Mean square displacement and reorientational correlation function in entangled polymer melts revealed by field cycling 1H and 2H NMR relaxometry

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Abstract

Mixtures of protonated and deuterated polybutadiene and polydimethylsiloxane are studied by means of field-cycling (FC) 1H NMR relaxometry in order to analyze the intra- and intermolecular contributions to spin-lattice relaxation. They reflect reorientational and translational dynamics,respectively. Master curves in the susceptibility representation $\pi''(\omega\tau_s)$ are constructed by employing frequency-temperature superposition with τ_s denoting the segmental correlation time. The intermolecular contribution is dominating at low frequencies and allows extracting the segmental mean square displacement $\langle R^2(t)\rangle$, which reveals two power-law regimes. The one at short times agrees with $t^{0.5}$ predicted for the free Rouse regime and at long times a lower exponent is observed in fair agreement with $t^{0.25}$ expected for the constrained Rouse regime of the tube-reptation model. Concomitantly the reorientational rank-two correlation function $C_2(t/\tau_s)$ is obtained from the intramolecular part. Again two power-law regimes $t^{-\epsilon}$ are identified for polybutadiene. The first agrees with t^{-1} of free Rouse dynamics whereas at long times $\epsilon = 0.49$ is obtained. The latter is corroborated by the 2H relaxation of deuterated polybutadiene, yet, it does not agree with $\epsilon = 0.25$ predicted for constrained Rouse dynamics. Thus, the relation $C_2(t) \propto \langle R^2(t)\rangle^{-1}$ as assumed by the tube-reptation model is not confirmed. © 2012 American Chemical Society.