Relaxation Processes in Semidilute and Dilute Solutions of Polymers in Liquid Crystal Solvents

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We investigate the relaxation phenomena in a polymer (polystyrene)/liquid crystal (4-cyano-4'-n-octyl-biphenyl) system, in its homogenous isotropic phase near the isotropic-isotropic, isotropic-nematic, and isotropic-smectic coexistence curve, using both polarized and depolarized Photon Correlation Spectroscopy (PCS). We study this system for different polystyrene molecular weights (4750, 12500, 65000 g/mol), different compositions (50%, 40%, 30% and 10% of polystyrene (PS) by weight), and different temperatures close to phase boundaries. First of all, we determine the phase diagrams of this system for the different molecular weights. The shape of the phase diagrams strongly depends on the molecular weight. However, in all cases, at low temperatures, these systems separate into an almost pure liquid crystalline (LC) phase and polystyrene-rich phase. PCS measurements show that the relaxation processes in the homogeneous phase are not affected by the proximity of the nematic, or smectic, boundaries (even at a temperature of 0.1°C above the phase separation in two phases). In polarized PCS experiments, we always see three relaxation processes well separated in time: one, very fast, with a relaxation time on the order of 10^{-5} s; a second one with a relaxation time within the range 10^{-2} – 10^{-3} s; and a last one, very slow, with a relaxation time on the order of 1 s. Both the fast and slow modes are independent of the wave vector magnitude, while the intermediate relaxation process is diffusive. In depolarized PCS experiments, the intermediate mode disappears and only the fast and slow relaxation processes remain, and they are independent of the magnitude of the wave vector. The diffusive mode is the classical diffusive mode, which is associated with the diffusion of polymer chains in all polymer solutions. The fast mode is due to the rotational diffusion of 8CB molecules close to polystyrene chains (transient network). Finally, we assign the slowest mode to reorientational processes of small aggregates of PS chains that are not dissolved in 8CB.