(16) Allinger, N. L.; Miller, M. A.; Catledge, F. A.; Hirsch, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 4345.
(17) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(18) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.
(19) Welsh, W. J.; Mark, J. E.; Riande, E. *Polym. J. (Tokyo)* **1980**, *12*, 467.
(20) Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 677; *J. Phys. Chem.* **1983**, *87*, 5304.
(21) Sundararajan, P. R. *Macromolecules* **1978**, *11*, 256.
(22) Suter, U. W. *J. Am. Chem. Soc.* **1979**, *101*, 6481.
(23) Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.
(24) Abe, A. *J. Am. Chem. Soc.* **1984**, *106*, 14.
(25) Sundararajan, P. R.; Flory, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 5025.
(26) Crescenzi, V.; Flory, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 141.

# Translational Diffusion of Linear and 3-Arm-Star Polystyrenes in Semidilute Solutions of Linear Poly(vinyl methyl ether)

**T. P. Lodge* and L. M. Wheeler**

*Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.*

*Received April 29, 1986*

ABSTRACT: The technique of dynamic light scattering from isorefractive ternary solutions has been used to investigate the translational diffusion behavior of linear and 3-arm-star polymers in linear polymer matrices. Diffusion coefficients have been obtained for four polystyrene (PS) samples present in trace amounts in solutions of poly(vinyl methyl ether) (PVME) in *o*-fluorotoluene over the range 0.001–0.1 g/mL in PVME concentration. The high molecular weight of the PVME sample, $1.3 \times 10^6$, guarantees that these concentrations extend well into the entangled regime. For PS with molecular weights around $4 \times 10^5$, a 3-arm star diffuses slightly more rapidly than its linear counterpart. However, when the PS molecular weight exceeds $1 \times 10^6$, a 3-arm star diffuses much less rapidly than its linear counterpart at the higher matrix concentrations. These data are interpreted as evidence for the importance of topology in determining diffusion rates for polymers in concentrated solutions. While this observation is consistent with the reptation mechanism, it is also apparent that reptation cannot dominate the diffusion process until the diffusing molecules are thoroughly entangled with the matrix.

Elucidation of the mechanisms by which polymer molecules in entangled solutions and melts diffuse, relax stress, or renew their conformations is an aim with great practical and theoretical importance. Over the past decade, a large number of experimental and theoretical studies have been undertaken to examine the validity and range of applicability of the reptation concept; the subject has recently been reviewed.[1] For polymer melts, diffusion coefficients measured by a wide variety of techniques are consistent with the $M^{-2}$ power law, which can be considered the signature of reptation. However, the experimentally well-established $M^{3.4}$ power law for shear viscosity is not in agreement with the reptation prediction. It is not yet clear whether this discrepancy can be explained by modifications to the basic reptation hypothesis, which was originally proposed for linear chains in fixed obstacles,[2] or whether fundamentally different molecular-level processes need to be invoked. In polymer solutions above the coil overlap concentration, the situation is even less clear. Reptation-based predictions for the molecular weight, concentration, and solvent quality dependence of the translational diffusion coefficient have all been compared with experimental results, with distinctly differing degrees of agreement.[1,3]

The solution situation may be more complicated than that of the melt due to several factors including the enhanced mobility of the molecules surrounding a test polymer, the role of solvent quality, and the concentration dependence of the monomeric friction coefficient. Among the possible contributing mechanisms that have been suggested, in addition to reptation, are (1) constraint release, or tube renewal, in which a test chain moves laterally into a vacancy created by the departure of a neighboring chain;[4-6] (2) the "noodle effect", in which a diffusing chain drags other entangling chains for finite distances;[7] (3) Stokes–Einstein diffusion, in which the test chain moving as a hydrodynamic sphere experiences only the bulk solution viscosity;[4,8] and (4) diffusion through a field of obstacles that generate hydrodynamic screening.[9-13] To design experiments to distinguish among these possibilities, given that they are not mutually exclusive, is challenging. One promising approach is to compare the diffusion coefficients of model branched polymers with those of linear molecules under identical conditions.

In the framework of reptation, the presence of long-chain branches should severely impede translational diffusion;[14] studies of 3-arm-star diffusion in the melt support this picture.[15-17] However, apparently no similar studies in solution have been reported. The pioneering diffusion studies of von Meerwall et al.[18,19] on dilute solutions of 3-arm-star polystyrenes, polyisoprenes, and polybutadienes did extend into the semidilute regime in some cases, but not for sufficiently high molecular weights to expect entanglement. These NMR measurements were performed on binary solutions, i.e., identical test and matrix polymers, and thus represent a different physical situation from that examined here. Nevertheless, these authors' conclusion that 3-arm-star and linear polymer diffusion behaviors are qualitatively indistinguishable is interesting in light of the results presented below. The importance of pursuing diffusion measurements in entangled solutions is underscored by considering that, unlike reptation, none of the four mechanisms listed above explicitly considers the topology of the diffusing polymer. As a result, linear and 3-arm-star polymers with either equal numbers of entanglements per molecule (cases 1 and 2) or equivalent hydrodynamic radii (cases 3 and 4) should diffuse at comparable rates. To test this hypothesis, diffusion data are presented for two 3-arm and two linear polystyrenes (PS) in semidilute solutions of linear poly(vinyl methyl ether)

0024-9297/86/2219-2983$01.50/0

**Table I**

| linear | | 3-arm | | linear | | 3-arm | |
|---|---|---|---|---|---|---|---|
| $M_w = 4.22 \times 10^5$ | | $M_w = 3.79 \times 10^5$ | | $M_w = 1.05 \times 10^6$ | | $M_w = 1.19 \times 10^6$ | |
| log $c^a$ | log $D^b$ | log $c$ | log $D$ | log $c$ | log $D$ | log $c$ | log $D$ |
| -2.997 | -6.72 | -2.996 | -6.67 | -3.009 | -6.91 | -2.996 | -6.95 |
| -2.853 | -6.75 | -2.851 | -6.66 | -2.858 | -6.94 | -2.851 | -7.00 |
| -2.694 | -6.79 | -2.706 | -6.71 | -2.705 | -6.98 | -2.714 | -7.02 |
| -2.524 | -6.83 | -2.527 | -6.77 | -2.526 | -7.06 | -2.524 | -7.10 |
| -2.393 | -6.89 | -2.401 | -6.80 | -2.399 | -7.19 | -2.395 | -7.20 |
| -2.225 | -6.97 | -2.221 | -6.91 | -2.222 | -7.20 | -2.223 | -7.31 |
| -2.097 | -7.05 | -2.097 | -6.98 | -2.101 | -7.30 | -2.102 | -7.44 |
| -2.003 | -7.19 | -2.000 | -7.06 | -2.012 | -7.39 | -2.003 | -7.56 |
| -1.861 | -7.24 | -1.854 | -7.18 | -1.862 | -7.57 | -1.860 | -7.78 |
| -1.699 | -7.45 | -1.703 | -7.33 | -1.706 | -7.80 | -1.714 | -8.04 |
| -1.523 | -7.75 | -1.519 | -7.59 | -1.530 | -8.16 | -1.529 | -8.49 |
| -1.398 | -7.94 | -1.407 | -7.76 | -1.403 | -8.47 | -1.402 | -8.80 |
| -1.215 | -8.36 | -1.222 | -8.13 | -1.219 | -8.98 | -1.220 | -9.45 |
| -1.100 | -8.75 | -1.097 | -8.47 | -1.100 | -9.37 | -1.095 | -9.96 |
| -1.003 | -8.83 | -0.996 | -8.79 | -1.009 | -9.65 | -1.000 | -10.51 |
| -0.959 | -9.11 | | | -0.959 | -9.81 | -0.947 | -10.81 |
| $D_0 = 2.11 \times 10^{-7}$ | | $D_0 = 2.24 \times 10^{-7}$ | | $D_0 = 1.36 \times 10^{-7}$ | | $D_0 = 1.19 \times 10^{-7}$ | |

[a] Concentrations in g/mL. [b] $D$ in cm$^2$/s.

(PVME) as a function of PVME concentration.

Diffusion coefficients have been measured by the technique of dynamic light scattering from isorefractive ternary solutions.[20,21] In this case, a small quantity of PS is dissolved in a PVME/*o*-fluorotoluene (*o*FT) solution. Because PVME and *o*FT are isorefractive ($\partial n/\partial c < 0.001$) at 30.0 °C, the observed scattered electric field intensity autocorrelation function is attributed solely to the PS component. The PS concentration is maintained at approximately one-tenth of the PS overlap concentration, so the decay rate is taken to reflect center-of-mass translation of the PS. Because PS and PVME are compatible, it is assumed that the two polymers are mixed on the molecular level and that, at least to a first approximation, the diffusion mechanisms available to the PS are the same as in binary PS/*o*FT solutions. The details of the solution preparation protocol,[22,23] DLS apparatus,[22] measurement technique,[23-25] and data analysis[24,25] are presented elsewhere. In brief, solutions were prepared by combining dilute, filtered binary PS/*o*FT and PVME/*o*FT solutions and evaporating *o*FT until the desired PVME concentrations were attained. Great care was taken to ensure solution homogeneity, minimal PVME degradation, and no significant deposition of polymer on the cell walls. Correlation functions were obtained on a home-built spectrometer[22] with a 128-channel multisample time correlator (Brookhaven Instruments BI-2030) in the homodyne mode. Decay rates were extracted both by cumulant analysis[24,26] and by the Provencher algorithm;[27] the results agreed to within 10%. The cumulant analysis was performed by taking into account the strong effect of small degrees of polydispersity when the molecular weight dependence of the diffusion coefficient increases with matrix concentration.[24] Each diffusion coefficient represents measurements at five or more angles and was obtained by regression from the slope of (linear) plots of decay rate vs. squared wave vector. The temperature was controlled to 30.0 ± 0.1 °C throughout. The polymer samples used were as follows: linear PS, NBS 1479 ($M_w = 1.05 \times 10^6$) and Toyo-Soda F-40 ($M_w = 4.22 \times 10^5$); 3-arm-star PS, PSJ-3A ($M_w = 1.19 \times 10^6$) and PSG-3 ($M_w = 3.79 \times 10^5$); PVME ($M_w = 1.3 \times 10^6$). The PVME sample was synthesized at NBS,[28] and the branched polystyrenes were synthesized at the University of Akron.[29] All the PS samples are relatively monodisperse, while the PVME has a polydispersity estimated to be 1.3. The PS concentrations employed were 0.46 ± 0.02, 0.76 ± 0.08, 0.50 ± 0.10, and 0.72 ± 0.07 mg/mL for PS 1479, PS F-40, PSJ-3A, and PSG-3, respectively. The uncertainties reported here represent the ranges of the actual concentrations used. It is recognized that the measured diffusion coefficients differ from the pure translational diffusion coefficient of the PS component, due to the finite values of $c_{PS}$. This effect may be accounted for by analogy with dilute binary solutions, i.e.

$$D_{measd} = D[1 + k_D c_{PS} + ...] \qquad (1)$$

However, the resulting correction would be small (less than 5% for the solutions studied here), and as there is evidence that $k_D$ is an unknown but decreasing function of matrix concentration,[25] no attempt has been made to compensate for this effect.

The measured diffusion coefficients for each of the four PS samples are displayed in Figure 1 as a function of PVME concentration over the range 0.001–0.1 g/mL; the data are also presented in Table I. The sample pairs were selected so that the linear and 3-arm star total molecular weights would be comparable. In fact, they are only matched to within 15%; however, on the basis of more extensive measurements on linear samples in this matrix,[25] it is possible to scale the linear data in Figure 1 to correspond to total molecular weights equivalent to the stars. This has not been done in this figure because the effect

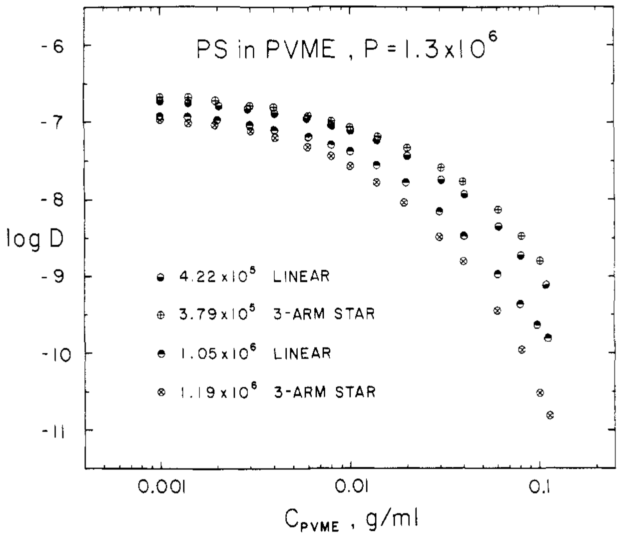

**Figure 1.** Diffusion coefficients for trace amounts of polystyrenes in poly(vinyl methyl ether)/*o*-fluorotoluene solutions.

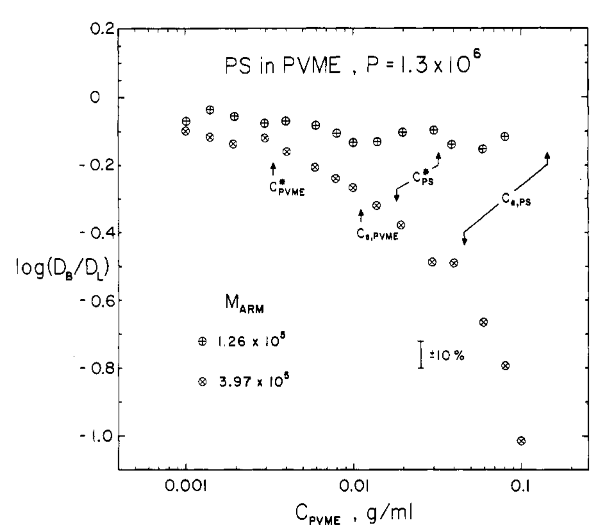

**Figure 2.** Ratio of the diffusion coefficients of 3-arm-star to 2-arm-star polystyrenes with equal arm molecular weight.

is small. The maximum vertical shift for both linear polymers would be less than 0.1 on a logarithmic scale and would have no effect on the conclusions discussed below.

Comparison of the data for the two lower molecular weight samples reveals that the branched molecule diffuses slightly more rapidly than its linear counterpart over the measured concentration range, even after accounting for the molecular weight difference, but more slowly than would a linear polymer of two-thirds the star molecular weight. This suggests that the mechanism of motion is governed primarily by overall hydrodynamic dimensions rather than by diffusant topology. In contrast, the diffusion data for the two higher molecular weight PS samples are distinctly different. As with the smaller polymers, the infinite dilution diffusion coefficients of the two are essentially equivalent, but by the highest PVME concentration, the 3-arm star is diffusing an order of magnitude less rapidly than its linear counterpart. This implies that at higher matrix concentrations there is a mechanism of motion available to the linear polymer that is not available to the 3-arm star, which is at least qualitatively consistent with the reptation model.

In order to emphasize the difference in behavior between the two stars, the data have been replotted in Figure 2 as the ratio of the measured diffusion coefficients of the stars ($D_B$) to interpolated diffusion coefficients ($D_L$) for linear polymers of molecular weight equal to two-thirds that of the corresponding star. In other words, the linear data may be viewed as representing 2-arm stars with the same arm molecular weight as the 3-arm molecules. The interpolation of these data involved two steps. The measured linear data were scaled to the appropriate molecular weight by using the exponents obtained in the same matrix.[25] In addition, the PVME concentrations varied slightly between star and linear polymer solutions; this effect was removed by scaling the linear data to the PVME concentrations actually employed for the star solutions, using the function suggested by Phillies:[3]

$$D(c) = D(0)\exp[-a(c_{\mathrm{PVME}})^u] \qquad (2)$$

Using $a$, $u$, and $D(0)$ as adjustable parameters, it was possible to get a reasonable fit to the data, simply for the purpose of this correction. Within the indicated uncertainty of the data, the ratio $D_B/D_L$ is essentially independent of matrix concentration for the smaller star, but strongly decreasing for the larger one. Also indicated on this plot are estimates of six potentially relevant concentration crossovers. The dilute/semidilute boundary ($c^*$) has been taken to be $1.5/[\eta]$ for the matrix polymer, and thus the majority of these solutions are semidilute in the matrix. However, it is well established that coil overlap does not guarantee entanglement;[30] consequently, the concentration for the onset of entanglement ($c_e$) has been estimated as $(\rho)P_c^\circ/P$, where $\rho$ is the polymer density and $P_c^\circ$ is the critical molecular weight for the onset of the $P^{3.4}$ dependence of the melt shear viscosity. In this case, $P_c^\circ$ has been taken to be 14 400 for PVME on the basis of the value of 7200 for $P_e$ obtained by Hashimoto et al.[31] The ratio $c_e/c^*$ for the matrix thus determined is 3.3, and almost half the data fall in the regime where the matrix is entangled.

For the diffusion of a probe chain, it is equally important to consider the concentrations at which the probe can be expected to overlap or entangle with the matrix. Thus, values of $c^*$ have been estimated for linear polystyrenes of molecular weight 253 000 and 793 000, assuming that these chains have effectively $\Theta$ dimensions. This assumption is based on the $k_D$ results referred to previously.[25] The corresponding $c_e$ values were obtained by taking a value of 35 000 for $M_c^\circ$ for polystyrene.[30] All of these crossover concentrations are simply intended as reasonable estimates of the demarcations between the corresponding regimes for linear polymers; there is inevitably some arbitrariness in their definition, but the conclusions discussed below are not sensitive to exact numerical values. One implication of the results in Figure 2 is that there may not be a straightforward scaling concentration by which the data for the two stars can be reduced to a master curve. For example, the smaller star shows no sign of being retarded relative to a linear polymer below its entanglement concentration, whereas the larger star shows just such a retardation virtually as soon as the matrix is overlapped. Given the complexity of describing the concentration and molecular weight dependence of diffusion even for linear polymers, the apparent lack of a scaling concentration is perhaps not surprising.

In terms of the possible diffusion mechanisms identified previously, the following points may be made. It is clear that for the larger star topology is an important factor in determining the diffusion rate, and this may be taken as suggestive of an onset of reptative motion for the linear polymer. At the same time, the behavior of the smaller star indicates that any crossover to reptation occurs at concentrations significantly beyond the coil overlap condition. The mechanism of constraint release cannot be invoked to explain these results. For a given matrix molecular weight, constraint release should become more important as the diffusant molecular weight increases, making the linear and branched diffusion coefficients more comparable, which is the opposite of the observed trend. The "noodle effect" is a relatively recent concept and as such may be subject to further development. However, its underlying physical picture introduces no dependence on topology and is thus in conflict with these data. The smaller star data are quite consistent with the Stokes–Einstein relation, while those of the larger star are not; it may therefore be possible to interpret these results as reflecting a crossover from Stokes–Einstein to reptation, as has been suggested for linear polymers.[8] From these data alone, however, it is not possible to deduce the corresponding crossover concentration, as pointed out previously. Finally, although the function represented in eq 2 can describe the data, as yet it offers no physical explanation for the behavior in Figure 2. This particular functional form has been suggested on the basis of the screening of hydrodynamic interactions and as such does not address the issue of molecular topology directly.

A more quantitative interpretation of these results will be appropriate after several related studies have been conducted. In addition to the measurements of linear PS diffusion in this matrix referred to previously,[25] measurements are in progress on linear and 3-arm-star PS in other PVME matrices. Light scattering studies are being undertaken to determine the PS coil dimensions as a function of matrix concentration, as is further rheological characterization of semidilute and concentrated PVME solutions. Nevertheless, it is evident from these data that reptation must be considered as a significant contribution to diffusion of linear polymers in thoroughly entangled solutions. However, it is equally clear that coil overlap is not a sufficient condition for reptation to be the dominant mechanism of diffusion.

**Acknowledgment.** We thank Dr. L. J. Fetters for generously providing the branched polymer samples and Dr. G. D. J. Phillies for making available a preprint of his paper. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

**Registry No.** PS, 9003-53-6; PVME, 9003-09-2.

### References and Notes

(1) Tirrell, M. *Rubber Chem. Technol.* **1984**, *57*, 523.
(2) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(3) Phillies, G. D. J. *Macromolecules* **1986**, *19*, 2367.
(4) Daoud, M; de Gennes, P.-G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1971.
(5) Klein, J. *Macromolecules* **1981**, *14*, 460.
(6) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(7) Fujita, H.; Einaga, Y. *Polym. J (Tokyo)* **1985**, *17*, 1131.
(8) Martin, J. E. *Macromolecules* **1986**, *19*, 922.
(9) Ogston, A. G.; Preston, B. N.; Wells, J. D. *Proc. R. Soc. London, A* **1973**, *333*, 297.
(10) Freed, K. F.; Edwards, S. F. *J. Chem. Phys.* **1974**, *61*, 3626.
(11) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 594.
(12) Cukier, R. I. *Macromolecules* **1984**, *17*, 252.
(13) Altenberger, A. R.; Tirrell, M.; Dahler, J. S. *J. Chem. Phys.* **1986**, *84*, 5122.
(14) de Gennes, P.-G. *J. Phys.* **1975**, *36*, 1199.
(15) Klein, J.; Fletcher, D.; Fetters, L. J. *Nature (London)* **1983**, *304*, 526.
(16) Bartels, C. R.; Crist, B., Jr.; Fetters, L. J.; Graessley, W. W. *Macromolecules* **1986**, *19*, 785.
(17) Antonietti, M.; Sillescu, H. *Macromolecules* **1986**, *19*, 798.
(18) von Meerwall, E.; Tomich, D. H.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1982**, *15*, 1157.
(19) von Meerwall, E.; Tomich, D. H.; Grigsby, J.; Pennisi, R. W.; Fetters, L. J.; Hadjichristidis, N. *Macromolecules* **1983**, *16*, 1715.
(20) Lodge, T. P. *Macromolecules* **1983**, *16*, 1393.
(21) Hanley, B.; Balloge, S.; Tirrell, M. *Chem. Eng. Commun.* **1983**, *24, 93*, 1983.
(22) Markland, P.; Lodge, T. P., submitted for publication in *Polymer*.
(23) Hanley, B.; Tirrell, M.; Lodge, T. P. *Polym. Bull. (Berlin)* **1985**, *14*, 137.
(24) Lodge, T. P.; Wheeler, L. M.; Hanley, B.; Tirrell, M. *Polym. Bull (Berlin)* **1986**, *15*, 35.
(25) Wheeler, L. M.; Lodge, T. P.; Hanley, B.; Tirrell, M., submitted for publication in *Macromolecules*.
(26) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(27) Provencher, S. W.; Hendrix, J.; De Maeyer, L.; Paulussen, N. *J. Chem. Phys.* **1978**, *69*, 4273.
(28) Bauer, B. J.; Hanley, B.; Muroga, Y., to be submitted.
(29) Huber, K.; Burchard, W.; Fetters, L. J. *Macromolecules* **1984**, *17*, 541.
(30) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley-Interscience: New York, 1980.
(31) Hashimoto, T., personal communication.

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# Thermodynamic Interactions in Copolymeric Hydrogels

**Malcolm B. Huglin,* Mahmoud M. A.-M. Rehab, and Mat B. Zakaria**[†]

*Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, England.* *Received July 31, 1986*

ABSTRACT: Xerogels comprising *n*-butyl acrylate and *N*-vinyl-2-pyrrolidone (30/70 wt/wt) and varying small amounts of a hexafunctional cross-linking agent have been prepared by $\gamma$-ray-initiated copolymerization to complete conversion and then swollen in water to equilibrium at several different temperatures ($T$) within the range 284–349 K. Photographic determination of the sample dimensions afforded the volume fractions of polymer ($\phi_2$) and water within the resultant hydrogels, and the effective cross-linking densities ($\nu_e$) were obtained via stress–strain measurements. Values of $\phi_2$ increased with increasing $T$ and with increasing $\nu_e$. The elastic moduli at 294 K lay within the range 0.21–1.07 MN m$^{-2}$. Although the enthalpic components ($\chi_H$) were negative, the large entropic components ($\chi_S$) were positive and dominant in the overall increase with $T$ of the polymer–water interaction parameter ($\chi$). The negative values for the enthalpy and entropy of dilution are compatible with structuring of water via enhanced hydrogen bonding and by hydrophobic interaction.

## Introduction

In previous reports[1,2] we have shown that by means of $\gamma$-irradiation *n*-butyl acrylate (BA) can be copolymerized with *N*-vinylpyrrolidone (VP) to more than 99.9% conversion to yield a series of xerogels having a range of hydrophilicity. These materials are insoluble in liquids that are capable of dissolving the corresponding low-conversion copolymers. Hence it is inferred that the $\gamma$-irradiation not only effects initiation but also induces some cross-linking into the copolymers. Incorporation of a hexafunctional cross-linking agent, 1,1,1-trimethylolpropane trimethacrylate (TPT),[3] into the feed mixture enhances the cross-linking and also reduces the water content of the hydrogels produced by swelling the xerogels in water. The influence of composition, dose, and dose rate on the swelling characteristics[4] of the copolymers and observations on the dissolved oxygen permeability coefficient[5] in the hydrogels have been reported.

In this paper an attempt is made to characterize some of these hydrogels more fully, with specific reference to (a) copolymer–water interaction and (b) the influence of temperature on the degree of swelling.

In addition to those abbreviations already indicated, PEO, PTFE, PU, and PVAL are used to denote poly-

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[†] Present address: Jabatan Kimia, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia.

0024-9297/86/2219-2986$01.50/0