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Polymer chain dynamics under nanoscopic confinements

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Abstract

It is shown that the confinement of polymer melts in nanopores leads to chain dynamics dramatically different from bulk behavior. This so-called corset effect occurs both above and below the critical molecular mass and induces the dynamic features predicted for reptation. A spinodal demixing technique was employed for the preparation of linear poly(ethylene oxide) (PEO) confined to nanoscopic strands that are in turn embedded in a quasi-solid and impenetrable methacrylate matrix. Both the molecular weight of the PEO and the mean diameter of the strands were varied to a certain degree. The chain dynamics of the PEO in the molten state was examined with the aid of field-gradient NMR diffusometry (time scale, 10--100 s) and field-cycling NMR relaxometry (time scale, 10⁻⁹-10⁻⁴ s). The dominating mechanism for translational displacements probed in the nanoscopic strands by either technique is shown to be reptation. On the time scale of spin-lattice relaxation time measurements, the frequency dependence signature of reptation (i.e., $T_1 \sim \nu^{3/4}$) showed up in all samples. A "tube" diameter of only 0.6 nm was concluded to be effective on this time scale even when the strand diameter was larger than the radius of gyration of the PEO random coils. This corset effect is traced back to the lack of the local fluctuation capacity of the free volume in nanoscopic confinements. The confinement dimension is estimated at which the crossover from confined to bulk chain dynamics is expected. © 2005 Elsevier Inc. All rights reserved.

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Keywords

Diffusion, Field cycling, Nanopores, NMR relaxation, Polymer dynamics, Reptation