1026 Corrections Macromolecules

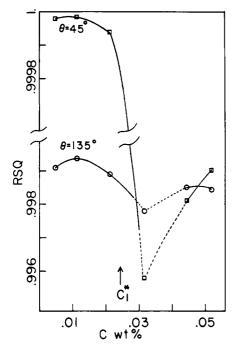


Figure 2. Plots of RSQ vs. concentration.

reformulated,³ such as C_0^* (= $M/N_A\rho_s(2r_g)^3$) or C_1^* $(=M/N_A\rho_s(^4/_3\pi r_g^3))$, and the separation between dilute and semidilute regions is not sharp. Figure 1 shows that the characteristic frequency $1/\tau$ goes through a maximum and then a minimum with increasing concentration. Near C_1^* , the polymer chain dynamics goes through a pseudo-transition region where the single characteristic frequency of the polymer chain $(1/\tau)$ slows down without appreciable entanglement formation. Qualitatively, we may consider that the slowdown is produced by interpenetration of some neighboring polymer molecules without creating a substantial amount of intermolecular polymer coil entanglement because the form of $|g^{(1)}(K,t)|$ has remained essentially unchanged. In the pseudo-transition region, the polymer solution is made up neither of individual polymer molecules in a homogeneous sea of solvent nor of entangled polymer coils where the distribution of entanglement

points becomes relatively uniform throughout the solution. The transition from the dilute solution to the semidilute solution gives rise to an anomalous concentration dependence⁶ which cannot be explained according to the classical Flory-Huggins theory. We believe that the slowdown of $1/\tau$ is related to the hydrodynamic screening effect⁵ and represents the first dynamical observation of this crossover transition region. In the neighborhood of the pseudotransition region, equilibration time becomes very long. Detailed experiments in this aspect will be reported in the full paper.

The emergence of the pseudo-gel motion in the semidilute region has been reported.3 At higher concentrations $(C > C_1^*)$, measurable amounts of entanglement have occurred and two characteristic frequencies appear. However, $|g_{m}^{(1)}(K,t)|$ can still be fitted according to eq 1 because the apparent characteristic frequency reflects mainly the diffusive chain motion. The apparent $1/\tau$ value increases with increasing concentration due to increasing contributions of the faster pseudo-gel mode which is related to the correlation length ξ ($\langle r_g \rangle$) between polymer entanglement points.

References and Notes

- (1) M. Adam and M. Delsanti, J. Phys. (Paris), 37, 1045 (1976);
- 38, L-271 (1977); Macromolecules, 10, 1229 (1977). E. Dubois-Violette and P. G. de Gennes, Physics (Long Island City, N.Y.), 3, 181 (1967).
- T. Nose and B. Chu, Macromolecules, 12, 347, 590, 599 (1979).
- (4) A. Z. Akcasu, Department of Nuclear Engineering, The University of Michigan, Ann Arbor, Mich., private communication. A. Z. Akcasu and M. Benmouna, Macromolecules, 11, 1193
- (1978).
- (6) M. Fixman, J. Chem. Phys., 33, 370 (1960).
- (7) (a) P. J. Flory, J. Chem. Phys., 10, 51 (1942); (b) M. L. Huggins, J. Phys. Chem., 46, 151 (1942).

Y.-H. Lin and B. Chu*

Department of Chemistry State University of New York at Stony Brook Long Island, New York 11794

Received December 10, 1979

CORRECTIONS

J. P. Jarry* and L. Monnerie: Fluorescence Depolarization Study of the Glass-Rubber Relaxation in a Polyisoprene. Volume 12, Number 5, September-October 1979, page 927.

Equation 6 for the characteristic time ρ of the diffusive rotational motions should read

$$\log \rho = \log \tau - 2 \log m$$

Accordingly, the model assuming diffusing motions along the chain backbones leads to a steeper temperature dependence of ρ than expected from eq 4.

Work supported by the National Science Foundation.