Deconvolution of the Excess Heat Capacity for the Room Temperature Transitions in Poly(tetrafluoroethylene)

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ABSTRACT: We have used a statistical mechanical approach to analyze the 19 and 30 °C crystalline transitions in poly(tetrafluoroethylene). Data from calorimetry, X-ray diffraction, and dynamic mechanical behavior were combined to derive information about the size of the units involved in the transitions between energy states. We conclude that the 19 °C transition involves a segment of about 180 CF_2 units which corresponds to a single stem in a crystal. The size of the unit involved in the 30 °C transition starts at this value, decreases with increasing temperature as the number of helix reversals increases, and ultimately reaches two CF_2 units at 116 °C.

It is well-known that there are two first-order crystalline transitions in poly(tetrafluoroethylene) (PTFE) at approximately 19 and 30 °C[1-5] with well-defined changes in the crystal structure[1,2] and the viscoelastic properties.[6,7]

At the 19 °C transition, there is a slight untwisting of the helical chain conformation from 13 to 15 CF_2 groups per 180° twist. It has also been shown that between 19 and 30 °C the chain segments are also disordered from a perfect lattice by small angular displacements about their longitudinal axes.[8] Above the 30 °C transition, the preferred crystallographic direction has been lost, and the molecular segments oscillate about their long axes with a random orientation in the lattice. Changes in the X-ray patterns at still higher temperatures suggest torsional motion, a twisting and untwisting of the chain molecules.

Changes in the infrared and Raman spectra above 19 °C[9-12] support the widely held concept of helix reversals, which occur in increasing numbers with increasing temperatures.[13-19]

Procedures for deconvoluting the excess heat capacity associated with first-order transitions have been presented by Freire and Biltonen,[20,21] who applied them to transitions in biopolymers such as the thermal unfolding of globular proteins. We have used this method to analyze the Brill transition in nylon 66.[22] This approach works reasonably well for a transition involving a single step between low- and high-energy states. It becomes increasingly difficult to invert heat capacity data when a large number of energy states is involved. Thus, it is helpful to use other information to guide the analysis.

Because of the ample evidence that there are two first-order transitions in this temperature region, we have used a model with three energy states. Moreover, we assume that the size of the molecular fragment undergoing the transition is fixed for the 19 °C transition and decreases with increasing temperature for the 30 °C transition.

Deconvolution Procedure

Given a system having a reference state and n higher energy states, the partition function is

$$Q = 1 + \sum_{i=1}^{n} \omega_i \exp(-\Delta G_i/RT) \tag{1}$$

where ω_i is the degeneracy of the ith state and ΔG_i is its Gibbs energy in excess of that of the reference state.

The fraction of units in the ith state is

$$F_i = \frac{\omega_i \exp(-\Delta G_i/RT)}{Q} \tag{2}$$

The excess enthalpy relative to the reference state is

$$\langle \Delta H \rangle = \sum_{i=0}^{n} \Delta H_i F_i = \frac{\sum_{i=0}^{n} \Delta H_i \omega_i \exp(-\Delta G_i/RT)}{Q} \tag{3}$$

where $\Delta H_i = (H_i - H_0)$ is the difference in enthalpy between the ith state and the initial state.

The excess enthalpy can be evaluated from the excess heat capacity, $\langle C_p \rangle$, which was found by subtracting the base line from a DSC curve.

$$\langle H \rangle = \int_{T_0}^{T} \langle C_p \rangle \, dT \tag{4}$$

The error from taking T_0, the temperature at which all units are in the reference state, as the point at which the DSC curve becomes tangent to the base line (rather than absolute zero) is very small. One must also consider whether there are differences in the heat capacities of the various states.

Equation 1 can be written in differential form as

$$d(\ln Q) = \frac{\langle \Delta H \rangle}{RT^2} \, dT \tag{5}$$

Thus, the partition function can be evaluated through numerical integration.

$$\ln Q = \int_{T_0}^{T} \frac{\langle \Delta H \rangle}{RT^2} \, dT \tag{6}$$

The fraction of units in the lowest energy state is given by

$$F_0 = \frac{1}{Q} = \exp\left(-\int_{T_0}^{T} \frac{\langle \Delta H \rangle}{RT^2} \, dT \right) \tag{7}$$

By analogy, the fraction in the highest energy state is given by

$$F_n = \exp\left(-\int_{T}^{T_n} \frac{\Delta H_n - \langle \Delta H \rangle}{RT^2} \, dT \right) \tag{8}$$

where ΔH_n is the overall enthalpy of the transition and T_n is the temperature at which all of the units are in the highest energy state.

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The fractions of units in intermediate states can be determined in the following way.[20,21] For a multistate transition, $\langle H\rangle/(1 - F_0)$ vs temperature is an S-shaped curve whose lower limit is equal to the enthalpy difference, $\Delta H_1{}^*$, between the first intermediate state and the initial state. At low temperatures, this quantity is not well determined because it is the ratio between two small quantities. Under these conditions, we assume the approximation that only the lowest and first intermediate states are populated.

We now consider only the states above the lowest and define a new excess enthalpy

$$\langle H_1\rangle = \langle \Delta H\rangle/(1 - F_0) - \Delta H_1^* \qquad (9)$$

and a new partition function

$$Q_1 = \exp\left(\int_{T_0}^{T}\frac{\langle \Delta H_1\rangle}{RT^2}\,\mathrm{d}T\right) \qquad (10)$$

The fraction of units above the lowest state that are in the first intermediate state, F'_i, is $Q_1{}^{-1}$, and the fraction in the overall population is

$$F_1 = F'_1(1 - F_0) \qquad (11)$$

In principle, this procedure can be repeated in a recursive manner to calculate the populations of a whole series of energy states. In practice, this often does not work well with real experimental data, and it is preferable to use other information to decide how many states should be considered.

The enthalpies and heat capacities in these equations are molar quantities while experimental data are obtained based on a gram of material. If c and h_n are the excess heat capacity and the enthalpy of the transition per gram

$$\langle C_p\rangle = cM \qquad (12a)$$

and

$$\Delta H_n = h_n M \qquad (12b)$$

where M is the molecular weight of the characteristic quantity of the transition. For a simple, one-step transition between two energy levels, it has been shown[21,22] that the value of M can be approximated by

$$M = \frac{4RT_{\max}{}^2 c_{\max}}{h_n{}^2} \qquad (13)$$

Application to Poly(tetrafluoroethylene)

We have used the heat capacity data reported by Lau, Suzuki, and Wunderlich[23] for a sample of highly crystalline, virgin granular PTFE. Their data are reported in terms of a mole of chain atoms (CF_2 units, and we will continue that usage. Lau et al. presented tabulated data for the base-line heat capacity of the crystal, and we subtracted these from the experimental data to obtain the excess heat capacity in the region of the crystal disordering transitions shown in Figure 1. Two endothermal transitions are seen, which are commonly known as the 19 and 30 °C transitions. We will use these terms for convenience even though the actual temperatures may be slightly different in some samples.

Since there is ample evidence based on crystallography,[1,2] mechanical behavior,[6,7] and other properties that there are only two discontinuities near these temperatures, we use a model based on three energy states whose fractions are F_0, F_1, and F_n. It has been found, however, that the excess heat capacity data cannot be fitted to a three-state model based on a constant value of M, the size of the unit undergoing the transitions. We have therefore used a model in which the transition from the lowest to the intermediate state has a fixed value of M, and the second transition involves a decreasing M with increasing temperature. This reflects the increasing number of helix reversals.

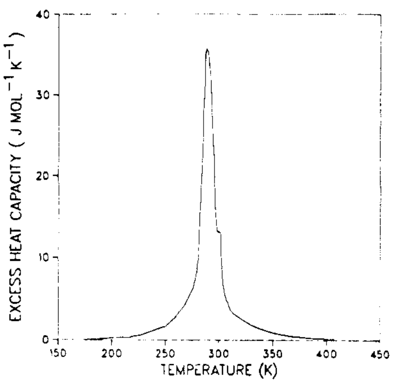

Figure 1. Excess heat capacity of highly crystalline PTFE.

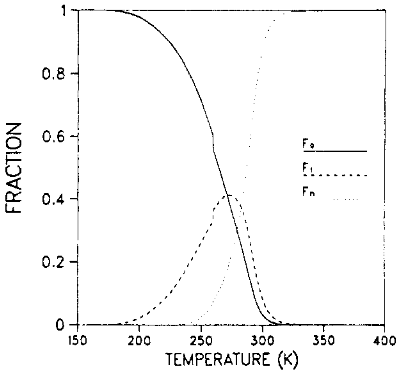

Figure 2. Energy-state fractions for $M_{0,1}$ = 194.

It is seen in Figure 1 that the 19 °C transition is much larger than the 30 °C transition. As a first approximation, we assumed that the 19 °C transition could be treated as a two-level, single-step transition up to the maximum in the heat capacity. Since $T_{\max}$ = 289 K, $c_{\max}$ = 35.7 J K^{-1} mol^{-1} of CF_2 units, and h_n = 714 J mol^{-1} of CF_2 units, we conclude from eq 13 that M = 194 CF_2 units. Using this value, we compute F_0 from eq 7 and F_1 from eq 11. Since there are only three states

$$F_n = 1 - (F_0 + F_1) = \exp\left(-\int_{T}^{T_n}\frac{M(\Delta h_n - \langle h\rangle)}{RT^2}\,\mathrm{d}T\right) \qquad (14)$$

$$\ln F_n = -\int_{T}^{T_n}\frac{M(\Delta h_n - \langle h\rangle)}{RT^2}\,\mathrm{d}T = \int_{T}^{T_n}\frac{M(\Delta h_n - \langle h\rangle)}{R}\,\mathrm{d}(1/T) \qquad (15)$$

$$\frac{\mathrm{d}\ln F_n}{\mathrm{d}(1/T)} = \frac{M}{R}(\Delta h_n - \langle h\rangle) \qquad (16)$$

F_0, F_1, and F_n are plotted in Figure 2.

The temperature-dependent value of M for the transition between the intermediate and upper energy states can be calculated from the slope of a plot of $\ln F_n$ vs $1/T$.

$$M(T) = \frac{R\dfrac{\mathrm{d}\ln F_n}{\mathrm{d}(1/T)}}{\Delta h_n - \langle h\rangle} \qquad (17)$$

As shown in Figure 3, the value of $M(T)$ decreases from

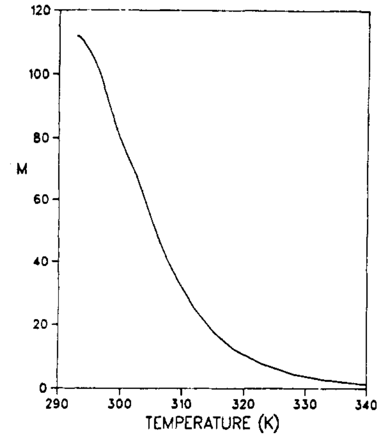

Figure 3. $M(T)$ vs T for $M_{0,1}$ = 194.

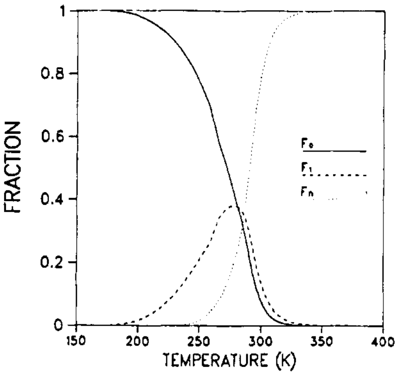

Figure 4. Energy-state fractions for $M_{0,1}$ = 145.

112 at 293 K to 1.4 at 339 K.

The approximation has at least two questionable aspects. All three energy states are populated at temperatures as low as 245 K, in violation of our assumption that only two states were required to characterize the 19 °C transition. The second problem concerns the discontinuity between the low-temperature value of M, which we now designate $M_{0,1}$ to signify its use to calculate F_0 and F_1, and the maximum value of $M(T)$. We believe that it is reasonable that M should vary continuously with temperature.

It turns out that the maximum value of $M(T)$ varies inversely with the value of $M_{0,1}$ from which it was derived. The value for which these two quantities are equal is 145 CF_2 units, and the temperature at which that equality occurs is very close to the nominal 19 °C transition temperature.

The energy-state fractions for this value of $M_{0,1}$ are plotted in Figure 4. As shown in Figure 5, $M(T)$ decreases from 145 at 294 K to 1.6 at 389 K. The high-temperature limit corresponds to a conformation approaching a planar zigzag with large-amplitude torsional oscillations.

It is suggested that the transition between the lowest and intermediate energy states involves a single crystal stem moving as a unit and that the transition to the highest state involves progressively smaller chain segments as the concentration of helix reversals increases with increasing temperature. From the broadening of the (0015) reflection in an X-ray diffractometer scan, the size of the crystallites along the chain has been estimated to be between 230 and 270 Å (176–207 CF_2 units).[24] A similar measurement on an oriented sample prepared by extruding the powder at 50 °C gave 267 Å or 203 CF_2 units.[25] Workers in the Soviet Union[26] have reported a value of 300 ± 40 Å for a sample of previously melted PTFE, and a value of 260–280 Å was deduced from the dependence of the turbidity of films on the wavelength of light.[27]

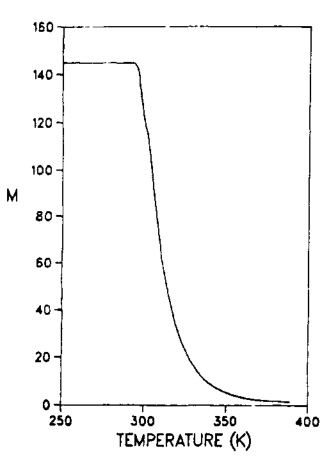

Figure 5. $M(T)$ vs T for $M_{0,1}$ = 145.

Up to this point we have not examined the assumption of Lau et al.[23] that the sample of virgin PTFE was 100% crystalline. They did recognize that the crystallinity might be as low as 84%. The measured heat of fusion was reported to be 4.10 kJ/mol of CF_2 units, which is equivalent to 19.6 cal/g. If we use the reported value of 24.4 cal/g for the heat of fusion for the crystal of virgin PTFE,[28,29] this would correspond to 80.3% crystallinity. The values of M calculated without this correction are proportionately too low. With the correction, $M_{0,1}$ becomes 181 CF_2 units or about 235 Å, in good agreement with the value from X-ray data. The limiting value of $M(T)$ at high temperatures is now two CF_2 units, i.e., 1.6 ÷ 0.803.

Viscoelastic Properties Just below the 19 °C Transition

We[7] and others[6] have found that there are discontinuities in the viscoelastic properties of PTFE at the 19 and 30 °C transitions. It must be emphasized that these are first-order thermodynamic transitions, not viscoelastic relaxations. Viscoelastic properties must be calculated from data in the regions of temperature below, between, and above the transitions. The effects of the crystalline phase were maximized by using a specimen made by extruding virgin granular polymer at 50 °C, far below its melting point. Measurements were made with the Polymer Laboratories dynamic mechanical thermal analyzer (DMTA). By shifting the data taken at various temperatures along the log (frequency) axis, we computed the following apparent activation energies: 24.5 kcal/mol below 19 °C, 122 kcal/mol between 19 and 30 °C, and 7.5 kcal/mol above 30 °C.[7] The very large apparent activation energy between 19 and 30 °C suggests that the type of motion is changing in this interval. These calculations did not consider the possibility that the unrelaxed and relaxed moduli might vary with temperature. This factor has now been added to the analysis.

Complex plane plots of E'' vs E' were constructed for the data taken at each temperature from −5 to +15 °C at 5 °C intervals. As shown in Figure 6, the data were fitted to least-squares circular arcs which are characteristic of the Cole–Cole empirical model.[30] That model is known to fit many secondary relaxations quite well. The intercepts of the arc with the E' axis define the values of the unrelaxed and relaxed moduli, E_u and E_r, for each temperature. These values are given in Table I. In all cases, the correlation coefficients were at least 0.9995, and the Cole–Cole parameter was 0.338 ± 0.007.

The distribution of activation free energies was calculated in the manner previously described.[31] The distri-

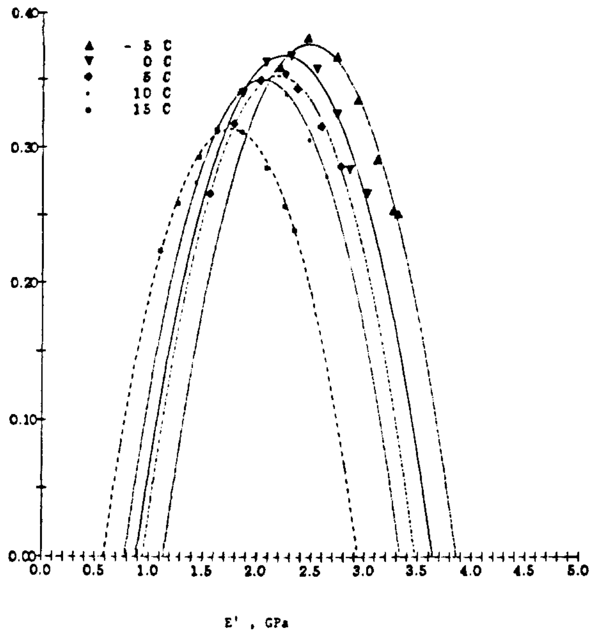

Figure 6. Complex plane plot.

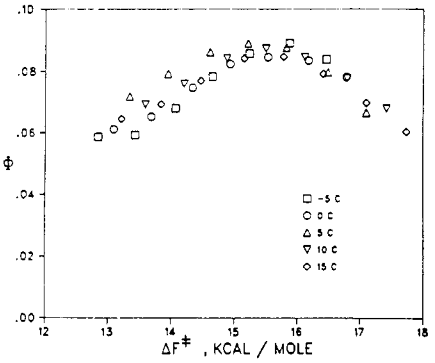

Figure 7. Distribution of activation free energies.

Table I
Unrelaxed and Relaxed Moduli

temp, °C	E_u, GPa	E_r, GPa
-5	3.86	1.14
0	3.64	0.88
5	3.48	0.95
10	3.34	0.78
15	2.94	0.58

bution of relaxation times is approximated by

$$\phi = \frac{2}{\pi}\frac{E''}{E_u - E_r}$$

and the activation free energy for each combination of temperature and frequency is

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} = T\Delta S^{\ddagger} = RT\,[\ln (k/2\pi h) + \ln (T/f)]$$

In a plot of the distribution of activation free energies, ϕ vs $\Delta F^{\ddagger}$, shown in Figure 7, the points for the various temperatures follow the same relationship. This indicates that $\Delta S^{\ddagger}$ is close to zero and $\Delta H^{\ddagger} \cong \Delta F^{\ddagger}$. The distribution has a maximum at ca. 15.5 kcal/mol, and the width at half-maximum is ca. 5.5 kcal/mol, a value that is similar to those for many other relaxations.[31]

The observations indicate that the form of the β-relaxation that exists below the 19 °C transition is a simple, noncooperative process. In contrast with this, the data taken between the 19 and 30 °C transitions indicate that this region is characterized by a large apparent activation energy and entropy.[7] This is consistent with a motion having a character that is changing rapidly with temperature.

Conclusions

The data from calorimetry, crystallography, and dynamic mechanical measurements are all consistent with a model in which single crystal stems are moving as a unit in the 19 °C transition from the lowest to the intermediate energy state. The fact that the activation entropy below the transition is close to zero indicates that these stems are acting independently of one another.

We conclude that in the region of the 30 °C transition, the size of the active unit decreases with increasing temperature as the number of helix reversals increases. Finally, at ca. 389 K, this process has reached the point where the conformation is equivalent to a planar zigzag modified by large and irregular local torsional oscillations.

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