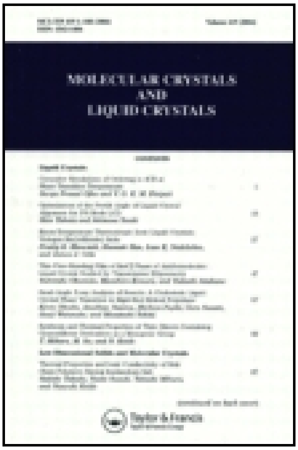

Molecular Crystals and Liquid Crystals

Heterogeneities in the Dynamics of a Molecular Tracer in Mesogenic and Nonmesogenic Azobenzene Copolymers

L. Andreozzi [a] , C. Autiero [a] , M. Faetti [a] , F. Zulli [a] , M. Giordano [a] & G. Galli [b]

[a] Dipartimento di Fisica e INFM, Università di Pisa, Pisa, Italy

[b] Dipartimento di Chimica e Chimica Industriale e INSTM, Università di Pisa, Pisa, Italy

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L. Andreozzi
C. Autiero
M. Faetti
F. Zulli
M. Giordano
Dipartimento di Fisica e INFM, Università di Pisa, Pisa, Italy

G. Galli
Dipartimento di Chimica e Chimica Industriale e INSTM,
Università di Pisa, Pisa, Italy

We studied by electron spin resonance (ESR) spectroscopy the reorientational dynamics of the cholestane spin probe dissolved in the matrix of the PMA4 40/60 copolymer containing methyl methacrylate (MMA, 40 mol%) and azobenzene methacrylate (MA4, 60 mol%) counits. Heterogeneities in the probe dynamics at the nanometer length scale were evidenced and attributed to the existence of molecular sites with slow and fast spinning correlation times. Different dynamic regimes were also observed with a crossover temperature T_C that was correlated with the glass transition temperature T_g of the copolymer, $T_C = 1.17\,T_g$. Even though the nematic-to-isotropic transition temperature could not be detected, the probe dynamics experienced the onset of nematic order at the molecular level. The results are compared with those of the closely related nematic PMA4 30/70 copolymer.

Keywords: azobenzene; cholestane probe; dynamic heterogeneity; liquid crystal polymer; nematic

INTRODUCTION

Side chain azobenzene polymers have been largely investigated due to their potential application as media for optical information storage [1–4]. In such materials, heterogeneities at molecular level may

Address correspondence to L. Andreozzi, Dipartimento di Fisica e INFM, Università di Pisa, 56127 Pisa, Italy. E-mail: laura.andreozzi@df.unipi.it

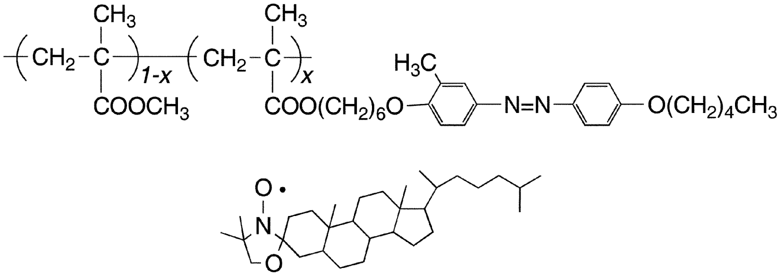

FIGURE 1 Structures of the PMA4 host matrices (homopolymer ($x = 1$), and 30/70 ($x = 0.7$) and 40/60 ($x = 0.6$) copolymers), and the cholestane tracer guest.

substantially affect the stability of the photochemically imprinted bit, thus seriously limiting the effectiveness of the azobenzene-based polymer matrices as erasable storage media at the nanometer length scale. We found that the homogeneity of azobenzene-containing polymethacrylates PMA4, homopolymers and copolymers with methyl methacrylate (MMA) (Fig. 1), critically depends on their thermal history [5–8], e.g. on isothermal annealing of the polymer at temperatures within the nematic phase or the isotropic phase.

Recently, it appeared that PMA4 copolymers [9] may be more suitable than the PMA4 homopolymers [10] for optical recording on the nanometer length scale in terms of both thermal stability and ultimate size of the optically induced bit due to the reduced influence of the nematic potential. Therefore, in this work we investigated a 40/60 copolymer incorporating a significant amount of nonmesogenic MMA counits ($x = 0.60$), which was expected to result in a further narrowing of the nematic range above the glass transition temperature of the copolymer. We studied by electron spin resonance (ESR) spectroscopy the reorientation dynamics of the cholestane probe dissolved in the copolymer over a broad temperature range and compared the results with those observed in a previous 30/70 copolymer ($x = 0.70$). In fact, ESR spectroscopy has proven to be a powerful technique to investigate heterogeneities [8] on the molecular length scale in simple and complex liquids of medium or high viscosity owing to its sensitivity to different molecular environments in the polymer matrix and their population as a function of temperature.

MATERIALS AND EXPERIMENTAL

The copolymers were prepared by free-radical polymerization of the respective MMA/MA4 comonomer feed mixtures according to a

TABLE 1 Physico-Chemical Characteristics of the Polymer Samples

Sample	M_w (g/mol)	M_w/M_n	T_g (K)	T_{NI} (K)
30/70 Copolymer	117000	3.54	314	345
40/60 Copolymer	93200	4.01	320	nd

nd: not resolvable from the glass transition.

literature procedure [11]. The 40/60 copolymer showed no isotropisation peak because of its proximity to the glass transition temperature T_g and was essentially nonmesogenic.

The average molar masses were determined by size exclusion chromatography (SEC) of chloroform solutions with a 590 Waters chromatograph that was equipped with two PL gel Mixed D columns and both RI R401 and UV LC75 detectors. Polystyrene standard samples ($M_n = 1 \cdot 10^3 - 5 \cdot 10^5$ g/mol) were used for calibration. Physico-chemical characteristics of the copolymers are reported in Table 1.

Differential scanning calorimetry (DSC) measurements were performed with a Perkin-Elmer DSC7 calorimeter calibrated with indium. A heating rate of 10 K/min was used.

Rheological measurements in oscillatory regime were performed with a Haake RheoStress RS150H rheometer in the plane-plate geometry. The temperature dependence of the structural relaxation time in the investigated regions, 335–438 K, was well described by the Vogel-Fulcher (VF) law with parameters $T_0 = 258 \pm 2$ K and $T_b = 1960 \pm 70$ K. Previous similar measurements provided VF parameters $T_0 = 266 \pm 5$ K and $T_b = 1570 \pm 50$ K for the 30/70 copolymer [6].

The ESR studies were performed on the polymeric matrix of interest in which the cholestane spin probe was dissolved. The 40/60 copolymer samples were prepared at room temperature by mixing two chloroform solutions containing predetermined amounts of polymer and cholestane, respectively. The resulting solution (10^{-3} cholestane/azobenzene repeat unit molar ratio) was evaporated to complete dryness by heating to 368 K under vacuum for 240 h.

An X band Bruker ER 200 SRL was used and the temperature control (± 0.1 K accuracy) was ensured by a Bruker BVT100 system. Simulation of the ESR spectra was performed by using a theoretical approach, based on the generalized Mori theory [12].

The cholestane spin probe exhibits nearly axial symmetry [13]. Its reorientational 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

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

ratio $\tau_{\perp}/\tau_{||}$ was found to be 15 over the whole temperature range. Therefore, only the temperature dependence of $\tau_{||}$ will be shown.

The principal components of the magnetic tensors of the spin probe were drawn by the powder lineshapes of the linear ESR recorded at 143 K, according to the procedure detailed elsewhere [14]. Powder lineshapes in both polymer samples were found to be coincident; the values of the Zeeman and hyperfine tensors in the molecular reference frame are listed in Table 2.

RESULTS AND DISCUSSION

The ESR equilibrium spectrum for the PMA4 40/60 copolymer was obtained quickly and no particular thermal procedure was needed to obtain reproducible results. The spectra were then taken on slowly heating the sample from room temperature up to 423 K. This is in contrast with the behavior of the PMA4 homopolymers [8] and 30/70 copolymer [5] for which particular thermal annealing procedures had to be devised in order to erase memory effects. This feature may be a manifestation of the nonmesogenic character of the 40/60 copolymer. Representative ESR spectra of the PMA4 40/60 copolymer recorded at different annealing times are reported in Figure 2.

The bimodal character of the distribution function of the spin probe sites is confirmed using a two δ-like distribution to simulate theoretical spectra at high temperatures, as reported elsewhere [8].

The temperature dependence of the spinning correlation time in the fast and slow molecular sites of cholestane in the 40/60 copolymer is shown in Figure 3 which also compares it with that of the 30/70 copolymer. Very similar trends are apparent for both copolymers. The slow component exhibited an Arrhenius behavior in the temperature region below T_g. The activation energy ΔE_a was found to value 29 kJ/mol, to compare with 31 kJ/mol for the 30/70 copolymer after annealing at 383 K [15].

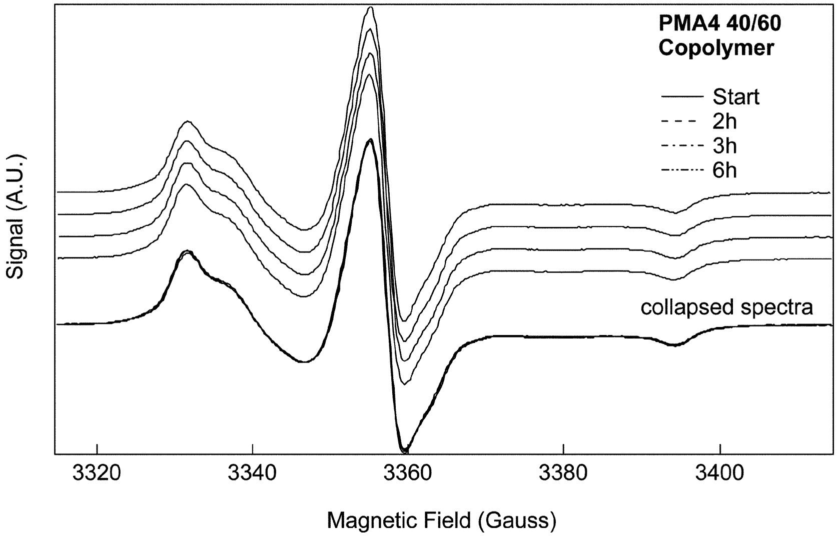

FIGURE 2 Time stability of the ESR lineshape during annealing of the 40/60 copolymer at 399 K.

Above T_g, two different dynamic regions, namely high temperature and intermediate temperature regions, were detected (Fig. 3). The temperature dependences of the spinning correlation time for

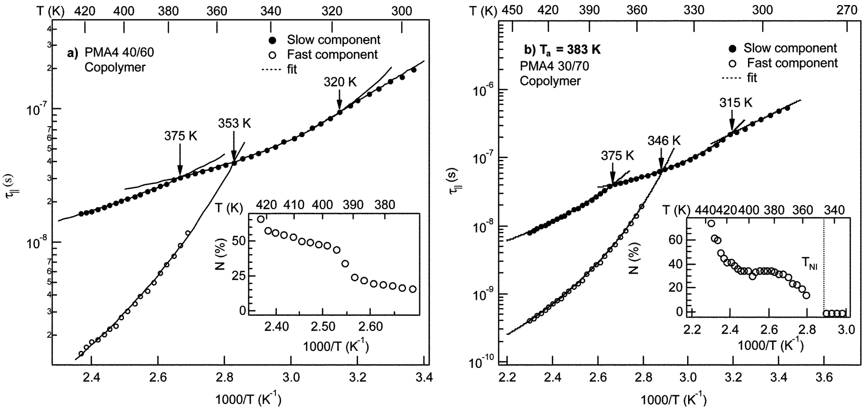

FIGURE 3 The temperature dependences of the spinning correlation time in the fast and slow sites of the cholestane spin probe for the 40/60 copolymer (a) and for the 30/70 copolymer ($T_a = 383\,\text{K}$) (b). The insets show the percent population of the fast sites as a function of temperature.

both fast and slow components could individually be described 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 the two copolymers are compared in Table 3. Since T_0 resulted of the same value as the corresponding Vogel temperature from rheological measurements in both high and intermediate temperature regions, $\tau_{||}$ can be expressed by a fractionary law of the structural relaxation time τ^{st}:

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

In Equation 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 results to be the ratio of the activation pseudo-energy, relevant to the ESR dynamics, to the T_b value of the structural relaxation time τ^{st} [16]. In [8] the decoupling of the dynamics of a paramagnetic tracer dissolved in the PMA4 homopolymer was taken as a measure of the decoupling degree of the probe dynamics from the α relaxation of the polymer. In particular, the observed decoupling in the high temperature region was ascribed to a steric hindrance due to the specific characteristic of the host matrix. The ratio ξ_C between the fractionary exponents for the intermediate and high temperature regions,

TABLE 3 Fit Parameters of the VF Temperature Dependence of the Fast (F) and Slow (S) Spinning Correlation Times $\tau_{||}$ in the High (H.T.) and Intermediate (I.T.) Temperature Regions

Temperature region	$\tau_{\|\|_0}$ (s)	T_0 (K)	T_b (K)
40/60 Copolymer			
H.T. (F)	$(1.4 \pm 0.3)\cdot 10^{-11}$	258 ± 4	760 ± 60
H.T. (S)	$(3.2 \pm 0.3)\cdot 10^{-9}$	258 ± 4	263 ± 25
I.T. (S)	$(9.4 \pm 0.2)\cdot 10^{-9}$	258 ± 4	138 ± 12
30/70 Copolymer ($T_\mathrm{a} = 383\,\mathrm{K}$)			
H.T. (F)	$(4.8 \pm 0.3)\cdot 10^{-12}$	266 ± 4	778 ± 62
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

resulted to be a measurement of the cooperativity degree in the probe dynamics in the intermediate region and $1/\xi_C$ the number of cooperative repeat units.

A crossover in the dynamics of the slow component occurs for both copolymers at the temperature of 375 K, that is well inside the isotropic phase (Fig. 3). Numerous observations in very different polymer systems evidenced that the crossover between different dynamic regimes intervened at temperatures in the range 1.1–1.2 T_g [17,18]. Such temperatures were often signaled by changes in the VF parameters and those variations were ascribed to the onset of cooperativity in dynamics at a critical temperature T_C [8,17,18, and references therein], according to the mode coupling theory [19].In the present copolymers the ratio $T_C/T_g = 1.17$ is in keeping with the above interpretation. Therefore, the onset of cooperativity in the copolymers appears to be responsible for the changes of the VF parameters relevant to the slow molecular site.

On lowering temperature, the spinning correlation time of the paramagnetic probe appears to be unaffected by the isotropic-to-nematic transition in the 30/70 copolymer (Fig. 3). In fact no changes in the dynamics of the slow component can be appreciated across T_{NI}. Thus, in both copolymers the molecular tracer weakly interacts with the mesogenic side groups. The smaller value of the pseudo-energy T_b in the 40/60 copolymer with respect to the 30/70 copolymer (Table 3) suggests that in the latter 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 sequences of azobenzene groups. Note that for the 40/60 copolymer $1/\xi_C \approx 2$, that is of the same order as that found for cholestane when it was dissolved in different poly-(ethyl acrylate) samples [18]. By contrast, the number of cooperative repeat units is much larger in nematic PMA4 homopolymer ($1/\xi_C \approx 5-10$ depending on the thermal history [20]) and 30/70 copolymer ($1/\xi_C \approx 3$) (Table 3) [15,20].

The temperature behavior of the fast dynamic sites is also worth emphasizing. In fact, in both 40/60 and the 30/70 copolymers, the fast molecular sites become unstable at certain temperatures that coincide in the latter with the corresponding T_{NI} (Fig. 3). Thus, it appears that at a molecular scale the onset of the nematic potential of the 40/60 copolymer is probed by the cholestane dynamics, even though the nematic phase cannot be clearly detected at a macroscopic length scale. Moreover, at temperatures lower than the crossing temperature between fast and slow dynamics, the cholestane dynamics becomes homogeneous.

CONCLUSIONS

ESR investigations may be considered preliminary to optical investigations oriented to optical writing and are very valuable in confirming the availability of homogeneous molecular sites in the polymer matrix. Homogeneity of the polymer is one relevant parameter in optical writing at the nanometer scale.

This work has investigated the capability of the 40/60 PMA4 copolymer to form homogeneous substrates at the nanometer length scale by looking at the dynamics of a molecular tracer dissolved in the polymeric matrix, in a comparison with the one of 30/70 copolymer, differing in the content of MMA counits.

It has been found that the 40/60 copolymer easily exhibits stable substrates without resorting to the thermal treatment, necessary in the 30/70 copolymer and the corresponding PMA4 homopolymer. These stable substrates have large intervals of temperature above the glass transition with single dynamic sites, and therefore they result homogeneous.

From this viewpoint, PMA4 copolymers could provide the best substrates for optical recording at *nanometer* length scale because of the reduced influence of the nematic potential. The consequence of this more local character of the intermolecular interaction would result in a reduced size of the optical imprinted bit, that is ultimately dictated by instrumental limitation. The 40/60 copolymer is expected to be a very effective material at the nanometer scale, although unsuitable in optical writing on the macroscopic scale.

REFERENCES

[1] Nakano, M., Yu, Y., Shishido, A., Tsutsumi, O., Kanazawa, A., Shiono, T., & Ikeda, T. (2003). *Mol. Cryst. Liq. Cryst.*, *398*, 1.

[2] Meier, J. G., Ruhmann, R., & Stumpe, J. (2000). *Macromolecules*, *33*, 843.

[3] Bubliz, D., Helgert, M., Fleck, B., Wenke, L., Hvilsted, S., & Ramanujam, P. S. (2000). *Appl. Phys. B*, *70*, 803.

[4] Yaroshchuk, O., Bidna, T., Dumont, M., & Lindau, J. (2004). *Mol. Cryst. Liq. Cryst.*, *409*, 229.

[5] Andreozzi, L. Faetti, M., Giordano, M., Palazzuoli, D., Laus, M., & Galli. G. (2002). *Macromol. Chem. Phys.*, *203*, 1636.

[6] Andreozzi, L., Faetti, M., Giordano, M., Palazzuoli, D., & Galli. G. (2004). *Mol. Cryst. Liq. Cryst.*, *411*, 515.

[7] Andreozzi, L., Faetti, M., Palazzuoli, D., Galli, G., & Giordano, M. (2003). *Mol. Cryst. Liq. Cryst.*, *398*, 87.

[8] Andreozzi, L., Faetti, M., Galli, G., Giordano, M., & Palazzuoli, D. (2001). *Macromolecules*, *34*, 7325.

[9] (a) Patanè, S., Arena, A., Allegrini, M., Andreozzi, L., Faetti, M., & Giordano, M. (2002). *Opt. Commun.*, *210*, 37.

(b) Likodimos, V., Labardi, M., Pardi, L., Allegrini, M., Giordano, M., Arena, A., & Patanè, S. (2003). *Appl. Phys. Lett.*, *82*, 3313.

[10] Labardi, M., Coppedè, N., Pardi, L., Allegrini, M., Giordano, M., Patanè, S., Arena, A., & Cefalì, E. (2003). *Mol. Cryst. Liq. Cryst.*, *398*, 33.

[11] Angeloni, A. S., Caretti, D., Laus, M., Chiellini, E., & Galli, G. (1991). *J. Polym. Sci., Polym. Chem. Ed.*, *29*, 1865.

[12] Grigolini, P. (1985). In: *Memory Function Approaches to Stochastic Problems in Condensed Matter*, Evans, M. W., Grigolini, P., & Pastori Parravicini, G. (Eds.), John Wiley & Sons: New York, p. 1.

[13] Carr, S. G., Kao, S. K., Luckhurst, G. R., & Zannoni, C. (1976). *Mol. Cryst. Liq. Cryst.*, *35*, 7.

[14] Andreozzi, L., Giordano, M., & Leporini, D. (1992). *Appl. Magn. Reson.*, *279*, 4.

[15] Andreozzi, L., Faetti, M., Galli, G., Giordano, M., Palazzuoli, D., & Zulli, F. (2005). *Mol. Cryst. Liq. Cryst.*, *429*, 29.

[16] Vrentas, J. S. & Duda, J. L. (1985). *J. Polym. Sci. Polym. Phys. Ed.*, *23*, 2475 and 2489.

[17] Beiner, M., Huth, H., & Schoeter, K. (2001). *J. Non-Cryst. Solids*, *279*, 126.

[18] Andreozzi, L., Faetti, M., Giordano, M., Zulli, F., & Castelvetro, V. (2004). *Phil. Mag. B*, *84*, 1555.

[19] Goetze, W. & Sjoegren, L. (1992). *Rep. Prog. Phys.*, *55*, 55 and references therein.

[20] Andreozzi, L., Faetti, M., Galli, G., Giordano, M., & Palazzuoli, D. (2004). *Macromolecular Symposia*, *218*, 323.