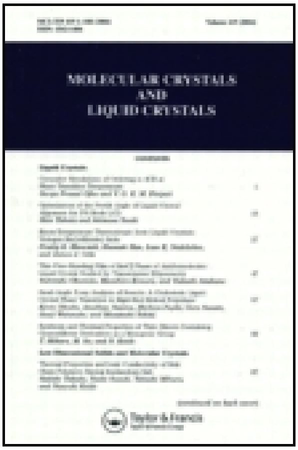

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Dynamics Heterogeneity and Optical Writing in a Liquid Crystalline Azobenzene Copolymer

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DYNAMICS HETEROGENEITY AND OPTICAL WRITING IN A LIQUID CRYSTALLINE AZOBENZENE COPOLYMER

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The dynamics of the cholestane spin probe dissolved in a nematic azobenzene copolymer was studied by ESR following a suitable thermal procedure. Heterogeneities in the dynamics of the guest molecule resulted to occur only in the high temperature region, slightly above the nematic-isotropic transition temperature. A temperature region above the glass transition was signalled, in which stable optical writing could be obtained. Optical birefringence and topological writing experiments were carried out on polymer films at the macroscopic and nanometer length-scales, respectively. SNOM analysis showed a very homogenous substrate that could be suitable for optical nanowriting.

Keywords: electron spin resonance; azobenzene; nematic copolymer; dynamics heterogeneity; optical writing

INTRODUCTION

Investigations on optical writing and bit stability are in a state of flux. In the last years liquid crystalline polymers have largely been investigated because of their potential application as media for optical information storage [1]. In particular, liquid crystalline polymers and copolymers with azobenzene side groups appeared to be suitable candidates to this aim [2]. Optical writing on the micrometer [3] and nanometer [4] length-scales in a nematic polymethacrylate (PMA4) containing a (3-methyl-4′-pentyloxy)azobenzene mesogenic unit has been presented. Some of the crucial

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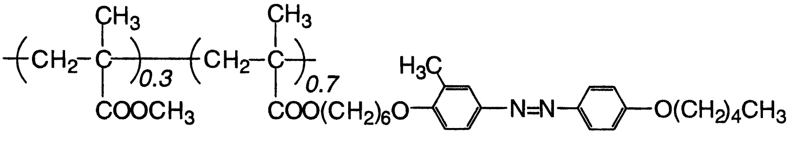

FIGURE 1 Chemical structure of the PMA4(30/70) copolymer.

parameters in data storage are bit stability, homogeneity at molecular level and working temperature range [3,5,6]. Homogeneity of the polymer matrix strongly depends on the thermal procedure [6]. On the other hand, relaxation processes at different time- and length-scales can affect the bit stability. Therefore, spectroscopic techniques which cover different time- and length-scales should be used in order to fully investigate the matrices of interest. Linear and non-linear ESR spectroscopies and rheological measurements have proved to be able to characterise homogeneity and cooperativity at molecular level; moreover, it has been shown that conformational rearrangements may affect the temperature dependence of the dynamics of spin probe dissolved in a liquid crystalline polymer matrix [3].

In this work we studied by ESR the dynamics of the cholestane spin probe dissolved in the random copolymer PMA4(30/70) that contained non-mesogenic units from methyl methacrylate (Fig. 1). We found that peculiarity in the dynamics of the molecular tracer signalled a temperature below which an optically induced bit was stable. A comparison between optical writing in homopolymer and copolymer matrices was made.

EXPERIMENTAL PART

The random copolymer PMA4(30/70), containing 30 mol% methyl methacrylate non-mesogenic units, was prepared following a literature general procedure [7]. Its molar mass ($M_w = 117000$ g/mol) and molar mass dispersity ($M_w/M_n = 3.54$) were evaluated by SEC measurements.

Differential scanning calorimetry measurements were carried out with a Perkin-Elmer DSC7 apparatus that had been calibrated with indium and zinc standards. The sample exhibited a nematic phase between the glass transition temperature ($T_g = 314$ K) and the nematic-isotropic transition temperature ($T_{NI} = 346$ K, $\Delta H_{NI} = 2.3 \pm 0.1$ J/g).

Rheological measurements in oscillatory regime were performed in the temperature range 400–324 K; the temperature dependence of the structural relaxation time in the investigated region was well described by a Vogel-Fulcher law with parameters $T_0 = 266 \pm 5$ K and $T_b = 1575 \pm 50$ K.

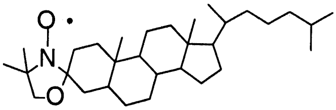

FIGURE 2 Chemical structure of the cholestane spin probe.

ESR studies were performed on the cholestane probe dissolved in the PMA4(30/70) matrix (10^{-3} cholestane/repeat unit molar ratio) according to the procedure in [6]. The structure of cholestane nitroxide spin probe(Aldrich) is shown in Figure 2.

In order to avoid memory effects a suitable thermal procedure [6] was followed by: i) maintaining the sample at the annealing temperature $T_a = 358$ K and monitoring the system evolution until a stable spectrum was recorded ($t_a = 64$ h) via the acquisition of ESR spectra; ii) recording spectra on cooling to different 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. By this procedure, the temperature range 358–280 K was fully investigated. Spectra in the upper temperature region were simply recorded on slowly heating the sample from 358 to 433 K.

ESR measurements were performed by an X band Bruker ER 200D SRC and the control of temperature was assured by a Bruker BVT100 system with ±0.1 K accuracy. ESR simulation spectra were performed by using a theoretical approach, based on the generalised Mori theory [9]. The principal components of the magnetic tensors of the spin probe were drawn by the powder lineshape [10] of the linear ESR recorded at 143 K, according to the procedure detailed elsewhere [11] (Table 1).

The cholestane spin probe exhibits nearly axial symmetry [8]. Its reorientational dynamics in PMA4 matrices 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 between them was found $\tau_{\perp}/\tau_{\|} = 18$ over the whole temperature range. Due to this relationship, only the temperature dependence of $\tau_{\|}$ will be shown.

TABLE 1 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

Optical induced topological experiments on copolymer films were carried out on a macroscopic length-scale and bit stability was assessed at 338 K (that is above T_g). Reasonably homogeneous films of about 4 μm thickness were prepared by solution casting. The optical observations were carried out with a Zeiss Axioplan 2 polarizing microscope connected to a videocamera for recording the images. The samples were placed between two crossed polarizers in a thermostated cell (accuracy 0.1 K). Trans-cis-trans optical cycles were induced in the azobenzene moieties due to the blue components of the microscope lamp. Typically, only a few irradiation seconds were necessary to provide a detectable effect. Readings were carried out by using an interferometric filter (wavelength center $\lambda = 650.2$ nm and bandwith $\Delta\lambda = 91$ nm) and rotating the sample by 45° with respect to the polarisation axes of the incident light.

Nanowriting experiments were done with a scanning near-field optical microscope (SNOM) based on a homemade setup [12], implemented with a tuning fork detection of the shear-force feedback [13,14]. The copolymer was locally irradiated at 325 or 488 nm through the aperture of a metallized tapered optical fiber. Commercial (Nanonics Ltd) tapered optical probes with a 50 nm nominal aperture were used.

RESULTS AND DISCUSSION

ESR measurements were performed on the PMA4(30/70) copolymer after annealing at 358 K, following a suitable procedure to obtain reproducible results (see Experimental Part). The ESR lineshapes were inhomogeneous in character, which was well taken into account by careful simulations with a two δ-like distribution function of molecular sites for the spin probe. This is consistent with what was previously found for the PMA4 homopolymer [15]. However, differently from the homopolymer inhomogeneity was present only in high temperature region above the T_{NI}. The temperature dependences of both fast and slow spinning correlation times are reported in Figure 3, that also illustrates the temperature dependence of the fast spin population, normalized to 100. In the temperature range 361–348 K reliable evaluation of the fast component percentage was not possible and these data are not included in Figure 3. On lowering the temperature an increasing instability of the fast component was detected until this completely disappeared. Thus, the thermal annealing performed at 358 K appeared to provide an homogeneous substrate, at least in the nematic temperature range ($T < 348$ K). This range resulted to be broader than in the PMA4 homopolymer ($T < 318$ K).

The fast component instability was probably due to the onset of cooperativity in the structural relaxation. This in fact would be expected to take

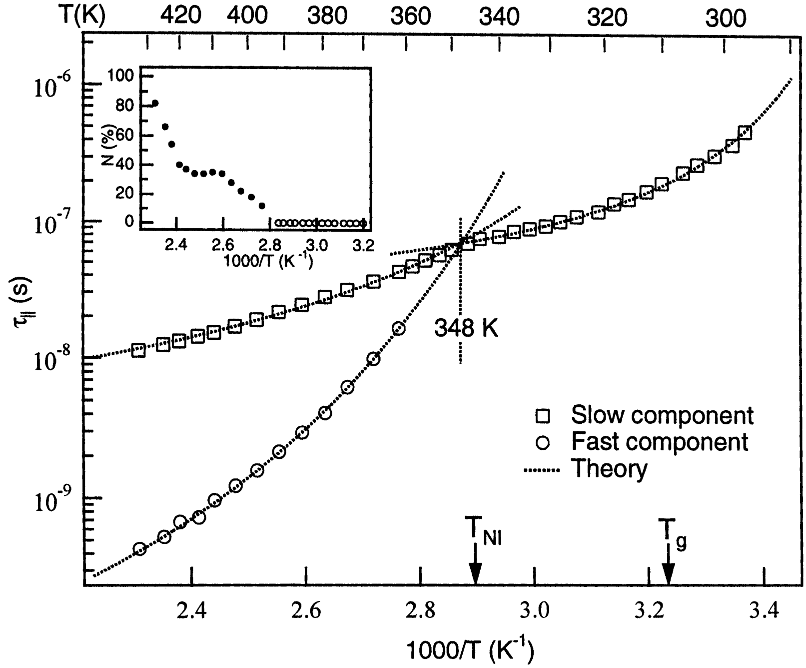

FIGURE 3 Temperature dependence of the spinning correlation time (the inset shows the population N of the fast site component vs. temperature).

place at a temperature T_c (critical or crossing temperature) [16,17] in the range $(1.1 \div 1.2)\cdot T_g$.

In the whole temperature range, the experimental data are well represented by Vogel-Fulcher (VF) laws:

$$\tau_{\parallel} = \tau_{\parallel_0} \cdot \exp\left(\frac{T_b}{T - T_0}\right) \qquad (1)$$

where $\tau_{\parallel_0}$ 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 both homopolymer and copolymer are reported in Table 2. Since the T_0 parameters coincided, within the experimental errors, with those obtained by rheological measurements, Eq. (1) can be written as a fractionary law:

$$\tau_{\parallel} \propto \tau_{\alpha}(T)^{\xi} \qquad (2)$$

where ξ, the fractional exponent, may vary between 0 and 1, with $\xi = 1$ corresponding to a complete coupling of the dynamics of the guest probe to the structural relaxation of the host matrix.

TABLE 2 Fit Parameters of the Temperature Dependence of $\tau_{\|}$ in PMA4 and PMA4(30/70) Annealed at 358 K

Temperature region	$\tau_{\|_0}$(s)	T_0(K)	T_b(K)
	PMA4		
H.T. (F)	$(3.3 \pm 0.2)\cdot 10^{-12}$	258 ± 9	799 ± 60
L.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
L.T. (S)	$(1.6 \pm 0.1)\cdot 10^{-08}$	258 ± 8	97 ± 7
	PMA4(30/70)		
H.T. (F)	$(2.9 \pm 0.2)\cdot 10^{-12}$	266 ± 7	820 ± 70
L.T. (F)			
H.T. (S)	$(2.0 \pm 0.1)\cdot 10^{-09}$	266 ± 6	290 ± 20
L.T. (S)	$(2.2 \pm 0.1)\cdot 10^{-08}$	266 ± 8	94 ± 6

ξ resorts to be the ratio of the activation pseudo-energy of the VF law relevant to the dynamics of the fast (and slow) component(s) over the value of the activation pseudo-energy of the structural relaxation time τ_α. In molecular glass formers, fractionary laws have been explained in terms of cooperativity [18], and ξ^{-1} has been interpreted as the size of the rearranging cooperative region. In liquid crystalline polymers [6], the decoupling of the probe dynamics from the α relaxation in the high temperature region (above T_c) was ascribed to steric hindrance, while the cooperativity effect in the dynamics was recognised in the VF branch at intermediate temperatures (above T_g). The size of the cooperative rearranging region resorted to be the ratio of the fractionary exponents in the high temperature region to that of the intermediate one.

The high pseudo-energy value relevant to the fast component, stable only at the higher temperatures, suggests [6,15] location of the fast molecular sites in proximity of the macromolecular main chain. To the contrary, the relatively low values [6,15] of the pseudo-energy relevant to the slow component, at both high and low temperatures, allow to locate the slow sites close to the mesogenic units, but away from the polymer backbone. This conclusion is also supported by the clear sensitivity of the probe dynamics to the nematic-isotropic transition.

Interestingly, the crossing between slow and fast spinning correlation time curves seems to be a signature of a structural conformation change of the polymer matrix, similar to what was found for a PMA4 homopolymer, that had been subjected to the same thermal annealing [3,15]. There, such a crossing occurred at 328 K and was ascribed to the freezing of conformational disorder of the polymer main chain driven by the nematic order. This was also manifested in a stable optical writing up to about 318 K, i.e. well above the T_g, and ten degrees below the temperature at which the fast reorienting component disappeared.

In order to evaluate the stability of the optically induced bit on the PMA4(30/70) copolymer, optical writing experiments through the trans-cis-trans isomerization cycles of the azobenzene groups were performed on polymer films at temperatures at which the slow component was only present (Fig. 4).

In Figure 4a, the images of maximum birefringence obtained right after sample irradiation and 48 h later at the constant temperature of 338 K are compared. It can be noted that no appreciable relaxation effect took place during this time and the optically induced bit remained quite stable. A different behaviour was found for the optical bit in the homopolymer matrix, following the same experimental procedure (Fig. 4b). As seen, the bit became blurred after a few seconds and the optically induced information was almost completely lost after 24 h.

Therefore, the instability of the ESR fast spinning component in the dynamics of the cholestane probe dissolved in a suitably annealed sample of the PMA4(30/70) copolymer may be taken as a signature of the possibility to get stable optical printing at temperatures above the T_g. This may result from the adoption of a conformation of the polymer main chain

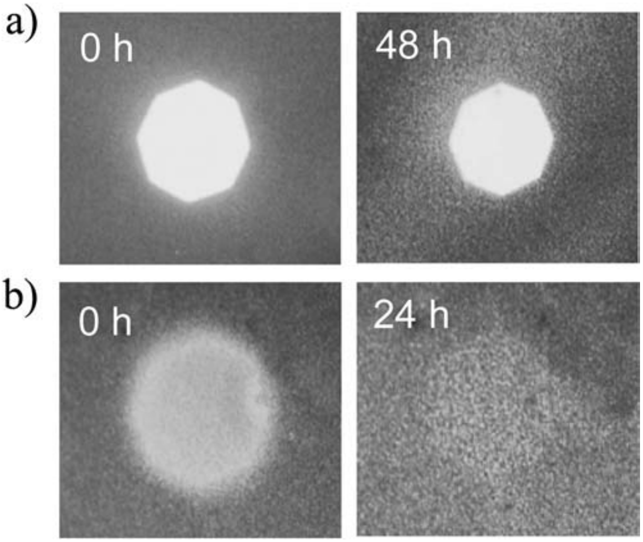

FIGURE 4 (see COLOR PLATE XXXIV) Induced birefringence in PMA4(30/70) copolymer (a) and PMA4 homopolymer (b) at 338 K after different times from irradiation (between crossed polarizers at $\pi/4$).

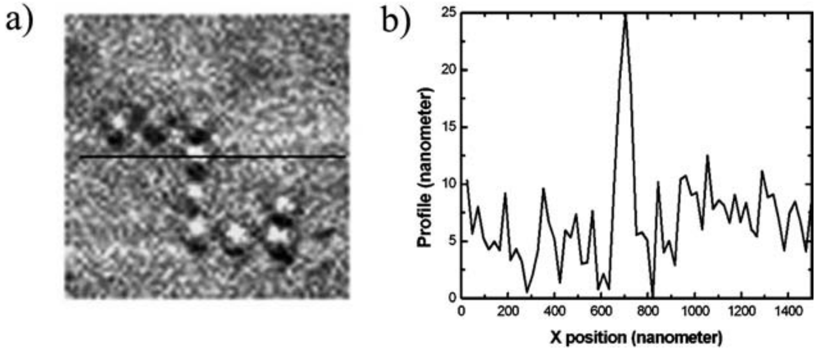

FIGURE 5 (see COLOR PLATE XXXV) Topographic image of PMA4(30/70) film ($\lambda = 488\,\mathrm{nm}$) (a) and profile analysis along the horizontal line (b) (courtesy of S. Patanè and M. Allegrini).

driven by the optically induced molecular reorientation of the side groups, which would be stabilised by the presence of the methyl methacrylate units.

Nanowriting SNOM experiments were also carried out on spin-coated films submitted to same thermal procedure [3] (Fig. 5). The surface roughness of the sample was estimated, prior to experiments, by studying the topography image obtained with the SNOM shear force signal. The film was remarkably flat with an average roughness of a few nanometers. Dots were about 80 nm in diameter, corresponding to 15 Gbit/cm^2.

Thus, the PMA4(30/70) films appeared to be suitable materials for optical nanolithography and high-density information storage.

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