compared to previous studies[8-10] might be caused by the fact that these previous studies extracted ν at very small concentrations (from the second virial coefficient) whereas the present study is based on the semidilute region. However, for the finite chain length the scaling prediction might lead to approximations of different quality in different regions of concentration. Okamoto's value $\nu = 0.574$,[12] which has also been obtained in the semidilute region, is comparable to the present value.

Summary

The scanning method was used to estimate the scaling function for the partition function of the SAW model on a five-choice simple cubic lattice in the semidilute region.

The Monte Carlo results for the scaling function are in perfect agreement with the power-law behavior predicted by the polymer-magnet analogy. From the exponent, which is the same as for Des Cloizeaux's scaling function for the osmotic pressure, one obtains the exponent for the end-to-end distance $\nu = 0.579 \pm 0.001$ for chain length $n = 60$ and $\nu = 0.579 \pm 0.002$ for $n = 80$. These results are in reasonable agreement with scaling predictions because the deviations from the commonly accepted value $\nu = 0.588 \pm 0.001$ are of order $1/n$.

Acknowledgment. I thank Prof. Dr. J. Honerkamp for stimulating my interest in polymer physics. The numerical calculations have been done on the University of Freiburg's UNIVAC 1100/80 computer.

References and Notes

(1) De Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(2) De Gennes, P. G. *Phys. Lett. A* **1972**, *38A*, 339.
(3) Des Cloizeaux, J. *J. Phys. (Paris)* **1975**, *36*, 281.
(4) Le Guillon, J. C.; Zinn-Justin, J. *Phys. Rev. B* **1980**, *B21*, 3976.
(5) Öttinger, H. C. *Macromolecules* **1985**, *18*, 93.
(6) Watts, M. G. *J. Phys. A* **1975**, *A8*, 61.
(7) Des Cloizeaux, J.; Noda, I. *Macromolecules* **1982**, *15*, 1525.
(8) McKenzie, D. S. *Phys. Rep.* **1976**, *27*, 35.
(9) McKenzie, D. S.; Domb, C. *Proc. Phys. Soc.* **1967**, *92*, 632.
(10) Bellemans, A.; Janssens, M. *Macromolecules* **1974**, *7*, 809.
(11) Okamoto, H.; Itoh, K.; Araki, T. *J. Chem. Phys.* **1983**, *78*, 975.
(12) Okamoto, H. *J. Chem. Phys.* **1983**, *79*, 3976.
(13) Khalatur, P. G.; Pletneva, S. G.; Papulov, Yu. G. *Chem. Phys.* **1984**, *83*, 97.
(14) Meirovitch, H. *Macromolecules* **1983**, *16*, 249.
(15) Meirovitch, H. *J. Phys. A* **1982**, *A15*, L735.
(16) Meirovitch, H. *Macromolecules* **1983**, *16*, 1628.
(17) Meirovitch, H. *J. Chem. Phys.* **1983**, *79*, 502.
(18) Rosenbluth, M. N.; Rosenbluth, A. W. *J. Chem. Phys.* **1955**, *23*, 356.

Relaxation Times of a Random Copolymer

M. CIEPLAK[†] and M. MUTHUKUMAR*

Department of Polymer Science and Engineering,
University of Massachusetts, Amherst,
Massachusetts 01003. Received October 16, 1984

The relaxation times of linear homopolymers[1,2] are well understood when the entanglement effects are not dominant. In this note, we present some results on the dependence of the relaxation times of a random copolymer on the randomly occurring bead friction coefficients. In infinitely dilute solutions where the hydrodynamic interaction among the beads is so strong that the relaxation times are independent of the bead friction coefficient, there should be no difference between the homopolymer and the random copolymer. On the other hand, at higher concentrations (but below the entanglement point) the hydrodynamic interaction is screened[3] and the differences in the bead friction coefficients are expected to significantly affect the chain relaxation times. The results presented below pertain to this Rouse regime.

The dynamics of a linear homopolymer with n beads and Kuhn step length l under Θ conditions is described by the Langevin equation[1,3]

$$\frac{\alpha \mathbf{R}_i}{\alpha t} + \frac{3k_{\mathrm{B}}T}{\zeta_{\mathrm{b}} l^2}\sum_{j=1}^{n}(2\delta_{ii} - \delta_{i,j+1} - \delta_{i,j-1})\mathbf{R}_j = \mathbf{f}_i \qquad (1)$$

where $\mathbf{R}_i$ is the position vector of the *ith* bead, $\mathbf{R}_i/\alpha t$ is its time derivative, ζ_{b} is the bead friction coefficient, and $\mathbf{f}_i$ is the Brownian force acting on the *ith* bead arising from the thermal fluctuations in the solvent. In eq 1, $k_{\mathrm{B}}T$ is the Boltzmann constant times the temperature and the inertial effects have been ignored. The diagonalization of the Rouse matrix appearing in eq 1 gives the eigenvalues λ_ν of the matrix from which the relaxation times $\tau_\nu \equiv 1/\lambda_\nu$ are obtained. Depending on the nature of the time-dependent correlation function under consideration, a numerical factor of 2 may appear in the relation between τ_ν and λ_ν. We here call the inverse of λ_ν as the relaxation time τ_ν. For the case of random copolymers, we generalize eq 1 to

$$\frac{\alpha \mathbf{R}_i}{\alpha t} + \frac{1}{\zeta_i}\sum_{j=1}^{n}(2\delta_{ij} - \delta_{i,j+1} - \delta_{i,j-1})\mathbf{R}_j = \mathbf{f}_i \qquad (2)$$

where ζ_i is a random variable. The random value of ζ_i clearly has two origins: random bead friction coefficient and the random Kuhn segment length. The calculation of the relaxation times thus involves the diagonalization of the random nonsymmetric marix of eq 2.

We have taken ζ_i to be a random variable taking a value of ζ_1 with the probability of $(1 - \sigma)$ and ζ_2 with the probability of σ. The data presented here correspond to the case of $\zeta_2/\zeta_1 = 10$, although the conclusions are independent of the numerical value of this ratio. The relaxation times for each sample obtained by the diagaonalization ofthe corresponding random matrix are then averaged over 100 samples. The average relaxation time of the longest mode is plotted vs. σ (which is the fraction of the second component) in Figure 1 for both the linear and ring chains. For the linear chain, the average relaxation time is linear in σ. For the uniform ring polymer, the Rouse modes are doubly degenerate. When the ring chain contains two components, the Rouse mode degeneracy is lifted and the two branches depend on σ nonlinearly. However, the average of these two branches depends on σ, similar to the case of linear chains.

For any value of σ, we have found for the linear copolymer that the average relaxation times ($\langle\tau_\nu\rangle$) of the lower modes are proportional to $\langle\zeta_i\rangle n^2$. The linear dependence of $\langle\tau_\nu\rangle$ on $\langle\zeta_i\rangle$ is demonstrated in Figure 2, where $\langle\tau_\nu\rangle/\langle\zeta_i\rangle$ is plotted vs. σ for the modes ν from 1 to 6. The corresponding plot for the ring random copolymer is presented in Figure 3. In this case the individual relaxation times of the two branches (belonging to a given original degeneracy) exhibit a nontrivial dependence on σ, while the average of these two relaxation branches is proportional to $\langle\zeta_i\rangle n^2$. The nonlinear dependence of the relaxation branches of cyclic copolymers on σ indicates that the random introduction of a second component in the polymer chain sequence affects the longest relaxation time more in the case of rings than the linear chains and that there exists an optimum concentration of the second component at which this effect is maximal. Also it is to

---

[†] Permanent address: Institute of Theoretical Physics, Warsaw University, 00-681 Warsaw, Poland

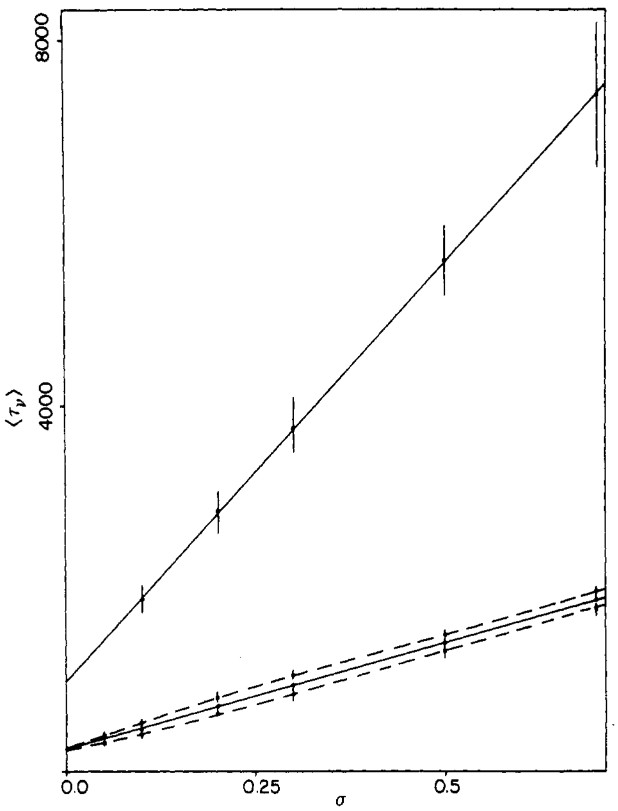

Figure 1. Plot of the longest average relaxation time of a random copolymer of 100 beads vs. the fraction σ of the second component. The solid line corresponds to the linear open chain while the broken curves correspond to the nondegenerate relaxation times of a ring copolymer. The vertical bars represent the error bars.

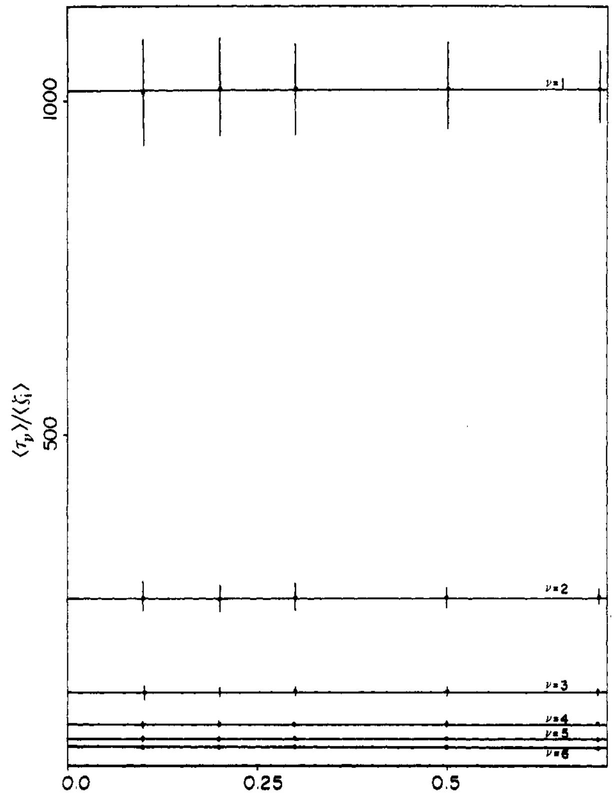

Figure 2. Plot of $\langle\tau_\nu\rangle/\langle\zeta_i\rangle$ for a linear copolymer against σ showing the proportionality of $\langle\tau_\nu\rangle$ to $\langle\zeta_i\rangle$ for all values of σ. $\nu = 1$ is the longest lived mode.

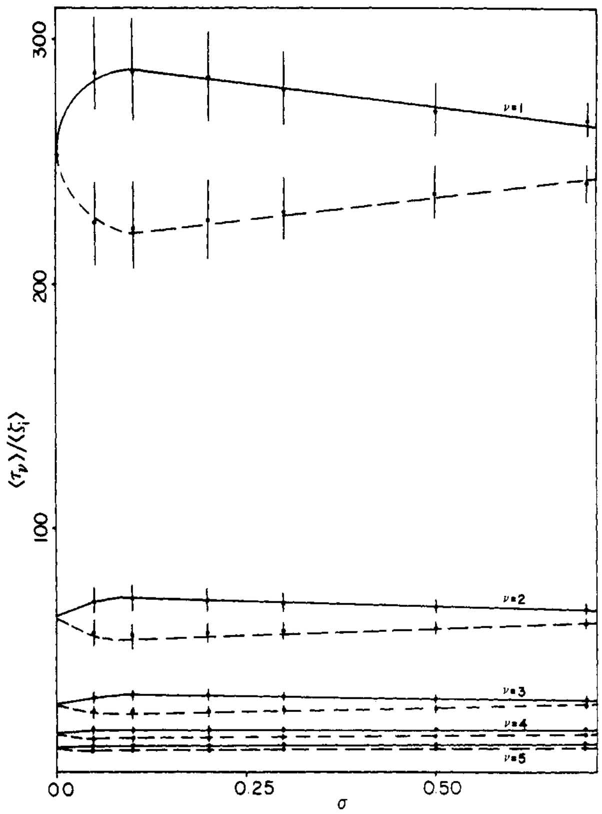

Figure 3. Plot of $\langle\tau_\nu\rangle/\langle\zeta_i\rangle$ for a ring copolymer vs. σ. The doubly degenerate modes of the uniform chain ($\sigma = 0$ or 1) split for $0 < \sigma < 1$, the branches depending on σ nonlinearly. The average of these two branches is independent of σ.

be noticed in Figures 2 and 3 that the longest $\langle\tau_\nu\rangle$ for linear chains stays roughly proportional to 4 times the longest $\langle\tau_\nu\rangle$ of the ring case, for all σ values, due to the choice of the boundary conditions in diagonalizing the random matrix.

The n dependence of $\langle\tau_\nu\rangle \sim n^2$ is not affected by the introduction of the second component, although the eigenmodes are now no longer associated with the familiar Rouse modes of the uniform cases. Furthermore, as shown in Figure 2 and 3, $\langle\tau_\nu\rangle$ is proportional to $\langle\zeta_i\rangle$ and not to $\langle 1/\zeta_i\rangle^{-1}$, even though, $1/\zeta_i$ appears in the matrix of eq 2. This is in agreement with the conclusion reached in the recent mode coupling theory[4] of diffusion in stationary disordered media.

Acknowledgment is made to the National Science Foundation (Grant No. DMR-8403581) and the Materials Research Laboratory at the University of Massachusetts for support of this research.

References and Notes

(1) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, 1972.
(2) J. D. Ferry, "Viscoelastic Properties of Polymers", 3rd ed., Wiley, New York, 1980.
(3) K. F. Freed and S. F. Edwards, *J. Chem. Phys.*, **61**, 3626 (1974).
(4) J. Machta, M. H. Ernst, H. Van Beijern, and J. R. Dorfman, *J. Stat. Phys.*, **35**, 413 (1984).

---

^{13}C NMR Relaxation Study on Amylose in Dimethyl Sulfoxide

PHOTIS DAIS

Department of Chemistry, McGill University, Montreal, Quebec H3A 2A7, Canada. *Received November 12, 1984*

Interest in the motional behavior of polysaccharide molecules in solution has grown in recent years. In par-

0024-9297/85/2218-1351$01.50/0