to assign a lower limit of about 1.0 kcal mole^{-1} to E_σ for the perfluoroalkane chain. Final conformational energy values incorporating this restriction are summarized in Table III.

The *gauche–trans* energy difference E_σ is thus found to be 1.4 ± 0.4 and 1.2 ± 0.2 kcal mole^{-1} for the four-state and three-state models, respectively. It is gratifying that these figures fall within the range of 1.1–2.3 kcal mole^{-1} predicted.[5] An earlier estimate of 4.3 kcal mole^{-1} by Starkweather and Boyd was based on the temperature coefficient of the recoverable elastic modulus in molten uncross-linked PTFE,[3a] as interpreted with a three-state model; but this result rests on the doubtful assumption that the number of "effective" cross-links does not vary with temperature and cannot be given great weight.

In the four-state model, $E_\omega = E(t^+t^-) - E(t^+t^+) = 1.1 \pm 0.7$ kcal mole^{-1}. This figure is in reasonable accord with paper I, where about 0.7 kcal mole^{-1} was found for the energy difference between $t^+t^-t^-$ and $t^+t^+t^+$ conformations in n-C_4F_{10}. It also overlaps energy differences of about 0.5 ± 0.2 kcal mole^{-1}, between unspecified rotational isomers, found from the ir spectra of simple liquid fluorocarbons by Szasz.[26] Finally, it is also consistent with the interpretation given by Brown[27] of the ir spectrum of PTFE. From the temperature dependence of the absorption in the region 600–650 cm^{-1}, he found an energy of 1.2 kcal mole^{-1} for a structural defect which he believed to be reversal of the helix and this was reinforced by his own semiempirical energy calculations.

The possibility cannot be ignored that the conformational energies of the fluorocarbon chain depend measurably on the solvent. Rather large effects have been observed[28–30] with other polymers bearing strongly polar bonds attached directly to the chain backbone. It would obviously be desirable to repeat the dipole moment measurements in some solvent other than benzene and it is hoped to do this in the near future. It is also planned to study some other homologous series $X(CF_2)_nX$, preferably with much bulkier substituents X than hydrogen, in order to reduce the sensitivity of the results to the effects of the end groups. In the meantime, the generally good agreement between the present results and the semiempirical calculations of conformational energies gives us some confidence that the solvent and end-group effects are not large.

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Conformational Energies of Perfluoroalkanes.[1] III. Properties of Polytetrafluoroethylene

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ABSTRACT: Properties of polytetrafluoroethylene which depend on the configurational statistics of the chain are discussed in terms of the four-state rotational-isomeric model used in the preceding paper to correlate the dipole moments of $H(CF_2)_nH$. Solution and melt viscosities are calculated from the predicted characteristic ratio, $\langle r^2\rangle_0/nl^2 = 30 \pm 15$ at 600°K, and are in satisfactory agreement with experimental data. The temperature coefficient $d \ln \langle r^2\rangle_0/dT$ is predicted to be $-(0.9 \pm 0.5) \times 10^{-3}$ deg^{-1}. The thermodynamics of both the solid–solid and solid–liquid phase transitions of the polymer are consistent with the four-state model. The calculated conformational entropy change on melting is 0.8 ± 0.1 cal deg^{-1} mole^{-1}, in good agreement with the experimental constant volume entropy of melting of 0.76 cal deg^{-1} mole^{-1}.

In the preceding paper[2] (hereafter II), it was found that a four-state rotational-isomeric model gave a good account of the observed dipole moments of the compounds $H(CF_2)_nH$. The rotational isomers consist of two *trans* states, $t^\pm$, at about ±15° from the planar zigzag conformation and two *gauche* states, $g^\pm$, at about ±120°; the potential energy differences $E_\sigma = 1.4 \pm 0.4$ kcal mole^{-1} and $E_\omega = 1.1 \pm 0.7$ kcal mole^{-1} determine the probabilities (relative to the most stable $t^\mp t^\pm$ helical conformation) of the bond sequences $t^\pm g^\pm$ and $t^\pm t^\mp$, respectively. A less convincing three-state model also can fit the dipole moments, but it does not account for the helical conformation of the chains in crystalline polytetrafluoroethylene.

In the present paper the rotational-isomeric model developed in II is used to discuss some of the properties of polytetrafluoroethylene (PTFE) which are related to chain conformation. These include chain dimensions, solution and melt viscosities, and phase transitions.

Temperature Dependence of Statistical Weights

Before attempting to discuss the properties of PTFE at temperatures exceeding 300°, it is prudent to inquire

(1) Supported by the National Science Foundation.
(2) T. W. Bates and W. H. Stockmayer, *Macromolecules*, **1**, 12 (1968).

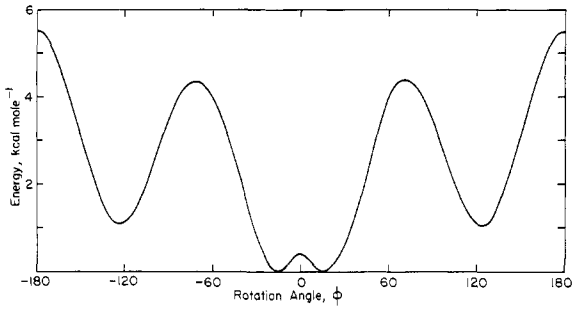

Figure 1. Potential energy for C–C bonds in perfluoroalkanes. The curve was calculated by means of eq 5 with $E_1 = 4.0$, $E_3 = 1.5$, and $E(0) = 0.4$ kcal mole^{-1}.

whether the statistical weight factors σ and ω at such temperatures can be estimated from the room-temperature values based on the dipole-moment analysis. In other words, we must ask whether the energies E_σ and E_ω in the expressions

$$\sigma = \exp(-E_\sigma/RT); \quad \omega = \exp(-E_\omega/RT) \qquad (1)$$

can be taken as independent of T. For the three-state model of polyethylene, Volkenstein[3] showed that this is an excellent approximation over a wide range of temperature; but it is not obviously so for our four-state model, in which the two *trans* rotational states are separated by a rather small angle. In the latter case, one might expect a different torsional frequency in the *trans* states than in the *gauche* states, leading in the classical harmonic-oscillator approximation to the modified expression

$$\sigma = (\nu_t/\nu_g) \exp(-E_\sigma/RT) \qquad (2)$$

where the ν's are torsional frequencies.

To investigate the above question, we follow Volkenstein and compute the average cosine of the internal-rotation angle for a single independent rotation

$$\langle \cos \phi \rangle = \frac{\int_0^{2\pi} \cos \phi \exp[-E(\phi)/RT]\, d\phi}{\int_0^{2\pi} \exp[-E(\phi)/RT]\, d\phi} \qquad (3)$$

This result for a continuous hindering potential $E(\phi)$ may be compared with the expression

$$\langle \cos \phi \rangle = \frac{\cos \phi(t) + \sigma \cos \phi(g)}{1 + \sigma} \qquad (4)$$

for a discontinuous potential consisting of four discrete rotational-isomeric states, $t^{\pm}$ and $g^{\pm}$. The statistical weight ω does not appear in eq 4 because of the symmetry of cos ϕ about $\phi = 0$. For the continuous potential we construct the function

$$E(\phi) = (E_1/2)(1 - \cos \psi) + (E_3/2)(1 - \cos 3\psi) + \Delta \qquad (5)$$

$$\psi = 12(\phi - \phi_m)/11; \quad \phi_m = \pi/12$$

where Δ is a graphical contribution differing from zero only near the origin and designed to make $dE/d\phi$ vanish at $\phi = 0$ while giving $E(0)$ some desired value. The above potential produces *trans* minima at $\sim+15°$ and *gauche* minima at $\sim+123°$. A plot of $E(\phi)$ against ϕ is shown in Figure 1.

Substitution of eq 5 into eq 3 allows $\langle \cos \phi \rangle$ to be found by numerical integration for given values of the temperature and the potential-energy parameters. Calculations were made over the temperature range 25–400° for the following ranges of these parameters: $E(g) = 0.74E_1$, from 1 to 2 kcal mole^{-1}; $E(\pi) = E_1 + E_3$, from 4 to 7 kcal mole^{-1}; and $E(0)$ from 0.3 to 0.8 kcal mole^{-1}, these figures being suggested by our previous work.[2,4]

The resulting values of $\langle \cos \phi \rangle$ were then used in eq 4 to obtain an equivalent value of σ for each temperature. Plots of log σ against T^{-1} gave satisfactory straight lines for all sets of the potential-energy parameters. In terms of eq 2, they correspond to a ratio ν_t/ν_g of about 1.4 and an energy E_σ about 0.2 kcal mole^{-1} higher than the energy $E(g)$ of the *gauche* minimum in the continuous potential $E(\phi)$ of eq 5. Analytical or graphical alternatives to eq 5 were not investigated, but they could produce only minor changes in the above results. Since the uncertainty in E_σ afforded by semi-empirical energy calculations[4] and the dipole-moment analysis is appreciably larger than 0.2 kcal mole^{-1} and since the uncertainty in E_ω is even larger, it may be concluded that the simple eq 1 is adequate for present purposes over the temperature range 25–400°. This equation is therefore used in all calculations to follow.

Chain Dimensions and Rotational Isomerism

Several authors[5-9] have derived expressions in the rotational-isomeric-state approximation for the "characteristic ratio" $\langle r^2 \rangle_0/nl^2$, where $\langle r^2 \rangle_0$ is the average over all configurations of the square of the end-to-end distance for an unperturbed chain of n bonds each of length l. We use the formula of Hoeve[7] for long chains in the Gaussian limit

$$\langle r^2 \rangle_0/nl^2 = 1 + 2\{(b_1 \times E_3)\mathfrak{J}[E_{3r} - (U \times E_3)\lambda_1^{-1}\mathfrak{J}]^{-1}(a \times E_3)\}_{11} \qquad (6)$$

In this expression, the statistical-weight matrix U, the coordinate-rotation supermatrix $\mathfrak{J}$, and the identity matrices E_3 and E_{3r} are the same as those used in II. In addition, λ_1 is the largest eigenvalue of U and a_1 and b_1 are the mutually normalized right-handed and left-handed eigenvectors, respectively, corresponding to this largest eigenvalue. The subscript 11 appended to the matrix in braces denotes the 11 element of that matrix. If the similarity transformation that diagonalizes U is written

$$BUA = \Lambda; \quad B = A^{-1}$$

then the columns a_k of A are found from

$$(U - \lambda_k E_r)a_k = 0$$

(3) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," S. N. Timasheff and M. J. Timasheff, Translators, Interscience Publishers, Inc., New York, N. Y., 1963, p 209.

(4) T. W. Bates, *Trans. Faraday Soc.*, **63**, 1825 (1967). This is paper I of the present series.

(5) (a) T. M. Birshtein and O. B. Ptitsyn, *Zh. Tekh. Fiz.*, **29**, 1048 (1959); T. M. Birshtein, *Vysokomol. Soedin.*, **1**, 748 1086 (1959); (b) S. Lifson, *J. Chem. Phys.*, **30**, 964 (1959).

(6) K. Nagai, *ibid.*, **31**, 1169 (1959); **37**, 490 (1962).

(7) C. A. J. Hoeve, *ibid.*, **32**, 888 (1960).

(8) P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, **51**, 1060 (1964).

(9) P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965).

TABLE I

CONFORMATIONAL PROPERTIES OF POLYTETRAFLUOROETHYLENE (AT 600°K UNLESS OTHERWISE NOTED)

	Three-state model[a]	Four-state model[b]	Exptl
Fraction of *gauche* states, $p(g^+) + p(g^-)$	0.33 ± 0.03	0.16 ± 0.07	...
Fraction of reversed *trans* bond pairs, $p(t^+t^-) + p(t^-t^+)$	...	0.25 ± 0.10	...
Characteristic ratio, $\langle r^2\rangle_0/nl^2$	11 ± 2	30 ± 15	24[c]
Temperature coefficient of unperturbed chain dimensions, $-10^3\ d\ \ln \langle r^2\rangle_0/dT$	0.6 ± 0.1	0.9 ± 0.5	5(?)[d]
Change in conformational entropy on melting, ΔS_c, cal/deg/mole	1.5 ± 0.1	0.8 ± 0.1	0.76[e]
Melt viscosity, 380°, $M_w = 2 \times 10^6$	2×10^9	10^{11}	(10^{11})[f]

[a] With $E_\sigma = E(g) - E(t) = 1.2 \pm 0.2$ kcal mole^{-1}. [b] With $E_\sigma = 1.4 \pm 0.4$ and $E_\omega = E(t^+t^+) - E(t^+t^-) = 1.1 \pm 0.7$ kcal mole^{-1}. [c] Based on solution viscosities.[18] Uncertain to perhaps five to ten units. [d] From ref 16, but uncertain; see text. [e] Entropy of melting at constant volume; see ref 16. [f] See ref 18.

where $k = 1, 2, \ldots r$, while the b_k are the row vectors of B. For the four-state model ($r = 4$) with U given by eq 8 of II, a_k and b_k are given by

$$a_k = [c_k, c_k(\lambda_k - \sigma)^{-1}, (\lambda_k - \sigma)^{-1}, 1]^T \quad (7)$$

$$b_k = \alpha_k[c_k, \sigma c_k(\lambda_k - \sigma)^{-1}, \sigma(\lambda_k - \sigma)^{-1}, 1] \quad (8)$$

where $c_k = (-1)^{k-1}$ and $(2\alpha_k)^{-1} = 1 + \sigma(\lambda_k - \sigma)^{-2}$. The eigenvalues of U are given by

$$(\lambda - 1)(\lambda - \sigma) = \sigma + c_k\omega(\lambda - \sigma) \quad (9)$$

with $\lambda_1 > \lambda_2 > \lambda_3 > \lambda_4$. For the three-state model, expressions 10 and 11 are obtained

$$A = \begin{bmatrix} \lambda_1 - \sigma & 0 & \lambda_3 - \sigma \\ 1 & -1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \quad (10)$$

$$B = (1/2)(\lambda_1 - \lambda_3)^{-1} \begin{bmatrix} 2 & \lambda_1 - 1 & \lambda_1 - 1 \\ 0 & \lambda_3 - \lambda_1 & \lambda_1 - \lambda_3 \\ -2 & 1 - \lambda_3 & 1 - \lambda_3 \end{bmatrix} \quad (11)$$

with

$$2\lambda_{1,3} = 1 + \sigma \pm (1 + 6\sigma + \sigma^2)^{1/2};\ \lambda_2 = \sigma \quad (12)$$

The foregoing equations were used to calculate the chain dimensions of PTFE at 600°K, which is the crystalline melting point. The results are summarized in Table I and displayed in Figure 2. They are based on a chain valence angle of 116° and rotational angles of ±15° for $\phi(t)$ and ±115° for $\phi(g)$. It was ascertained that increasing $|\phi(t)|$ to 25° and $|\phi(g)|$ to 125° had no appreciable effect on the numerical results. It is seen that the characteristic ratio is rather sensitive to the choice of model. Acceptable values of E_σ and E_ω (see II) lead to 30 ± 15 for the four-state model and 11 ± 2 for the three-state model. In the next section it is indicated that the meager evidence from solution viscosities tends to favor the four-state model, which is of course *also* to be preferred on other grounds.

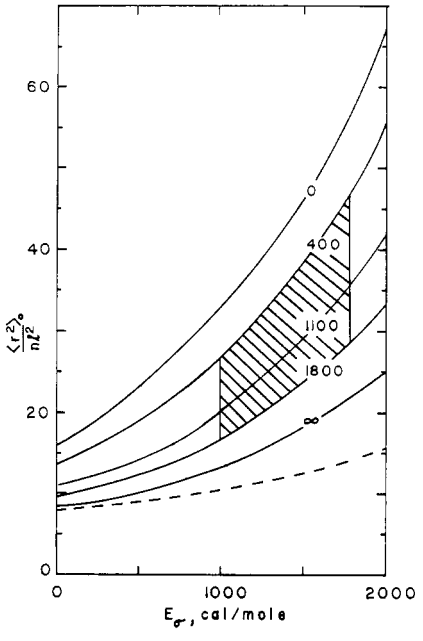

Figure 2. Effect of conformation energies E_σ and E_ω on the characteristic ratio, $\langle r^2\rangle_0/nl^2$, of PTFE at 600°K. Solid curves were calculated for the four-state model, values of E_ω being shown on each curve. The dashed curve was calculated for the three-state model. The shaded region corresponds to ranges of E_σ and E_ω found in II.

The predicted characteristic ratio for PTFE may be compared with the experimental figure[10] of 6.8 for polyethylene at 140°, just above the melting point. The PTFE chain clearly has a greater persistence of direction, which is due to a quite different population of the rotational-isomeric states. For long chains, the fraction $p(\beta)$ of bonds in a rotational-isomeric state β is given[11] by

(10) R. Chiang, *J. Phys. Chem.*, **69**, 1645 (1965).

(11) T. M. Birshtein and O. B. Ptitsyn, "Conformations of Macromolecules," S. N. Timasheff and M. J. Timasheff, Translators, Interscience Publishers, Inc., New York, N. Y., 1966, p 114.

$$p(\beta) = \sum_{\alpha=1}^{r} \partial \ln \lambda_1 / \partial \ln u_{\alpha\beta} = a_{\beta 1} b_{1\beta} \quad (13a)$$

while the fraction $p(\alpha,\beta)$ of bond pairs $i-1$, i in states α and β, respectively (*i.e.*, the second-order distribution function), is given by

$$p(\alpha,\beta) = \partial \ln \lambda_1 / \partial \ln u_{\alpha\beta} = u_{\alpha\beta} a_{\beta 1} b_{1\alpha} / \lambda_1 \quad (13b)$$

where the $u_{\alpha\beta}$ are elements of statistical weight matrix U and $a_{\beta 1}$ and $b_{1\beta}$ (or $b_{1\alpha}$) are elements of the eigenvectors a_1 and b_1, respectively. For the four-state model, the fraction of *gauche* bonds, $p(g^+) + p(g^-)$, is 0.16 ± 0.07 at 600°K, or considerably smaller than the figure of 0.41 ± 0.04 for polyethylene at 140°; the three-state model of PTFE yields a less credible value of 0.33 ± 0.03.

It is also found with the four-state model that the fraction, $p(t^+t^-) + p(t^-t^+)$, of all bond pairs in $t^{\pm}t^{\mp}$ sequences is about 0.25 ± 0.10 at 600°K. Since the two *trans* states differ in rotational angle by only about 30°, such sequences are not very destructive of persistence in direction. The relatively large fraction of such sequences, and the complete exclusion of both $t^{\pm}g^{\mp}$ and $g^{\pm}g^{\mp}$ sequences, accounts qualitatively for the large predicted characteristic ratio of PTFE with the four-state model.

Although calculations for chains of finite length could be made from the equations furnished by Flory and Jernigan,[9] we have not troubled to perform these in view of the large uncertainties in the statistical weights. However, fairly good[12] though not highly accurate[13] estimates may be obtained with the wormlike chain model.[14] With a characteristic ratio of 30 and a contour length of 1.30 Å per CF_2 unit, the persistence length q is given by

$$q = (30nl^2)/2(1.30n) \cong 28 \text{ Å} \quad (14)$$

a figure that seems compatible with the X-ray diffraction measurements on molten PTFE by Kilian and Jenckel.[15] The wormlike chain formula may be written as

$$\langle r^2 \rangle_0 / 30nl^2 = (x - 1 + e^{-x})/x; \quad x = 1.30n/q \quad (15)$$

We find that the characteristic ratio attains half of its limiting Gaussian value at a chain length of about 50 bonds and reaches 95% of the limit only after about 425 bonds. Similar estimtes for the three-state model are easily made.

Temperature coefficients of the unperturbed chain dimensions of PTFE were also evaluated. If eq 1 holds

$$-\frac{d \ln \langle r^2 \rangle_0}{d \ln T} = \ln \sigma \frac{d \ln \langle r^2 \rangle_0}{d \ln \sigma} + \ln \omega \frac{d \ln \langle r^2 \rangle_0}{d \ln \omega} \quad (16)$$

where of course the last term is omitted for the three-state model. Plots of $d \ln \langle r^2 \rangle_0 / dT$ at 600°K as a function of E_σ are shown in Figure 3. Unlike the characteristic ratio itself, the temperature coefficient turns out to be rather insensitive to the choice of model; the acceptable values are $-(0.9 \pm 0.5) \times 10^{-3}$ deg^{-1} for the four-state model and $-(0.6 \pm 0.1) \times 10^{-3}$ deg^{-1} for the three-state model. In no case does the temperature coefficient come close to the value[16] of about -5×10^{-3} deg^{-1} based on the measurements by Nishioka and Watanabe[17] of creep recovery in PTFE specimens above the melting point. However, as already remarked in II, this result must be regarded with caution because it is based on the assumptions (a) that the effective number of network junctions in the uncross-linked rubbery polymer is independent of temperature and (b) that the observed deformations are at least proportional to those that would be observed at mechanical equilibrium for a cross-linked specimen. The value of E_σ required to reproduce such a large temperature coefficient is[16] about 4.3 kcal mole^{-1}, which is far beyond the range admitting agreement with the dipole moment results of II.

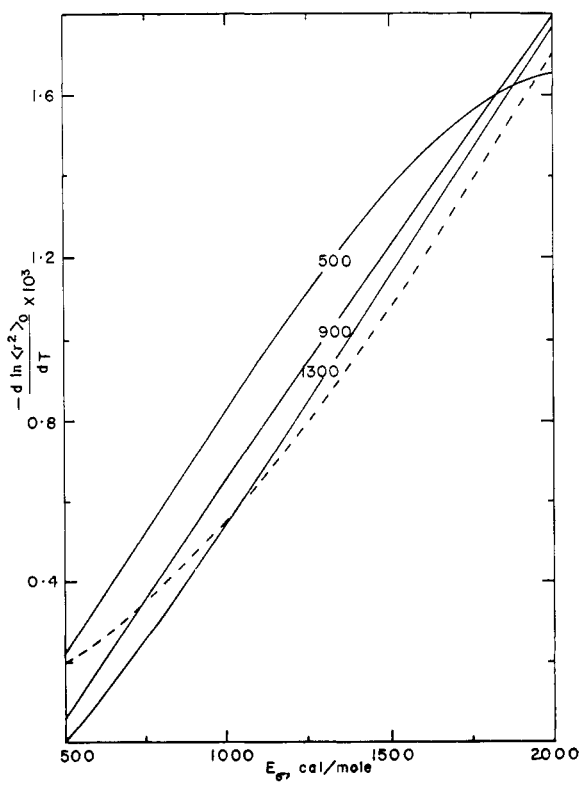

Figure 3. Effect of conformation energies E_σ and E_ω on the temperature coefficient of $\langle r^2 \rangle_0$. Solid curves were calculated for the four-state model, values of E_ω being shown on each curve. The dashed curve was calculated for the three-state model.

Intrinsic and Melt Viscosities

A few intrinsic viscosity measurements have been reported[18,19] for PTFE in fluorinated solvents ("per-

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(13) R. L. Jernigan and P. J. Flory, *Polymer Preprints*, **8**, 252 (1967).
(14) O. Kratky and G. Porod, *Rec. Trav. Chim. Pays-Bas*, **68**, 1106 (1949).
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(18) R. C. Doban, A. C. Knight, J. H. Peterson, and C. A. Sperati, "The Molecular Weight of Polytetrafluoroethylene," 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1956.
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fluorokerosene") at 300°, but these were not accompanied by direct measurements of molecular weights. However, Doban, Knight, Peterson, and Sperati[18] did determine for their samples the specific gravity following a standard fabricating cycle (ASTM specification D 1457-56T). A relationship between this quantity and the number-average molecular weight[18,20] was established by measuring the concentration of end groups derived from a radioactive initiator[21] and then making the kinetically plausible[20] assumption that each PTFE chain has two such ends. In this way, it was found that unfractionated samples with intrinsic viscosities of 2.9 and 9.2 dl g^{-1} correspond to number-average molecular weights of $(0.65 \pm 0.2) \times 10^6$ and $(4.5 \pm 1) \times 10^6$, respectively. A third polymer sample with $[\eta] = 20$ dl g^{-1} had a standard specific gravity outside the range of the end-group calibration.

The above figures quickly dispose of any suggestion that the PTFE molecules in solution are rigid rods. From the theoretical formula of Kirkwood and Auer,[22] a PTFE chain with a molecular weight of 10^6 and the dimensions[21] of the helix found in crystalline PTFE (length 1.30 Å per CF_2 and diameter *ca.* 5 Å) would have an intrinsic viscosity of about 1500 dl g^{-1}. On the other hand, the data are in reasonable accord with the chain dimensions we have calculated, as will now be shown.

To estimate the chain dimensions from the number-average molecular weights and solution viscosities quoted above, we must consider two important corrections, those associated with the long-range expansion factor or "excluded volume effect" and with polydispersity of the samples. A corresponding-states comparison with the behavior of polyethylene in *n*-alkanes[23] indicates that the solvent power of "perfluorokerosene" for PTFE at 300° cannot be great and we shall therefore assume an expansion factor close to unity; in other words, the dimensions of the chain in such solvents must be close to the unperturbed values. As to polydispersity, we may pursue the kinetic assumptions made in relating end-group counts to molecular weights: if termination is entirely by combination of radicals, the ratio M_w/M_n of the weight-average to the number-average molecular weight is $^3/_2$ at low conversion and increases somewhat with conversion, by an amount depending on the relative rates of initiator and monomer depletion. In the absence of further evidence, it is reasonable to pick a ratio of 2, which corresponds to a viscosity-average molecular weight M_v of about $1.8M_n$. Since partial hydrodynamic draining can also be safely neglected for the molecular weights and dimensions here involved,[24] the Flory–Fox equation[25] for the present case may be written

$$[\eta] \cong [\eta]_\theta = K(M_v)^{1/2} \cong K(1.8M_n)^{1/2} \qquad (17)$$

The experimental data then lead to $K = \Phi(\langle r^2\rangle_0/M)^{3/2} = 3.0 \times 10^{-3}$ in conventional units. With the preferred[26] figure of 2.5×10^{21} for Φ, we obtain $\langle r^2\rangle_0/M = 1.15 \times 10^{-16}$ mole cm^2 g^{-1} and hence the characteristic ratio $\langle r^2\rangle_0/nl^2 \cong 24$. This figure, which is seen to be in quite satisfactory agreement with our calculations based on the four-state model and the dipole-moment data, could obviously be raised or lowered a few units by making alternative assumptions with respect to polydispersity or expansion factor. It therefore remains possible, though surely improbable, that a three-state model could account for the existing solution-viscosity data.

Melt viscosities of about 10^{10} to 10^{11} P at 380° have been reported for commercial samples of PTFE by several groups of workers.[17–19,27] These figures imply a longest relaxation time[28,29] in the range 10^4 to 10^5 sec; on this basis the true Newtonian melt viscosities are probably somewhat higher than the quoted values, for which the time of observation would then be too short[17] or the shear stress too high[27] for observation of Newtonian steady-state behavior. In any case, application of the semiempirical melt viscosity relations of Fox and Allen,[30] as recently amended and extended by Berry and Fox,[31] shows that the calculated chain dimensions for PTFE are consistent with the existing melt viscosity data. According to these authors, Newtonian melt viscosities for various polymers of high molecular weight, well above the onset of entanglement coupling between chains, can be correlated by the equation

$$\eta = (N_A X_c \zeta/6)(X/X_c)^{3.4}$$
$$X = (M_w l^2/6M_0^2 v)(\langle r^2\rangle_0/nl^2) \qquad (18)$$

where N_A is the Avogadro number, ζ the frictional coefficient per chain atom, M_w the weight-average molecular weight of the polymer, v the specific volume, M_0 the molecular weight per chain atom, and X_c an approximately universal constant with the numerical value 4×10^{-15} mole cm^{-1}. The friction constant in turn is to be estimated from the equation[31]

$$\log \zeta = -10.6 + \frac{W}{2.3T} + \frac{1000}{57.5 + T - T_g} \qquad (19)$$

where T_g is the glass temperature and W is a parameter depending slightly on chain structure and probably[30] related to the internal-rotation barriers within the chain. For a number of polymers, W varies from about 400 to about 1500°K, being larger for those considered to have "stiff" chains, and we take the high figure for PTFE. With T_g equal to[32] 400°K and with

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(32) R. F. Boyer, *J. Polymer Sci.*, C **14**, 3 (1966). It should be noted that there are two distinct "glass transitions" in PTFE, but for considerations of the motions of extended sections of the chain, such as are involved in melt flow, the upper temperature is the pertinent one.

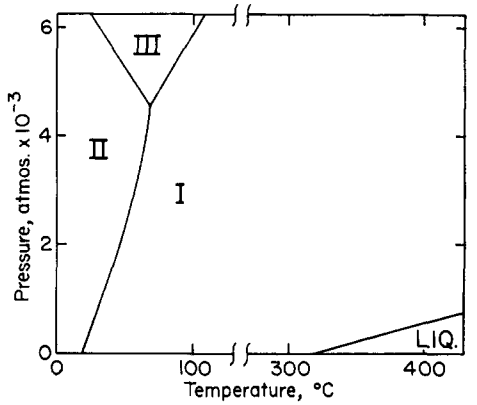

Figure 4. Phase diagram for PTFE, as given by Sperati and Starkweather,[20] based on data of Beecroft and Swenson[40] and of P. L. McGeer and H. C. Duus (*J. Chem. Phys.*, **20,** 1813 (1952)).

the four-state model result of 30 ± 15 for $\langle r^2\rangle_0/nl^2$, eq 18 and 19 lead to

$$\log \eta = 10 \pm 1 + 3.4 \log (10^{-6}M_w) \qquad (20)$$

at 380°. This relation predicts a viscosity of about 10^{11} P for a polymer with $M_w = 2 \times 10^6$. For the three-state model, the predicted viscosity would be about $^1/_{50}$th as large, which is somewhat less compatible with the existing experimental evidence. Thus the above result implies the simultaneous success of the Berry–Fox correlation and of our calculations of chain dimensions for PTFE (or possibly a fortuitous compensation of errors).

It would obviously be desirable to have a more reliable estimate of ζ for PTFE. Unfortunately, a lack of experimental data prevents such an estimate from being made at the present time. Thus an attempt to determine ζ by extrapolating to infinite chain length some viscosity data[33] for fluorinated oils was unfruitful, since the viscosities did not extend to sufficiently high molecular weights or temperatures.

In eq 18 for the melt viscosity, the temperature dependence of the factor ζ dwarfs that of the other quantities. Thus the temperature coefficient of the melt viscosity may be estimated from eq 19 alone. With the aforementioned numerical assumptions, an apparent activation energy

$$E_{app} = -RT^2 \, \mathrm{d} \ln \zeta/\mathrm{d}T \cong 25 \text{ kcal mole}^{-1} \qquad (21)$$

is obtained for 350–380°. This is somewhat smaller than the figure of about 35 ± 5 kcal mole^{-1} derived from the creep data of Nishioka and Watanabe;[17] but, as already remarked, these probably do not refer to Newtonian conditions.

Phase Transitions

There are at least three well-defined crystalline modifications of PTFE. Although polymorphism is by no means confined to this polymer (there are, for example, three different crystalline forms of polyoxacyclobutane[34]), it is the only one for which we are aware of an equilibrium phase diagram. The latter[20] is reproduced in Figure 4. A self-consistent account of the structures and thermodynamic properties of the various phases can be based on the foregoing treatment of the conformational properties of the perfluoroalkane chain. For a more detailed description of the structures of the crystalline modifications, the review article of Starkweather and Sperati[20] may be consulted.

Solid form II is the stable phase below 19° at atmospheric pressure. X-Ray measurements by Bunn and Howells[35] show that the conformation of the chains in this phase is that of a helix with a twist of 180° per 13 CF_2 groups. As Bunn and Holmes[36] emphasized, the stability of the helical form is almost certainly due to *intra*molecular interactions. Semiempirical calculations[8,37–39] of conformational energies support the view that the helix observed in phase II is also the most stable configuration of an isolated molecule. It is on this basis that the four-state model was accorded *a priori* preference in our treatment of the conformational properties of single perfluoroalkane chains.

Transition II ⇌ III. For the transition[40] from phase II to the high-pressure form III, $\Delta V \cong -0.58$ ml (mole of CF_2)$^{-1}$ (corrected to 100% crystallinity) and $\mathrm{d}P/\mathrm{d}T \cong -40$ atm deg^{-1}. Then from the Clapeyron equation, $\Delta S = +0.56$ cal deg^{-1} mole^{-1} and $\Delta H \cong$ 170 cal mole^{-1} at about 5000 atm. From the thermodynamic recipe $(\partial \Delta H/\partial P)_T = \Delta V - T(\partial \Delta V/\partial T)_P$, we then find that at atmospheric pressure $\Delta H \cong 230$ cal mole^{-1}, with an estimated error of possibly ±50 cal mole^{-1} due to uncertainties in $\mathrm{d}P/\mathrm{d}T$, the volume change, and the thermal expansions. Since $\Delta(PV)$ is very small, we also have $\Delta E \cong 230 \pm 50$ cal mole^{-1} for the II → III transition at low pressure.

Thus phase III has a higher density, higher entropy, and higher energy than form II. These facts, together with the ir spectrum,[41] are consistent with Brown's suggestion[41] that the PTFE chain adopts the planar zigzag conformation in phase III. This form of chain can be packed more efficiently[35] than the helical form, thus accounting for the higher density, and the energy change is of the expected sign and order of magnitude. To elaborate this point, we may write

$$\Delta E = \Delta E(\text{intra}) + \Delta E(\text{inter}) \qquad (22)$$

and estimate the last term from the known volume change and the cohesive energy density. For the latter we may either take the theoretical lattice-energy calculations of Brandt[42] or employ suitable values[20] of the thermal expansion α and the compressibility β to get the internal pressure $T(\alpha/\beta)$. We thus find $\Delta E(\text{inter}) \cong -80 \pm 30$

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cal mole^{-1} and hence the intramolecular energy change is 0.3 ± 0.1 kcal mole^{-1}, a figure which is in satisfactory agreement with those obtained in the more refined semi-empirical energy calculations.[4,37,38]

Huggins[43] has examined the effects of interchain forces on polymer chain conformations and crystal structures. His treatment of polyethylene amplifies the present discussion of the energetics of phase III in PTFE.

The higher entropy of phase III, despite its smaller volume, is also in accord with the above picture, for the unfavorable intramolecular energy must reduce the force constants for torsional oscillations of the chain. If the entire entropy change were due to this effect, we should have, for the ratio of the torsional frequencies in the two phases

$$\nu(\mathrm{II})/\nu(\mathrm{III}) \cong \exp(\Delta S/R) = 1.3 \qquad (23)$$

since there is one such degree of freedom per CF_2 unit, but the frequencies of other modes of motion may well increase on passing to phase III, so the above ratio for the torsional frequencies is only a lower limit, with an upper limit lying perhaps near 1.5. These figures seem reasonable.

Transition II ⇌ I. Solid phase I is interesting because of its configurational disorder, which is evident in both X-ray diffraction patterns[44] and ir spectra.[41] The transition II ⇌ I is not sharp and in fact comprises two transitions centered at about 19 and 30°, the upper one being rather diffuse as judged by the observed heat capacity.[45,46] The sharp transition at 19° results in a change of helical pitch (from 13 to 15 CF_2 groups per 180° twist) and of unit cell symmetry from probably triclinic to hexagonal. Disorder appears rapidly through the 30° transition and thereafter grows steadily with further increase in temperature.

For the purposes of discussing the properties of phase I above 30°, it is convenient to lump together[20] the changes in properties through the two transition regions. This gives ΔV = 0.29 ml mole^{-1} and ΔS = 0.54 cal deg^{-1} mole^{-1} for the overall change II → I. Again following Starkweather and Sperati,[20] we can split the total observed entropy increase into two parts: a "normal" contribution of $(\alpha/\beta)\Delta V$ = 0.20 cal deg^{-1} mole^{-1} related to the change in volume and a remainder of 0.34 cal deg^{-1} mole^{-1}. Such a subdivision is of course meaningless without some underlying physical picture. As for simple solids,[47] the first contribution may be related to changes in vibrational frequencies with density; if we again blame the whole change on the torsional motions as in eq 23 we get $\nu(\mathrm{II})/\nu(\mathrm{I}) \cong 1.1$. The remaining 0.34 cal deg^{-1} mole^{-1} is identified as an increase in configurational entropy due to imperfections in the helical chain structure. Rigorously, the problem would be that of a three-dimensional cooperative phenomenon, with relatively strong interactions in one spatial direction (intramolecular)) and relatively weak interactions in the other two directions (intermolecular). However, as clearly demonstrated by the behavior of two-dimensional anisotropic Ising lattices,[48] it is an excellent approximation to treat the disorder at temperatures *above* the transition region as that of a one-dimensional system involving only the strong interactions. Physically, this means that phase I at temperatures above 30° may be regarded as an assembly of quasi-independent chains admitting a single type of structural defect. This is the model used by Brown[41] to explain the temperature dependence of the ir spectrum and he obtained a defect energy of 1.2 kcal mole^{-1}, a figure he regarded as of the correct order of magnitude but uncertain by a factor of perhaps 2 or 3. Brown suggested that the defects were in fact reversals in the sense of the helix; that is, t^+t^- or t^-t^+ sequences in our nomenclature.

The statistical thermodynamics of the above model are familiar. The statistical-weight matrix is just

$$U = \begin{bmatrix} 1 & \omega \\ \omega & 1 \end{bmatrix} \qquad (24)$$

and the corresponding configurational partition function is

$$Z_c = (1 + \omega)^N \qquad (25)$$

The entropy per mole of bonds is then given by

$$S_c/R = \ln(1 + \omega) - \omega \ln \omega/(1 + \omega) \qquad (26)$$

Since phase II has no disorder of this type, we may equate the above entropy to 0.34 cal deg^{-1} mole^{-1}, as explained above. This gives ω = 0.034, which at the mean transition temperature of 295°K corresponds to a defect energy of $E_\omega \cong$ 1.8 kcal mole^{-1}. This result is in adequate agreement with Brown's 1.2 kcal mole^{-1}. It also just touches the range 1.1 ± 0.7 kcal mole^{-1} obtained[1] for isolated perfluoroalkane chains and indeed might be expected slightly to exceed the latter because of packing restrictions in the crystal.

With the above model, there is a conformational contribution to the heat capacity of about 0.4R per mole just above the transition. This amounts to only 0.016 cal deg^{-1} g^{-1} and in fact agrees very well with the observed[46] difference in heat capacity above and below the transition region. The model also predicts a conformational energy increase through the transition of $E_c = \omega E_\omega/(1 + \omega)$, which amounts to 80 cal mole^{-1} as compared to a total ΔH for the transition of 160 cal mole^{-1}. The difference between these figures is largely if perhaps not completely accounted for by a "normal" cohesive contribution of $T(\alpha/\beta)\Delta V \cong$ 60 cal mole^{-1}, the remainder perhaps reflecting the weak intermolecular order–disorder energy.

Transition I ⇌ Liquid. The thermodynamics of melting of PTFE at 327° have been previously discussed by Starkweather and Boyd.[16] They discovered that for polyethylene and polyoxymethylene the estimated entropy increase at constant volume $(\Delta S_m)_v$ was

(43) M. L. Huggins, *Makromol. Chem.*, **92**, 260 (1966).
(44) E. S. Clark and L. T. Muus, *Z. Krist.*, **117**, 119 (1960).
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(47) J. C. Slater, "Introduction to Chemical Physics," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, Chapter XIII.
(48) G. F. Newell and E. W. Montroll, *Rev. Mod. Phys.*, **25**, 359 (1953), Figure 15.

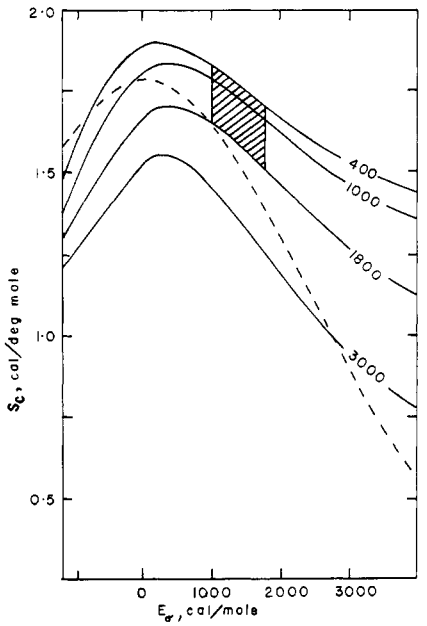

Figure 5. Conformational entropy S_c of PTFE at 600°K as a function of E_σ. Solid curves are from eq 27 for the four-state model with various values of E_ω cal mole^{-1} as labeled. The shaded region corresponds to ranges of E_σ and E_ω found in II. The dashed curve is for a three-state model.

essentially equal to the conformational entropy change ΔS_c, as calculated from three-state models for those chains. This result involves somewhat fortuitous cancellation of other contributions to the total entropy of fusion and has therefore been criticized.[49] However, its success justifies extension to other examples. For PTFE, we may compute S_c for the liquid from our previous results for the four-state model, but we must not ignore the conformational entropy of solid I. From eq 26, with $E_\omega = -RT \ln \omega = 1.8$ kcal mole^{-1}, the latter amounts to 0.90 cal mole^{-1} deg^{-1} at 600°K. The conformational entropy in the liquid is given by

(49) R. P. Smith, *J. Polymer Sci.*, **A2**, 4, 869 (1966).

$$S_c(\text{liq})/R = \ln \lambda_1 - \frac{\sigma(\lambda_1 - \omega) \ln \sigma + \omega(\lambda_1 - \sigma) \ln \omega}{\lambda_1(2\lambda_1 - 1 - \sigma - \omega)} \quad (27)$$

where λ_1 is the largest eigenvalue of the four-state matrix U, as given by eq 9. Plots of S_c(liq) for various values of the energies E_σ and E_ω are shown in Figure 5. At 600°K the allowed ranges of these energies give S_c(liq) = 1.7 ± 0.1 cal deg^{-1} mole^{-1}. We arrive, therefore, at

$$\Delta S_c = S_c(\text{liq}) - S_c(\text{I}) = 1.7 - 0.9 = 0.8 \pm 0.1 \text{ cal deg}^{-1} \text{ mole}^{-1} \quad (28)$$

The experimental constant-volume entropy of melting is $(\Delta S_m)_v = 0.76$ cal deg^{-1} mole^{-1}, in remarkable agreement with the above prediction. The three-state model predicts S_c(liq) = 1.5 ± 0.1 cal deg^{-1} mole^{-1}, but is incapable of extension to the solid.

Conclusion

Results of the principal calculations described and discussed in the preceding sections are summarized in Table I. Since the experimental information is neither voluminous nor precise and since the ranges of the conformational energies E_σ and E_ω consistent with the dipole-moment results of II are rather wide, it cannot be claimed that a unique description of the perfluoroalkane chain has been achieved. The three-state model obviously cannot account for the structure of the crystalline polymer or for the entropy of fusion. The four-state model, on the other hand, permits an adequate and self-consistent explanation of the presently known conformational properties of the system.

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