The Journal of Chemical Physics 1994 vol.101 N1, pages 822-832

Nuclear spin-lattice relaxation dispersion and segment diffusion in entangled polymers. Renormalized Rouse formalism

Fatkullin N., Kimmich R.

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

Abstract

A formalism for polymer melts was derived linking the spin-lattice relaxation time T1, the correlation function of chain tangent vectors and the mean-square segment displacement with memory functions. Potential normal-mode number dependences are included. In the limit of infinitely fast decaying memory functions the theory reproduces known expressions characteristic for Rouse dynamics. Interchain excluded-volume forces were taken into account in the frame of the renormalized Rouse approach [K. S. Schweizer, J. Chem. Phys. 91, 5802 (1989)]. The power law limits predicted on this basis are T 1, ∝ω1/2, T1∝ω1/4, and T1∝ω1/5 for the T1 dispersion in a sequence of regimes from high to low frequencies. The mean-square segment displacement obeys □r2□∝t1/4, □r2□∝ t3/8, and □r2□∝2/5 in a sequence of limits for increasing times. The spin-lattice relaxation dispersion of different polymers was studied mainly by the aid of the field-cycling NMR technique. The covered proton frequency range is less than 103 Hz to more than 108 Hz. The frequency dependence can be described by a series of power laws arising from chain dynamics. Two of these, namely T 1∝ω0.5 and T1∝ω0.25 tending to appear at high and low frequencies, respectively, can be perfectly explained on the basis of the derived renormalized Rouse limits. The third power law, T1∝ω0.44, which was observed only at rather low frequencies, has no theoretical counterpart in the frame of the renormalized Rouse theory. Some hints that farther reaching polymer theories such as the mode-mode coupling approach [K. S. Schweizer, J. Chem. Phys. 91, 5822 (1989)] can help to understand this finding are discussed. © 1994 American Institute of Physics.