Molecular Organization of the Polymer Backbone in a Side Group Liquid Crystal Polymer. An ESR Investigation

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Received March 18, 1997; Revised Manuscript Received May 27, 1997[⊗]

ABSTRACT: We have investigated the orientational order in the nematic glass formed by the side group liquid crystal polymer poly[6-(4-methoxy-4′-oxyazobenzene)hexyl methacrylate]-*co*-poly[methyl methacrylate] using ESR spectroscopy. In one experiment the order of the polymer backbone was investigated using a nitroxide attached to it via an ester link while in the other the nitroxide probe was dissolved in the polymer. The results of the experiments suggest that whereas the mesogenic side groups have a high orientational order the polymer backbone does not.

Introduction

Side group liquid crystal polymers continue to be the focus of much research activity. This interest arises not only as a result of their application potential in a range of advanced electro-optic technologies[1,2] but also because of their demanding challenge to our understanding of self-assembly in polymeric systems.[3,4] A side group liquid crystal polymer consists of three distinct structural components: a mesogenic group, a polymer backbone, and, connecting these, a flexible spacer. The spacer plays a critical role in determining the liquid crystalline behavior of the polymer, and without it liquid crystallinity is rarely observed. In essence, the spacer is thought to decouple, to a certain extent, the self-assembling tendency of the mesogenic groups from that of the polymer backbone to adopt random coil conformations. The implication of this model is that the orientational order of the mesogenic groups should be significantly higher than for the polymer backbone. Electron spin resonance spectroscopy (ESR) offers a powerful technique with which to see if this difference in orientational order actually occurs.

The ESR experiment requires the sample either to be spin-labeled, *i.e.*, in which a free radical is covalently attached to the sample, or spin-probed, in which the radical is simply physically dispersed in the sample. The behavior of a spin label should reflect the properties of the region of the system to which it is attached. In comparison, the spin probe will experience a range of environments, and hence its behavior will be an average over these. Indeed, chemical intuition is needed to judge which region of the system is being probed, and a degree of ambiguity may arise in interpreting the results. If these two types of experiment are performed on the same sample, however, then complementary information is normally obtained. ESR spectroscopy has been shown to be a valuable technique with which to study the orientational order of a mesophase.[5] If the reorientational motion of the spin probe or label is fast on the ESR time scale then the orientational order of the probe/label is reflected by the positions of the spectral lines. For the case of a nitroxide radical, the rotational correlation times need to be smaller than about 10^{-9} s. This situation normally obtains for low molar mass mesogens. For polymeric liquid crystals, especially in their glassy phases, this limit is not reached since the correlation times are much longer than 10^{-9} s. In this slow motion limit the positions of the lines in the powder spectrum are independent of the orientational order which is now reflected by the intensities of the spectral features.

In this paper, we use ESR spectroscopy to characterize the molecular organization within a nematic phase exhibited by a side group polymer. Two samples have been studied: a spin-labeled polymer in which the nitroxide is attached directly to the backbone, **1**, and the analogous polymer without the label, **2**, but with the cholestane spin probe, **3**. The spin probe was selected in the expectation that it would reside preferentially in the regions comprising the mesogenic groups while the label provides information concerning the backbone.

Experimental Section

The synthesis of copolymers **1** and **2** has been described in detail elsewhere.[6] The thermal behavior of the two polymers was identical: copolymer **1** exhibits a glass transition at 69 °C and a nematic-isotropic transition at 118 °C while the corresponding temperatures for **2** are 68 and 114 °C, respectively.

The spin probe selected for this investigation was the cholestane nitroxide (3-spiro-[2′-*N*-oxy-3′,3′-dimethyloxazolidine]-5α-cholestane, **3**, which was purchased from Aldrich Chemicals and used without further purification. It has a highly anisotropic structure and so is found to be well ordered in a liquid crystal solvent. Indeed it is frequently employed in studies of order and dynamics in liquid crystals.[7] The probe was introduced into the copolymer, poly[6-(4-methoxy-4′-oxyazobenzene)hexyl methacrylate]-*co*-poly[methyl methacrylate] in the following manner. It was first dissolved in dichloromethane and the solution placed in a 4 mm internal diameter Pyrex tube, the solvent was removed under vacuum, and then the copolymer was added to the tube. Any dissolved oxygen, which would broaden the spectral lines, was removed by a freeze−pump−thaw cycle. A macroscopically aligned sample of the nematic glass was obtained using a magnetic field. In one set of experiments, the sample was placed in the

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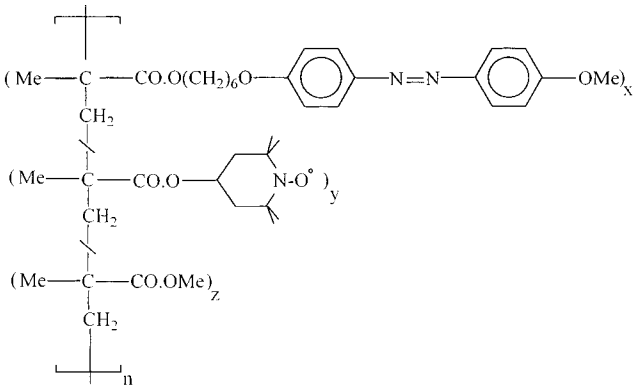
[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S0024-9297(97)00365-3 CCC: $14.00



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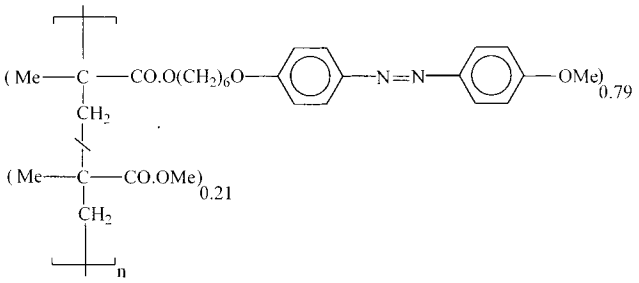

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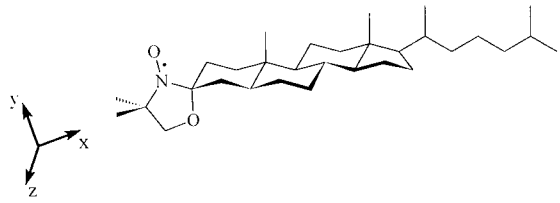

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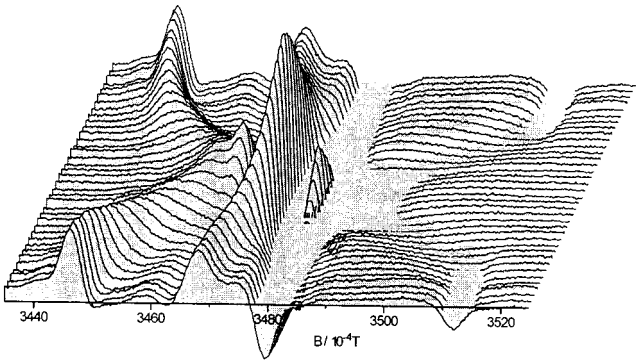

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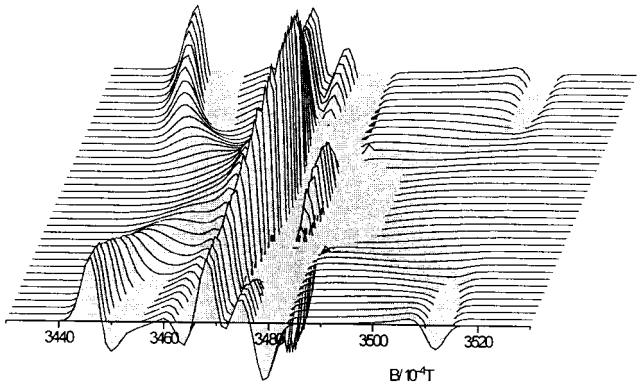

b

Figure 1. (a) Angular dependence (0−180°) of the ESR spectrum for the cholestane spin probe dissolved in the aligned nematic glass of the copolymer poly[6-(4-methoxy-4′-oxyazobenzene)hexyl methacrylate]-*co*-poly[methyl methacrylate] recorded at 27 °C. (b) Simulated angular dependence of the spectrum for the spin probe using a Maier−Saupe distribution function for the molecular long axis.

microwave cavity of a Bruker ECS 106 ESR spectrometer and the field was increased to its maximum value of 0.6 T. The sample was then heated just into the isotropic phase and the temperature was then lowered at 1 °C h^{-1}. This very slow cooling rate was used to ensure that the director was well aligned in the temperature regime where the bulk viscosity of the sample was as low as possible. When the sample was 10 °C below the nematic-isotropic temperature the rate of cooling was increased to 10 °C min^{-1} and the nematic glass so produced was studied at 27 °C. In particular the ESR spectrum was measured as a function of the angle between the magnetic field and the director. The computer-controlled goniometer, Bruker ER 218 PG1, was used in these experiments. To ensure that a perfect monodomain sample could be obtained in this way, a much larger magnetic field was employed to align the director. The sample was now placed in the probe of a Bruker MSL 200 NMR spectrometer where the magnetic field is 4.7 T. Since the magnetic torque is quadratic in the field, this represents a factor of 61 greater than that available with the ESR magnet. The sample was again heated into the isotropic phase and also cooled at a rate of 1 °C h^{-1} until 10 °C below T_{NI}. At this point the cooling rate was increased to 10 °C min^{-1} until a nematic glass was obtained at room temperature. The sample was then transferred to the ESR spectrometer and its spectrum again recorded as a function of the angle between the director and the magnetic field.

The spin-labeled polymer was aligned using the magnetic field of the ESR spectrometer in the same way as the sample doped with the cholestane spin probe. The ESR spectrum of the aligned nematic glass was also recorded as a function of the angle between the director and the magnetic field.

Results and Discussion

The angular dependence of the ESR spectrum of the cholestane spin probe in the nematic glass is shown in Figure 1a for a rotation of the sample through 180° in steps of 5°; the spectra at the edges of the top and bottom of the stack plot are for the field at 90° to the director while the spectrum in the center is that when the director is parallel to the field. The spectra shown in this figure are for the sample aligned with the magnetic field (0.6 T) of the ESR spectrometer; an identical angular dependence was obtained for the nematic glass aligned with the much higher magnetic field of the NMR spectrometer. It would seem, therefore, that the field of 0.6 T available from the ESR spectrometer is sufficient to align the director when the side group liquid crystal is cooled in the manner described in the Experimental Section.

An ESR powder pattern of an organic nitroxide is expected to contain certain distinctive features associated with the spectra found when the magnetic field is parallel to the principal axes of the nitrogen hyperfine tensor. Since the components of this tensor are about 3.3 mT for the parallel and 0.6 mT for the perpendicular component, the powder spectrum is expected to contain two triplets with just these hyperfine spacings. As the g tensor is not quite isotropic, the central lines of these two triplets do not overlap exactly; the angular dependent spectra show just these features (see Figure 1a). When the magnetic field is orthogonal to the director, the outer absorption-like spectral features correspond to a hyperfine interaction of 3.3 mT although the other features corresponding to the perpendicular hyperfine interaction are not really apparent until the sample has the director parallel to the magnetic field. This change in the spectrum when the sample is rotated by 90° clearly demonstrates the orientational order of the

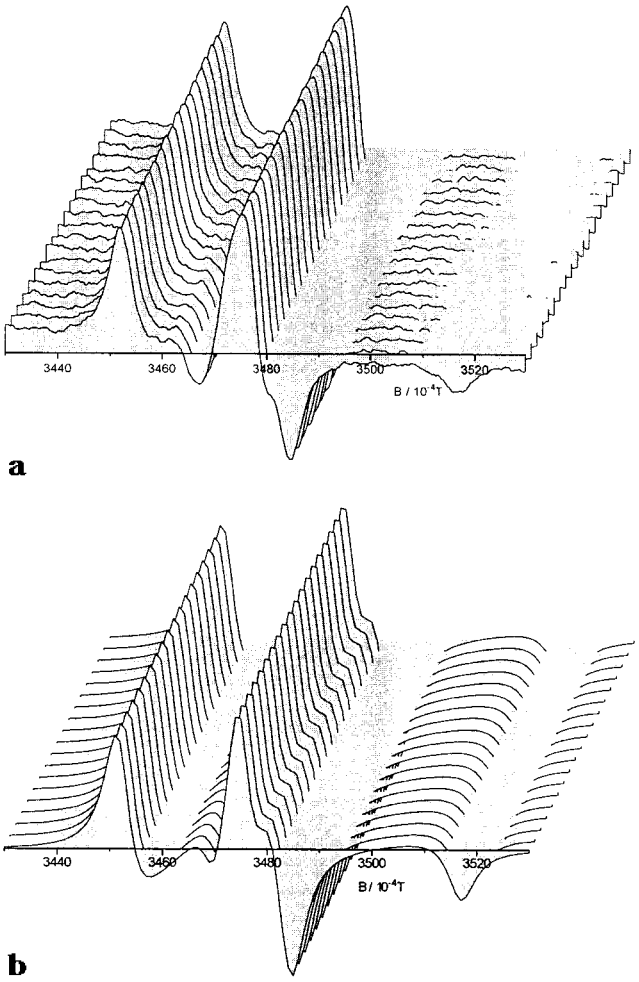

Figure 2. (a) Angular dependence (0−180°) of the ESR spectrum of the spin labeled copolymer poly[6-(4-methoxy-4′-oxyazobenzene)hexyl methacrylate]-*co*-poly[methyl methacrylate] recorded at 27 °C for the aligned nematic glass. (b) Simulated angular dependence of the spectrum for the spin label assuming an isotropic distribution of the nitroxide.

cholestane spin probe and may be understood in the following, qualitative way. The parallel component of the nitrogen hyperfine tensor corresponds to an axis orthogonal to the plane of the oxazolidine ring and so to the long axis of the cholestane probe (see the chemical structure). The perpendicular component is associated, therefore, with the directions in the plane of the oxazolidine ring, which also contains the long axis of the molecule. In the aligned nematic glass, when the field is parallel to the director, it will also tend to be parallel to the molecular long axis, and so the nitrogen hyperfine spacing will be the perpendicular component, which is about 0.6 mT, as we observe. When the sample is rotated by 90°, the field will now tend to be orthogonal to the molecular long axis. Since the ordering of the spin probe is essentially cylindrically symmetric about the long axis,[8] both the parallel and perpendicular axes of the hyperfine tensor will be parallel to the field with the same probability. We expect, therefore, to find both the parallel and the perpendicular features of the spectrum when the field is orthogonal to the director, as we can see in Figure 1a. A more detailed analysis of the ESR powder pattern requires its simulation, and we shall turn to this shortly.

The ESR spectrum of the spin-labeled copolymer, **1**, in its aligned glassy nematic state is shown as a function of the angle between the director and the magnetic field in Figure 2a. The most striking feature of the spectra is that they do not change with the orientation of the director. This suggests that the nitroxide is not aligned within the glassy nematic phase. Since it is attached to the polymer backbone, this result could be taken to imply that the backbone itself is not ordered within the nematic phase. Indeed this conclusion would seem to be consistent with the results of both neutron scattering studies of side group liquid crystal polymers which find that the anisotropy in the radius of gyration is rather small[9] and NMR studies which find that the order of the polymer chain is rather low[10] in comparison with the mesogenic groups. In contrast the strong angular dependence of the intensities of the lines in the ESR spectrum of the cholestane spin probe shows that this is highly ordered orientationally. Since the probe is expected to be localized near the mesogenic groups in the liquid crystal polymer, it seems reasonable to conclude that they do have a high orientational order. It would appear, therefore, that the hexyl spacer is very effective in decoupling the behavior of the mesogenic groups from that of the polymer backbone, as planned in the design of these materials.

To be able to quantify the statements which we have made concerning the orientational order of the spin probe and the spin label in the nematic glass, it is necessary to simulate the powder patterns which we have recorded, and we now describe how this is achieved. We begin by noting that whereas the nitrogen hyperfine tensor approximates quite closely to cylindrical symmetry, the g tensor does not; the principal components are $g_{xx} = 2.0063$, $g_{yy} = 2.0103$, and $g_{zz} = 2.0025$ where z is the symmetry axis for the nitrogen hyperfine tensor (see the chemical structure). This biaxiality in the g tensor complicates the simulation of the ESR spectrum and its angular variation. We have, therefore, taken the g tensor also to be cylindrically about z; this is a reasonable approximation since the biaxiality in the g tensor does not have a major influence on the form of the spectrum. With this approximation the resonance fields $B_m(\theta)$ for the nitroxide probe when the field makes an angle θ with the z axis are given, to first order, by[5]

$$B_m(\theta) = \frac{h\nu}{g(\theta)\mu_B} - \frac{hK(\theta)m}{g(\theta)\mu_B} \qquad (1)$$

where h is the Planck constant, μ_B is the Bohr magneton and m is the nitrogen spin quantum number. The g factor is

$$g(\theta) = \{g_\perp^2 + (g_\parallel^2 - g_\perp^2)\cos^2\theta\}^{1/2} \qquad (2)$$

and the angular dependent hyperfine interaction is

$$K(\theta) = \{A_\perp^2 g_\perp^2 + (A_\parallel^2 g_\parallel^2 - A_\perp^2 g_\perp^2)\cos^2\theta\}^{1/2}/g(\theta) \qquad (3)$$

The form of the first derivative of the spectral line shape $L(B_m(\theta), B, T_2^{-1})$ is taken to be Gaussian where T_2^{-1} is the width of the line which is assumed to be independent of the orientation of the probe with respect to the magnetic field. The observed spectrum is the sum of such lines for all orientations of the nitroxide, that is

$$L(B) = \sum_m \int L(B_m(\theta), B, T_2^{-1}) \sin\theta \, d\theta \qquad (4)$$

when the probe is distributed isotropically. This expression was used to simulate the spectrum of the spin-labeled copolymer using the parameters given in Table 1. The simulated spectrum is shown in figure 2b as a stack plot in order to facilitate comparison with the

Table 1. Parameters Used for Simulation of the ESR Spectra of the Spin-Labeled and -Probed Copolymer

	$A_{\|}$/ mT	$A_{\perp}$/ mT	T_2^{-1}/ mT	$g_{\|}$	ν/ GHz
spin-labeled copolymer	32.6	5.8	1.76	2.0025	9.75
spin-probed copolymer	32.2	6.8	3.80	2.0025	9.75

observed spectra; there is clearly good agreement with experiment, thus confirming that the spin label is not orientationally ordered.

When the probe molecule is ordered the theoretical expression for the powder pattern becomes

$$L(B) = \sum_m \int L(B_m(\theta), B, T_2^{-1}) f(\theta) \sin\theta \, d\theta \qquad (5)$$

where $f(\theta)$ is the normalized distribution function for finding the symmetry axis z for the g and hyperfine tensors at an angle θ to the magnetic field. According to the Maier-Saupe theory of nematics,[11] the singlet orientational distribution function for the molecular long axis with respect to the director is

$$f(\beta) = Z^{-1} \exp(-XP_2(\cos\beta)) \qquad (6)$$

where the factor Z ensures that the distribution function is normalized. The same form is obtained by a maximum entropy analysis based on the dominance of the second rank order parameter.[12] This prediction for $f(\beta)$ is supported by neutron scattering studies of 4,4′-dimethoxyazoxybenzene[13] as well as computer simulation investigations of the Gay−Berne model mesogen.[14] However, although the form of the distribution function for the molecular long axis is known with some certainty, what we require is the distribution function for an axis orthogonal to the long axis. Provided the ordering of the molecule about its long axis is cylindrically symmetric, the distribution function is

$$f(\beta') \propto \exp\left\{\left(-\frac{3}{4}X\right)\sin^2\beta'\right\} I_0\left\{\left(-\frac{3}{4}X\right)\sin^2\beta'\right\} \qquad (7)$$

where β' is the angle between the magnetic symmetry axis and the director and I_0 is a modified Bessel function. To use this distribution function to simulate the ESR spectrum when the director makes an angle γ with the magnetic field requires that θ in the expression for the resonant fields $B_m(\theta)$ is replaced with β', γ, and α, where α is the azimuthal angle for the magnetic symmetry axis in a laboratory frame defined by the director and the field. This change in the orientational variables allows us to write the form of the powder pattern as

$$L(\beta,\gamma) = \sum_m \int L(B_m(\beta', \alpha, \gamma), B, T_2^{-1}) f(\beta') \sin\beta' \, d\beta' \, d\alpha \qquad (8)$$

which uses the cylindrical symmetry of the nematic phase with respect to the director.

The angular dependence of the ESR spectrum of the cholestane spin probe ordered in the nematic glass was calculated using the distribution function given by eq 7. In these calculations the components of the nitrogen hyperfine tensor were given the values shown in the table. They differ slightly from those for the spin label in keeping with the different structures of the two nitroxides. The parallel component of the g tensor was set equal to 2.0025 as for the spin label. However, the value of $g_{\perp}$ was changed slightly according to the orientation of the director with respect to the magnetic field.

The angular dependence of the spectrum for the spin probe was then calculated for different values of the strength parameter X. The best qualitative fit was found when X was given the value −4.26, and the spectra calculated with this are shown in Figure 1b. The simulated spectra are clearly in good agreement with the experimental spectra confirming, at least semiquantitatively, the model for the orientational distribution function which we have adopted. Using the value of X obtained in this way, the second rank orientational order parameter $\bar{P}_2$ is calculated from

$$\bar{P}_2 = \int P_2(\cos\beta) f(\beta) \sin\beta \, d\beta \qquad (9)$$

where $P_2(\cos\beta)$ is the second Legendre polynomial, and found to be 0.73. This clearly supports the view that the spin probe has a high orientational order and we also note that it is similar to that expected for the mesogenic groups at a relatively low reduced temperature. Of course, the orientational order parameter which we have determined is not for the nematic glass at the temperature of the ESR measurements but rather for the spin probe ordered in the nematic phase when the viscosity has been so high that the order does not change with further reduction in the temperature during the time taken to perform this experiment. This temperature is likely to be at the glass transition, which corresponds to a reduced temperature of 0.88 and for which the order parameter $\bar{P}_2$ is found to be about 0.7 for low molar mass nematogens.[13]

Acknowledgment. We are grateful to EPSRC for a Grant (GR/H 96904) with which to purchase the Bruker ECS 106 ESR spectrometer. We also wish to thank the EC for a grant, made under the TEMPUS scheme, which made D.I.'s visit to Southampton possible.

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MA970365C