[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Specific Heat of Synthetic High Polymers. V. A Study of the Order-Disorder Transition in Polytetrafluoroethylene

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The specific heat of polytetrafluoroethylene (Teflon) has been measured from −25 to 120° on powdered and drawn samples. Drawing the Teflon into fiber form has no effect on the heats of the order-disorder transitions at 20 and 28° None of the order-disorder theories developed for order-disorder in alloys is accurately applicable to the Teflon data, although qualitative agreement suggests that the transition is an order-disorder transition. A modified order-disorder theory is presented which agrees somewhat better with the data but which has serious theoretical difficulties.

Introduction

Polytetrafluoroethylene, or Teflon, exhibits a rather unusual first-order transition at 20° as discovered by Rigby and Bunn[1] and another barely perceptible transition at 30° as discovered by Quinn, Roberts and Work,[2] both on the basis of a dilatometric study. These two transitions were confirmed by specific heat measurements on powdered, molded and annealed Teflon by Furukawa, McCoskey and King.[3] The transitions and phases of Teflon at high pressures have been studied by Bridgman[4] and Weir.[5]

Because of the fact that specific heat studies of drawn 6-6 and 6 Nylon[6,7] demonstrated that drawing linear polymers into fiber form had the effect of considerably reducing the magnitude of the glass transition (sometimes called the second-order transition), it seemed of interest to measure the specific heat of drawn Teflon to see if either the temperatures or the heats of transition of the two transitions in Teflon would be affected by the drawing process.

We realized, of course, that the transitions in Teflon were an entirely different type from that in 6-Nylon, inasmuch as the course of the specific heat temperature curve was completely different and the Teflon transitions were reversible. As will be seen from the theoretical discussion in this paper, the Teflon transitions are probably order-disorder transitions for which we have developed a new order-disorder theory.

Experimental

The specific heat equipment and its operation were the same as that previously described.[7,8] The samples of Teflon studied were used as supplied[9] by the E. I. du Pont de Nemours and Co. except for drying. The description of the samples was as follows.

"Virgin" polymer, TE-3058, Lot-30012.

"A sample of highly drawn (16.6 × at 370°) monofil made from this batch of polymer. This monofil is very highly oriented, as shown by its X-ray diffraction pattern." Because of the high temperature of drawing this polymer, the drawn Teflon may possibly be considered to be like annealed Teflon.

Experimental Results

Above 40° our specific heat data can be expressed by the equations

Powdered Teflon

$$c_p = 0.2227 + 2.50 \times 10^{-4}t \quad (1)$$

Drawn Teflon

$$c_p = 0.2277 + 2.39 \times 10^{-4}t \quad (2)$$

where c_p is the specific heat in cal. g.$^{-1}$ deg.$^{-1}$ and t is the temperature in degrees centigrade. Over the range 45 to 125° the average deviation of eight results from eq. 1 amounted to ±0.33% with −1.0 and +0.6% being the lower and upper limits of the differences. In the case of eq. 2 the average deviation of seven results was ±0.20% with −0.33 and +0.21% being the lower and upper limits. The agreement between our results and those of Furukawa, McCoskey and King[3] is satisfactory above 40°, but below the transition region, in the range 0 to −23°, the NBS data on powdered Teflon are about 3.5% higher than ours. This difference may be caused by a difference in the samples, but this is considered unlikely as above 40° the NBS data and ours agree within the uncertainty limits of our experiments. The difference may be the result of the difference in time allowed to reach thermal equilibrium during the measurements, not more than 30 minutes in the NBS work, but an hour or more in our experiments.

Discussion

In Fig. 1, our data for powdered and drawn Teflon are compared over the transition temperature range. It can be seen that drawing the polymer has little effect on the transition other than to narrow slightly its temperature range, but this may be the result of the heat treatment during the drawing process. We have attempted to compute the heat of transition by subtracting from the total measured enthalpy change between −20 and +50°, 18.1 cal./g. in the case of the powdered Teflon and 17.9 cal./g. in the case of the drawn fibers, the estimated enthalpy change assuming a linear increase in specific heat over the entire temperature range, but with the slope of eq. 1 and 2 above 30° and a slope equal to 7.0 × 10^{-4} cal. g.$^{-1}$ deg.$^{-2}$ below 30°. This latter slope was estimated from the NBS data which were more extensive than ours below 0°, but ran parallel to the data which we had obtained. The

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[1] H. A. Rigby and C. W. Bunn, *Nature*, **164**, 583 (1949). An early indication of such a transition at 50° was obtained during an unpublished X-ray study of an experimental Teflon sample by C. E. Black.

[2] F. A. Quinn, Jr., D. E. Roberts and R. N. Work, *J. Appl. Phys.*, **22**, 1085 (1951).

[3] G. T. Furukawa, R. E. McCoskey and G. J. King, *J. Research Natl. Bur. Standards*, **49**, 273 (1952).

[4] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **76**, 55 (1948).

[5] C. E. Weir, *J. Research Natl. Bur. Standards*, **50**, 95 (1953).

[6] R. C. Wilhoit and M. Dole, *J. Phys. Chem.*, **57**, 14 (1953).

[7] P. Marx, C. W. Smith, A. E. Worthington and M. Dole, *ibid.*, **59**, in press (1955).

[8] A. E. Worthington, P. Marx and M. Dole, *Rev. Sci. Instru.*, **26**, 696 (1955).

[9] Kindly sent to us by J. D. Grandine, 2nd, of the Pioneering Research Division.

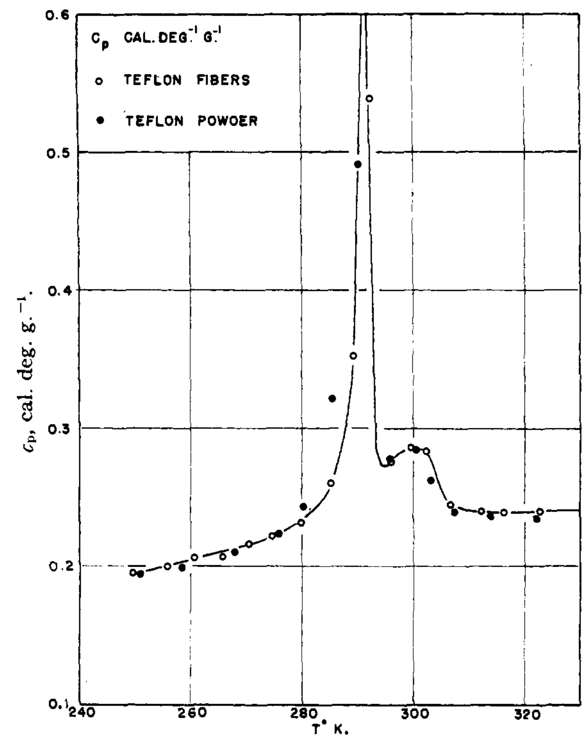

Fig. 1.—Specific heat of Teflon.

heats of transition for the two transitions combined amounted to 2.79 and 2.36 cal./g. for the powdered and drawn samples, respectively. Furukawa, McCoskey and King[3] similarly found that the heats of transition were greater for the powdered form than for the annealed by about 0.36 cal./g., close to our difference of 0.43 cal./g.

By estimating the slope of the individual specific heat–temperature curves for the two transitions, we have computed that 83% of the total heat of transition is to be ascribed to the 20° transition, or 2.31 cal./g. in the case of powdered Teflon and 1.96 cal./g. in the case of the drawn. Our estimate of 83% agrees well with a similar estimate of 85% obtained by Quinn, Roberts and Work[2] from their dilatometric study. Weir[5] estimated a heat of transition of 1.54 cal./g. from the slope of the pressure–temperature curve representing the transition between solid phases I and II, but this calculation is greatly dependent on the uncertain estimate of the slope. For example, a similar calculation made by us from an estimate of the slope of Weir's data yielded 1.96 cal./g. in exact agreement with the thermochemical value for drawn Teflon.

X-Ray studies of Teflon[1,10] indicate that the transition of Teflon at 20° is probably an order–disorder transition inasmuch as no new well defined crystal structure is revealed by X-rays above 20°, but only a disorientation or weakening of the structure that exists below 20°. In the words of Rigby and Bunn,[1] "There is evidently a change of crystal structure; it is, however, not a change from one precise arrangement to another, but a change from a 3-dimensional (fully crystalline) order below 20° to a lower order degree of order above 20°C."

Theories of the specific heat of order–disorder transitions have been developed for order–disorder transitions in alloys.[11] These range from the pioneering treatment of Bragg and Williams[12] to a more exact development[13] of Wakefield.[14] In general, these theories differ in their manner of computing the increase of entropy as the long or short range order decreases. All the theories assume a linear decrease of the energy required to make the transition from an ordered site to a disordered site with increase in the degree of disorder. In Fig. 2 we have plotted the trend of the specific heat with temperature according to the Bragg–Williams[12] theory of long range order, and also similar specific heat values based on Wakefield's refinement[14] of the order–disorder theories. The constants of the equations have been adjusted so that the critical temperature agrees with the temperature of the maximum of the observed specific heat temperature curve, and so that the molecular weight of the segment making the transition in any one jump will reproduce the observed maximum. The dotted straight lines of Fig. 2 represent the base specific heat, that is, the specific heat Teflon would have above and below the 20° transition if no order–disorder phenomena occurred. The specific heat calculated from the order–disorder theories has been added to the base specific heat to obtain the theoretical curves of Fig. 2.

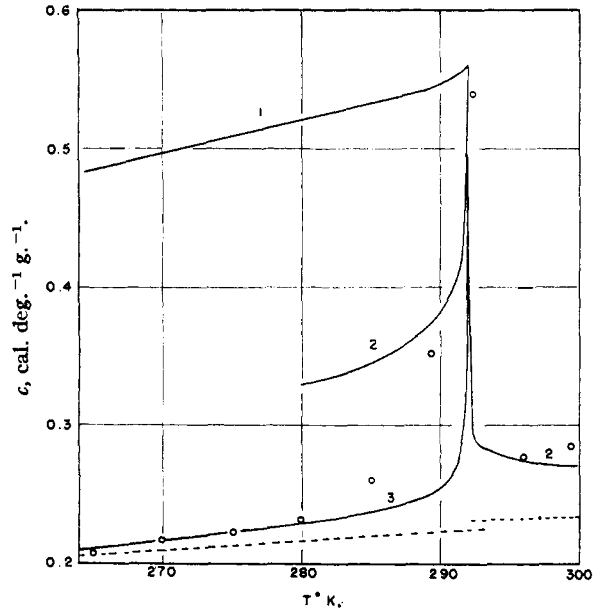

Fig. 2.—Measured specific heat of Teflon (open circles) compared with the theory of Bragg and Williams, curve 1, the theory of Wakefield, curve 2, and the theory of this paper, curve 3.

The qualitative agreement may be considered satisfactory, leading us to believe that an order–disorder theory especially developed for long-chain

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(10) C. E. Black, private communication; see also C. W. Bunn, *Nature*, **174**, 549 (1954).

(11) See J. Frenkel, "Kinetic Theory of Liquids," Oxford, 1946, Chap. II, for a description of order–disorder theories.

(12) W. L. Bragg and E. J. Williams, *Proc. Roy. Soc.* (*London*), **A145**, 699 (1934).

(13) For a recent review of order–disorder theories see G. F. Newell and E. W. Montroll, *Revs. Mod. Phys.*, **25**, 353 (1953).

(14) A. J. Wakefield, *Proc. Camb. Philos. Soc.*, **47**, 419 (1951)

molecules instead of simple atoms might be quantitatively successful. It has seemed to us that the energy required for one group to make the transition say from site α to site β might vary with the degree of disorder by a power higher than the first. Each long chain segment is bound by primary valence forces to the rest of the chain with the result that the transition of one segment affects the potential energy of the segments at both of its ends. A transition of one segment probably takes place by a rotation of several CF_2 groups through an angle of 180° or less. Thus, a segment is assumed to consist of several repeating units.

Following in general the method of Bragg and Williams[12] let n_α be the number of segments on an α-site, or having the orientation of an α-group, let n_β be the corresponding number of β-segments. If n is the total number of segments, then

$$n = n_\alpha + n_\beta \tag{1}$$

Let E_0 be the energy per mole required for the transition of a segment from an α- to a β-site initially at complete order, then we assume that

$$E_i = E_0\zeta^2/N \tag{2}$$

where ζ is the degree of order (equals unity at complete order and zero at complete disorder)

$$\zeta = 1 - 2n_\beta/n \tag{3}$$

N is Avogadro's number, and E_i is the energy required for the transition of a segment when the degree of order is equal to ζ. As stated above we have made E_i a function of the degree of order to the second power. The total energy E of the transition is found by integrating (2) from ζ equal to unity to ζ.

$$\begin{aligned} E &= \int_0^{n_\beta} E_i \, \mathrm{d}n_\beta \\ &= -\left(\frac{n}{2N}\right)E_0\int_1^{\zeta}\zeta^2\mathrm{d}\zeta \\ &= \left(\frac{n}{6N}\right)E_0\,(1-\zeta^3) \end{aligned} \tag{4}$$

We now make the crude assumption that the entropy of the order–disorder transition can be calculated from the equation

$$S = k \ln \frac{n!}{n_\alpha! n_\beta!} \tag{5}$$

Letting A, the free energy, equal $E - TS$ and minimizing A with respect to n_β which introduces the assumption of thermodynamic equilibrium, we obtain the expression

$$\frac{n_\beta}{n_\alpha} = e^{-E_0\zeta^2/RT} \tag{6}$$

From (6) it follows that

$$\zeta = \frac{1-z}{1+z} \tag{7}$$

where z is $\exp(-E_0\zeta^2/RT)$. Figure 3 illustrates a plot of ζ as a function of T/T_0 where T_0 is equal to $E_0/2R$. This function is compared in Fig. 3 with a similar function of Bragg and Williams.[12]

To obtain the contribution to the specific heat, ΔC, due to the disordering of the crystal, (4) is differentiated with respect to T. The result is

$$\Delta C = \frac{\mathrm{d}E}{\mathrm{d}T} = \frac{nE_0}{NT}Z \tag{8}$$

where

$$Z = \frac{\zeta^2}{\dfrac{(1+z)^2}{zr} - \dfrac{4}{\zeta}} \tag{9}$$

In (9) r equals $E_0\zeta^2/RT$. Equation 9 is of such a form that as the temperature increases, the two terms in the denominator approach each other causing ΔC to approach infinity rapidly at a critical temperature, and then to become negative. The useful values of ζ, *i.e.*, values of ζ such that ΔC is positive, lie between 0.8 and 1.0.

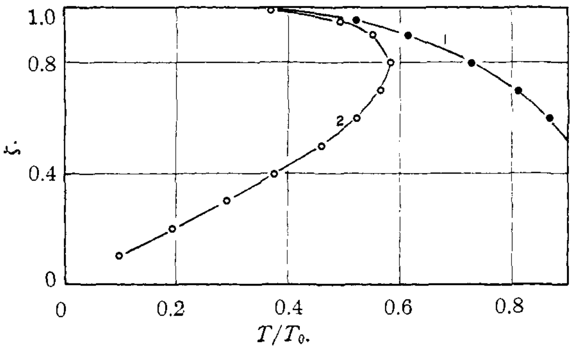

Fig. 3.—Comparison of the ζ function of Bragg and Williams, curve 1, with that of this paper, curve 2.

The following procedure was used in applying eq. 9. Values of ζ from zero to unity were selected and z calculated from the expression

$$z = \frac{1-\zeta}{1+\zeta} \tag{10}$$

From z, r was readily calculated and from ζ, z and r, Z was determined. The maximum value of the specific heat increment, $\Delta C_{\max}$, occurs at the maximum value of ζ^2/r. Knowing the temperature of the maximum to be 292°K., E_0/R was calculated to be 1002°. The temperatures associated with a certain value of ζ were then found by multiplying ζ^2/r by 1002°. Finally $(n/N)E_0$ was calculated from $T_{\max}\,\Delta C_{\max}/Z_{\max}$. Thus the constants (n/N) and E_0 were chosen so that the maximum measured increment to the specific heat and the temperature of the maximum would coincide with those calculated from eq. 9. By $Z_{\max}$ we do not mean infinity which is the maximum value of Z, but a value of Z at 292°K. which fits the calculated curve to the observed. In the Bragg–Williams[12] theory, Z is given by the equation

$$Z = \frac{\zeta}{\dfrac{(1+z)^2}{zr} - \dfrac{2}{\zeta}} \tag{11}$$

where r equals $E_0\zeta/RT$.

In Fig. 2 curve 3 represents values of the specific heat calculated from eq. 8. Agreement with the observed values is fair except in the neighborhood of the critical temperature where the observed specific heat rises with temperature more gradually than the calculated. The total transition energy for our model is obtained by setting ζ equal to zero in eq. 4 and introducing the value of 8.75 for $(n/N)E_0$. As E_0 is equal to 1993 cal./mole as calculated by multiplying 1002° by the gas constant R, n/N has the value 0.0044, which is the number of moles of segments making the order–disorder transition in one gram of Teflon. The molecular weight of the segments thus is calculated to be 227 or about 4.5 CF_2 units. The total energy E for ζ equal to zero is 1.46 cal./g. as compared to the observed value of 1.96 cal./g.

The difficulties with the present order–disorder model are the transition of ΔC from positive to negative values at ζ equal to 0.8 and the two values of T that can satisfy eq. 7 at a single value of ζ (Fig. 2). A negative contribution of ΔC is certainly physically possible and may explain the decrease of c_p with rising temperatures frequently observed in high polymers. Negative values of ζ are impossible because a negative ζ can only be produced by a negative T. But the two values of T at a single value of ζ have no meaning thermodynamically. We conclude that the theoretical model presented here can have only limited validity, if any.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Specific Heat of Synthetic High Polymers. VI. A Study of the Glass Transition in Polyvinyl Chloride

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Data are given for the specific heat of powdered and annealed L-38 polyvinyl chloride over the temperature range −20 to 120°. The glass transition is shown to be pronounced, indicating the amorphous nature of the polymer. The specific heat below T_g can be represented by an equivalent Einstein solid with 18 modes of vibration per structural unit, and a single vibrational frequency. Above T_g this is no longer possible, suggesting that interchain interactions contribute greatly to the specific heat above T_g. The maximum value of the dielectric loss factor, ϵ'', occurs at a temperature about 20° above T_g at 60 cycles.

Introduction

The previous papers[1–4] of this series dealt with linear polymers whose crystallinity was at least 50% or greater. Polyvinyl chloride represents the first highly amorphous polymer whose specific heat has been investigated by us. It is an especially interesting material to study because of the extensive dielectric measurements made on it by Fuoss[5] and by Davies, Miller and Busse,[6] whose results coupled with those of this paper make possible a correlation between the thermal and electrical properties. Polyvinyl chloride is also interesting because of the magnitude of the rise in specific heat at the glass transition temperature.

Previous specific heat determinations on polyvinyl chloride (German trade name "Igelit PCU") have been carried out by Vieweg and Gottwald,[7] Heuse[8] and Badoche and Shu-Hua-Li,[9] but these authors determined only the average specific heats over large temperature intervals. Gast,[10] on the other hand, obtained results that are comparable to ours and to which we shall refer later.

Experimental Details

Through the courtesy of R. M. Fuoss, a sample of powdered L-38 polyvinyl chloride used by him was obtained from the General Electric Co., their number SN-85114. It was used as received except for drying. The apparatus and technique of carrying out the specific heat measurements were the same as those previously described.[3,4,11]

The temperature range of the measurements was limited on the low temperature side to −20° because of the nature of the apparatus, and on the high temperature side by the tendency of polyvinyl chloride to decompose. Because of the danger of decomposition, 120° was set as the upper limit. Although the polyvinyl chloride became discolored during the specific heat measurements, no silver chloride could be detected (the polymer was heated in silver trays) and the weight loss during each series of measurements was only 0.12% which is considered to be negligible.

Experimental Data

Figure 1 illustrates our specific heat data for the original polyvinyl chloride (PVC), curve 1, while curve 2 is the specific heat of the annealed material. By "annealed" we mean PVC that had previously been heated to 120° and then slowly cooled. The dotted line represents the data of Gast.[10] Below 60° the specific heat of the L-38 PVC is given by the equation

$$c_p = 0.2092 + 7.29 \times 10^{-4}t \qquad (1)$$

where t is in degrees centigrade while the specific heat of the annealed PVC follows the equation

$$c_p = 0.2048 + 8.46 \times 10^{-4}t \qquad (2)$$

The peculiar fluctuations in the specific heat curve of the original PVC were observed in three different series of measurements, so we have no doubt as to their reality. They are probably the result of a slight amount of crystallization taking place in the polymer. The total change in enthalpy for the annealed PVC between 0 and 100° was 26.2 cal./g. while the original PVC gave the value 25.9 cal./g. with an uncertainty of about 0.1 cal./g. The

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(1) M. Dole, W. P. Hettinger, Jr., N. R. Larson and J. A. Wethington, Jr., *J. Chem. Phys.*, **20**, 781 (1952).

(2) R. C. Wilhoit and M. Dole, *J. Phys. Chem.*, **57**, 14 (1953).

(3) P. Marx, C. W. Smith, A. E. Worthington and M. Dole, *ibid.*, **59**, in press (1955).

(4) P. Marx and M. Dole, THIS JOURNAL, **77**, 4771 (1955).

(5) R. M. Fuoss, *ibid.*, **59**, 1703 (1937); **60**, 451, 456 (1938); **61**, 2329, 2334 (1939); **63**, 369, 385, 2401, 2410 (1941).

(6) J. M. Davies, R. F. Miller and W. F. Busse, *ibid.*, **63**, 361 (1941).

(7) R. Vieweg and F. Gottwald, *Kunststoffe*, **30**, 138 (1940).

(8) W. Heuse, *ibid.*, **39**, 41 (1949).

(9) M. Badoche and Shu-Hua-Li, *Compt. rend.*, **231**, 50 (1950); *Bull. soc. chim. France*, 546 (1951).

(10) T. Gast, *Kunststoffe*, **43**, 15 (1953).

(11) A. E. Worthington, P. Marx and M. Dole, *Rev. Sci. Instr.*, **26**, 698 (1955).