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MAGNETIC RESONANCE STUDIES OF POLYMERIC MESOPHASES

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Abstract A detailed analysis of the microscopic properties characterizing some selected polymeric mesophases is currently in progress by using the Electron Spin Resonance spectroscopy. A thorough microscopic lineshape-theory has been developed in order to draw valuable informations both about microdynamics and spatial arrangements of these phases.

1. Introduction

Thermotropic liquid-crystal polymers with mesogenic groups inserted either in side positions or in the main chain have attracted increasing current interest, both because of their theoretical and technological aspects. However, relatively few works appeared, providing insight into their microscopic properties. Magnetic spectroscopies appear to naturally accomplish to these task, in the last decades having been widely applied to investigate low-weight liquid crystals. Being polymers diamagnetic in nature, it is customary to solve spin probes in the host matrix and then detect the related ESR signal. This technique was proven to be able to characterize both the microscopic order and the dynamics of probes from which informations about the mesophase may be inferred.

2. Results and discussion

We report results concerning the polyacrylate side-chain polymer Poly[[4-(6-hexyloxy)-4'-methoxy] azobenzene] acrylate, exhibiting a glass/ nematic transition at 338 ± 5 °K and a nematic/ isotropic transition at 400 ± 5 °K. The probe used is the cholestane radical. In the nematic phase the ESR spectral simulations confirmed that a good alignment of the local director is reached by plunging the samples in magnetic fields of about 2.3 T and is retained after restoring the usual value of .33 T to observe the ESR

signal. Even if similar behaviours are customary in low-weight mesophases, it must be remarked that ordering in polymers is easily hindered by entanglement of the chains and subsequent increased viscosity. On the other hand, differently from low-weight mesophases, ordering is retained in solid phase, suggesting appealing applications in the realm of erasable/ programmable storage devices. However, so far in our samples the induced orientation unlocks for time intervals longer than about two weeks. Evidence of both structural and dynamical changes has been experimentally derived by recording the ESR spectrum in the isotropic and nematic phases (see figure). The marked spectral changes, which are typical for spin probes incorporated into macroscopically aligned environments, have been theoretically simulated by resorting to a stochastic Liouville equation accounting for the diffusional orientation of the probe. The theory computes analytically the spectrum in terms of a continued fraction and accounts for the strong slowing-down of the microscopic motion. In order to investigate the viscosity of these phases some experiments concerning the orientation recovery properties have been performed. There, after creating in the sample a non-equilibrium orientation distribution of the local director, the recovery of the thermal equilibrium distribution is observed by repeated ESR recordings. Depending on both the sample and its temperature, the times needed to reach the equilibrium range from few hours in the nematic phase to several days in the glassy state. The dynamic law of the equilibrium recovery is dependent on microviscosity and local order.

