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Polymer dynamics under nanoscopic constraints: The "corset effect" as revealed by NMR relaxometry and diffusometry

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Abstract

A spinodal demixing technique was employed for the preparation of linear poly(ethylene oxide) (PEO) confined in nanoscopic strands, which in turn are embedded in a quasi-solid methacrylate matrix impenetrable to PEO. Both the molecular weight of the PEO and the mean diameter of the strands are variable to a certain degree. Chain dynamics of the PEO in the molten state were examined with the aid of field-gradient NMR diffusometry and field-cycling NMR relaxometry. The dominating mechanism for translational displacements in the nanoscopic strands is shown to be reptation. A formalism for the evaluation of NMR diffusometry is presented, which permits the estimation of the mean PEO strand diameter. Samples of different composition revealed diameters in the range 9-58 nm, in reasonable agreement with electron micrographs. The time scale of the diffusion measurements was 10-300 ms. On the much shorter time scale of field-cycling NMR relaxometry, 10-9-10-4 s, a frequency dispersion of the spin-lattice relaxation time characteristic for reptation clearly showed up in all samples. An effective tube diameter of only 0.6 nm was found even when the strand diameter was larger than the radius of gyration of the PEO chain random coils. The finding that the tube diameter effective on the short time scale of field-cycling NMR relaxometry is much smaller than the diameter of the confining structure is termed the "corset effect", and is traced back to the lack of local free-volume fluctuation capacity under nanoscale confinements. The order of magnitude of the "pore" diameter, at which the cross-over from confined to bulk chain dynamics is expected, is estimated.

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Keywords

Diffusion, Nanostructures, NMR spectroscopy, Polymers, Relaxation