

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

Herrmann A., Kresse B., Wohlfahrt M., Bauer I., Privalov A., Kruk D., Fatkullin N., Fujara F., Rössler E.

Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

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 $\chi''(\omega\tau_s)$ 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 $t^{-\varepsilon}$ are identified for polybutadiene. The first agrees with t^{-1} of free Rouse dynamics whereas at long times $\varepsilon = 0.49$ is obtained. The latter is corroborated by the ^2H relaxation of deuterated polybutadiene, yet, it does not agree with $\varepsilon = 0.25$ 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.

<http://dx.doi.org/10.1021/ma301099h>
