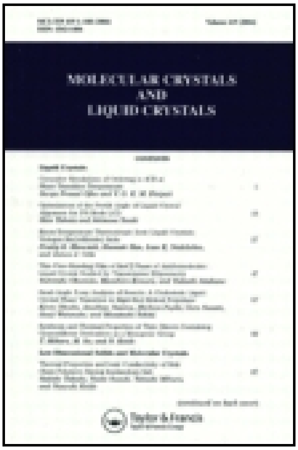

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Effects of Thermal Annealing on the Heterogeneities in the Dynamics of a Paramagnetic Probe Dissolved in Azobenzene Polymethacrylates

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The rotational dynamics of the cholestane spin probe dissolved in nematic azobenzene polymethacrylates (homopolymer and copolymer) was studied by electron spin resonance spectroscopy. Upon isothermal annealing in the isotropic phase, dynamic nanoscale heterogeneities were induced in both polymers, with slow and fast sites being available for reorientation of the spin probe. The stability with temperature of the different sites was found to be very different in the homopolymer and copolymer. In any case, the rotational correlation time in both the isotropic and nematic phases was well represented by the Vogel-Fulcher law. By comparing the probe dynamics with the polymer structural relaxation, it was possible to locate the reorientation sites at different positions of the polymer structure. Finally, the annealing of the copolymer in the isotropic phase resulted in a dynamically very homogeneous sample in the nematic phase.

Keywords: azobenzene; dynamics; electron spin resonance; liquid crystal polymer

INTRODUCTION

Electron Spin Resonance (ESR) spectroscopy is a powerful technique to investigate molecular dynamics in simple and complex liquids [1–3]. In particular, ESR studies proved to be very sensitive to details

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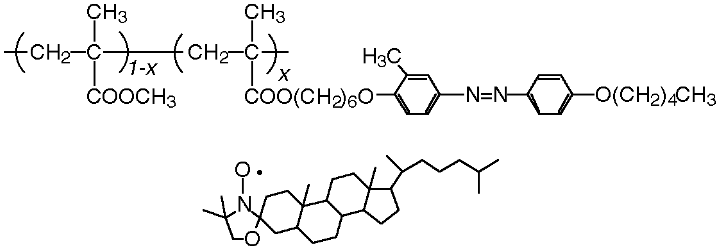

FIGURE 1 Structures of the azobenzene PMA4 homopolymer ($x = 1$) and 70/30 copolymer ($x = 0.7$) host matrices and the cholestane spin probe guest.

of the molecular rotation in liquids of medium or high viscosity [3]. Diamagnetic systems are often investigated by dissolving very small quantities of suitable paramagnetic tracers, so called spin probes, in the host matrix [1]. The cholestane spin probe is an excellent molecular tracer, especially in the study of reorientation processes of liquid crystal polymers [4].

We are interested in the reorientation dynamics of cholestane in the nematic polymethacrylate system PMA4 based on the 3-methyl-4'-pentyloxy-azobenzene mesogenic unit connected at the 4-position by a hexamethylene spacer to the main chain (Fig. 1). This system appears a very promising material for nanorecording [5–7].

In this work, we investigated the copolymer with 30 mol% methyl methacrylate counits ($x = 0.7$) that was subjected to isothermal annealing treatments at different temperatures. We found heterogeneities in the dynamics of the spin probe reorienting in slow and fast sites. In particular, thermal annealing in the *isotropic* phase was able to modulate the stability of different sites in the polymer. The effects of the annealing were also compared with those of analogous treatments on the azobenzene homopolymer ($x = 1$).

MATERIALS AND EXPERIMENTAL

The PMA4 homopolymer and 70/30 copolymer were synthesized according to a literature procedure [8]. They present nematic and glassy phases (Table 1). Molar mass and polydispersity data are also collected in Table 1.

The transition temperatures were determined by differential scanning calorimetry (10 K/min heating rate) with a Perkin-Elmer DSC7 apparatus on samples (*ca.* 15 mg) that had been previously heated to 358 K for 4 h and then rapidly cooled to 250 K.

TABLE 1 Physico-chemical Characteristics of the Polymer Samples

PMA4 Sample	M_w (g/mol)	M_w/M_n	T_g (K)	T_{NI} (K)
Homopolymer	59000	3.17	294	353
70/30 Copolymer	117000	3.54	314	345

Rheological measurements were performed with a Haake RheoStress RS150H rheometer in the plane-plate geometry [9]. The temperature dependence of the shearflow structural relaxation time τ^{st} was well described by the Vogel-Fulcher (VF) law:

$$\tau^{st} = \tau_0^{st} \exp\left(\frac{T_b}{T - T_0}\right) \tag{1}$$

T_0 and T_b being the Vogel temperature and the activation pseudo-energy in K, respectively. The VF parameters for τ^{st} were $T_0 = 259 \pm 5\,\mathrm{K}$, $T_b = 1300 \pm 50\,\mathrm{K}$, $\tau_0^{st} = (7.0 \pm 0.8) \cdot 10^{-13}\,\mathrm{s}$ for the homopolymer, and $T_0 = 266 \pm 5\,\mathrm{K}$, $T_b 1570 \pm 50\,\mathrm{K}$ and $\tau_0^{st} = (1.7 \pm 0.2) \cdot 10^{-12}\,\mathrm{s}$ for the 70/30 copolymer.

ESR measurements [2,10] were done with an X band Bruker ER 200 SRL with a Bruker BVT100 temperature control system (±0.1 K accuracy). The samples were prepared at room temperature by mixing chloroform solutions containing predetermined amounts of polymer and cholestane. The resulting solution (cholestane/repeat unit $\approx 10^{-3}$ molar ratio) was evaporated to complete dryness by heating to 358 K under vacuum for 72 h. The sample was finally sealed in a standard ESR tube. The above evaporation temperature was used for all samples, independent of their subsequent thermal treatments.

The components of the magnetic tensors of the spin probe were detected by the powder lineshape [11] of the linear ESR recorded at 143 K, according to the procedure described in Ref. [12]. The values of the Zeeman and hyperfine tensors in the molecular frame are listed in Table 2. The ESR lineshape analysis was performed according to

TABLE 2 Values of the Principal components of the Zeeman and Hyperfine Tensors in the Molecular Reference Frame for the Cholestane Spin Probe

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

the theoretical approach based on the generalized Mori theory [13]. The cholestane spin probe exhibits nearly axial symmetry, and its reorientation dynamics is characterized by a spinning motion around its own symmetry axis and a tumbling motion of the symmetry axis itself, with correlation times $\tau_{\|}$ and $\tau_{\perp}$, respectively. The anisotropy ratio $\tau_{\perp}/\tau_{\|}$ for the copolymer and the homopolymer after annealing at 383 K was 20 and 15, respectively, over the whole temperature range. Due to this relationship, only the temperature dependence of $\tau_{\|}$ is shown here.

RESULTS AND DISCUSSION

The rotational dynamics of the paramagnetic probe dissolved in the polymer matrix of interest was studied by following a specific thermal procedure that consisted [2] of: i) choosing the annealing temperature T_{a}; ii) holding the sample at T_{a} until a stable ESR lineshape was obtained; iii) performing acquisition of ESR data on cooling to the selected temperature for about 1 h; iv) re-heating the sample to T_{a} for 2 h; v) confirming that the ESR spectrum at the lowest temperature in a series of measurements was coincident with the first one of the successive series; vi) repeating the steps iii)–v).

By this procedure the temperature range 383–280 K was investigated. The spectra at higher temperatures were simply recorded on slowly heating the sample from 383 K to 438 K. This procedure was found to be optimal to prevent strong memory effects in the local polymer structure affecting the measurement reproducibility.

Figure 2 shows the time evolutions of the ESR lineshape of cholestane in the 70/30 copolymer, during the annealing at $T_a = 383$ K and 358 K and compares them with those previously detected for the homopolymer at the same T_{a} [2,10,14]. The experimental ESR lineshapes could only be fitted with a two-δ distribution function of the correlation times with fast and slow reorienting sites for the cholestane probe [2].

The temperature dependence of the spinning correlation time $\tau_{\|}$ in the fast and slow molecular sites of cholestane in the 70/30 copolymer and homopolymer, after annealing at 383 K or 358 K, is shown in Figure 3 for a large temperature range. Both slow and fast components, whenever the latter was present, typically exhibited an Arrhenius behavior in the temperature region below T_{g}. The activation energy ranged approximately from 31 kJ/mol to 33 kJ/mol. Above T_{g}, two different dynamic regions were detected, namely high temperature and intermediate temperature regions (Fig. 3). The temperature dependence of $\tau_{\|}$ for both fast and slow components was described

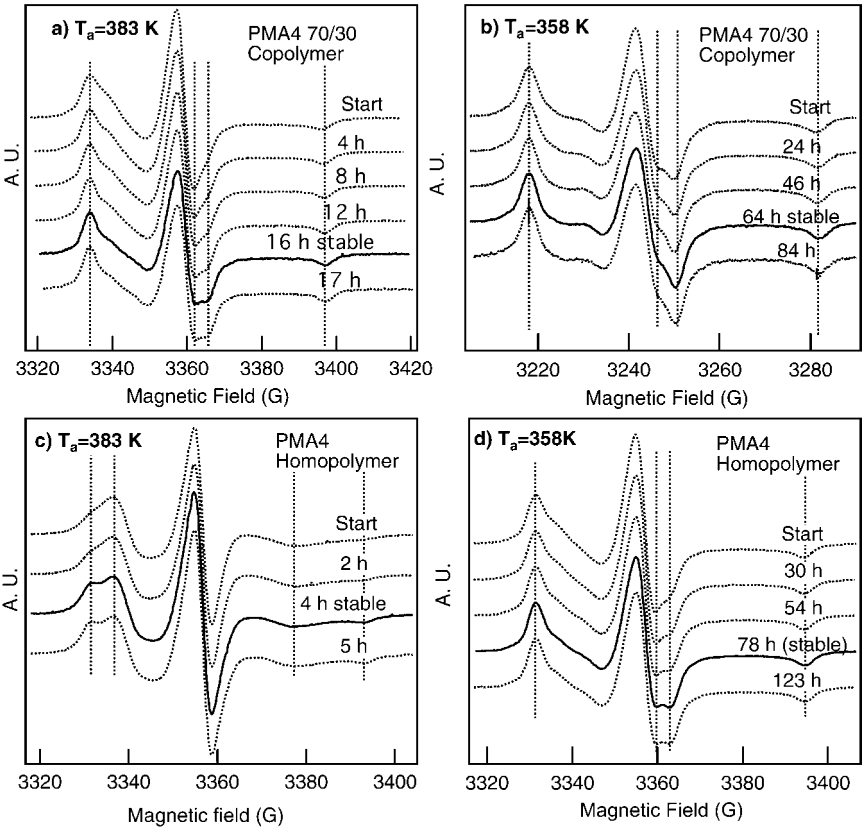

FIGURE 2 Time evolution of the ESR lineshape on annealing of the homopolymer and 70/30 copolymer at different temperatures ($T_a = 383\,\mathrm{K}$ or $358\,\mathrm{K}$).

by the VF law:

$$\tau_{\|} = \tau_{\|_0} \exp\left(\frac{T_b}{T - T_0}\right) \tag{2}$$

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 for $\tau_{\|}$ in the various temperature regions are collected in Table 3. Since T_0 resulted in all cases, in both the high and intermediate temperature regions, of the same value as the corresponding Vogel temperature from rheological measurements, $\tau_{\|}$ can be expressed by a fractionary law of the structural relaxation

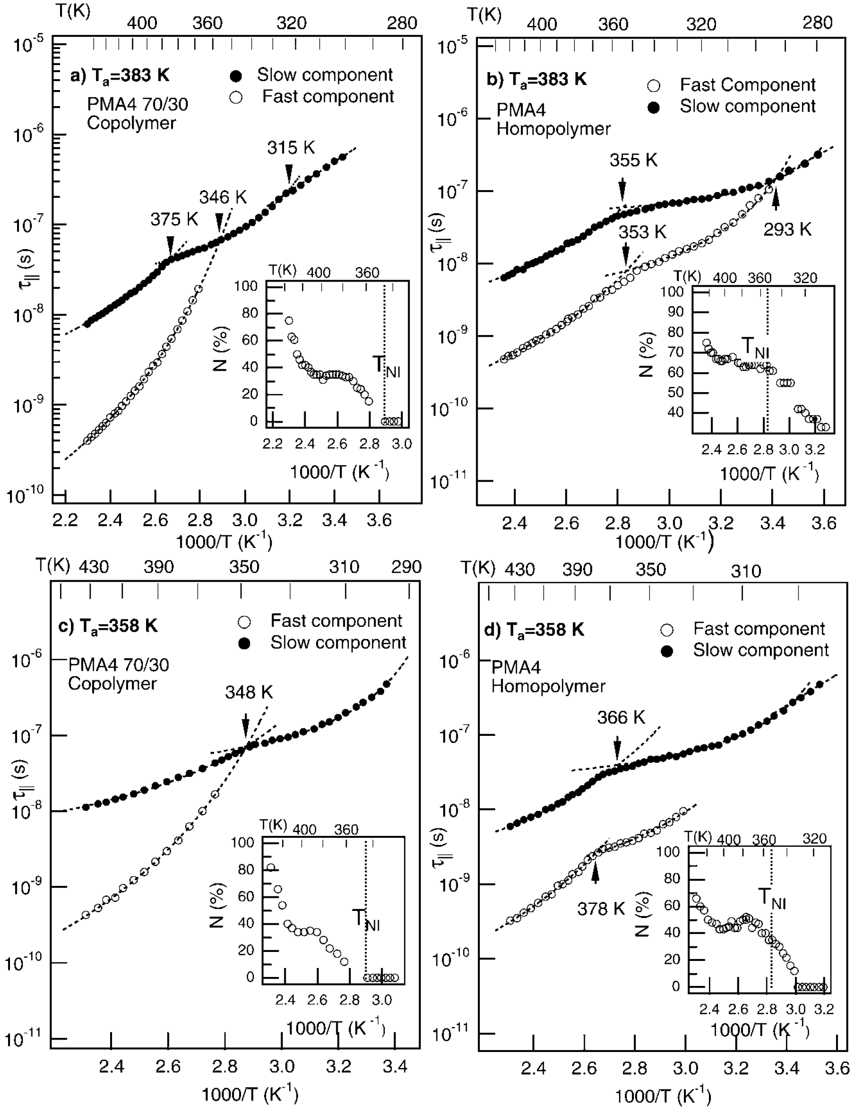

FIGURE 3 Temperature dependences of the spinning correlation time in the fast and slow sites of the cholestane spin probe after annealing at $T_a = 383\,K$ of the copolymer (a) and homopolymer [2] (b), and at $T_a = 358\,K$ of the copolymer [14] (c) and the homopolymer [10] (d). The insets show the percent population N of the fast sites as a function of temperature.

TABLE 3 Fit Parameters of the VF Temperature Dependence of $\tau_{\|}$, Fast (F) and Slow (S) in the High Temperature (H.T.) and Intermediate Temperature (I.T.) Regions After Annealing at the T_a Temperature

70/30 Copolymer			
Temp. region	$\tau_{\|0}$ (s)	T_0 (K)	T_b (K)
$T_a = 383\,\mathrm{K}$			
H.T. (F)	$(4.8 \pm 0.3)\cdot 10^{-12}$	266 ± 4	778 ± 62
I.T. (F)	–	–	–
H.T. (S)	$(4.4 \pm 0.3)\cdot 10^{-10}$	266 ± 5	493 ± 39
I.T. (S)	$(1.1 \pm 0.2)\cdot 10^{-8}$	266 ± 5	147 ± 12
$T_a = 358\,\mathrm{K}$			
H.T. (F)	$(2.9 \pm 0.2)\cdot 10^{-12}$	266 ± 7	820 ± 70
I.T.(F)	–	–	–
H.T. (S)	$(2.0 \pm 0.1)\cdot 10^{-9}$	266 ± 6	290 ± 20
I.T. (S)	$(2.2 \pm 0.1)\cdot 10^{-8}$	266 ± 8	94 ± 6

Homopolymer			
Temp. region	$\tau_{\|0}$ (s)	T_0 (K)	T_b (K)
$T_a = 383\,\mathrm{K}$			
H.T. (F)	$(1.2 \pm 0.1)\cdot 10^{-11}$	259 ± 3	608 ± 27
I.T. (F)	$(1.4 \pm 0.1)\cdot 10^{-9}$	258 ± 8	164 ± 9
H.T. (S)	$(3.3 \pm 0.3)\cdot 10^{-10}$	259 ± 3	497 ± 4
I.T.(S)	$(3.6 \pm 0.3)\cdot 10^{-8}$	259 ± 4	47 ± 2
$T_a = 358\,\mathrm{K}$			
H.T. (F)	$(3.3 \pm 0.2)\cdot 10^{-12}$	258 ± 9	799 ± 60
I.T. (F)	$(3.0 \pm 0.2)\cdot 10^{-10}$	258 ± 7	258 ± 15
H.T. (S)	$(3.0 \pm 0.2)\cdot 10^{-10}$	258 ± 7	527 ± 20
I.T. (S)	$(1.6 \pm 0.1)\cdot 10^{-8}$	258 ± 8	97 ± 7

time τ^{st}:

$$\tau_{\|} \propto \tau^{st}(T)^{\xi} \tag{3}$$

In Eq. (3), the fractional exponent ξ 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. The fractional exponent resorts to be the ratio of the activation pseudo-energy T_b, relevant to the ESR dynamics, to that of the structural relaxation time τ^{st}. The decoupling of the dynamics of a paramagnetic tracer dissolved in a liquid crystalline polymer was taken as a measure of the decoupling degree of the probe dynamics from the α relaxation of the polymer sample [2].

It can be seen, Fig. 3a, that in the 70/30 copolymer annealed at 383 K, the fast molecular site becomes unstable at about T_{NI}. Note that the fast molecular sites are characterized by a high value of the T_{b} constant (see Table 3), denoting its position in the proximity of the polymer main chain. Identical results, within the experimental error, were found for the 70/30 copolymer after annealing at 358 K. Thus, interestingly, the cholestane dynamics becomes homogeneous at temperatures below T_{NI}.

On the other hand, one should note the crossover in the dynamics of the slow component occurring at the temperature of 375 K that is well inside the isotropic phase (Fig. 3a). Such temperature is about 30 K higher than T_{NI} at which temperature a dynamics change was detected in the copolymer that was annealed at 358 K (Fig. 3c).

Numerous observations in very different polymer systems evidenced [15,16] that the crossover between different dynamic regimes occurred at temperatures in the range $1.1-1.2 \cdot T_{\mathrm{g}}$. The temperatures at which crossover occurred were often signaled by changes in the VF parameters, and many authors attributed [2,15,16] those variations to the onset of cooperativity in dynamics at a temperature T_{C}, according to the mode coupling theory [17]. In the present copolymer annealed at 383 K the ratio $T_{\mathrm{C}}/T_{\mathrm{g}} = 1.19$ is in keeping with the above interpretation. Therefore, the onset of cooperativity of the azobenzene copolymer appears to be responsible for the changes of VF parameters relevant to the slow molecular site. This suggests that the isothermal annealing at appropriate temperatures can enable discrimination between phenomena associated with the main chain cooperativity and the nematic potential of the side groups.

Moreover, looking at Figure 3a it is worth mentioning that $\tau_{\|}$ of the paramagnetic probe is unaffected by the isotropic-to-nematic transition; in fact no changes in the dynamics of the slow component can be appreciated at T_{NI}. Thus, the annealing at 383 K would promote polymer overall configurations leading to molecular sites weakly interacting with the mesogenic side groups, in which cholestane slowly reorients. The greater pseudo-energy value in the copolymer annealed at 383 K with respect to the one annealed at 358 K (Table 3) shows that in the former case the slow molecular sites are situated closer to the polymer main chain. This may be explained by positioning the slow component in regions near the methyl methacrylate units comprised between different sequences of azobenzene groups.

CONCLUSIONS

We show that the annealing of the 70/30 copolymer at temperatures in the isotropic phase favors formation of homogeneous nematic polymeric substrates. Such effect is detected when annealing was performed at a T_a just above T_{NI} (358 K) or much higher than T_{NI} (383 K). This behavior is in marked contrast with that of the homopolymer, for which a homogeneous substrate was observed in a limited temperature region after annealing at 358 K. Therefore, the 70/30 copolymer appears to be a more suitable substrate for optical writing in the nematic phase. This can be attributed to the greater mobility of the side groups due to the presence of the methyl methacrylate units, which weaken the nematic potential.

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