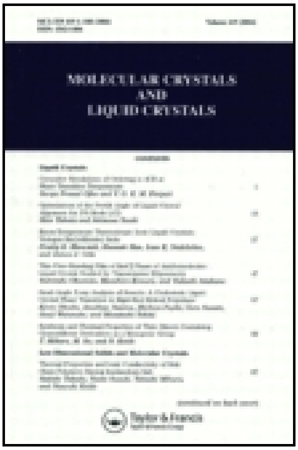

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On the Dynamics of the Cholestane Spin Probe in a Nematic Azobenzene Side Group Oligomer

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ESR studies were carried out on the rotational dynamics of the cholestane spin probe dissolved in a nematic methacrylate oligomer containing azobenzene side groups from well above T_{NI} to below T_g. Only one molecular site was detected in contrast to analogous high molar mass samples, for which distributions of molecular sites were found depending on their thermal histories. The probe dynamics was coupled to that of either the methacrylate main chain or the azobenzene side groups in different temperature regions.

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

INTRODUCTION

In the last few years great attention has been paid to devices for rewritable optical storage based on polymers with functional side groups [1]. In particular, polymers with azobenzene mesogenic units can undergo photochemically induced *trans-cis* isomerization of the azo moiety [2–4] which can trigger a variety of physical effects [5]. In these

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systems nanowriting and information storage rest on bit stability and homogeneity at the molecular level.

ESR spectroscopy has proven to be a powerful tool to investigate heterogeneities on the nanoscale and in singling out suitable thermal procedures to control them in a number of azobenzene methacrylate polymers [6]. In general, ESR investigations performed in molecular and polymeric glass matrices have shown [7,8] that the reorientational correlation times of molecular probe guests follow fractional power laws η^{ξ} in the supercooled region, η being the shear viscosity of the host. 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 possibility to express the spinning correlation time by a fractional law of viscosity of the host matrix rests on the fact that the dependences on temperature, for both viscosity and spinning correlation time, in these systems follow Vogel-Fulcher laws, the Vogel temperatures of which coincide with each other within the experimental errors. Moreover, an accurate evaluation of the spin dynamics in highly heterogeneous polymer systems has very seldom been carried out. Nonetheless, precise analysis of the ESR lineshapes can provide information on dynamics heterogeneity, when the lifetime of heterogeneity becomes larger than the measuring observation time, and on space heterogeneity, due to the distribution of sites available to the rotating molecule. To cite a few examples, very different molecular sites can be populated depending on the polymer polydispersity index [9], thermal treatment [8,10], and presence of plasticizing impurities [11]. ESR investigations on azobenzene methacrylate polymers and co-polymers pointed out that molecular sites available to the probe rotation exhibited a discrete distribution depending on the thermal treatment [12].

In this work we studied the ESR dynamics of a new azobenzene methacrylate PMA4 oligomer with a narrow molar mass dispersity using cholestane as the tracer (Fig. 1). A comparison with experimental results obtained on azobenzene methacrylate polymers with different high molar masses and molar mass distributions is also presented [13].

MATERIALS AND EXPERIMENTAL BACKGROUND

The PMA4 oligomer was prepared by atom transfer radical polymerization (ATRP) of the methacrylate monomer by using the methyl 2-bromoisobutyrate/hexamethyl tetraethylenetetramine/CuBr system under similar conditions to the ATRP of other azobenzene methacrylates

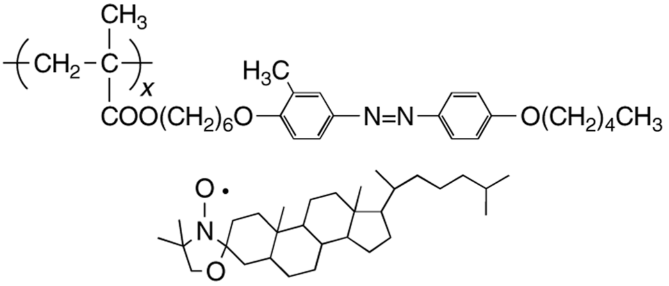

FIGURE 1 Structures of the oligomer PMA4 host matrix and the cholestane spin probe guest.

[14]. It forms a nematic phase between the glass transition ($T_{\mathrm{g}} = 294\,\mathrm{K}$) and the isotropization temperatures ($T_{\mathrm{NI}} = 344\,\mathrm{K}$). Molar mass data and thermal transition parameters are collected in Table 1 and compared with those of two homopolymers S1 and S5.

Differential scanning calorimetry traces were recorded with a Perkin-Elmer DSC7 apparatus calibrated with indium and zinc standards. Annealing experiments were carried out on samples (*ca.* 13 mg) heated to 358 K and maintained at this temperature for 4 h. Then, the sample was rapidly cooled to 250 K and the DSC trace was immediately recorded at a 10 K/min heating rate (Fig. 2). Both T_g and T_{NI} slightly rise with the molar mass of the samples, in agreement with a general trend of such transition temperatures for liquid crystal polymers. Moreover, a conformational transition is also present in the high molar mass homologues at T_c that was not detected in the oligomer. Such conformational transition was previously ascribed [8] to the increased nematic potential when temperature was lowered toward T_g. Probably, the oligomer chain length is shorter than the cooperative length of the polymer main chain in the S1 and S5 polymers.

TABLE 1 Physico-Chemical Characteristics of PMA4 Oligomer and Polymer Samples of Different Molar Masses and Molar Mass Distributions from [13]. The Given Values of T_g, T_c, and T_{NI} are Measured according to the Enthalpic [15], Onset, and Onset Methods, Respectively

PMA4	M_n (g/mol)	M_w/M_n	T_g (K)	T_c (K)	T_{NI} (K)
Oligomer	5800	1.23	294	–	344
Polymer S1	18600	3.17	294	320	353
Polymer S5	29900	2.43	305	337	357

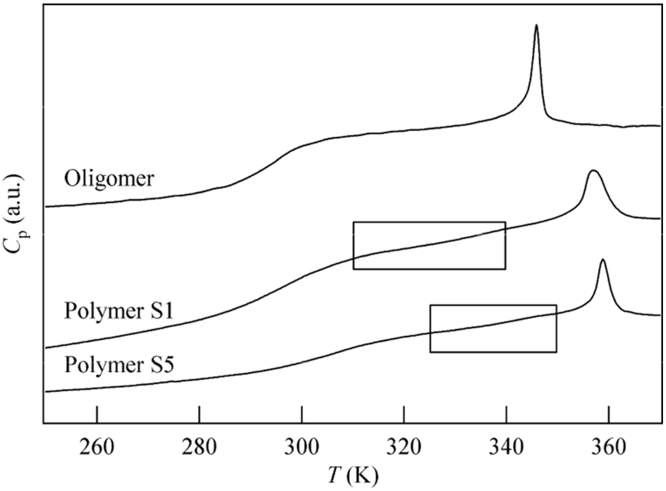

FIGURE 2 DSC heating scans for the PMA4 oligomer and for S1 and S5 polymers. The signalled temperature ranges identify the region of conformational transition (the curves in the figure are vertically shifted to avoid overlap).

A linear viscoelastic characterization of the S1 and S5 samples was presented previously [13]. The shear viscosity data were found to follow a Vogel-Fulcher (VF) law [16,17] over the whole investigated temperature range:

$$\eta(T) = \eta_\infty \exp\left(\frac{T_b}{T - T_0}\right) \tag{1}$$

The VF parameters for the S1 and S5 polymers are given in Table 2.

ESR studies on the oligomeric matrix, in which the cholestane molecular tracer was dissolved (10^{-3} cholestane/repeat unit molar ratio), were performed with an X band Bruker ER 200 SRC equipped with a Bruker BVT100 temperature controller (±0.1 K accuracy). ESR simulation spectra were performed by using a theoretical approach based on the generalised Mori theory [18]. The cholestane spin probe

TABLE 2 Vogel-Fulcher Best-Fit Parameters for the PMA4 S1 and S5 Polymers [13]

PMA4	η_∞ (Pa s)	T_b (K)	T_0 (K)
Polymer S1	$(2.12 \pm 0.03) \cdot 10^{-3}$	1300 ± 30	259 ± 5
Polymer S5	$(3.70 \pm 0.05) \cdot 10^{-3}$	1100 ± 30	278 ± 3

TABLE 3 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}
2.0025	2.0088	2.0062	33.0	6.5	5.5

exhibits nearly axial symmetry [19]. Its reorientational dynamics in the host matrix was characterized by a spinning motion around its own symmetry axis and a tumbling motion of the symmetry axis itself with correlation times $\tau_{\parallel}$ and $\tau_{\perp}$, respectively. The anisotropy ratio $\tau_{\perp}/\tau_{\parallel}$ was found to be 15 over the whole temperature range. Therefore, only the temperature dependence of $\tau_{\parallel}$ will be presented. The principal components of the magnetic tensors of the spin probe were drawn by the powder lineshapes [20] of the linear ESR recorded at 143 K, according to the procedure detailed elsewhere [21] (Table 3).

RESULTS AND DISCUSSION

A previous linear viscoelastic characterization of the S1 and S5 polymer samples showed that the shear viscosity data followed a Vogel-Fulcher (VF) law over the whole investigated temperature range (Table 2) [13]. Thus, it is possible to estimate the VF pseudo-activation energy T_b for the temperature behavior of the viscosity of the narrow dispersity PMA4 oligomer, while ESR results should provide the value of T_0. In fact, the pseudo-activation energy depends on the molar mass according to the law $T_b(M) = T_b(\infty)/(1 + M_{T_b}/M)$ [17]. Taking into account the typical number of units (about 5) that affects the mass value of the parameter M_{T_b} [17], we extrapolated $T_b \approx (1000 \pm 200)$ K for the oligomer from the T_b parameters of the S1 and S5 samples. Unfortunately, due to the different polydispersities of the S1 and S5 samples, this procedure provides a rough estimation only.

A further argument can provide an alternative estimation. In fact, it is known that the parameter $c_1^g = T_b/(T_g - T_0) \times \ln\ 10$ is almost molar mass independent in series of homologous monodisperse polymers [17]. Moreover, for monodisperse samples of poly(meth)acrylates (PMMA [22], poly(alkyl acrylate)s of different molar masses [17] and side-chain lengths [23,24]) a value of *ca.* 12 was found for c_1^g, which might imply for the oligomer PMA4 a $T_b \approx (1300 \pm 200)$ K. Thus, average values of $T_b \approx (1150 \pm 150)$ K and $T_0 = 244$ K in the following were assumed as VF parameters for the temperature dependence of η of the oligomer.

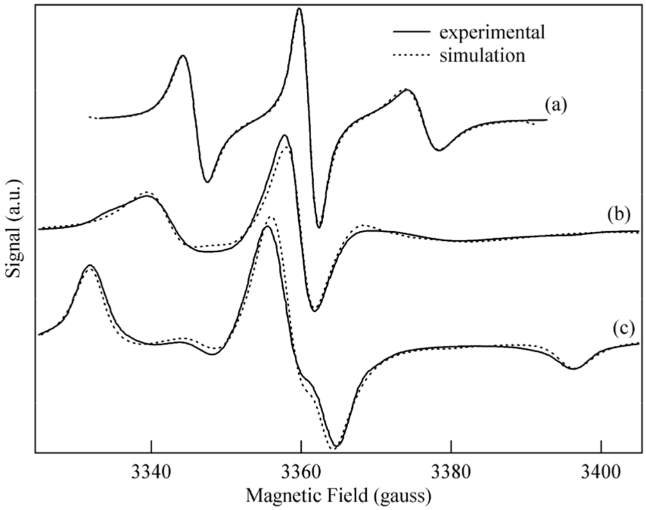

FIGURE 3 ESR spectra with relevant simulations at different temperatures: (a) $T = 442\,\mathrm{K}$ - $\tau_{\|} = 3.78{\cdot}10^{-10}\,\mathrm{s}$; (b) $T = 383\,\mathrm{K}$ - $\tau_{\|} = 1.78{\cdot}10^{-9}\,\mathrm{s}$; (c) $T = 307\,\mathrm{K}$ - $\tau_{\|} = 6.15{\cdot}10^{-8}\,\mathrm{s}$.

The dynamics of the cholestane probe in the PMA4 oligomer was studied by ESR. Typical spectra and relevant theoretical simulations at different temperatures in the isotropic, nematic and glassy states are illustrated in Figure 3. Careful simulations proved the homogeneous character of the ESR lineshapes; in fact a single value of spinning reorientational correlation time was necessary to reproduce the experimental ESR lineshapes.

The time evolution of the ESR lineshapes during the annealing procedure at two temperatures T_a is reported in Figure 4. As one can see, equilibrium spectra were quickly reached, whereas very different behaviors were observed in PMA4 homopolymers [8,10] and copolymers [25,26], where the setting up of complex competitive molecular processes led to very slow evolution of molecular peculiarities on the nanometer and nanosecond scales experienced by the cholestane probe.

The temperature dependence of the spinning correlation time of the cholestane spin probe dissolved in the PMA4 oligomer is shown in Figure 5. For both intermediate regions (II and III) the temperature dependence was well described by VF laws:

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

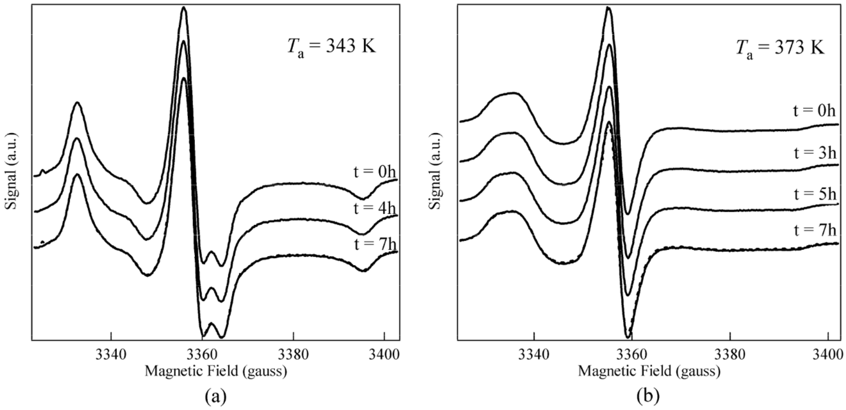

FIGURE 4 Evolution with time of the ESR spectra at $T_a = 343\,\mathrm{K}$ (a) and $T_a = 373\,\mathrm{K}$ (b). Note that the first spectrum is superimposed (dashed line) to the last one.

where $\tau_{\|\infty}$ and T_b, the pseudo-activation energy in kelvin, are parameters dependent also on the spin probe, and T_0 is the Vogel temperature. Arrhenius trends with activation energies ΔE_a were followed in the extreme temperature regions. The values of the fit parameters are reported in Table 4.

The Arrhenius behavior exhibited below 290 K, in the temperature region around the glass transition temperature (onset of the glass transition at 288 K), presents $\Delta E_a \approx 10\,\mathrm{kJ/mol}$, to be compared with 31–35 kJ/mol for PMA4 homopolymers and copolymers [12] and various poly(alkyl acrylate)s at temperatures below T_g [23,24]. In molecular glass formers activation energies of 14–15 kJ/mol are found.

TABLE 4 Fit Parameters for the Temperature Dependence of Cholestane Spinning Correlation Time in the PMA4 Oligomer

			Fit parameters			
Region	Temperature range	Physical law	$\tau_{\|\infty}$(s)	ΔE_a (kJ/mol)	T_0 (K)	T_b (K)
I	$T > 408\,\mathrm{K}$	Arrhenius	$(8.2 \pm 0.1) \cdot 10^{-13}$	21 ± 4	–	–
II	$347\,\mathrm{K} < T < 408\,\mathrm{K}$	Vogel-Fulcher	$(6.0 \pm 0.1) \cdot 10^{-13}$	–	244 ± 4	1070 ± 50
III	$290\,\mathrm{K} < T < 347\,\mathrm{K}$	Vogel-Fulcher	$(8.8 \pm 0.1) \cdot 10^{-9}$	–	244 ± 6	122 ± 7
IV	$T < 290\,\mathrm{K}$	Arrhenius	$(1.8 \pm 0.1) \cdot 10^{-9}$	10 ± 2	–	–

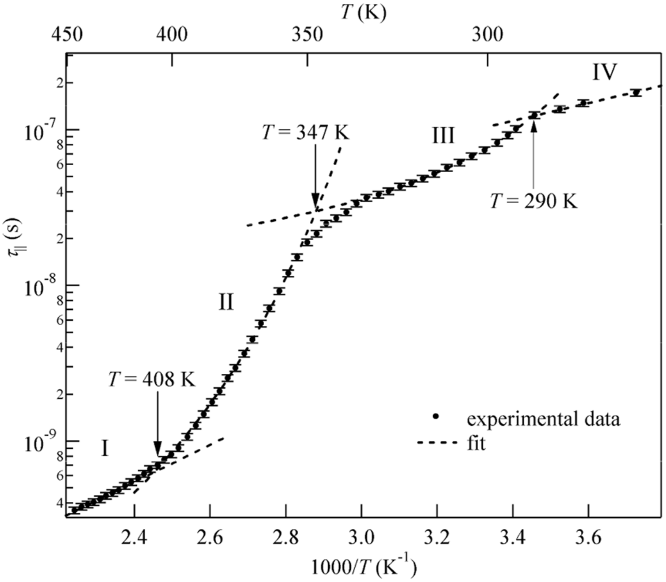

FIGURE 5 Temperature dependence of the spinning correlation time.

Moreover, the activation energy for various oligomer samples investigated by dielectric spectroscopy [27] ranged between 27 kJ/mol and 32 kJ/mol. Thus, the present small values of ΔE_a would suggest a sort of segregation mechanism in this temperature region.

Above 290 K, two different dynamic regions, namely high temperature and intermediate temperature regions II and III, were detected (Fig. 5). The temperature dependence of the spinning correlation time for both regions is well described by the VF law, whose parameters are reported in Table 4. One should note the very high value of the pseudo-activation energy in the high temperature region II. We previously found that in S1 polymer two molecular sites, namely fast and slow sites, were available to the cholestane probe [12]. A comparison with the VF parameters determined for the dynamics in the S1 sample submitted to thermal annealing at different T_a may be in order (Table 5). The higher T_b values in S1 were attributed [12] to the fractional coupling of the probe dynamics to that of the polymer main chain. In all our studies on polymers [12,24,26, and references therein], the ESR T_0 values resulted within the experimental error of the same value as the corresponding Vogel temperature from rheological measurements.

In the case of the oligomer PMA4, the value of T_b relevant to the high VF temperature region results to be 1070 ± 50 K (Table 4), the

TABLE 5 Fit Parameters of the VF Dependence of the Spinning Correlation Time of Cholestane in the PMA4 S1 Polymer in the High Temperature (HT) and Intermediate Temperature (IT) Regions, for Fast (F) and Slow (S) Molecular Sites

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

highest value found in all our studies in polymers for the cholestane probe. The fractional coefficient was $\xi \approx 1$, which suggests the probe dynamics be fully coupled to that of the polymer main chain. Similar results have been found for the cholestane probe solved in OTP and SALOL molecular glass formers [28].

The crossover in the dynamics to the intermediate VF regime occurs at 347 K in correspondence of T_{NI}. The low value of the pseudo-activation energy for the intermediate VF region indicates that the relevant molecular sites are likely situated away from the main chain along the mesogenic side group near the terminal alkyl tails of the repeat unit. The fractional exponent in the VF intermediate region, defined as the ratio of the T_b of the ESR dynamics to that of the structural relaxation time, coincides with the cooperativity coefficient ξ_c [8]. For the PMA4 oligomer we found $\xi_c = 0.11$ that corresponds to $1/\xi_c \approx 9$ cooperative repeat units.

An Arrhenius law with activation energy of $(21 \pm 4)\,\text{kJ/mol}$ fits the activated regime in the highest temperature zone above 408 K. An activated region at high temperature has already been found for many unentangled polymer chains by ESR and other techniques [29]. In [24] this region was studied for different poly(alkyl acrylate) samples varying the side-chain length and the molar mass, and a constant activation energy of about 12 kJ/mol and an onset temperature dependent on the molar mass of the samples have been found. This region with relaxation times in the range 10^{-10}–10^{-12} s was ascribed to changes of the conformers along the main chain when they are able to rotate without restrictions by their neighbors [24]. The higher activation energy of the PMA4 oligomer in comparison with other linear homopolymers should be due to the greater resistance opposed by the bulkier azobenzene side group.

CONCLUSIONS

The dynamics of the cholestane spin probe dissolved in a PMA4 azobenzene oligomer was investigated in a wide temperature range. Interestingly, the oligomer chain length is of the same order of the long axis of the molecular tracer. On the length scale of the probe, the matrix appears to be homogenous over the entire temperature interval investigated. Moreover, calorimetric measurements showed that no conformational disorder transition occurs between T_g and T_{NI} in contrast to PMA4 polymers.

Four regions characterize the dynamic behavior of the probe. I) An Arrhenius behavior at the highest temperatures, essentially due to conformational changes along the polymer main chain. II) A VF behavior at high temperatures where a substantially complete coupling of the probe dynamics with that of the main chain is observed, for the first time in azobenzene polymers. III) A VF region at intermediate temperatures where highly cooperative reorientations occur. IV) An Arrhenius trend, below the glass transition, where the azobenzene side groups modulate the probe dynamics.

Finally, comparison with the dynamics of previous polymer samples emphasizes the significance of spatial-temporal nanoscale processes. In particular, we identified nematic PMA4 samples with M_n and M_w/M_n values in a suitable range to undergo a conformational transition that stabilizes a homogeneous dynamic substrate. This in turn can be exploited for reversible optical nanowriting through the azobenzene photochemistry.

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