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HETEROGENEITY IN THE DYNAMICS OF A MOLECULAR TRACER DISSOLVED IN LIQUID CRYSTAL HOMOPOLYMER AND COPOLYMER

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ESR studies were carried out on the rotational dynamics of cholestane molecular tracer dissolved in liquid crystal homopolymer and copolymer from well above T_{NI} down to below T_g . Rheological measurements also provided the flow relaxation properties of the polymer matrices. The distribution functions of molecular sites were determined, and their stability was monitored as a function of thermal history. The different molecular site distributions and cooperativity degrees were compared and discussed.

Keywords: cooperativity; dynamics heterogeneity; electron spin resonance; molecular tracer; nematic polymer

INTRODUCTION

Devices for re-writable optical storage may be achieved by use of LC polymers with functional mesogenic side groups [1]. Among these, polymers with azobenzene units [2] can undergo photochemically induced *trans-cis* isomerization of the azo moiety [3]. Thus, alignment can be effectively photoinduced by the combination of photoorientation and thermotropic self-organization [4]. However, nanowriting and information storage rest on bit stability and homogeneity at molecular level, which represent key features in the effectiveness of polymer matrices in erasable storage devices at the nanometer length-scale [5,6]. Homogeneity of the polymeric

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matrix strongly depends on the thermal procedure [7]. On the other hand, different spatial-temporal relaxation processes can affect the bit stability. The properties of the material should, therefore, be characterized with spectroscopic techniques which can cover various time- and length-scales.

We are investigating the heterogeneity in the dynamics of polymers with azobenzene side groups by electron spin resonance (ESR) using suitable molecular tracer guests in the host polymer matrix. In this work we have studied an azobenzene polymethacrylate homopolymer ($x = 1$) and its 70/30 ($x = 0.7$) random copolymer with non-mesogenic methyl methacrylate using cholestane as the tracer (Fig. 1).

MATERIALS AND EXPERIMENTAL

The homopolymer and 70/30 copolymer (Table 1) were prepared by free-radical polymerization according to a literature procedure [8].

Rheological measurements in oscillatory regime were carried out in the temperature ranges 400–304 K and 400–324 K for the homopolymer and copolymer, respectively. The temperature dependences of the structural relaxation time in the investigated regions were well described by Vogel-Fulcher (VF) laws with parameters $T_0 = 259 \pm 5$ K and $T_b = 1300 \pm 50$ K for the homopolymer and $T_0 = 266 \pm 5$ K and $T_b = 1570 \pm 50$ K for the copolymer.

ESR studies were performed on the polymeric matrices of interest in which the cholestane molecular tracer was dissolved (10^{-3} cholestane/repeat unit molar ratio). An X band Bruker ER 200 SRL was used and the temperature control (± 0.1 K accuracy) was ensured by a Bruker BVT100 system.

Strong memory effects in the temperature dependence of the probe dynamics forced us to identify a suitable thermal procedure in order to obtain reproducible results. The preferred protocol consisted in

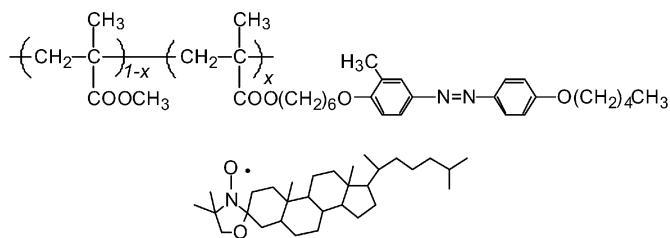


FIGURE 1 Structures of the homopolymer ($x = 1$) and copolymer ($x = 0.7$) host matrices and the cholestane tracer guest.

TABLE 1 Physico-chemical Characteristics of the Polymer Samples

Sample	M_w (g/mol)	M_w/M_n	T_g (K)	T_{NI} (K)
Homopolymer	59,000	3.17	294	353
Copolymer	117,000	3.54	314	345

i) maintaining the sample at the annealing temperature $T_a = 358$ K, and monitoring the system evolution until stable spectra were recorded via the acquisition of ESR spectra (78 h, homopolymer; 64 h, copolymer); ii) recording spectra on cooling to various predetermined temperatures for an overall measuring time $t_r = 1$ h; iii) re-heating the sample and maintaining it at T_a during a time $t_w = 5$ h; iv) repeating steps ii)–iii) to cover the whole temperature range of interest [9]. By this procedure, the temperature ranges of 358–280 K (homopolymer) and 358–297 K (copolymer) were fully investigated. Spectra in the upper temperature region were taken on slowly heating the samples from 358 to 433 K.

ESR simulation spectra were performed by using a theoretical approach based on generalised Mori theory [10]. The cholestane spin probe exhibits nearly axial symmetry [11]. Its reorientational dynamics in the present polymer matrices was characterized by a spinning motion around its own symmetry axis and a tumbling motion of the symmetry axis itself with correlation times $\tau_{||}$ and τ_{\perp} , respectively. The anisotropy ratio $\tau_{\perp}/\tau_{||}$ was found to be 15 for the homopolymer and 18 for the copolymer over the whole temperature range. Therefore, only the temperature dependence of $\tau_{||}$ will be shown. The greater anisotropy ratio found in the copolymer denoted that the reorientation of the molecular tracer occurred in a more rigid molecular environment.

The principal components of the magnetic tensors of the spin probe were drawn by the powder lineshapes [12] of the linear ESR recorded at 143 K, according to the procedure detailed elsewhere [13]. Powder lineshapes in both polymer samples were found to be coincident; the values of the Zeeman and hyperfine tensors in the molecular frame are listed in Table 2.

TABLE 2 Values of the Principal Components of the Zeeman and Hyperfine Tensors in the Molecular reference Frame for Cholestane

g			A (gauss)		
g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}
2.0026	2.0092	2.0069	32.6	5.5	5.0

RESULTS AND DISCUSSION

Typical ESR spectra and relevant theoretical simulations at different temperatures in the isotropic, nematic and glassy states for the homopolymer and copolymer are illustrated in Figure 2.

ESR measurements were carried out on both samples after annealing at 358 K, that is in the isotropic phase, following the thermal procedure delineated in the experimental section. Careful simulations proved that the inhomogeneous character of the ESR lineshapes was well taken into account by a two δ -like distribution function of the molecular tracer sites, in agreement with previous results [14].

The evolution of the ESR lineshapes from the beginning of the annealing procedure and the time at which stable spectra were recorded is shown in Figure 3.

The temperature dependences of the fast spin population, normalized to 100, in the homopolymer and copolymer are reported in Figure 4. Interestingly, only the dynamics of the spin probe dissolved in the homopolymer appeared significantly inhomogeneous at T_a . On lowering the temperature, qualitatively similar behaviours were observed consisting of a decrease of the fast component, a plateau where population percentage became about 50% (homopolymer) and 35% (copolymer), and then a further decrease down to its complete disappearance. In the temperature ranges 334–328 K for the homopolymer and 361–348 K for the copolymer, evaluation of the site populations was somewhat unreliable and these data are not

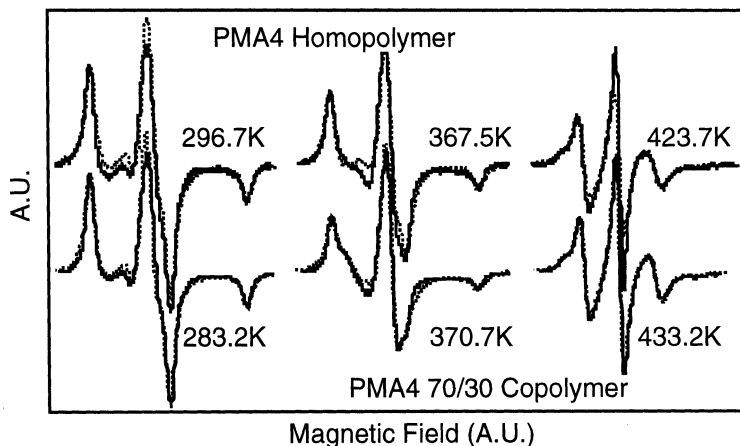


FIGURE 2 ESR spectra with relevant simulations at different temperatures.

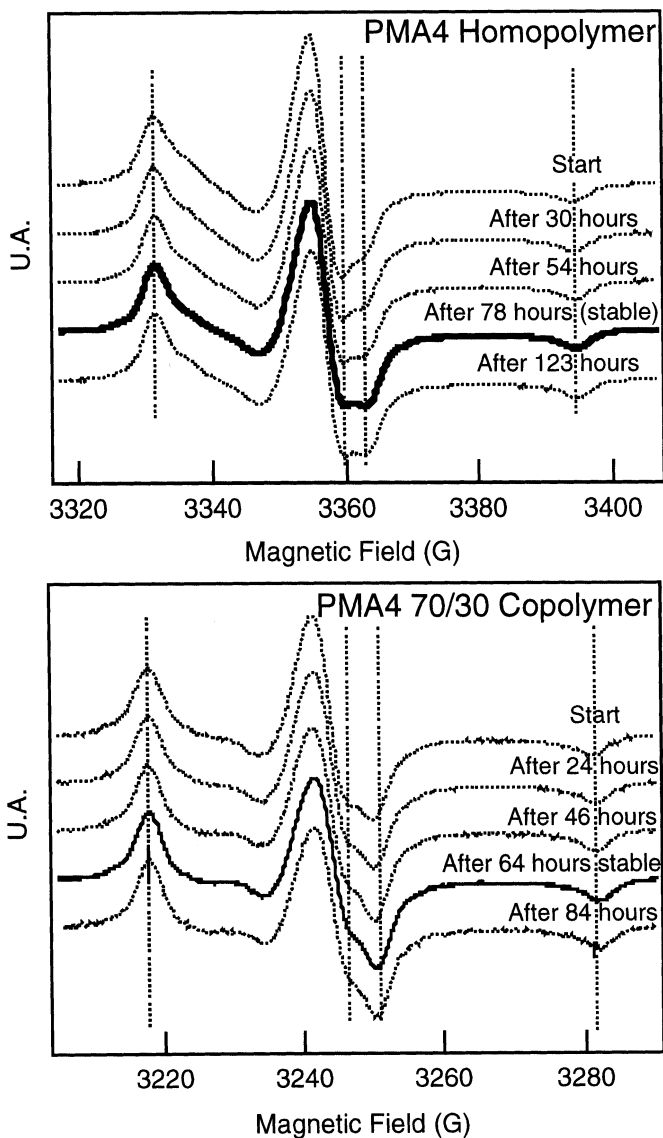


FIGURE 3 Evolution with time of the ESR spectra at $T_a = 358$ K.

reported in Figure 4. The fast component in the homopolymer remained stable down to -328 K, well inside the nematic region, whereas that in the copolymer disappeared at -348 K, about T_{NI} . This suggests that different physical mechanisms underlie the fast site instability.

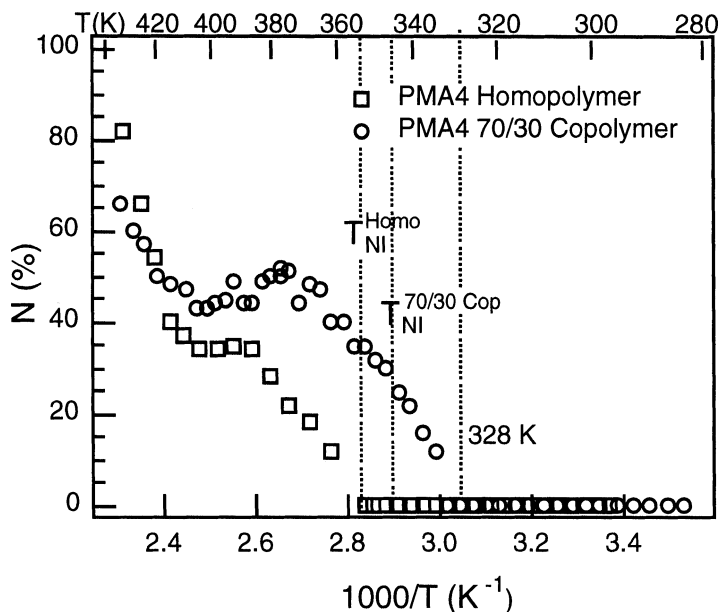


FIGURE 4 Population N of the fast site component vs. temperature.

The temperature dependences of the fast and slow components for the homopolymer and copolymer are reported in Figure 5. For both polymers, above the glass transition temperature the temperature dependences of the slow and fast spinning correlation times were well described by VF laws:

$$\tau_{||} = \tau_{||0} \exp\left(\frac{T_b'}{T - T_0'}\right) \quad (1)$$

where $\tau_{||0}$ and T_b' , the activation pseudo-energy in K, are constants depending also on the spin probe, and T_0' is the Vogel temperature. The values of the fit parameters are reported in Table 3. The slow component of the molecular probe in the homopolymer matrix exhibited an Arrhenius behaviour below the glass transition temperature.

Note that the T_0' values relevant to the temperature dependence of the spinning correlation times of the spin probe dissolved in both homopolymer and copolymer coincided with the corresponding T_0 values obtained by rheological measurements. Therefore, the spinning correlation time behaviour could be expressed by a fractionary law of the structural relaxation time τ_α :

$$\tau_{||} \propto \tau_\alpha(T)^\xi \quad (2)$$

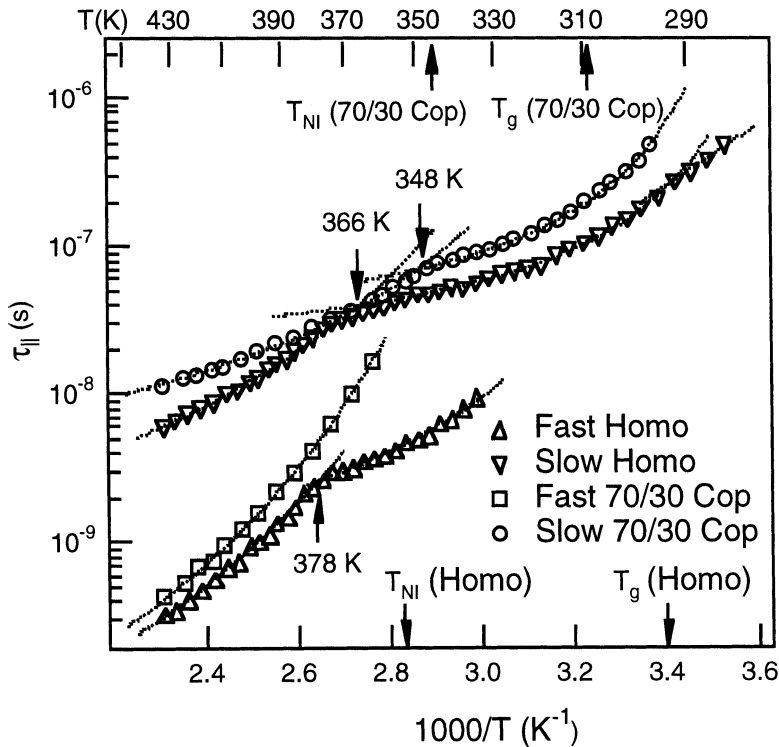


FIGURE 5 Temperature dependence of the spinning correlation times.

TABLE 3 Fit Parameters for the Slow and Fast Components in the High Temperature (HT) and Low Temperature (LT) Regions of the Polymers

	Slow component		Fast component	
	HT	LT	HT	LT
Homopolymer				
$\tau_{ 0}$ (s)	$(3.0 \pm 0.2)10^{-10}$	$(1.6 \pm 0.1)10^{-8}$	$(3.3 \pm 0.2)10^{-12}$	$(3.0 \pm 0.2)10^{-10}$
T_b' (K)	527 ± 20	97 ± 7	799 ± 60	258 ± 15
T_0' (K)	258 ± 7	258 ± 8	258 ± 9	258 ± 7
Copolymer				
$\tau_{ 0}$ (s)	$(2.0 \pm 0.1)10^{-9}$	$(2.2 \pm 0.1)10^{-8}$	$(2.9 \pm 0.2)10^{-12}$	
T_b' (K)	290 ± 20	94 ± 6	820 ± 70	
T_0' (K)	266 ± 6	266 ± 8	266 ± 7	

in which ξ , the fractional exponent, may vary between 0 and 1, with $\xi = 1$ corresponding to a complete coupling of the probe dynamics to the structural relaxation of the host matrix. In molecular glass formers the onset of fractionary relationships has been explained in terms of cooperativity [15], and ξ^{-1} has been interpreted as the size of the rearranging cooperative region.

By inspection of Table 3 one notes the high pseudo-energy values relevant to the fast component at higher temperatures for both polymer samples. The decoupling degrees ξ_d from the α relaxation were evaluated by the ratio (T_b'/T_b) of the VF pseudo-energy values pertinent to the spinning dynamics over the ones from rheological measurements [7]. We found $\xi_d = 0.61$ for the homopolymer and $\xi_d = 0.52$ for the copolymer, which implies a weaker coupling in the latter sample. In a recent work [9] it was suggested that fast sites could be localised in the homopolymer between the flexible spacers and the polymer main chain. Accordingly, the spin probe sites relevant to the fast component of the copolymer seemed to be situated near the polymer main chain but segregated from the mesogens possibly near the methyl methacrylate unit. The instability of the fast sites in the copolymer at $T < -348$ K was probably driven by the onset of cooperativity in the main chain dynamics. In fact, the crossing or mode coupling critical temperature T_c [16,17] occurs in polymers at 1.1–1.2 T_g . Differently the fast component instability in the homopolymer at $T < -328$ K was ascribed to conformational disorder [9].

The variations of both slow dynamics (Figure 5), occurring in proximity of the T_{NI} , indicate that the molecular tracer resided in the mesogenic regions. Greater decoupling degrees from structural relaxation characterised the slow component dynamics in both polymer samples. In the high temperature region ξ_d^{HT} was found to be 0.40 for the homopolymer and 0.18 for the copolymer. Thus, the slow components appeared to be sited in the mesogenic region at varying distance from the main chain. In the low temperature region further decouplings from the α relaxation were observed: ξ_d^{LT} values of 0.08 and 0.06 were determined for the homopolymer and copolymer, respectively, thus suggesting location of the slow molecular sites far from the polymer main chain and near the alkyl tail of the repeat unit. It can be noted that the molecular segregation in the copolymer resulted stronger than in the homopolymer. On the other hand, the more rigid molecular environment characterising the dynamics of the probe in the copolymer would point to the occurrence of a larger size of rearranging cooperative region (ξ_c^{-1}) than in the homopolymer. By contrast, we found that $\xi_c^{-1} = \xi_d^{HT}/\xi_d^{LT}$ was 3 units for the copolymer and 5 units for the homopolymer. This may be explained by positioning the slow component, below the clearing point, between different mesogenic regions astride the methyl methacrylate units.

CONCLUSIONS

Two molecular sites, fast and slow, in which the probe reorients have different localisations with respect to the polymer main chain. The instability of the fast sites resulted in a homogeneous spin probe dynamics over a wider temperature range in the copolymer than in the homopolymer. This may suggest consideration of the copolymer as a more suitable substrate for application in optical nanowriting. Studies on other copolymers with varying compositions of mesogenic/non-mesogenic units are in progress.

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