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ESR studies of the orientational and reorientational properties of mesomorphic polymers

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The orientational properties of two mesomorphic azobenzene-containing polyacrylates are investigated by ESR spectroscopy using the spin probe technique. Procedures to achieve a uniform alignment of the director in the presence of a static magnetic field are described in detail. The recovery of the alignment after the creation of controlled non-equilibrium states in the presence of a magnetic field is studied. It is found that the recovery time is proportional to the reciprocal square of the static magnetic field, analogous to that which occurs in low molar mass liquid crystals.

1. Introduction

Molecular rearrangements in the ordered state of polymeric mesophases are hampered by the high viscosity of these materials. In particular, the reorientation processes which arise in the presence of external electric and magnetic fields occur on time scales much longer than those recorded for low molar mass liquid crystals [1]. Investigations focused on variables governing the kinetics of the alignment provide insights into both the equilibrium structure and the dynamics of polymeric mesophases. Moreover, the alignment process may have some implications of practical relevance such as those connected to lock in the glassy state of the macro-order, as acquired on cooling from the mesophase.

The present paper reports on the bulk orientational properties of two azobenzene-containing mesomorphic polymers in the presence of a high magnetic field [2]. The determination of the degree of orientational order established, the alignment persistence above the glass transition temperature, and the recovery time of the oriented structure after the onset of controlled non-equilibrium orientational distributions will be also discussed. The dependence of the orientational behaviour on the thermal history is investigated by analysing the ESR lineshape of stable radicals (spin probes) dissolved in the polymeric hosts [3].

A rigorous evaluation of the ESR lineshape can be accomplished along the guidelines of the memory-function approach that has been published elsewhere [4]. However, the slow dynamics of the probe affects only in a minor way the ESR lineshape, which, instead, is largely determined by its angular equilibrium distribution. It follows that the ESR lineshape is very similar to the asymptotic form of the ESR 'powder' spectrum [5, 6]. Since the present investigation is focused on the orientational properties of the host phase, it is enough for our purposes to carry out the analysis of

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the ESR lineshapes of a probe in the ultra-slow motion regime, by resorting to the efficient algorithms which evaluate the powder ESR lineshape. According to this procedure, the estimated values of the g-tensor (A tensor) exhibit errors not larger than $\pm 3 \times 10^{-4}$ ($\pm 0{\cdot}4$ Gauss) [7].

2. Experimental

2.1. *Materials*

2.1.1. *Side chain liquid crystal polymers*

In figure 1 are represented the structural formulae of the mesomorphic polymers containing the azobenzene chromophore substituted in the 4′-position with an ethoxy (PA1) and a methoxy (PA2) group; these were synthesized by radical polymerization of the acrylates [2]. The structures of the polymers have been checked by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The value of $\bar{M}_n$ corresponds to medium degrees of polymerization, with $\bar{x}_n = 100$–200. Transition temperatures, together with relevant thermodynamic quantities for PA1 and PA2 attained by DSC, are listed in table 1.

2.1.2. *Spin probe*

The cholestane spin probe was the one of choice. Its selection was dictated by its fairly high declared thermal stability (450 K onset of decomposition) [8], and by its structure which is suitable to intercalate among the mesogenic side chain branches, spaced from the polymer backbone by a six methylene spacer. The spin probe was tested for its thermal stability in the two polymer matrices and was found to be about 70 K below the declared threshold. In figure 2 there are represented the profiles of the cholestane thermal decay with time at three different values of the reduced temperature $T^* = T/T_i$ (T_i is the temperature of the clearing point), and for an initial concentration $C = 10^{-2}$ (mol/mol) as referred to the azobenzene containing monomeric units.

2.2. *Sample preparation*

The samples have been prepared according to the following procedure. The molarity of the polymer solution has been defined as the number of moles of the

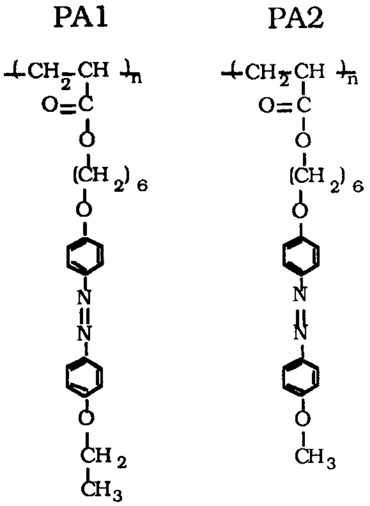

Figure 1. Structures of the mesomorphic polymers and their acronyms.

Table 1. Transition temperatures and thermodynamic properties of the polymeric mesophases at the clearing point.

	T_g/K	T_m/K	T_i/K	ΔH_i/KJ mol^{-1}	ΔS_i/J K^{-1} mol^{-1}
PA1	257·7	360	433	0·83	1·89
PA2	258·8	370	413	0·78	1·88

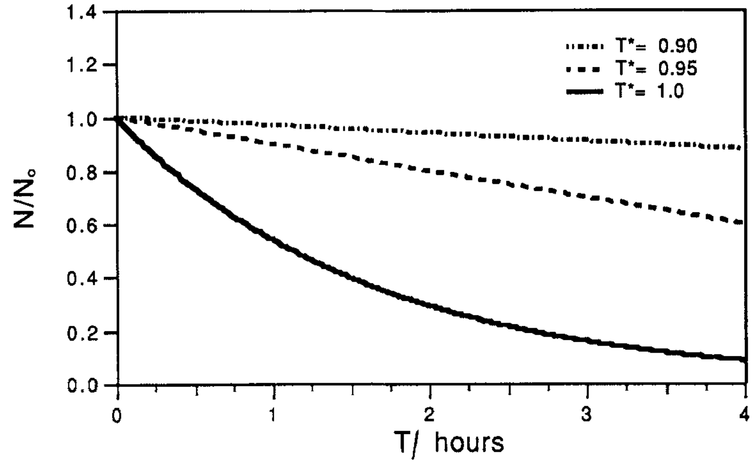

Figure 2. Percentage loss of the cholestane spin probe with time in solution in polymers PA1 and PA2. Spin probe concentration $N_0 = 10^{-2}$ (mol/mol).

repeating monomeric unit per litre of solution. Spin probe solutions of known molarity have been added to the polymer solution and the solvent thoroughly evaporated under vacuum. The concentration of the spin probe as referred to the monomeric unit was $C = 10^{-2}$. The mesophase alignment was practically unaffected by the spin probe concentration, and the profiles of the ESR spectra were very little broadened by the dipolar coupling. By comparing the ESR spectra recorded for samples both in sealed tubes under ultrapure nitrogen and in unsealed tubes, no appreciable differences were detected.

2.3. *Instrumental*

The ESR spectra were recorded using an X-band spectrometer (Bruker ER200D SRL). The field modulation frequency was 100 kHz. The spectrometer magnet itself provided the aligning field (maximum value 23 kGauss). The temperature control system was based on a Bruker VT100 central unit controlling the temperature of a nitrogen stream. The temperature was measured by a thermocouple placed as close as possible to the sample without perturbing the microwave field inside the resonating cavity. Good thermal contact between the thermocouple and the sample tube was guaranteed by a high thermal conductivity foam.

3. Results and discussion

The investigation of the orientational properties of polymers PA1 and PA2 required the identification of suitable thermal histories to achieve the uniform alignment of the sample.

The standard orientational procedure, which was selected to get a complete macroscopic alignment of small-sized samples (about 4 mg), is briefly described. At first, in order both to reduce the defects between domains and favour the spin probe diffusion, the sample is annealed for about 2 hours at the reduced temperature $T^* = 0{\cdot}90$ in the absence of any external field [9]. Then, the annealing was continued for an

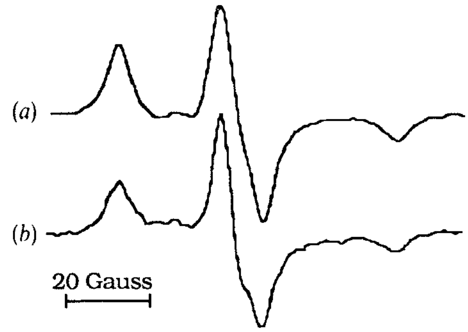

Figure 3. Comparison between the isotropic (*a*) ESR spectrum of PA2 and that for the partially oriented sample (*b*) after the preliminary aligning treatment. See text for details. No appreciable improvement is achieved by extending the duration of the alignment process. $T = 300$ K.

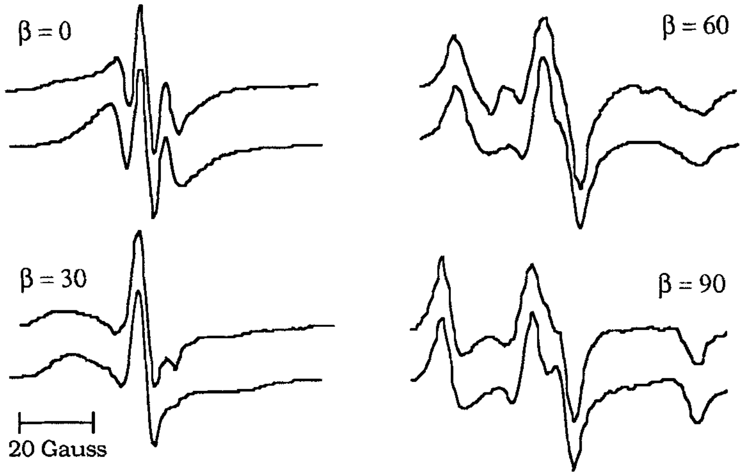

Figure 4. Angular dependence of the ESR lineshape of the cholestane spin probe in PA1 with uniform director. $T = 300$ K. β is the angle between the static magnetic field and the director. For each pair, the upper curve is the experimental spectrum and the lower curve is the simulated lineshape. The magnetic parameters (molecular frame) used in the simulations are: $g_{xx} = 2{\cdot}0030$, $g_{yy} = 2{\cdot}0085$, $g_{zz} = 2{\cdot}0064$, $A_{xx} = 32{\cdot}5$ G, $A_{yy} = 6{\cdot}2$ G, $A_{zz} = 5{\cdot}5$ G. Residual linewidth $T_2^{-1} = 3{\cdot}0$ Gauss. $P_2 = 0{\cdot}71$.

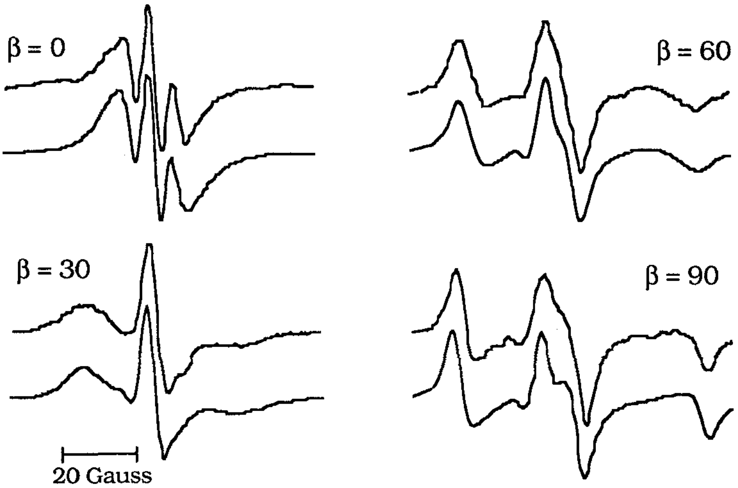

Figure 5. Angular dependence of the ESR lineshape of the cholestane spin probe in PA2 with uniform director. $T = 300$ K. β is the angle between the static magnetic field and the director. For each pair the upper curve is the experimental spectrum and the lower curve is the simulated lineshape. The magnetic parameters (molecular frame) used in the simulations are: $g_{xx} = 2{\cdot}0030$, $g_{yy} = 2{\cdot}0090$, $g_{zz} = 2{\cdot}0075$, $A_{xx} = 33{\cdot}9$ G, $A_{yy} = 6$ G, $A_{zz} = 4{\cdot}9$ G. Residual linewidth $T_2^{-1} = 3{\cdot}3$ Gauss. $\bar{P}_2 = 0{\cdot}81$.

additional 2 hours in the presence of a static magnetic field $B = 23$ kGauss. No appreciable improvement in the alignment is achieved by extending the duration of the treatment. Figure 3 illustrates the negligible alignment of the probe after the above thermal treatments.

Successively, the sample was then annealed at room temperature (which is above T_g) for ten hours with $B = 0$ and then at $T^* = 0{\cdot}94$ for 40 minutes with $B = 23$ kGauss.

The efficiency of the alignment procedure can be monitored by studying the dependence of the ESR lineshape on the angle β between the static magnetic field and the sample director. In figures 4 and 5, the comparison between the experimental results and the theoretical lineshapes for the PA1 and PA2 polymeric matrices, respectively, is represented. Some of the g-tensor components used in the simulations are slightly different from those usually used for polymeric systems [3, 10]. In our opinion, these deviations may be ascribed both to the polarity of the host matrix and to the interstitial position of the doxyl group of the paramagnetic probe [3].

The simulations assume a uniform director across the sample (uniaxial macro-order) and a local aligning potential of the Maier–Saupe form. The results of the simulations are given in terms of the averaged second order Legendre polynomial $\bar{P}_2$ which provides quantitative characterization of the orientational order of the probe [4]. Some small discrepancies are ascribed to minor deviations of the director from the uniform alignment.

In a different aligning procedure, the sample was annealed for 2 h at $T^* = 0{\cdot}90$. Then, the temperature was raised to $T^* = 0{\cdot}94$ and the static magnetic field was set at $B = 23$ kGauss for a certain time interval Δt. The results for PA2 samples at $\Delta t = 1$ h and 2 h, respectively are shown in figure 6. In both cases a partial alignment of the sample is apparent. With increasing Δt the alignment of the sample improves, but a consistent depletion of the spin probe takes place.

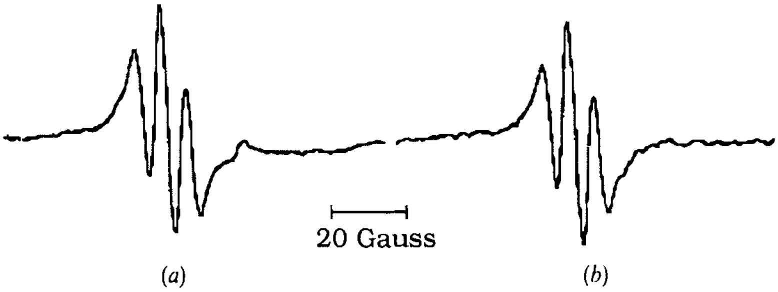

Figure 6. Alignment of PA2 after 2 h at $T^*=0{\cdot}90$ and Δt at $T^*=0{\cdot}94$ with $B=23$ kGauss. $T=300$ K. (a) $\Delta t=1$ h; (b) $\Delta t=2$ h.

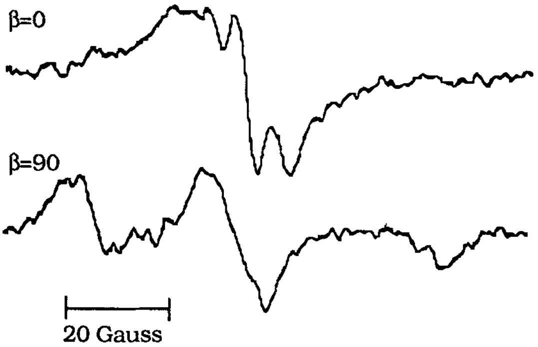

Figure 7. Residual alignment of PA1 after 1 month. Angular dependence of the ESR lineshape of the cholestane probe. $T=300$ K. β is the angle between the static magnetic field and the director.

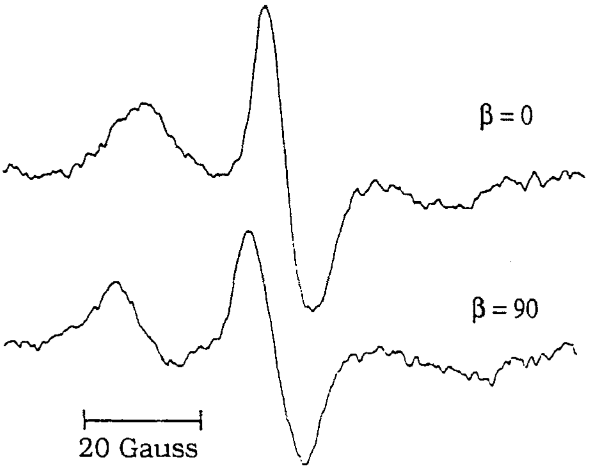

Figure 8. Residual alignment of PA2 after 20 days. Angular dependence of the ESR lineshape of the cholestane probe at $T=300$ K. β is the angle between the static magnetic field and the director.

On the contrary, in the adopted aligning scheme, following the annealing at room temperature which is above T_g, only 40 min at $T^* = 0{\cdot}94$ were needed in order to achieve a uniform director alignment. It is worth stressing that, before the annealing at room temperature, the alignment was fairly low, as confirmed by figure 3.

In conclusion, the experimental results provide some hints that at high temperatures the organization of the mesogenic groups must compete with the tendency of the flexible backbone to assume disordered configurations, in spite of the increased fluidity of the sample, that should in principle favour polymer alignment. At lower temperatures, the blurring action of the polymer backbone is somewhat hindered, thus allowing achievement of alignment of the coupled side chains in a fairly short time after the annealing at room temperature.

It must be pointed out that the orientational procedure which has been adopted for small-sized samples has been found to be unsatisfactory for large samples ($\cong$50 mg), which seems to indicate that surface effects may play a role in the alignment of the small sample.

In figures 7 and 8 the residual alignment of PA1 and PA2 is shown after the samples were maintained for some weeks at room temperature (i.e. above the glass transition temperature of both PA1 and PA2). In the case of PA1, a small anisotropy of the ESR lineshape is detected. In contrast, in the case of PA2, the ESR lineshape of the cholestane probe does not exhibit any anisotropy. In the case of the PA1 sample, the degree of orientation is maintained even after 30 days permanently at room temperature, whereas for sample PA2, that differs from PA1 by the substitution of a methoxy group for an ethoxy group in the *para*-position of the azobenzene cromophore, the alignment is almost completely cancelled after 20 days. At this stage, it appears of interest to investigate structurally analogous types of polymer, possessing different spacers and different substituents in the *para*-position of the azobenzene rings.

3.1. *Reorientational properties*

The reorientational properties of macroscopically aligned PA2 samples have been investigated by creating non-equilibrium orientational distributions in the sample and

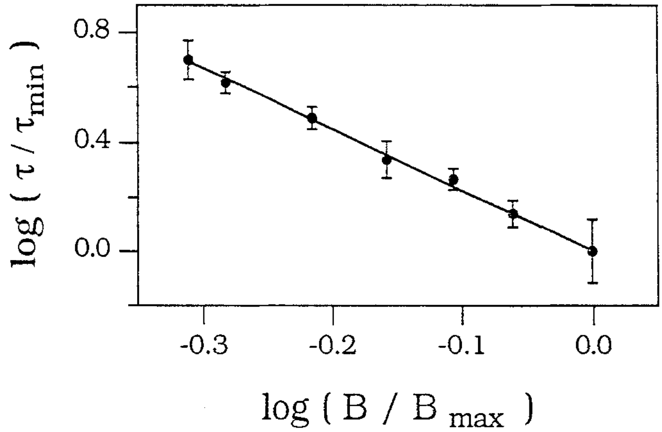

Figure 9. Orientational recovery of PA2. τ is the time needed to recover the equilibrium state in the presence of the static magnetic field B. $B_{max} = 23$ kGauss $\tau_{min} = 630$ s. Fitting the data to a straight line yields a slope $\alpha = 2{\cdot}12$. $T = 368$ K.

following the subsequent reorientation in the presence of a static magnetic field. The procedure is briefly detailed. By following the sample alignment along the direction of the static magnetic field of amplitude B, a reference ESR spectrum has been preliminarly recorded. Then, the direction of the B field has been switched to be at right angles to the director. The reorientational process has been monitored at constant intervals, by decreasing the static magnetic field to the value $B_{\mathrm{res}} = 3400$ Gauss (appropriate for an X-band ESR measurement), recording the ESR spectrum and then raising the magnetic field again to the original value B. The reorientational process has been assumed to be completed when the ESR spectrum recovered the reference pattern.

The recovery to the equilibrium state was monitored in the temperature range 358–388 K. Due to the high viscosity of PA2, no appreciable effect on the reorientation was observed up to $T = 380$ K under B_{res}. At temperatures lower than $T = 368$ K, the reorientational processes became extremely slow.

Figure 9 shows the behaviour of the reorientational time τ plotted against the magnetic field at 368 K. H_{max} and τ_{min} are the values of the maximum applied magnetic field and the minimum reorientation time, respectively. The superimposed straight line comes from the best fit of the experimental data. The slope α over the range of temperatures investigated agrees with the theoretical value $\alpha = -2$ which is expected for liquid crystals of low molecular weight [11]. Similar results were found at $T = 378$ K (see table 2).

4. Conclusions

The orientational properties of two mesomorphic azobenzene-containing polyacrylates in the presence of static magnetic fields have been investigated by ESR spectroscopy using the spin probe technique.

It is found that the uniform director alignment of the polymeric mesophase is favoured by thermal treatments which include low-temperature annealing of the sample above the glass temperature. On the contrary, thermal treatments operating at temperatures which are close to the clearing point are less effective, in spite of the reduced viscosity. In order to interpret these experimental findings, consideration has been given to the antagonistic roles played by the mesogenic side chains and the flexible polymer backbone.

The recovery of the alignment after the creation of controlled non-equilibrium director distributions in the presence of a magnetic field has been studied. It is found that the recovery time is proportional to the reciprocal square of the static magnetic field, as occurs in low molar mass liquid crystals.

These results when connected with the capability of locking-in ordered structures obtained by the combined actions of magnetic fields and annealing above T_g, allow one to envisage practical outlets in the area of optical memory for polymers of the structures investigated and also those of related structures. The presence of the azo-chromophore could permit one to drive a device and store and erase optical information, not only by thermal treatments, but also by photophysical means.

Table 2. Reorientational properties of PA2 samples. See text for details.

T/K	B_{max}/kGauss	τ_{min}/min	α
368	23	10·5	−2·12
378	23	4·5	−1·98

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