coil conformation of the polymer backbone is only overcome when the proportion of cyanoazobenzene moieties is high. Thus the tendency for self-organization is decreased with an increasing proportion of the rodlike side groups and only a proportion of cyanobiphenyl groups of 20% or less results in liquid-crystalline properties of the materials. These polymers are the subject of the present investigation, the physical properties of which are given in Table 1. LC1 and LC2 liquid-crystalline side-chain polymers exhibit a low enthalpic stability of the liquid-crystalline phases, as measured by DSC [$\Delta H(\mathrm{LC} \rightarrow i) = 1.8$ and 3.8 J/g,[20] respectively]. Therefore, amorphous films which are transparent, optically isotropic, and nonscattering can easily be prepared by cooling a polymer film quickly (20 deg/min) from the isotropic melt into the glassy state. The samples were prepared this way to avoid any preferred alignment of the mesogenic groups on slow cooling, as these samples have a tendency to do. Alignment of the liquid-crystal mesogenic groups has been discussed fully both theoretically[21] and experimentally[13,22-26] and can be induced by applying a strongly directing ac electrical field to the liquid-crystal film, resulting in the alignment of the groups parallel, or perpendicular, to the directing ac electrical field, depending on its frequency. Also, upon irradiation with linearly polarized laser radiation, the cyanoazobenzene moieties undergo angular-dependent $E \leftrightarrow Z$ photoisomerization and a wavelength-dependent photostationary equilibrium between rodlike E isomers and Z isomers with a modified geometrical shape is established. Irradiation at a wavelength which produces only a low proportion of Z isomers but results in high rates of both $E \rightarrow Z$ as well as $Z \rightarrow E$ isomerization yields a reorientation of the cyanoazobenzene side groups and may trigger the physical reorientation of the other mesogenic groups in the same direction, *i.e.* perpendicular to the plane of polarization.[27,28] Therefore the overall alignment is changed and is frozen in because the isomerization cycle causes a net perturbation in the supramolecular structure. The mechanism for reorientation has been described in more detail by Läsker *et al.*[8,10]

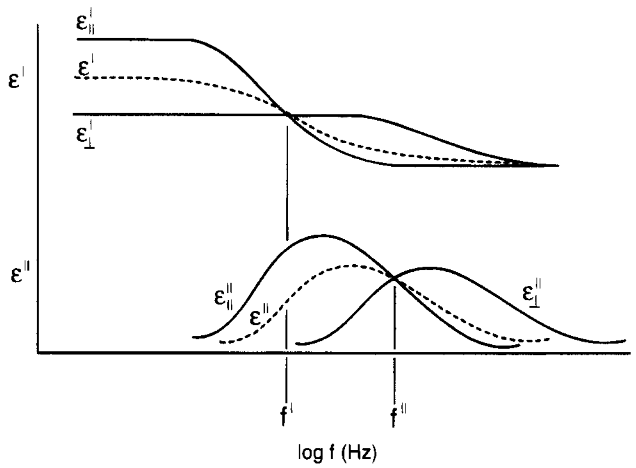

Figure 1. Plot of the real and imaginary parts of $\epsilon_{\|}$, ϵ, and $\epsilon_{\perp}$ against log f for a side-chain liquid-crystalline polymer.

Experimental Section

In order to study the effects of both an applied ac electrical field and polarized laser radiation on the liquid-crystalline side-chain polymers, samples were melted on a hot plate and sandwiched between two conducting indium tin oxide (ITO) coated glass electrodes. Temperatures just above their clearing temperature, T_C, were chosen for the melting process since amorphous films had to be produced by quickly cooling from the isotropic melt but decomposition of the LC polymer samples at much higher temperatures had to be avoided. PTFE spacers were used to maintain a constant thickness (about 45 μm) and to insulate one electrode from the other. The sample area was *ca.* 1.21 cm^2. The glass cells containing the samples were mounted in a thermostatically-controlled Linkam hotstage which was connected to a Novocontrol dielectric thermal analyzer (DETA) system comprising a Solartron SI1260 frequency response analyzer with dielectric interface. The whole system was coupled to a computer running Novocontrol's WINDETA software to collect, store, and manipulate the dielectric data thus acquired.

For each frequency, f, the equivalent parallel capacitance, C_P, and conductance, G_P, were measured for the sample. From these, various other quantities can be calculated, in particular the relative permittivity, ϵ', and loss factor, ϵ'', that are the real and imaginary parts of the complex permittivity, $\epsilon = \epsilon' - i\epsilon''$. These are related to C_P and G_P as follows:

$$\epsilon' = C_P/C_O \qquad \epsilon'' = G_P/\omega C_O \tag{1a,b}$$

where C_O is the geometrical capacitance of the interelectrode space and ω ($=2\pi f$) is the angular frequency of the measurement. Thus plots of ϵ' and ϵ'' indicate the dielectric relaxation behavior in the samples being studied.

Theoretical Considerations

The effects of macroscopic alignment on the dielectric properties of a liquid-crystalline side-chain polymer material can best be described by referring to theoretical permittivity and loss curves for a "dielectrically-positive" material; these are shown schematically in Figure 1. ϵ' and ϵ'' show the dielectric permittivity and loss of a randomly orientated material in which all the mesogenic groups in the LC material are randomly directed, $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the permittivities of samples with the average LC director aligned parallel (homeotropic, h) or perpendicular (homogeneous or planar, p), respectively, to the direction of the applied ac field.

Semimacroscopic theory for the complex permittivity states[15,23] that formation of homeotropic alignment should shift the frequency of maximum loss to lower frequencies, and planar alignment to higher frequencies, since the loss curves comprise different weighted sums of the underlying dipole relaxation modes 00, 01, 10, and 11 where

$$\epsilon = (1 + 2S_d)\epsilon_{\parallel}/3 + 2(1 - S_d)\epsilon_{\perp}/3 \qquad (2)$$

S_d is the macroscopic director order parameter where

$$S_d = \langle 3\cos^2\theta_{nZ} - 1\rangle/2 \qquad (3)$$

and θ_{nZ} is the angle between the director axis and the measuring field direction. S_d is equal to 0 for an unaligned sample (a weighted average of all underlying relaxation modes) and +1.0 and −0.5 for fully h- and p-aligned samples, respectively. This leads to the conclusion that for all values for S_d there may be a frequency with the same loss value for all sample orientations. An analogous isosbestic point also arises for the permittivity, ϵ', of differently-aligned samples, but its value is different from that for the loss factor.

It follows from Figure 1 that if a strongly directing ac electrical field of frequency f is applied to the material, then for $f < f'$, $\Delta\epsilon' > 0$ and h-alignment is favored while for $f > f'$, $\Delta\epsilon' < 0$ and p-alignment is favored. However, a frequency that is too low, and in the conductivity tail, will result in dielectric heating of the sample, which leads to thermal instabilities and flow, hence reducing the extent of the alignment that can be achieved. Using this "two-frequency" addressing principle, h-aligned samples may be prepared by cooling from the isotropic melt in the presence of a strong low-frequency field, as has been described elsewhere.[15,17,29] The dominant loss peak in a h-aligned LCSC polymer is the δ process (00 mode), as described earlier.[15-17] On formation of a p-aligned sample the δ process is effectively removed, leaving a small loss curve (α process) arising at higher frequencies.

As for the effect of polarized laser radiation on an isotropic side-chain liquid-crystalline material, certain rodlike mesogenic groups will undergo $E \leftrightarrow Z$ photoisomerization; in the present case isomerization of the cyanoazobenzene groups will result. The angular-dependent photoselection combined with rotational diffusion within the photostationary equilibrium of the $E \leftrightarrow Z$ isomerization will result in a preferred orientation of the groups perpendicular to the electric vector of the light. This 90° effect has been discussed comprehensively by Birenheide *et al.*[30] The photoinduced isomerization and therefore reorientation of the cyanoazobenzene moieties perpendicular to the direction of polarization in the laser radiation may affect the overall orientation of the cyanobiphenyl moieties in the same direction due to their strong polarization field. This orientation will then be frozen into the material. However, since the large area of the film is parallel to the x–y plane of the laboratory frame and the light passes through the sample along the z direction and is polarized along the x direction, then the mesogenic groups will be aligned perpendicular to the x direction, *i.e.* the y or z direction. The dielectric assembly is such, however, that only the induced anisotropy within the y direction will be observed. Any observed difference in alignment in the y direction can therefore be explained in terms of a preferred alignment, since alignment in the z direction may occur also but is not measured in the present experiment.

Results and Discussion

LC1 and LC2 were selected in this study in order to observe dielectrically the effect of a directing ac electrical field on the macroscopic ordering within sample films, while the effect of polarized light on liquid crystal samples of this type was studied on LC2 only, in order to observe the changes, if any, of the alignment in the material. The two dielectric processes observed in LC1 and LC2 can be compared to gauge the effectiveness of an applied field of light in aligning the mesogenic groups in the materials, and to determine theoretically from these results the loss curves of their p-aligned liquid-crystalline phases.

Electrical Alignment. The samples of LC1 and LC2 liquid-crystalline side-chain polymers were aligned by applying a field of 240 Hz, 40 V for 3 h at 120 °C (LC1) and 3 Hz, 40 V for 3 h at 104 °C (LC2) and then cooling very slowly into the LC state with the field maintained (a later experiment using 60 V for the ac electrical alignment resulted in electrical breakdown in the liquid-crystal films). The upper temperatures used ensured that the samples were in the isotropic melt during the application of the ac electrical field before cooling with the field applied. Frequencies of 240 and 3 Hz were selected because they are away from the dielectric loss maxima and conductivity tails; frequencies used in other regions would result in dielectric heating, as discussed earlier. These frequencies are well below the crossover frequency as the melt becomes the LC phase. Therefore h-alignment is predicted to occur (see Figure 1) under these conditions. Initial results for the electrical alignment of LC1 and LC2 exhibited a high conductivity tail at lower temperatures which made it difficult to examine the loss spectra at lower temperatures. It is expected therefore that important data to indicate the change in the loss peaks during the alignment process would be obscured by this conductivity process. This was even more so for LC2 than for LC1 because with a lower T_C, most of the loss-peak data were partly obscured by the low-frequency conductivity process.

In order to remove this low-frequency conductivity process from the loss spectra, a procedure of conductivity subtraction was undertaken. This takes advantage of the fact that at high temperatures the conductivity process dominates at low frequencies. The functional behavior of this can be calculated over the frequency range and the theoretical curve subtracted from the original data to reveal a "cleaned" loss spectrum. For a true dc conductivity process, the loss factor should be proportional to $1/f$. However, it is usually found for organic solids that a $1/f^n$ law applies. The low-frequency conductivity process can be represented by

$$\log(\epsilon'') = A - n\log f \qquad (4)$$

If a plot of $\log(\epsilon'')$ *vs* $\log f$ is made, values of A and n can be found from the interception and slope of the resulting linear equation. Table 2 gives the values of A and n for the conductivity subtraction process for unaligned LC1 as an example. Although their values calculated this way do not vary much within the

Table 2. Values of n and A Calculated for the Conductivity Subtraction Process of the Data for the Unaligned LC1

temp/°C	n	A
100	0.90	3.020
103	0.92	3.162
106	0.94	3.311
112	0.94	3.467
115	0.99	3.631
118	0.95	3.715
121	0.98	3.891
124	0.97	3.981

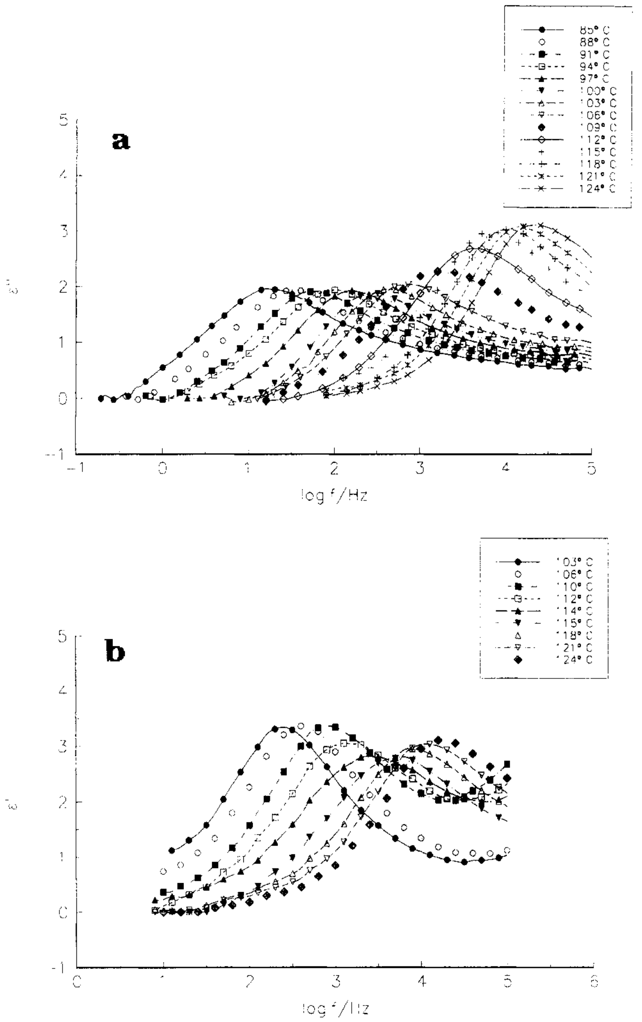

Figure 2. ϵ'' *vs* log f of LC1 over a range of temperatures around T_C for (a) the unaligned sample with the conductivity process subtracted and (b) the ac h-aligned sample (40 V, 240 Hz, 3 h, 120 °C) with the conductivity process subtracted.

temperature range, there is a tendency for n and A to increase with temperature. This is in accordance with a previous study on liquid-crystalline polyacrylate-containing spiropyran groups.[31] Values of A have a good linear relationship over the temperature range; this shows that the conductivity increases with a simple Arrhenius relation as temperature is increased, while values of n are near 1.0, which indicates a nearly-pure conductivity process with little dispersive transport of ions.

By subtracting the calculated loss due to the conductivity process from the observed loss curves, the features due to the dipole relaxation are obtained and are shown in Figures 2 and 3 for LC1 and LC2, respectively. It can be seen from Figures 2a and 3a that the loss curves in the liquid-crystalline state are well-defined with a Δ log f (the full width of the loss curve at half-height) of about 2.1, which is typical of an unaligned LC film and indicates a mixture of α and δ processes, as described previously. The loss peaks are broad and bimodal in the sense that a small high-frequency tail is observed in addition to the main peak. The loss curves in Figures 2a and 3a are assigned to a weighted sum of relaxation modes 00, 01, 10, and 11 (as has been discussed earlier in refs 15, 16, and 32) in which the longitudinal dipole moment μ_l and the transverse dipole moment μ_t associated with the mesogenic groups in the copolymer are relaxed. Alignment should cause an enhancement of the longitudinal moment μ_l associated with the δ-relaxation process (00 mode) in relation to that of the α-relaxation process. As the clearing temperature is approached in LC1, the loss peaks increase as the liquid-crystalline phase melts and becomes an isotropic liquid (Figure 2a, 3a). Once the sample has melted, there are no significant changes observed in peak height or width as the temperature is increased further. The same is true for LC2. Examining the loss curves for the homeotropically aligned samples (Figures 2b and 3b), one can see that preferred homeotropic alignment leads to an increase in the height of the loss peaks over the liquid-crystal phase up to the clearing temperature. Beyond this, the loss curves fall to those for the sample in its isotropic state, as the liquid-crystalline properties

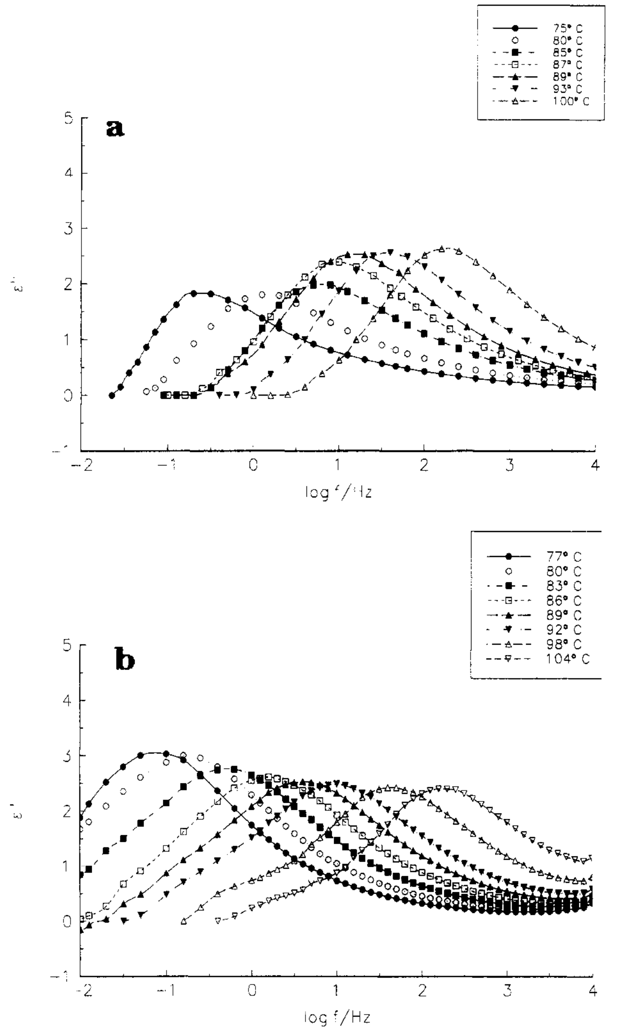

Figure 3. ϵ'' *vs* log f of LC2 over a range of temperatures around T_C for (a) the unaligned sample with thee conductivity process subtracted and (b) the ac h-aligned sample (40 V, 3 Hz, 3 h, 105 °C) with the conductivity process subtracted.

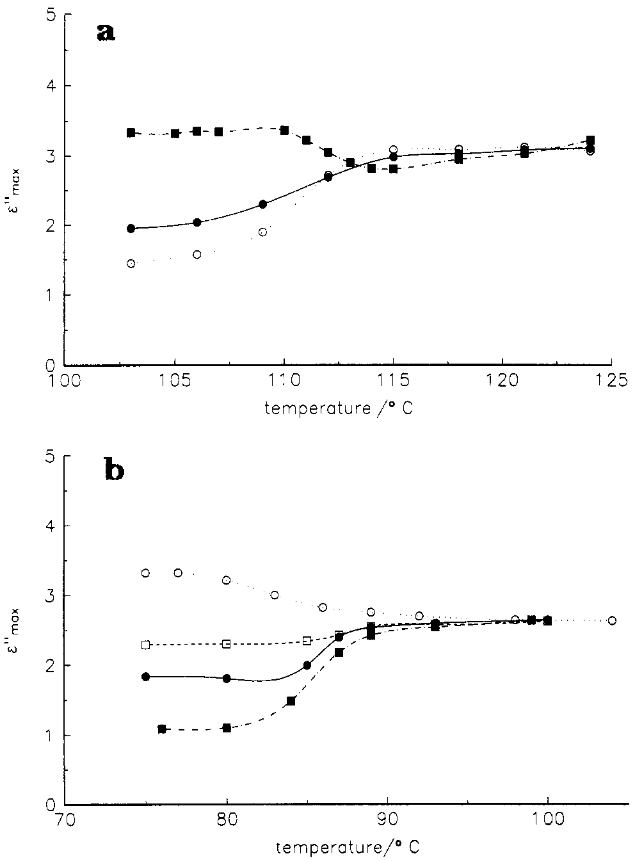

Figure 4. Plot of ϵ'' at the loss peak against temperature for (a) LC1 (h-aligned [■], unaligned [●], and predicted p-aligned [○] samples) and (b) LC2 (h-aligned [○], unaligned [●], irradiated [□], and predicted p-aligned [■] samples).

have been lost. The change in intensity of the loss peaks at temperatures below T_C on alignment is a result of the enhancement of the δ process, or "00" mode, arising from the changes in the rotational fluctuations of the mesogenic groups around their short axes which occurs on alignment. This phenomenon is well-known dielectrically for LCSC polymers (see a review by Williams[33]). Also, the alignment was maintained even when the field was removed for a long period of time, as with earlier work with siloxane polymers[15,31] where it was found that no disalignment occurred for aligned samples for $T < T_C$, as monitored by the dielectric spectrum. Parts a and b of Figure 4 show the plots of the value of maximum loss *vs* the temperature at which the values were measured for LC1 and LC2, respectively. These show clearly the changes in the intensity of the loss peaks with temperature before and after electrical alignment; there is an observed divergence in the ϵ''_{max} values, $\Delta\epsilon''_{max}$, between unaligned and homeotropically aligned samples of about 1.3, which is caused by the enhancement of the δ-relaxation process on alignment. The enhancement of the δ process observed dielectrically is of the same magnitude for both samples, as h-alignment is created by the action of the ac electric field, and is due to the change in the distribution of relaxations of the longitudinal (μ_l) and transverse (μ_t) dipole moments of the mesogenic groups from a weighted sum of the four relaxation modes 00, 01, 11, and 10 (unaligned sample) to predominantly the 00 mode (in the h-aligned sample). This is observed dielectrically by an increase in the δ process in relation to the α process.

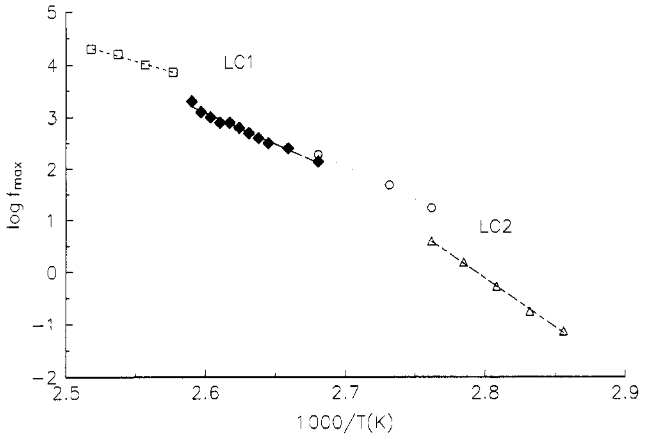

Figure 5. Plots of log f_{max} *vs* T^{-1} for unaligned [□, ○] and h-aligned [◇, △] samples of LC1 and LC2, respectively.

Activation Energies. Plots of log f_{max} *vs* T^{-1} for the isotropic and h-aligned samples of both LC1 and LC2 are shown in Figure 5. The line for the aligned sample lies at slightly lower frequencies than that for the isotropic sample, which is a feature seen previously for a siloxane polymer[31] and arises from the fact that the loss curve for the unaligned sample is a weighted sum of all four relaxation modes, where the frequencies of the 01, 10, and 11 modes lie above that for the 00 mode which dominates the loss peak for the h-aligned sample. The slopes of these linear fits obey the relationship

$$\log f_{max} = \log A - E_a/2.303RT \qquad (5)$$

where R is the gas constant and E_a is the activation energy of the sample phase. The activation energies of each phase are therefore approximately independent of temperature. The values derived are 240.6 and 303.0 kJ mol^{-1}, respectively, for LC1 and LC2 in their liquid-crystalline phases. The derived activation energies for the δ process are extremely large, which emphasizes the cooperative nature of the process and that it is coupled to the chain backbone motions. In contrast, the activation energies for the conductivity process, as obtained from the slopes of log A (from Table 2) *vs* T^{-1}, is 12.3 kJ mol^{-1} for LC1 in its liquid-crystalline phase and is similar for the two samples and is not more than 9% of that for the dipole relaxation process. This enables the dipole relaxation process to emerge from the conductivity process when a sample is heated.

The calculated activation energies for h-aligned LC1 and LC2 are typical of the apparent activation energies associated with the relaxation of mesogenic groups within a LCSC polymer. It is also evident that the activation energy for LC2 should be higher than that for LC1 since the motions of the mesogenic groups are more strongly coupled to the motion of the main backbone of the polymer since the concentration of the cyanoazobenzene moieties is less.

Planar Alignment. In many cases, liquid-crystalline samples may be aligned homeotropically, but in the present cases experiments fail to prepare planar-aligned material. This is due to the fact that either the frequency where $f > f'$ required to prepare p-aligned samples is too high for the ac generator in the temperature range where p-alignment is possible or $\Delta\epsilon$ is too small to allow planar realignment within practical time scales. In these cases the dielectric data for unaligned and h-aligned liquid-crystalline samples can be used to

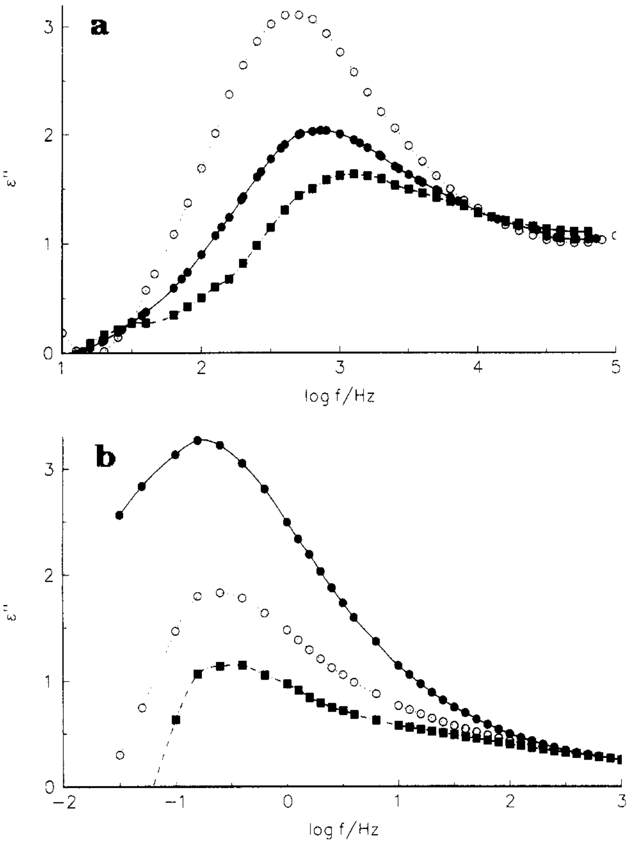

Figure 6. Plot showing (a) unaligned [●], h-aligned [○], and predicted p-aligned [■] loss curves for LC1 at 106 °C and (b) unaligned [○], h-aligned [●], and predicted p-aligned [■] loss curves for LC2 at 80 °C.

calculate p-aligned data. By using $S_d = 0$ and 1 for unaligned and fully h-aligned samples, respectively, in eq 2, we can deduce eq 6, where ϵ'' and $\epsilon_\parallel''$ are known

$$\epsilon_\perp'' = {}^1/_2[3\epsilon'' - \epsilon_\parallel''] \quad (6)$$

for each temperature studied. Parts a and b of Figure 6 show the experimental loss curves for LC1 and LC2, respectively, for unaligned and h-aligned samples and the p-aligned loss curves calculated using eq 6 at one representative sample temperature. It is evident that the p-aligned loss curves are lower in intensity, but shifted to higher frequencies, when compared with those for the unaligned material. The changes reflect different weightings of the component 00, 01, 10, and 11 processes, as we have described earlier.[15]

The isosbestic points for ϵ'' in the two samples are at $10^{4.1}$ and $10^{2.4}$ Hz for LC1 at 106 °C and LC2 at 80 °C, respectively (see Figure 6), and those for ϵ' at the same temperatures are found to be at 10^3 and 10 Hz, respectively. Also, as can be seen from Figure 4a,b, $\Delta\epsilon''$ values on electrical alignment are about 0.5 and 0.8, respectively, for LC1 and LC2. This means that by selecting a frequency greater than the isosbestic point in the ϵ' plots, as indicated by the "two-frequency" addressing principle,[15,17,29] p-alignment in these samples should be possible; the frequencies are within the range of the present experiment and $\Delta\epsilon''$ values are reasonable, although lower than for h-alignment. Unfortunately, initial experiments to do this have failed, a result found too by Bormuth and Haase,[34] who found that they could align carbon-chain LC polymers to obtain homeotropically aligned samples, but it was not found possible to obtain fully planar-aligned materials.

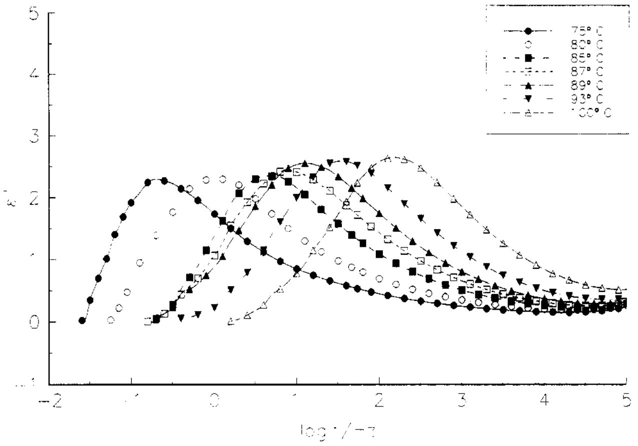

Figure 7. ϵ'' *vs* log *f* of LC2 over a range of temperatures around T_C for the irradiated sample with the conductivity process subtracted.

Laser-Induced Alignment. After the ITO cell with the unaligned LC2 sample was mounted in the hotstage, it was heated to 70 °C slowly, a temperature that is just above the glass transition temperature, T_g, of the sample. The alignment of the mesogenic groups in the sample was altered using a 514 nm mode-locked pulse laser. This had a pulse half-width of 20 ps, which repeated at a rate of 82 MHz. A beam expander was mounted so that a uniform intensity of light impinged on the liquid crystal sample, and a polarizer was placed after the diffuser so that there was only one vector in the actinic laser radiation transmitting onto the sample perpendicular to the large area of the liquid-crystal layer. The average power density on the sample surface was 54 mW cm^{-2}. The light was incident on the sample during a very slow heating process, heating to above the T_g (75 °C) of the sample at a rate of about 0.6 °C/min. The sample was then slowly cooled at the same rate to well below the T_g of the polymer (50 °C); this ensured that the macroscopic alignment in the sample induced by the temporary production of Z isomers was maintained.

As with the electrical alignment results, the process of conductivity subtraction was undertaken. The results of the laser light on the loss curves of LC2 are shown in Figure 7. Comparing the results with those in Figure 3a, it can be seen that irradiation of the sample has caused a change in the intensity of the loss curves, increasing from the unaligned state to the irradiated one. It is also evident from a comparison with Figure 3b that the change is not as marked as when the sample was aligned with an ac field. The differences in intensities induced by the irradiation of the sample is compared more clearly with that of the electrical alignment in Figure 4b. This shows the ϵ''_{max} data obtained for the irradiated LC2 sample. It can be seen that there is an increase in the intensity of the loss peaks up to the clearing temperature, although the phenomenon is not as marked as with the electrical alignment of the same sample, $\Delta\epsilon''_{max}$ being much less, with a value of 0.5 compared to 1.3 with electrical alignment. The fact that the change in alignment from the unaligned state caused by the laser light is less marked than before (isotropic → electrically aligned) is due to the fact that in the present experiment we are measuring the change in the alignment of the mesogenic groups in the *z* direction, as discussed earlier, but the changes in the *y* direction, that are equally possible, are not being measured. Using eq 2, a prediction of the macroscopic order parameter of the irradiated sample of LC2 can be calculated using the results of the h-aligned and unaligned samples. This calculation gives a value of $S_d = 0.4$, which compares with a value of 1 for fully h-aligned and 0 for unaligned samples. Only some macroscopic alignment has thus been measured in the LC2 film by irradiation.

Conclusions

The present investigation has shown that dielectric relaxation spectroscopy can be used effectively to measure the changes in the alignment in the mesogenic groups of these novel liquid-crystalline side-chain polymers induced by an applied ac electrical field of 40 V and 240 Hz at 120 °C for 3 h (LC1) and 40 V and 3 Hz at 105 °C for 3 h (LC2) and by polarized laser radiation of 514 nm at a uniform power of 54 mW cm^{-2} (LC2). Different physical processes occur in each, with the ac electrical field invoking homeotropic alignment within the LC1 and LC2 samples, while a preferred homeotropic alignment with $S_d = 0.4$ was induced in LC2 with polarized laser radiation, increasing the loss due to the δ process (00 mode) measured with alignment. This may be because not all changes that may occur in the sample are being measured because the direction perpendicular to the direction of polarization is not as clear as would be anticipated. The method of irradiation may have to be modified by the use of circular polarized light as a possibility of inducing more homeotropic alignment in the samples than was possible in the present experiment. Also, it has been shown that it is possible to predict from these results what the dielectric loss behavior of planar-aligned LC1 and LC2 would be.

Acknowledgment. The authors would like to thank S. Kostromin and V. Shibaev for supplying the samples in the study and gratefully acknowledge funding from the Engineering and Physical Sciences Research Council for a grant for the provision of the dielectric instrumentation used in the study, and for a postdoctoral award to one of us (S.R.A.).

References and Notes

(1) Various authors *Adv. Polym. Sci.* **1986**, *60/61*.
(2) Attard, G. S.; Williams, G. *Chem. Br.* **1986**, *22*, 919.
(3) Ciles, H. J. In *Developments in Crystalline Polymers*; Bassett, D. C., Ed.; Applied Science, Vol. 2; Elsevier: New York, 1988, p 297.
(4) McArdle, C. B. *Side-chain Liquid Crystal Polymers*; Blackie: Glagow, 1989.
(5) Eich, M.; Wendorff, J. H.; Reck, B.; Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 59.
(6) Tredgold, R. H.; Allen, R. A.; Hodge, P.; Khoshdel, E. *J. Phys. D: Appl. Phys.* **1987**, *20*, 1385.
(7) Xie, S.; Natansohn, A.; Rochan, P. *Macromolecules* **1992**, *25*, 2268 and 5531.
(8) Läsker, L.; Fischer, T.; Stumpe, J.; Kostromin, S.; Ivanov, S.; Shibaev, V.; Ruhmann, R. *Mol. Cryst. Liq. Cryst.* **1994**, *246*, 347.
(9) Fischer, T.; Läsker, L.; Stumpe, J.; Kostromin, S. *J. Photochem. Photobiol. A: Chem.* **1994**, *80*, 453.
(10) Läsker, L.; Fischer, T.; Stumpe, J.; Kostromin, S.; Ivanov, S.; Shibaev, V.; Ruhmann, R. *Mol. Cryst. Liq. Cryst.* **1994**, *252*, 293.
(11) Natansohn, A.; Rochon, P.; Pezolét, M.; Audet, P.; Brown, D.; To, S.; *Macromolecules* **1994**, *27*, 2580.
(12) Williams, G. In *Comprehensive Polymer Sciences*; Allem, G., Bevington, J. C., Eds.; Vol. 2, *Polymer Properties*; Price, C., Booth, C., Eds.; Pergamon Press: Oxford, U.K., 1989; p 601.
(13) Attard, G. S.; Araki, K.; Moura-Romos, J. J.; Williams, G. *Liq. Cryst.* **1988**, *3*, 861.
(14) Kozak, A.; Moura-Ramos, J. J.; Simon, G. P.; Williams, G. *Makromol. Chem.* **1989**, *190*, 2463.
(15) Attard, G. S.; Araki, K.; Williams, G. *Br. Polym. J.* **1987**, *19*, 119.
(16) Araki, K.; Attard, G. S.; Kozak, A.; Williams, G.; Gray, G. W.; Lacey, D.; Nestor, G. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1067.
(17) Nazemi, A.; Williams, G.; Attard, G. S.; Karasz, F. E. *Polym. Adv. Technol.* **1992**, *3*, 157.
(18) Haase, W.; Pranoto, H.; Bormuth, F. J. *Macromolecules* **1985**, *18*, 960.
(19) Bormuth, F. J.; Haase, W. *Mol. Cryst. Liq. Cryst.* **1987**, *148*, 1.
(20) Kostromin, S. G.; *et al.* To be published.
(21) Kozak, A.; Moscicki, J. K.; Williams, G. *Mol. Cryst. Liq. Cryst.* **1991**, *201*, 1.
(22) Kozak, A.; Simon, G. P.; Moscicki, J. K.; Williams, G. *Mol. Cryst. Liq. Cryst.* **1990**, *193*, 149.
(23) Kozak, A.; Moura-Ramos, J. J.; Williams, G. *Makromol. Chem.* **1989**, *190*, 2463.
(24) Attard, G. S.; Araki, K.; Moura-Ramos, J. J.; Williams, G.; Griffin, A. C.; Bhatti, A. M.; Hung, RSL. *Polymer Association Structures, Microemulsions and Liquid Crystals*; ACS Symposium Series No. 384; American Chemical Society: Washington, DC, 1989.
(25) Simon, G. P.; Kozak, A.; Williams, G.; Wetton, R. E. *Mater. Forum* **1991**, *15*, 71.
(26) Attard, G. S.; Williams, G.; Fawcett, A. H. *Polymer* **1990**, *31*, 928.
(27) Ivanov, S.; Yakovlev, I.; Kostromin, S.; Shibaev, V.; Läsker, L.; Stumpe, J.; Kreysig, D. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 709.
(28) Wiesner, U.; Antonietti, M.; Boeffel, C.; Spiess, H. W. *Makromol. Chem.* **1990**, *191*, 2133.
(29) Attard, G. S.; Williams, G. *J. Mol. Electron.* **1986**, *2*, 107.
(30) Birenheide, R.; Budesheim, K. W.; Wendorff, J. H. *Makromol. Chem.* **1991**, *185/186*, 319.
(31) Keller, E. J. C.; Williams, G.; Krongauz, V.; Yitzchaik, S. *J. Mater. Chem.* **1991**, *1*, 331.
(32) Attard, G. S.; Williams, G. *J. Liq. Cryst.* **1986**, *1*, 253.
(33) Williams, G. In *The Encyclopedia of Advanced Materials*; Bloor, D., Brook, R. J., Flemmings, M. C., Mahajan, S., Eds.; Pergamon Press: Oxford, U.K., 1994; p 1310.
(34) Bormuth, F. J.; Haase, W. *Liq. Cryst.* **1988**, *3*, 881.

MA9505890