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ESR Studies of Molecular Dynamics of A Liquid Crystalline Polyether

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Introduction

Fundamental knowledge of macroscopic chain dynamics within a polymer melt is essential for a clear understanding of molding properties, adhesion and mechanical properties of engineering resins. A model liquid crystalline (LC) polymer system was developed and its melt diffusion was studied by Forward Recoil Spectrometry (FRES)^{1,2} for diffusion slower than 10^{-10} cm²/s. Recently, a new technique called Dynamic Imaging of Diffusion by Electron Spin Resonance (DID-ESR) has been developed to measure translational diffusion of LC in the range of 10^{-5} to 10^{-8} cm²/s with much success.^{3,4} The material must be labeled with a paramagnetic species, usually a stable free radical. As a microscopic technique, ESR is effective in studying the conformation and dynamic molecular structure. DID-ESR combines the precision of microscopic techniques with the long-time scales (for Fickian diffusion) of mass transport techniques. Its primary advantage is its ability to measure rotational diffusion coefficients and order parameters on the same sample that is used for translational diffusion measurements. In this way, macroscopic and microscopic properties of a sample can be related to an unprecedented degree.

The investigation reported here is the initial work to adapt the DID-ESR technique to study short chain LC polymers. The same model polymer system used in previous FRES studies was spin labeled. This publication focuses on the behavior of low molecular weight LC polymers for which liquid crystalline behavior may be important. Melt diffusion coefficients are measured for samples with degrees of polymerization ranging from 12 - 66.

The principles of DID-ESR have been well described previously.^{3,4} The formula for measuring the translational diffusion D_x by DID-ESR (in the case of unrestricted, one-dimensional diffusion) is usually given by:

$$\ln \left\{ \frac{I_g(\xi, t)}{I_g(\xi, t')} \right\} = -4\pi^2 D_x (t-t') \xi^2 \cdot G^2 \quad (1)$$

where I_g on the LHS of Eq.(1) are the Fourier transform of the ESR spectra with the field gradient on at initial time, t' , and final time, t , respectively. ξ is in units of inverse magnetic field and G is the magnetic field gradient. D_x therefore can be calculated from two gradient-on spectra at known times, t' , t , and the gradient value G .

The microscopic properties measurable by ESR include the rotational diffusion constants R_{\parallel} and R_{\perp} , for motion about directions parallel and perpendicular to z' (a unit vector along the long axis of the spin-labeled molecule), and the molecular order parameter S . S is defined as the ensemble average of the quantity $[3(z' \cdot \hat{d})^2 - 1]/2$, where \hat{d} is a unit vector along the director axis defining the direction of liquid crystalline ordering. Thus, S ranges in value from 1 (for perfect order with $z' \parallel \hat{d}$) to -0.5 ($z' \perp \hat{d}$). S may refer either to macroscopic ordering of the LC polymer or to ordering within microscopic domains of the sample. In the macroscopically aligned samples studied, \hat{d} coincides with the direction of the spectrometer field B_0 . Samples that were not macroscopically aligned were analyzed using a model of microscopic ordered and macroscopic disorder (MOMD) in which the microscopic directors have a uniform distribution of orientations. The quantities R_{\parallel} , R_{\perp} , and S are obtained by least-squares fitting of spectral simulations to the ESR spectrum measured in the absence of a gradient.

Experimental

1. Materials and Methods

The nematic model system used was a main-chain LC polyether, based on 4,4'-dihydroxy- α -methylstilbene and mixed aliphatic linking groups of 7 and 9 carbons in length (DHMS-7,9). Monomer and polymer syntheses have been described previously.⁵ The free radical (3-carboxy-2,2,5,5-tetra-methyl-1-pyrrolidinyloxy) was attached to the chain end. Molecular weights were determined by gel permeation chromatography.

2. DID-ESR sample preparation

The samples for DID-ESR experiment were composed of three layers in a 1.7 mm ID glass tube with a thin layer of labeled LC polymer (the tracer) in the middle of unlabeled LC polymer (the matrix) to form an inhomogeneous distribution of spin concentration in the x -direction (perpendicular to the z -direction of the static magnetic field B_0). The spin concentration in the tracer was chosen low enough to avoid Heisenberg spin exchange.

3. DID-ESR Measurement

An optimum choice of tracer thickness in combination with magnetic field gradient was found for these particular samples, which provided an acceptable S/N ratio and a reasonable measuring time (several hours). The maximum non-saturating microwave power, and a large time constant and short data acquisition time were used for taking the gradient-on spectra to maximize the S/N ratio without any distortion of the spectra. Averaging over a time period during which the diffusion process was negligible was also used. Gradient-off spectra were taken during each DID-ESR measurement and later fitted by simulation.

Results

1. The characterization of materials

Low MW fractions of DHMS-7,9 were chosen to achieve melt diffusion coefficients in a range optimal for DID-ESR. Data on weight-average molecular weights (M_w), number-average molecular weights (M_n) and transition temperatures are reported in Table 1. The combination of three tracers and three matrices yielded nine DID-ESR samples. A temperature of 120°C was chosen to measure the diffusion coefficient, because it is in the nematic regime of the matrices.

2. Alignment of LC polymers in the ESR magnetic field

Experiments showed macroscopic alignment of some of the LC polymers was occurring in the nematic phase in a magnetic field of 3300 gauss, a field not normally strong enough to align polymer samples. The degree of alignment depends largely on the matrix rather than the tracer. While the matrix of smaller MW ($P=4,470$) could be well aligned within one hour, the larger MW matrix ($P=22,400$) showed only partial alignment after twenty hours, and the ESR spectra consisted of superposition of aligned and unaligned components.

3. Translational diffusion coefficients

The diffusion coefficients reported in this paper were measured after the gradient-off spectra became time-independent, i.e., after the alignment process had finished. In Figure 1 is plotted $\log_e |I_g(\xi, t)| - \log_e |I_g(\xi, t')|$ vs. ξ^2 from one pair of gradient-on spectra of sample 1 over the time period ($t-t'$). By fitting a straight line over the appropriate range of ξ^2 to get the slope, the diffusion constant (D) was calculated. Several pairs of gradient-on spectra with the same time interval ($t-t'$) were used in calculating the diffusion coefficient for each sample. The translational diffusion coefficients for all 9 samples are listed in Table 2. Under optimal experimental conditions, a diffusion rate of 2×10^{-8} cm²/s can be measured within an hour with a 10% uncertainty.

4. Magnetic parameters of the spin label

A rigid limit spectrum of a labeled DHMS-7,9 sample was taken on a 250 GHz Far-Infrared ESR spectrometer in order to obtain the magnetic g and A tensors of the spin label. The result is shown in Figure 2. The values

of the g and A tensors were assumed to be independent of temperature and the MWs of the samples, and were fixed through all simulations.

5. Rotational diffusion and ordering parameter

The gradient-off spectra of the first 6 samples were simulated using a non-linear least squares fitting program. For samples 3 and 6, a MOMD model was applied. The order parameter, S , the perpendicular component of the rotational diffusion, R_{\perp} , and the rotational anisotropy, N ($N=R_{\perp}/R_{\parallel}$), are listed in Table 2. The experimental and simulated ESR spectra of the first three samples are shown in Figure 3.

Discussion

From the simulated results on the gradient-off ESR spectra of the DID-ESR samples, an important correlation was found between the order parameter S and $\langle D \rangle$ of the samples that showed significant macroscopic alignment, (i.e., samples 1, 2, 4 and 5). The geometry of the DID-ESR experiment resulted in the nematic director being aligned parallel to the magnetic field and perpendicular to the direction of diffusion; thus, the DID-ESR of a perfectly aligned sample is a measurement of the perpendicular component of the translational diffusion, D_{\perp} . The observation that $\langle D \rangle$ decreases when S increases indicates that D_{\perp} tends to be smaller than the average diffusion coefficient of an unaligned nematic sample, $\langle D \rangle$.

Acknowledgments

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Table 1 MWs and transition temperatures of DHMS-7,9

	M_w	M_n	D_{pw}	T_m (°C)	T_{ni} (°C)
Matrix	4470	2730	13	90	160
	11000	7000	32	102	155
	22400	16000	66	91	190
Tracer	4212	3072	12	92	118
	7792	5108	23	96	120
	10504	6256	31	82	121

Table 2 Diffusion coefficients and order parameter of DHMS-7,9

#	Matrix (M_w)	Tracer (M_w)	$\langle D \rangle$ ($10^{-6} \text{cm}^2/\text{s}$)	S	R_{\perp} (10^6s^{-1})	N
1	4470	4212	1.59 ± 0.01	0.44	1.70 ± 0.02	2.2
2	4470	7792	2.0 ± 0.2	0.33	1.60 ± 0.02	1.7
3	4470	10504	1.8 ± 0.2	0.20	1.9 ± 0.5	1.6
4	11000	4212	2.3 ± 0.1	0.30	3.28 ± 0.07	3.9
5	11000	7792	2.42 ± 0.02	0.25	2.22 ± 0.05	3.5
6	11000	10504	0.81 ± 0.02	0.26	3.6 ± 0.7	1.6
7	22400	4212	1.20 ± 0.06			
8	22400	7792	0.92 ± 0.04			
9	22400	10504	0.71 ± 0.01			

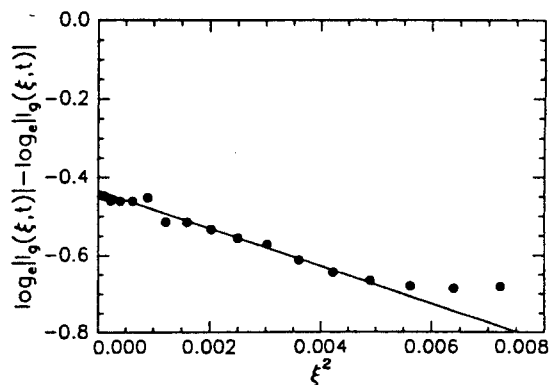


Figure 1 Plot to get $\langle D \rangle$ from a pair of gradient-on spectra for DID-ESR sample 1. The slope equals to $-4\pi^2(t-t')G^2$.

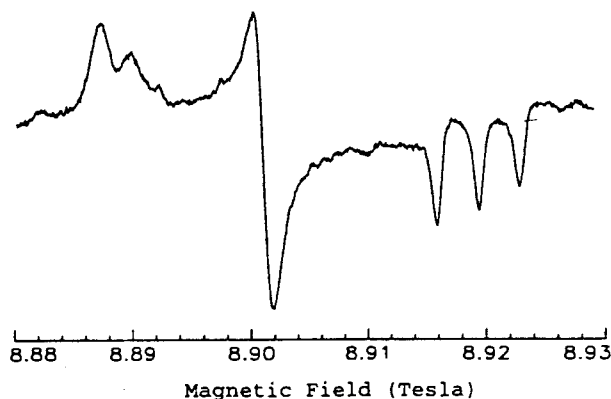


Figure 2 250 GHz FIR-ESR spectrum of a spin labeled DHMS-7,9 sample at -154 °C. The magnetic g and A tensors were measured as $g_{xx}=2.0087$, $g_{yy}=2.0060$, $g_{zz}=2.0018$, $A_{xx}=5.18$ g, $A_{yy}=4.31$ g, $A_{zz}=34.37$ g.

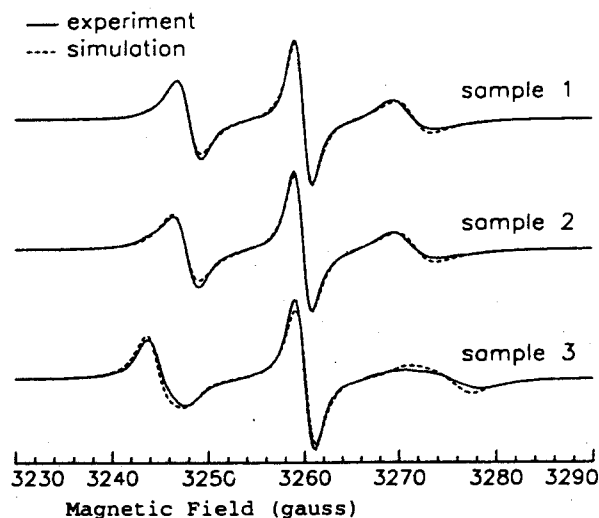


Figure 3 Experimental and simulated ESR spectra (gradient-off) of some DID-ESR samples (matrix $P=4,470$)