IV. Conclusions

The first, and more important, prediction of this paper concerns the sedimentation coefficient, or the related permeation coefficient λ of eq II.9a. More systematic studies on the concentration dependence of λ would be most helpful.

The second result concerns the cooperative diffusion coefficient D_c, which should be a linear function of concentration; D_c can be measured by macroscopic means or by photon beat methods.

The third point is negative; it does not seem possible to probe the rubber-like behavior of an entangled solution by inelastic scattering of light. Equation III.12 suggests that when the scattering wave vector $\mathbf{q}$ is increased, the line width $\Delta\omega_{\mathbf{q}}$ never becomes of order $\lambda E_{\mathrm{gel}}\mathbf{q}^2$ but saturates at a value $\rho^{-1}T_r^{-1}$. This lack of a rubbery regime appears to be confirmed by preliminary experiments of Adam and Delsanti (unpublished); it was, in fact, their observations which induced us to perform the analysis of section III.

Of course there are some limitations to the model and to our discussion. (a) Our analysis in section III assumes a single relaxation time T_r for the entanglements (eq III.3) and this is an over simplification. (b) We constantly assumed that $\mathbf{q}\xi \ll 1$. The regimes at larger $\mathbf{q}$'s could be interesting, since they could probe the distance between entanglement points. However, the $\mathbf{q}$ values of interest are too large for photon beat studies, and the corresponding $\Delta\omega_{\mathbf{q}}$ are too small for neutron inelastic scattering experiments; this part of the problem belongs to a rather distant future.

(c) We have not discussed the disentanglement time T_r. An estimate of T_r can in fact be constructed from the reptation model[17] and is of the form

$$T_r = (\text{constant})\,\frac{\eta_s a^3}{T}\,N^3(f_s c a^3)^{3/2}$$

However, this suffers from the usual defect of being proportional to N^3 rather than $N^{3.3}$ as suggested by the mechanical data. It is of interest to note that at the lower concentration limit ($c = c^*$) T_r is still comparatively large (proportional to $N^{9/4}$). This means that the self-knots of a single coil do not disentangle easily.

Acknowledgments. We are indebted to Drs. Mijnlieff and Varoqui for pointing out to us the existence (and interest) of sedimentation studies in semidilute solutions, to professor W. Stockmayer for a discussion of mechanical experiments in the dilute regime, and especially to M. Adam and J. Delsanti who convinced us that the cooperative diffusion coefficient $\tilde{D}_c$ was not observed in their photon beat experiments at $T = \Theta$.

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Notes

The Sorption of Chemicals by Perfluorocarbon Polymers

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One of the most useful and familiar properties of poly(tetrafluoroethylene) (PTFE) is its resistance to chemical attack.[1-3] Only a few substances such as molten alkali metals, chlorine trifluoride, and gaseous fluorine can attack the polymer, and there are no known solvents below the melting point. This does not mean, however, that there is no penetration by relatively small molecules.

In a general way, Sperati[3] has referred to the sorption of certain solvents. A number of investigators have studied the adsorption of various substrates on the surface of fine powders of nascent PTFE which is very crystalline.[4-7] In a study of the kinetics for the adsorption of carbon tetrachloride on PTFE, Wade[8] concluded that there must be diffusion into the bulk. There have also been a few reports of significant levels of swelling at elevated temperatures, e.g., 3.7% carbon tetrachloride at 200 °C[9] and 2% perchloroethylene and 0.7% methylene chloride at their boiling points.[3]

The sorption of various compounds at room temperature was investigated for two kinds of 2 mil perfluorocarbon film. One sample was a commercial film of PTFE made by casting an aqueous dispersion followed by sintering. This material was then melted and quenched in ice water. The degree of crystallinity estimated from the density[2] was 41%. The other sample had been melt-extruded from a copolymer of tetrafluoroethylene and hexafluoropropylene (FEP resin). It was estimated to be 42% crystalline. Samples of both materials were immersed in the test liquids until the weight no longer increased. They were wiped dry and weighed quickly to minimize evaporation. The weight gains are presented in Table I, together with solubility parameters taken from the literature.[10,11]

The test compounds can readily be divided into two categories, those which contain hydrogen and those which do not. The sorption of the hydrogen-containing compounds is always low, less than 1% in most cases, and does not depend on the solubility parameter over a wide range. While this behavior might reflect an adsorption process, this is considered unlikely in view of the relatively small amount of surface. The perfluorocarbon polymers absorb up to 11% of compounds which do not contain hydrogen. As shown in Figure 1, the weight gain is strongly dependent on the solubility parameter, δ, declining from the maximum amount near $\delta = 6$ to less than 1% at $\delta = 10$. Admittedly, compounds such as chloroform, methylene chloride, the dichloroethanes, and bromoform which contain relatively small amounts of hydrogen and have solubility

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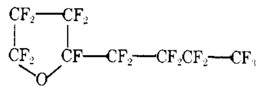
Table I
Sorption of Various Compounds by Perfluorocarbon Polymers

Compd	Solubility parameter, $(\mathrm{cal/cm^3})^{1/2}$	Wt gain, % PTFE	Wt gain, % FEP Resin
Compounds containing hydrogen			
Isooctane	6.85	0.8	0.4
n-Hexane	7.3	0.7	0.5
Diethyl ether	7.4	0.8	0.6
n-Octane	7.55	1.2	0.5
Cyclohexane	8.2	1.1	0.4
Toluene	8.9	0.4	0.3
1,1-Dichloroethane	9.1	1.5	0.6
Benzene	9.15	0.4	0.3
$CHCl_3$	9.3	1.4	1.4
CH_2Cl_2	9.7	0.5	0.6
1,2-Dichloroethane	9.8	0.8	0.4
$CHBr_3$	10.5	0.5	0.2
	Av	0.8	0.5
	Stand dev	0.4	0.3
Compounds without hydrogen			
FC-75[a]		10.6	11.0
Perfluorokerosene	6.2	11.2	6.1
Perfluorodimethylcyclohexane	6.1	10.1	10.4
C_6F_{12}[b]		9.1	8.4
1,2-Br_2TFE		6.5	7.2
$SiCl_4$	7.6	5.2	3.6
CCl_4	8.6	2.4	1.8
$SnCl_4$	8.7	3.4	2.0
$TiCl_4$	9.0	2.2	1.3
$CCl_2{=}CCl_2$	9.3	1.9	1.4
CS_2	10.0	0.4	0.2
Br_2	11.5	0.7	0.7

[a] Structure



[b] Cyclic dimer of hexafluoropropylene.

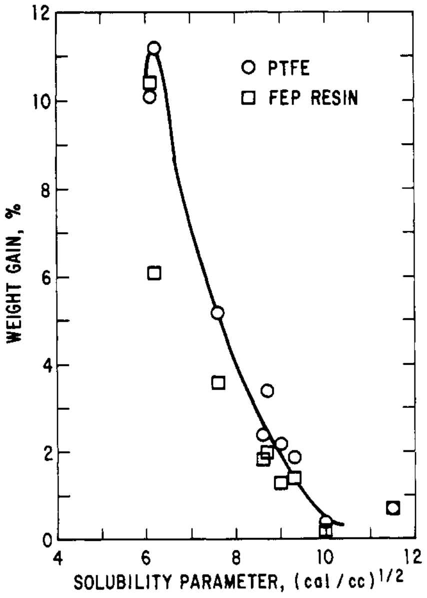


Figure 1. Sorption of compounds not containing hydrogen.

Table II
Effect of Various Compounds on the Modulus of Poly(tetrafluoroethylenes)

Compd	Wt gain, %	Tensile modulus, psi
Control		68 000
$CHCl_3$	1.3	47 000
CCl_4	2.3	31 500
FC-75	6.9	22 000

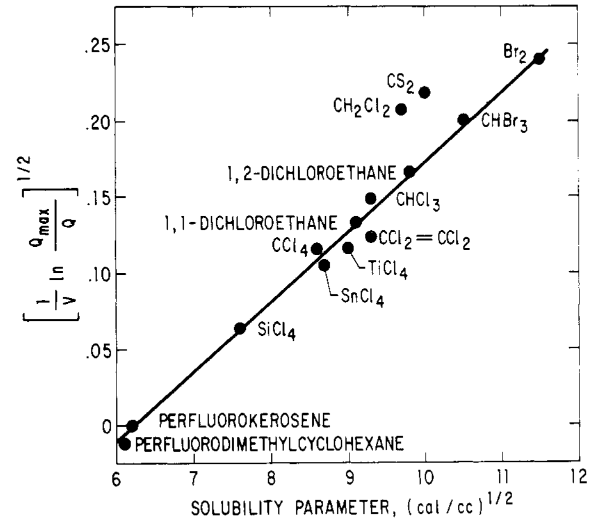


Figure 2. Gee plot for the sorption of liquids by PTFE.

parameters greater than 9 could have been placed in either category.

The contrast between the two groups of liquids can be illustrated by normal octane and $SiCl_4$ which have essentially the same solubility parameter. However, more than four times as much $SiCl_4$ is absorbed. This contrast is in line with the well-known anomalously low miscibility of fluorocarbons and hydrocarbons.[12,13]

For some of the compounds in Table I, the solubility parameters are not known. Perfluorokerosene was assigned a value of 6.2 based on estimates in the literature.[14,15] For PTFE, the sorptions of perfluorokerosene, FC-75, and perfluorodimethylcyclohexane are all 10–11%, and those compounds are presumed to have similar solubility parameters. Since PTFE and FEP resin absorbed similar amounts of the last two compounds, it is considered that the lower level of perfluorokerosene in FEP Resin reflects a failure to reach equilibrium.

The pattern in Figure 1 is a normal one for the dependence of swelling on the solubility parameter. Although suitable liquids with lower solubility parameters were not available, the points fall fairly well on a portion of a Gauss error curve. This is demonstrated in Figure 2 where

$$\left[\frac{1}{V}\ln\frac{Q_{\max}}{Q}\right]^{1/2}$$

is plotted against δ according to the method of Gee.[16] Here, V is the molar volume of the liquid and Q is the swelling expressed as cubic centimeters of liquid per gram of polymer. In this figure, the compounds containing relatively low levels of hydrogen have been included. All of the points lie reasonably close to a straight line except methylene chloride and carbon disulfide for which the sorption was less than expected.

In most cases, the weight gain for FEP resin is lower than for PTFE. The reason for this is not known, and the differences may not be significant.

In another series of experiments, a 1-mil dispersion cast film of PTFE was immersed in selected liquids without the melting and quenching treatment. After reaching an apparently stable weight, the initial tensile modulus at 23 °C was determined

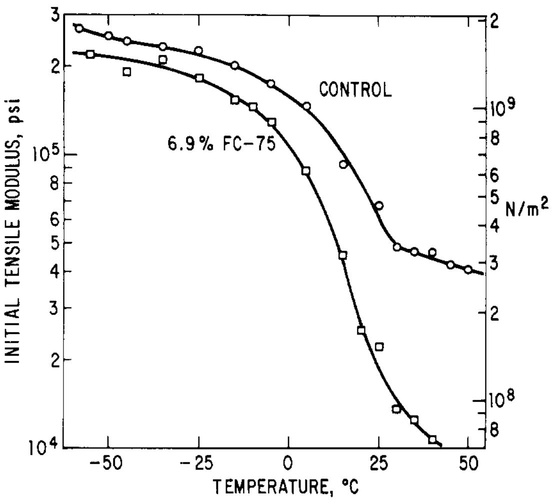


Figure 3. Effect of FC-75 on the tensile modulus of PTFE.

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.

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Radius of Gyration for Chains and Rings in Semidilute Polymer Solutions

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Received April 11, 1977

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 $S_0^2 = N^{-2}\,\Sigma_{i<j}\,\langle r_{ij}^2\rangle_0$ 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 $n < N$, $\langle R^2\rangle_0 \sim Nn^{2\nu-1}$; 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