

Bifurcation of the dye diffusion coefficient in bulk polymer below the glass transition temperature

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The forced Rayleigh scattering (FRS), or holographic (grating) relaxation technique [1–3] shows itself as particularly sensitive method for estimation of heterogeneities at nanometer scale. The ranges of diffusion coefficients D and spatial scales Λ on which the latter can be measured are $D = 10^{-10} - 10^8 \mu\text{m}^2\text{s}^{-1}$ and $\Lambda = 10^{-1} - 10^2 \mu\text{m}$, respectively, which makes FRS ideal not only for slow diffusion measurements of molecules and particles in polymer systems, but also allows for reaching the superresolution conditions in terms of relaxation times' measurements. The smaller the spatial period Λ the more sensitive is the technique to heterogeneities.

Among other techniques, suitable for heterogeneities sensing, FRS demonstrates superior stability at long times of the measurement. Despite that the minimum spatial scale of this optical technique is in the range of hundreds of nanometers, its sensitivity to the molecular motion is approximately 10 times lower. For example, for a grating distance of 180 nm the characteristic intensity function decreases by a factor e if the particle under investigation performs root mean square displacements (RMSD) of 30 nm: $\text{RMSD} = (2Dt)^{1/2} = \Lambda/2\pi$, where D is the diffusion coefficient and Λ is the spatial period of the induced grating [3].

Holographic (grating) relaxation gives insight into diffusion of the dye molecules in complex environment. It was shown, that this method is particularly useful for investigation of the heterogeneities in wet latex films [4–6], and in dry films with nanofillers [7]. In [4] it was shown that diffusion coefficients in various types of latex film domains and their characteristic size may be defined selectively: in latex particles themselves and in the water-enriched space in between. Core-shell systems were investigated in [5] and [7], while by the same technique the presence of heterogeneities in pure polycarbonate polymer was shown in [6].

In this study the dynamics of 9,10-phenanthrenequinone molecules in the melt of short poly(4-methyl styrene) chains of 15 kg/mol molecular weight with polydispersity of 1.05, which was obtained by freeze drying its non-entangled solution, was investigated below the glass transition temperature (T_g 106 °C) by means of FRS. The bifurcation behaviour of the diffusion coefficient dependency was revealed in this temperature region. Temperature and spatial scale dependencies of apparent diffusion coefficients have shown that the dynamics of the slower process obeys the Williams-Landel-Ferry law, while the faster one demonstrates an activation mechanism of the dye movement. These dependencies were interpreted as evidence for the presence of dynamical heterogeneities in bulk polymer below T_g .

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