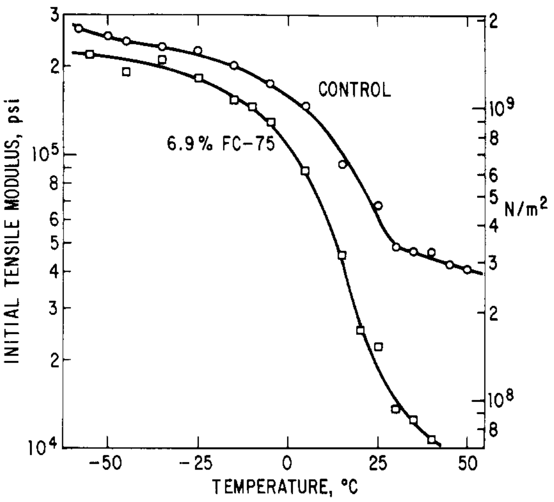

Figure 3. Effect of FC-75 on the tensile modulus of PTFE.

on an Instron tester. The results are shown in Table II. For chloroform and carbon tetrachloride, the weight gain was close to that observed earlier. For FC-75, it was about one-third less. All three compounds reduced the modulus of PTFE and the magnitude of the reduction increased with increasing weight gain.

The dependence of the modulus on temperature for a control and the sample containing 6.9% FC-75 is shown in Figure 3. The modified sample had a lower modulus at all temperatures investigated, but the plasticizing effect of FC-75 became greater near room temperature and above. This is the region of the β relaxation which has been attributed to motions in the crystalline regions of PTFE.[2,17] It is surprising that such a process would be affected by an additive which is more likely to be in the amorphous regions. However, it has been reported that the distribution of relaxation times changes abruptly at the 19 °C first-order transition.[18,19] Presumably, the additive has a greater effect on the relaxation times in the higher temperature region. Thus the magnitude of the softening process is increased with little if any change in its temperature, and the modulus continues to decrease gradually above 25 °C.

It is concluded that as long as one focuses on compounds containing little or no hydrogen, the sorption behavior of perfluorocarbon polymers is the familiar one for nonpolar partially crystalline polymers. The plasticizing effect of such additives also conforms to a familiar pattern. This has apparently not been generally recognized, because most applications involve exposure to substances such as hydrocarbons and polar compounds for which there is very little sorption.

References and Notes

(1) M. M. Renfrew and E. E. Lewis, *Ind. Eng. Chem.*, **38**, 870 (1946).
(2) C. A. Sperati and H. W. Starkweather, *Adv. Polym. Sci.*, **2**, 465 (1961).
(3) C. A. Sperati, "Polymer Handbook", 2nd ed., J. Brandrup and E. H. Immergut, Ed., Wiley, New York, N.Y. 1975, p V-29–36.
(4) J. W. Whalen, W. H. Wade, and J. J. Porter, *J. Colloid Interface Sci.*, **24**, 379 (1967).
(5) J. J. Chessick, J. H. Healey, and A. C. Zettlemoyer, *J. Phys. Chem.*, **60**, 1345 (1956).
(6) D. Graham, *J. Phys. Chem.*, **66**, 1815 (1962); **68**, 2788 (1964); **69**, 4387 (1965).
(7) W. H. Wade and J. W. Whalen, *J. Phys. Chem.*, **72**, 2898 (1968).
(8) W. H. Wade, *J. Colloid Interface Sci.*, **47**, 676 (1974).
(9) S. Sherratt, "Kirk-Othmer Encyclopedia of Chemical Technology", Vol. 9, 2nd ed., Interscience, New York, N.Y., 1966, p 805–831.
(10) J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes", 3rd ed, Reinhold, New York, N.Y., 1950.
(11) H. Burrell, ref 3, p IV-337–359.
(12) R. L. Scott, *J. Phys. Chem.*, **62**, 136 (1958).
(13) J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions", Van Nostrand-Reinhold, New York, N.Y., 1970.
(14) P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
(15) A. V. Tobolsky, "Properties and Structure of Polymers", Wiley, New York, N.Y., 1960, p 66.
(16) G. Gee, *Trans. Inst. Rubber Ind.*, **18**, 266 (1943).
(17) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York, N.Y., 1967.
(18) K. H. Illers and E. Jenckel, *Kolloid-Z.*, **160**, 97 (1958).
(19) K. Nagamatsu, T. Yoshitomi, and T. Takemoto, *J. Colloid Sci.*, **13**, 257 (1958).

Radius of Gyration for Chains and Rings in Semidilute Polymer Solutions

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A recent article by Daoud et al.[1] includes a theory to describe the configuration of monomer segments in a "semidilute" polymer solution. This important contribution has motivated us to examine their argument for the square radius of gyration S_0^2 for open chains and to extend the analysis to the case of the square radius of gyration S_r^2 for ring polymers in semidilute solutions.

The mean-square separation between monomer segments $\langle r_{ij}^2 \rangle$ is concentration dependent. In analogy to ref 1 we shall assume for an open chain in dimensionless units

$$\begin{aligned} \langle r_{ij}^2 \rangle_0 &= |i-j|^{2\tau} n^{2\nu - 2\tau} \qquad |i-j| \leq n \\ &= |i-j| n^{2\nu-1} \qquad |i-j| > n \end{aligned} \tag{1}$$

where n is a dimensionless screening length measured along the chain; it depends upon the monomer concentration ρ according to $n \sim \rho^{-1/(3\nu-1)}$. This treatment of $\langle r_{ij}^2 \rangle_0$ in the *semidilute region* is reminiscent of the physical ideas that underlie nonuniform expansion parameters for a single chain in the *dilute region.*[2]

For open chains the result for $S_0^2 = N^{-2} \sum_{i<j} \langle r_{ij}^2 \rangle_0$ is

$$\frac{S_0^2}{\langle R^2 \rangle_0} = \frac{1}{6} + \left(\frac{1}{2\tau + 1} - \frac{1}{2} \right) x^2 + \left(\frac{1}{3} - \frac{1}{2\tau + 2} \right) x^3 \tag{2}$$

where $\langle R^2 \rangle_0$ is the mean-square end-to-end distance. In the semidilute region $n < N$, $\langle R^2 \rangle_0 \sim N n^{2\nu-1}$; here N is the number of monomers per chain. The quantity x in eq 2 is a reduced density parameter $x = n/N$. Daoud et al. consider the case $\tau = \nu$ but give an incorrect result for $S_0^2/\langle R^2 \rangle_0$; the numerical difference between eq 2 for $\tau = \nu$ and the result given by Daoud et al. (their equation IV.11) is small.

Our motivation for considering the case $\tau \neq \nu$ comes from the interpretation of light-scattering experiments and Monte Carlo calculations.[3] Most recently, Mazur and McIntyre[4] (MM) have advocated the use of the value $2\tau = 1.1$ in place of the more conventional excluded volume result $2\tau = 2\nu = 6/5$.[5] They consider only the dilute region where $x = 1$ $(n = N)$, $\langle R^2 \rangle_0 = N^{2\nu}$, and

$$\frac{S_0^2}{\langle R^2 \rangle_0} = \frac{1}{(2\tau + 1)(2\tau + 2)} \tag{3}$$

MM chose τ so that his ratio gives 0.153, which results from their more fundamental equation for the mean-square separation and which is close to the Monte Carlo results; the choice $\tau = \nu$ gives 0.142 for this ratio. We generalize the MM argument for the dilute case to the semidilute regime according to eq 1. In Figure 1 we plot the result for $S_0^2/\langle R^2 \rangle_0$ vs. $1/x$ for the choice $2\tau = 1.1$ and $\tau = \nu$.

For the case of a *ring*-polymer solution the influence of shielding on $\langle r_{ij}^2 \rangle_r$ is more conjectural. We propose

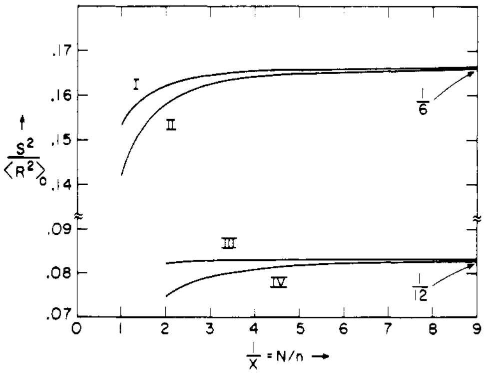

Figure 1. The square ratio of the radius of gyration and the open-chain end-to-end distance as a function of $1/x$. (I and II) radius of gyration for open chains, $2\tau = 1.1$ and $2\tau = 2\nu$, respectively; (III and IV) radius of gyration for rings, $2\tau = 1.025$ and $2\tau = 2\nu$, respectively.

$$\begin{aligned} \langle r_{ij}{}^2\rangle_r &= |i-j|^{2\tau}\left(1-\frac{|i-j|}{N}\right)n^{2\nu-2\tau} \\ &\qquad |i-j| \leq n \\ &= |i-j|\left(1-\frac{|i-j|}{N}\right)n^{2\nu-1} \\ &\qquad |i-j| > n \end{aligned} \tag{4}$$

The result for $S_r{}^2$ is

$$\frac{S_r{}^2}{\langle R^2\rangle_0} = \frac{1}{12} + \left(\frac{1}{2\tau+1}-\frac{1}{2}\right)x^2 + \left(\frac{1}{3}-\frac{1}{2\tau+2}\right)x^3 \tag{5}$$

Other reasonable choices for $\langle r_{ij}{}^2\rangle_r$ in the region $|i-j| \leq n$ are possible, but $S_r{}^2/\langle R^2\rangle_0$ will only differ by terms of order $(2\tau-1)x^3$. In particular, note that eq 4 is not symmetric about $(N/2)$ in the region $|i-j| \leq n$. We adopt this form rather than the symmetric form which would be obtained by raising the second factor to the (2τ) power for the following three reasons. First, the present form is continuous at $|i-j| = n$. Second, for $x < 1/2$, the two arcs of the ring $|i-j|$ and $[N-|i-j|]$ have different lengths relative to n when $|i-j| \leq n$ and accordingly will feel the influence of excluded volume differently. Finally, the only discrepancy arises near $x = 1/2$ where a symmetric form would be preferred, but this is where the form for $|i-j| > n$ is questionable. As indicated, a change in functional form has only a minor effect on the numerical values presented below.

The value of τ may be chosen in a variety of ways, e.g., to match the enumeration results of Rapaport[6] for the dilute case $x = 1/2$. This leads to $2\tau = 1.025$. In Figure 1 the ratio $S_r{}^2/\langle R^2\rangle_0$ is plotted vs. $1/x$ for the choices $2\tau = 1.025$ and $2\tau = 2\nu = 6/5$. We see that the concentration dependence for $2\tau = 1.025$ is much less than that exhibited for the choice $\tau = \nu$. However, the uncertainty in Rapaport's enumeration work does not exclude values of 2τ which are larger, up to about $2\tau = 1.1$.

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References and Notes

(1) M. Daoud, J. P. Cotton, B. Farnoux, G. Jannink, G. Sarma, H. Benoit, R. Duplessix, C. Picot, and P. G. De Gennes, *Macromolecules*, **8**, 804 (1975).
(2) Y. Chikahisa and T. Tanaka, *J. Polym. Sci., Polym. Symp.*, **30**, 105 (1970).
(3) See, e.g., A. J. Hyde, J. H. Ryan, F. T. Wall, and T. F. Schatzki, *J. Polym. Sci.*, **33**, 129 (1958); F. T. Wall and J. J. Erpenbeck, *J. Chem. Phys.*, **30**, 637 (1959).
(4) J. Mazur and D. McIntyre, *Macromolecules*, **8**, 464 (1975).
(5) For the uniform-expansion approximation, $2\tau = 1$, however, see H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971.
(6) D. C. Rapaport, *J. Phys. A: Gen. Phys.*, **8**, 1328 (1975).

Huggins Coefficients in Heterodisperse Solutions of Macromolecules

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In 1942 Huggins[1] proposed the following expression for the viscosity of a solution of macromolecules

$$\eta = \eta_0(1 + [\eta]c + K[\eta]^2c^2) \tag{1a}$$

where η and η_0 are the viscosities of the solution and the solvent, respectively, c is the mass concentration of the solute,

$$[\eta] = \lim_{c\to 0}\frac{\eta-\eta_0}{\eta_0 c}$$

is the intrinsic viscosity of the solute, and K is the Huggins coefficient. Equation 1a is more than a formal expansion of η with respect to c. By the introduction of the factor $[\eta]^2$ in the coefficient of c^2, the remaining Huggins coefficient may be expected to provide information about the interactions between the macromolecules.

This can be seen from considering Einstein's equation for the viscosity of a solution of hard spheres. The viscosity depends on the volume fraction ϕ only

$$\eta = \eta_0(1 + 2.5\phi + k\phi^2) \tag{1b}$$

Since k in (1b) can be calculated for hard spheres and the volume of the macromolecule is expressed by $[\eta]$, the effect of introducing the factor $[\eta]^2$ in the coefficient of c^2 in eq 1b is to obtain a Huggins coefficient K which can be compared with a theoretical value for hard spheres. Since the second-order terms in both (1a) and (1b) represent the interactions between the solute molecules, comparison between the experimental Huggins coefficients and those calculated for hard spheres gives not only an insight in the hydrodynamic interaction between the macromolecules, that is in the "hardness" and the interpenetration of the spheres, but reveals also the occurrence of specific thermodynamic interactions, if the latter are present.

Experimentally Huggins coefficients have been determined for many different polymer–solvent systems. In solutions without strong association the values range from 0.5 to 0.7 and are nearly independent of molecular weight. They depend on the branching and the stiffness of the macromolecules and are sensitive to specific interactions.

Theoretical calculations of k and K yield different results. For random coil polymers under theta conditions the result of the calculations depends strongly on the models used for the interpenetration of the macromolecules, the draining, and the segment distribution. Besides, for hard spheres the effect of the correlation between the positions of the particles in a shear field gives rise to different results.

Some results compiled from the literature are given in Table I.

For hard spheres the calculations of Peterson and Fixman appear the most reliable; for deformable and interpenetrable coils the results of Sakai can be used with some confidence.

For a dilute ternary system we can write in analogy to (1)

$$\begin{aligned} \eta = \eta_0\{1 &+ [\eta]_1c_1 + [\eta]_2c_2 + K_1[\eta]_1{}^2c_1{}^2 \\ &+ K_2[\eta]_2{}^2c_2{}^2 + 2K_{12}[\eta]_1[\eta]_2c_1c_2\} \end{aligned} \tag{2}$$

where the symbols need no explanation. The coefficient K_{12} is often[12-16] called the "interaction coefficient", but incorrectly.

If we call the total polymer concentration c and the intrinsic viscosity of the mixture $[\eta]_m$ we have

$$c = c_1 + c_2; \quad [\eta]_m c = [\eta]_1c_1 + [\eta]_2c_2, \tag{3a}$$