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Field-Cycling Relaxometry as a Molecular Rheology Technique: Common Analysis of NMR, Shear Modulus and Dielectric Loss Data of Polymers vs Dendrimers

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Abstract

© 2015 American Chemical Society. Linear poly(propylene glycol) (PPG) as well as a poly(propyleneimine) (PPI) dendrimer with different molar masses (M) are investigated by field-cycling (FC) ^1H NMR, shear rheology (G) and dielectric spectroscopy (DS). The results are compared in a reduced spectral density representation: the quantity $R1(\omega\alpha)/R1\alpha(0)$, where $R1(\omega\alpha)$ is the master curve of the frequency dependent spin-lattice relaxation rate with α denoting the local correlation time, is compared to the rescaled dynamic viscosity $n'(\omega\alpha)/n'\alpha(0)$. The quantities $R1\alpha(0)$ and $n'\alpha(0)$, respectively, are the zero-frequency limits of a simple liquid reference system. Analogously, the dielectric loss data can be included in the methodological comparison. This representation allows quantifying the sensitivity of each method with respect to the polymer-specific relaxation contribution. Introducing a "cumulative mode ratio" $F_i(M)$ for each technique i , which measures the zero-frequency plateau of the rescaled spectral density, characteristic power-law behavior $F_i(M) \propto M^{\alpha_i}$ is revealed. In the case of PPG, $F_{\text{NMR}}(M)$, $F_G(M)$, and $F_{\text{DS}}(M)$ essentially agree with predictions of the Rouse model yielding characteristic exponents α_i . The crossover to entanglement dynamics is identified by a change in α_i around $M \cong 10$ kg/mol. The analysis is extended to the dendrimer which exhibits a relaxation behavior reminiscent of Rouse dynamics. Yet, clear evidence of entanglement is missing. The M -dependencies of the dendrimer diffusion coefficient D obtained by pulsed field-gradient NMR and the zero-shear viscosity are found to be $D(M) \propto M^{-1.6 \pm 0.2}$ and $\eta(M) \propto M^{1.9 \pm 0.2}$, respectively, in good agreement with our theoretical prediction $\eta(M) \propto M^{1/3}$ $D^{-1}(M)$. The close correspondence of $R1(\omega\alpha)$ with $n'(\omega\alpha)$ establishes FC NMR as a powerful tool of "molecular rheology" accessing the microscopic processes underlying macroscopic rheological behavior of complex fluids.

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