ments 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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EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

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

BY SAUL ALFORD AND MALCOLM DOLE

RECEIVED MARCH 11, 1955

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).

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

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(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).

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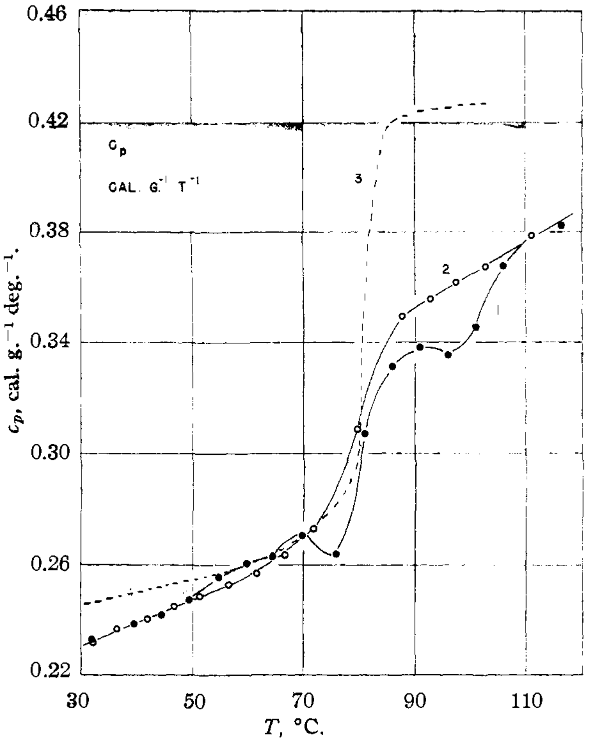

Fig. 1.—Specific heat of polyvinyl chloride: powdered (curve 1); powdered and annealed (curve 2); data of Gast[10] (dotted line, curve 3).

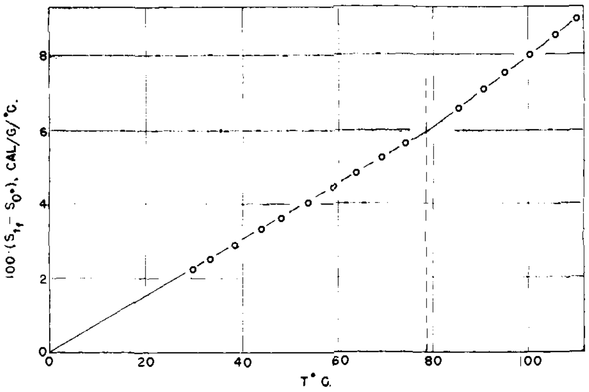

Fig. 2.—Entropy per gram of polyvinyl chloride between 0 and 110°; dotted line indicates glass transition temperature.

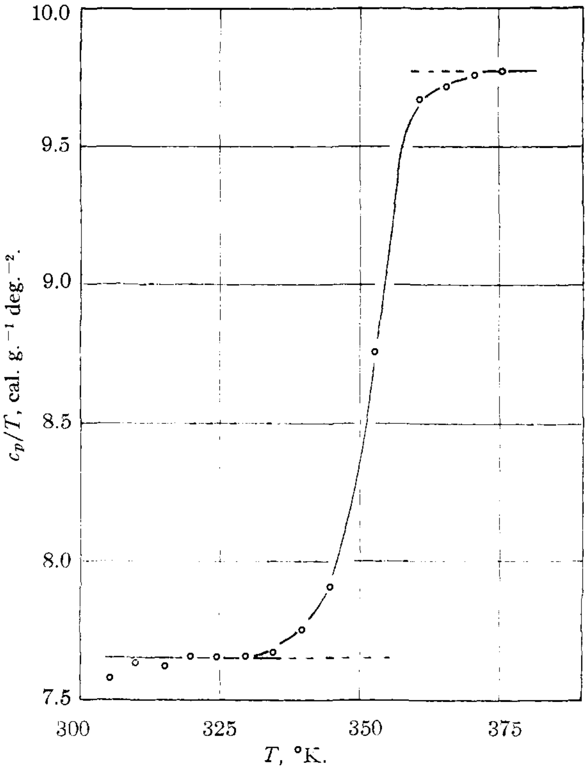

Fig. 3.—Variation of c_p/T for polyvinyl chloride through the glass transition range.

specific heat data were probably reliable to ±0.2% over most of the temperature range.

We have no explanation for the difference between our results and those of Gast.[10] In any of the polymers which we have studied we have never observed such a sharp, abrupt glass transition as exhibited by Gast's data. Perhaps Gast's PVC had a smaller spread in its molecular weight than did ours.

Interpretation of the Data

If the difference in entropy of the annealed PVC between t° and 0° is plotted as a function of the centigrade temperature as in Fig. 2, it can be seen that there are two linear branches of the curve which meet sharply at the glass transition temperature, T_g. The entropy–temperature curve seems to constitute the best curve based on thermal data from which to calculate the glass transition temperature. The straight lines of Fig. 2 signify that c_p/T must be constant above and below T_g but with different values. Figure 3 illustrates this relation. The approximate constancy of C_p/T below T_g indicates that the constant of eq. 2 should be zero if the temperature is expressed in degrees absolute. This is nearly true; hence c_p must rise nearly linearly with T from the absolute zero to 60°. T_g occurs at 78.5° as estimated from Fig. 2. This is lower by a degree or two than T_g as estimated from the inflection point in the specific heat temperature curve.

The rather considerable rise in the specific heat at T_g, amounting to about 25%, might be thought to be the result of the activation of additional vibrational modes of the solid. That the rise in specific heat cannot be explained solely on the basis of this simple picture is suggested by the following crude theoretical treatment. Omitting the zero point energy, the average energy of the linear harmonic oscillator $\bar{\epsilon}$, can be expressed by the equation

$$\bar{\epsilon} = \frac{h\nu}{e^{\theta/T} - 1} \qquad (3)$$

where h is Planck's constant, ν is the frequency of the vibration, θ is $h\nu/k$, T the absolute temperature and k Boltzmann's constant. Inasmuch as the heat capacity of PVC at 60° per repeating unit is (0.2555)(62.50) or 15.97, which is only a little greater than 0.44 of the classical value of 18R, the guess can be made that the Einstein frequencies of vibration are such that at 60° θ/T is large enough so that unity may be neglected in comparison to $e^{\theta/T}$ in the denominator of (3). In this case we can write the equation for the specific heat per degree of freedom as

$$c_i = R\frac{\theta^2}{T^2}e^{-\theta/T} \tag{4}$$

Making the gross assumption that the major frequencies of vibration are such that they all have nearly enough the same frequency to express the heat capacity per gram by the equation

$$c_v = xNk\frac{\theta^2}{T^2}e^{-\theta/T} \tag{5}$$

where x is the number of modes of vibration per gram of PVC, we can rearrange (5) into a linear equation of the form

$$\ln T^2 c_v = \ln x R\theta^2 - \frac{\theta}{T} \tag{6}$$

This expression can be tested by plotting log $T^2 c_v$ as a function of the reciprocal temperature. Such a plot is shown in Fig. 4 where c_p represents the heat capacity per gram of PVC. For convenience we have neglected the difference between c_p and c_v. From the slope of the straight lines above and below T_g, θ can be calculated and from θ, the major contributing frequency. At infinite temperature T^2, c_v is equal to $xR\theta^2$ in the case of this approximation, hence x can be estimated from the intercept at infinite temperatures of the curves of Fig. 4 for the temperature range both above and below T_g. A least squares calculation of the data from the two linear sections of the curve yielded a frequency of 835 cm.$^{-1}$ in the high temperature region and 690 cm.$^{-1}$ in the low. These are reasonable values. For example, Thompson and Torkington[12] in their study of the absorption spectrum of PVC found strong bands in the neighborhood of 600–700, 950 and 1250 cm.$^{-1}$.

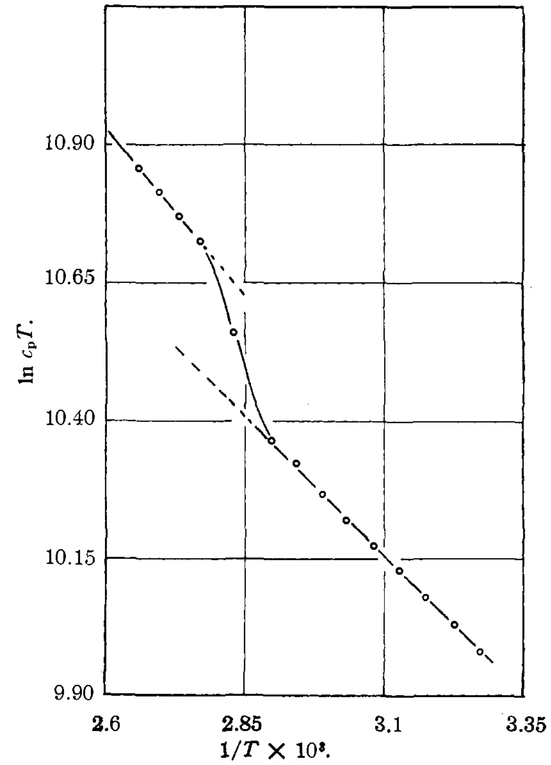

Fig. 4.—Test of eq. 6.

The extrapolation of the straight lines of Fig. 4 to infinite temperature yielded values of x equal to 0.285 and 0.445 at the lower and upper temperatures, respectively. On multiplying by the molecular weight per repeating unit, or 62.5, 17.8 and 27.8 were obtained. The first number is almost identical with the expected value of 18 degrees of freedom for the six atoms in the repeating unit. Thus the specific heat of PVC below 60° can be represented by 6 Einstein oscillators, each having the same frequency of oscillation equal to 690 cm.$^{-1}$. This frequency might be called the Einstein equivalent frequency.

The value of 27.8 degrees of freedom calculated from the data of the upper curve is without significance, as far as the model of a simple Einstein oscillator is concerned, because this value is above the maximum theoretical limit of 18 degrees of freedom. This fact suggests that other factors beside oscillations, vibrations or rotations are contributing to the specific heat, such as interchain interactions involving a potential energy.

The calorimetric and dielectric behavior of PVC are compared in Fig. 5 where the dielectric loss factor, ϵ'', taken from the data of Fuoss[13] up to 105° and the data of Davies, Miller and Busse[6] above 105°, are plotted along with the specific heat of annealed PVC. It can be seen that the sharp rise in the specific heat and in ϵ'' begins at about the same temperature, but that the maximum in ϵ'' does not occur until a temperature of about 98° is attained. At this temperature the glass transition in PVC has been completed. In fact, the glass transition seems to have been completed at about 90°. That the two phenomena do not coincide exactly is not surprising inasmuch as both c_p and ϵ'' are time dependent phenomena with not necessarily the same time dependence. Thus, the temperature at which ϵ'' passes through a maximum rises with the frequency; the specific heat values would also possibly

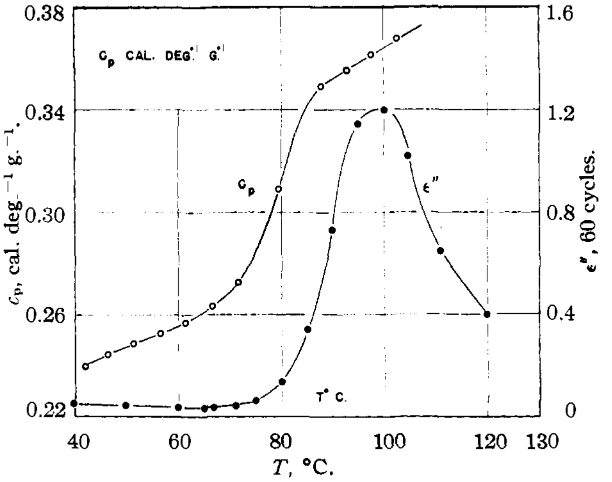

Fig. 5.—Comparison of specific heat and dielectric loss factor for polyvinyl chloride.

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[12] H. W. Thompson and P. Torkington, *Proc. Roy. Soc.* (*London*), **A184**, 21 (1945); see also E. J. Ambrose, A. Elliott and R. B. Temple. *ibid.*, **A199**, 183 (1949).

[13] R. M. Fuoss, Amer. Documentation Inst. Document No. 1460, Library of Congress, Washington, D. C.

be a function of the rapidity of heating if this could be varied significantly.

Nevertheless, it is apparent that the molecular processes responsible for the glass transition must necessarily be partly responsible for the increase in the dielectric loss. We picture these processes as occurring in the amorphous region of the polymer where, with rise of temperature, the viscosity of this region falls to a value low enough for the observed phenomena to occur.

Acknowledgment.—Grateful appreciation is expressed for support of this project by the Office of Ordnance Research, U. S. Army.

EVANSTON, ILLINOIS

NOTES

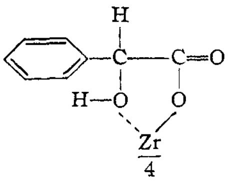
Studies of Zirconium Tetramandelate[1]

BY RICHARD B. HAHN AND LEON WEBER[2]

RECEIVED APRIL 13, 1955

In studying the reactions of various organic acids with zirconyl ions, Kumins[3] observed that a precipitate was formed when a zirconyl chloride solution was treated with a solution of *d,l*-mandelic acid (phenylglycolic acid). The precipitate was shown to be zirconium tetramandelate, $Zr(C_8H_7O_3)_4$. Using mandelic acid as a reagent, Kumins developed an analytical method for the determination of zirconium in the presence of various other ions. Hahn[4] found that quantitative precipitation of zirconium tetramandelate occurs even in strongly acid solution and that hafnium was also precipitated by mandelic acid.

Kumins considered the zirconium tetramandelate precipitate as a simple salt, $Zr(C_8H_7O_3)_4$, whereas Feigl[5] postulated a chelate type structure



Kumins observed that zirconium tetramandelate dissolves in aqueous ammonia. This he attributed to the formation of a soluble complex with ammonia, although no experiments were made to substantiate this. The solvent action displayed by ammonia on zirconium tetramandelate was explained by Feigl as being due to the presence of acidic (OH) groups in zirconium tetramandelate. The acidity of the weakly acidic alcoholic (OH) group of mandelic acid is enhanced by the coördination of the zirconium with the oxygen atom of an (OH) group as shown in the above structure. The binding of the hydrogen atom is loosened and hence it becomes more mobile, or more acidic. If all four mandelate groups are linked to zirconium in this inner complex manner, one can assume that all four hydrogen atoms could be replaced by ammonia; however, if only two molecules of mandelic acid are so linked and two bound normally, then only two hydrogen atoms would be replaced by ammonia. The first condition would assign zirconium the coördination number of 8, which is quite rare, and the second would assign the more common value of 6. In order to clarify the structure and the reactions of zirconium tetramandelate the following investigations were made.

Experimental

Reagents.—Chemically pure zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$ (Fisher Scientific Co.), was used in all experiments. This was checked spectrographically and found to be free of impurities except for a small amount of hafnium. A solution was prepared by dissolving the salt in water. This solution was standardized by precipitation with mandelic acid.

d,l-Mandelic acid (Eastman Kodak Co. No. 722 melting point 119–121°) was used. A saturated aqueous solution (about 15%) was used in all experiments.

Sodium mandelate (Mallinckrodt) was purified by several recrystallizations from 95% ethyl alcohol. The final salt was assumed to be $NaC_8H_7O_3$.[6]

Reaction of Zirconyl Ions with *d,l*-Mandelic Acid.—When a solution containing zirconyl ions is treated with mandelic acid a precipitate does not form immediately. A clear solution is obtained which persists for a moment or two even when a large excess of mandelic acid is present. If the mandelic acid is added dropwise, a precipitate does not form until almost equivalent amounts are mixed. It was considered that an intermediate soluble complex may be formed first which then reacts with more mandelic acid to form a precipitate. In order to check this hypothesis a conductometric titration was carried out. Standard solutions of zirconyl chloride and sodium mandelate were prepared. The zirconyl chloride was titrated with the standard sodium mandelate solution using the apparatus described by Willard, Merritt and Dean.[7] The results are shown in Fig. 1.

50.0 ml. of 0.0163 M zirconyl chloride was found to react with 1.9 ml. of 1 M sodium mandelate. This indicates that approximately 2.3 moles of sodium mandelate react with 1 mole of zirconyl ion to form a soluble complex. The reaction might be formulated as

$$ZrO^{++} + 2HC_8H_7O_3 \longrightarrow ZrO(C_8H_7O_3)_2 + 2H^+$$

When an excess of mandelate ion is added a precipitate of zirconium tetramandelate results

$$ZrO(C_8H_7O_3)_2 + 2HC_8H_7O_3 \longrightarrow Zr(C_8H_7O_3)_4 + H_2O$$

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(1) This study was supported in part by a grant from the Atomic Energy Commission, AT(11-1)213.

(2) Submitted as a thesis by Leon Weber in partial fulfillment for M.S. degree in chemistry, Wayne University.

(3) C. A. Kumins, *Anal. Chem.*, **19**, 376 (1947).

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(5) F. Feigl, "Chemistry of Specific, Sensitive, and Selective Reactions," Academic Press, Inc., New York, N. Y., 1949.

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(7) H. H. Willard, L. L. Merritt and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand Co., New York, N. Y., 1951, p. 224.