

Dynamics of PPI dendrimers: A study by dielectric and ^2H NMR spectroscopy and by field-cycling ^1H NMR relaxometry

Mohamed F., Hofmann M., Pötzschner B., Fatkullin N., Rössler E.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© 2015 American Chemical Society. We investigate bulk poly(propyleneimine) dendrimers of generation (G) 2-5 by dielectric spectroscopy (DS), solid-state ^2H NMR, and field-cycling ^1H NMR relaxometry (FC ^1H NMR) in a large temperature range (120-400 K). Three relaxation processes are identified by DS: a main (α -) relaxation ($T > T_g$) and two secondary processes ($T < T_g$). The α -process exhibits a super-Arrhenius temperature dependence typical of glass-forming liquids and changes only weakly with G, yielding $T_g \sim 200$ K. The temperature dependence of the secondary relaxations is governed by an Arrhenius law. While one secondary process exhibits features characteristic for glasses, the other is atypical. Its time constant is virtually independent of G, and its spectral width does not increase with lowering temperature as is usually observed for sub- T_g relaxations. Regarding FC ^1H NMR probing the dispersion of the spin-lattice rate R_1 in the frequency range 200 Hz-30 MHz, transformation to the susceptibility representation, $\pi''(\omega) \propto \omega R_1(\omega)$, and applying frequency-temperature superposition, an effective frequency range of 9 decades is covered by a master curve $\pi''_{\text{Prime}}(\omega\tau\alpha)$. In addition to the segmental time $\tau\alpha(T)$, which complements the results from DS up to high temperatures, a longer terminal relaxation $\tau(T)$ is identified. In between, an intermediate power-law regime is observed in $\pi''_{\text{Prime}}(\omega\tau\alpha)$ with an exponent of about 0.8. The broad relaxation spectrum is attributed to local dynamics, breathing modes, and overall tumbling and diffusion of the dendrimer molecule. In the low-frequency limit, $R_1(\omega)$ is determined by intermolecular relaxation from which the molar mass dependence of the translational diffusion coefficient can be estimated. We find $D(M) \propto M^{-1.2 \pm 0.2}$.

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