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Diffusion in Entangled Polymer Solutions: Constraint Release[1]

E. VON MEERWALL, J. RANDALL, S.-Q. WANG, Univ. Akron — We have used the proton pulsed-gradient spin-echo NMR method to measure the self-diffusion D of entangled polybutadienes (PBD) in tetrachloromethane at 70°C, in order to elucidate the origins of the departure of the molecular-weight (M) exponent of D from the reptational -2.0, and to characterize any differences between melt and solution behavior. M(PBD) ranged from 12 kDa to 100 kDa; PBD concentration (volume fraction) v was 0.350, 0.422, and 0.514. Entanglement ratios R were calculated as $M/M_e(v)$, where for PBD $M_e(1) = 4.5$ kDa and $M_e(v) = M_e(1)/v^{1.2}$, yielding a range of R between 2 and 25. Preliminary results, plotted in the form log $(DM^2v^{1.2})$ *vs.* log R, adhere to a master curve with slope near -1, suggesting at most modest differences from the known behavior of melts. The relatively rapid approach to the melt asymptote, near R = 20, supports our earlier contention that constraint release rather than contour length fluctuation is the cause of the observed M-exponent of D. Further work, using solutions of binary blends based on high-M PBD, is in progress.

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Ernst von Meerwall
Physics and Polymer College, Univ. Akron

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