DTA Evidence for Physical Orientation (Crystallinity) in PVC

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Synopsis

A difference has been observed in the DTA and DSC curves for the glass transition of both PVC homopolymer and acetate copolymer, depending on the rate of quenching or annealing below the glass transition temperature. The difference has the appearance of an endothermal peak added to the glass transition curve and is attributed to an alignment of stereoregular chain segments of adjacent polymer molecules. The lengths of chain segments are assumed to be so short that no x-ray evidence of crystallinity was obtained. The orientation process involved has an activation energy of 47.8 kcal./mole in the homopolymer and 43.6 kcal./mole in the copolymer. The measured rate of the process agrees with the principle of time–temperature superposition, the rates becoming equal for homopolymer and copolymer at equal temperatures below their glass transition temperatures.

INTRODUCTION

In a previous publication[1] minor anomalies in the differential thermal analysis (DTA) curves obtained in determining the glass transitions of PVC polymers and copolymers were illustrated. These variations were correlated with the thermal history of the sample, that is, whether the sample had been cooled quickly (quenched) from above the glass transition temperature or had been cooled slowly (annealed) through this temperature. It was suggested that the observed increase in depth of the T_g endotherm might be an indication of a slight amount of crystallinity in PVC developed by the annealing process.

There has been extended and detailed examination of the effect of annealing on the measurement of physical properties of crystalline and semicrystalline polymers.[2–6] Crystallinity in PVC is much less pronounced, and this polymer is generally considered to be amorphous. Böckman[7] has obtained increased crystallinity through specialized polymerization procedures. Reding[8] and associates have also examined methods of production of crystallinity in PVC. They conclude that the increased crystallinity produced by polymerization at lower temperatures results from an increase in the internal syndiotactic structure of the polymer molecules. They also call attention to the enhancement of the degree of crystallinity on plasticiz-

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ing the polymer and in a critical experiment involving the annealing of an oriented, plasticized sample of conventional PVC were able to obtain x-ray diffraction evidence for an increased amount of crystallinity resulting from this procedure. This increased crystallinity obtained by annealing physically stretched sheets is certainly not due to any change in stereoregularity of the skeletal structure of individual molecules. Reding et al. conclude that they have obtained qualitative evidence "that the chains in poly(vinyl chloride) line up laterally to a quite high degree of perfection when annealed but that the crystallite perfection along the chain axis is very poor at best."

In the present investigation we have assumed initially that the changes in the PVC produced by slow cooling as evidenced by the DTA curves are similar in origin to those obtained by Reding and associates, differing only in that the number and size of the areas involved in physical orientation are insufficient to yield an x-ray pattern. For this reason the term physical orientation has been used rather than crystallinity.

The DTA equipment used in the present evaluation is similar to that described by Keavney and Eberlin[9] employing chromel–alumel thermocouples. Time studies have been made in the differential scanning calorimeter (DSC) (Model DSC-1, Perkin-Elmer Corp., Norwalk, Conn.). All of the PVC polymers investigated have been commercial materials (Exon, Firestone Plastics Company; Opalon, Monsanto Chemical Company; Geon, B. F. Goodrich Chemical Company).

EXPERIMENTAL RESULTS

In the experimental procedure quenched samples were prepared by heating the sample and reference material in the aluminum block of the DTA apparatus to 120°C., far above the 70–80°C. glass transition region, maintaining that temperature for 15 min., then surrounding the aluminum block with Dry Ice for rapid cooling. The slowly cooled samples were prepared by the same technique initially but were allowed to cool from 120°C. with the aluminum block surrounded by its heating jacket (heating element disconnected) and insulating mantle thereby achieving a cooling rate of 0.2–0.3°C./min. to well below the glass transition region.

Quenched samples produced the normal T_g curve in every case and the slowly cooled samples produced a T_g curve with the added endothermal peak. This is illustrated with the PVC homopolymer Exon 965 in Figure 1 and the acetate copolymer Exon 487 in Figure 2. The difference in the total height of the endothermal peaks in the two cases is mainly due to the difference in sample weight required to fill the constant volume cell of the DTA apparatus. Similar results were obtained for plasticized PVC, as illustrated in Figure 3, with the homopolymer Geon 101EP plasticized with 20 phr butyl benzyl phthalate.

Effect of Cooling Rate on Height of Endothermal Peak

The DTA equipment used in this study had not been constructed to provide closely controlled cooling. However, a difference in the rate of slow
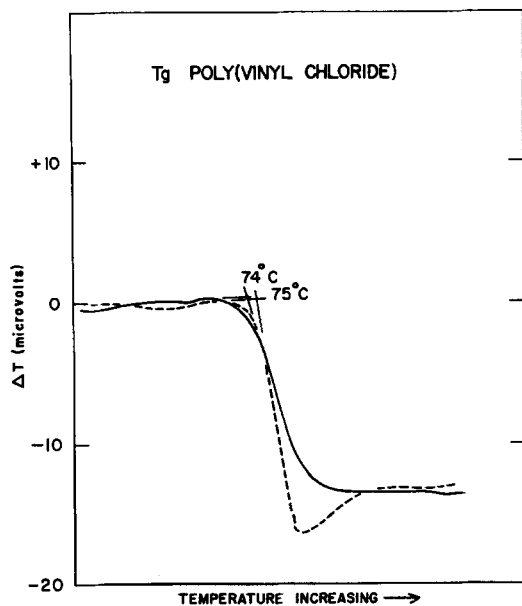
Fig. 1. DTA curves for PVC (Exon 965), illustrating annealing peak on T_g endotherm: (——) quenched; (– –) annealed. Sample weight 1.0 g.
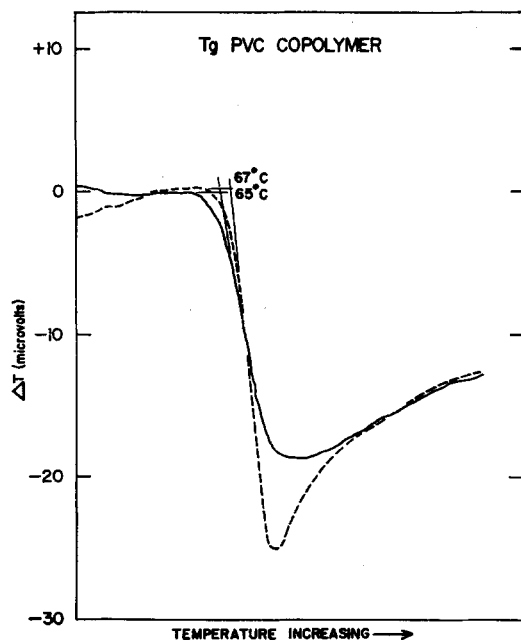

Fig. 2. DTA curves for PVC copolymer (Exon 487), illustrating annealing peak on T_g endotherm: (——) quenched; (– –) annealed. Sample weight 1.3 g.
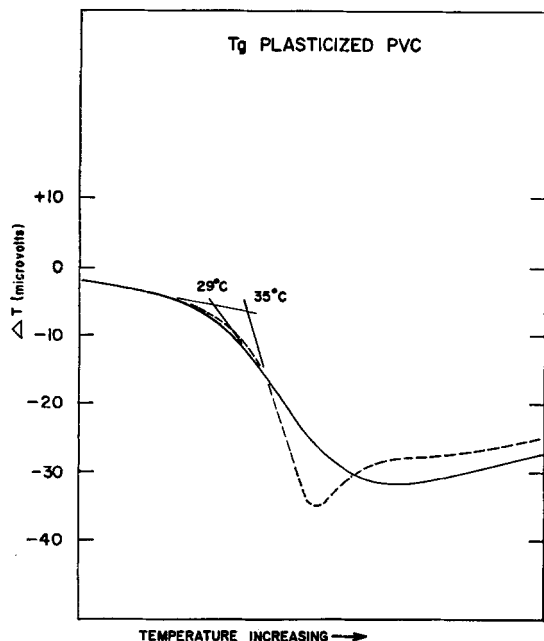
Fig. 3. DTA curves for plasticized PVC (Geon 101 E.P.), illustrating annealing peak on T_g endotherm: (———) quenched; (– –) annealed. 20 phr plasticizer, sample weight 1.3 g.

cooling was achieved by removal of the insulating jacket from the sample-containing aluminum block and it appeared that the depth of the endo-thermal peak developed was roughly inversely proportional to the rate of cooling. Such an investigation of the time versus temperature factors in cooling the polymer in the glass transition region was more easily performed in the differential scanning calorimeter (DSC). The results of a series of measurements on a single sample (27 mg.) of a 13% acetate PVC copolymer (Exon 487) are collected in Figure 4a. The initial curve is shown as a dashed line. In each case the rate of heating during the scanning was 20°C./min. and was maintained to 120°C. At that temperature cooling was initiated and maintained at the indicated rate. After the tempera-ture reached 0°C., another scanning curve was made. Each successive curve has been drawn on the chart by repositioning the baseline 0.2 in. The increasing depth of the peak as the cooling rate is decreased is clearly evident. It is obvious that whatever the phenomenon related to the forma-tion of the endothermal peak, it is highly dependent on and proportional to the rate of cooling through the glass transition region.

A similar analysis was made using 27 mg. of the PVC homopolymer Opalon 630, the results of which are shown in Figure 4b. At comparable cooling rates over the same temperature range the homopolymer appears to behave in a manner similar to that of the copolymer, except that the
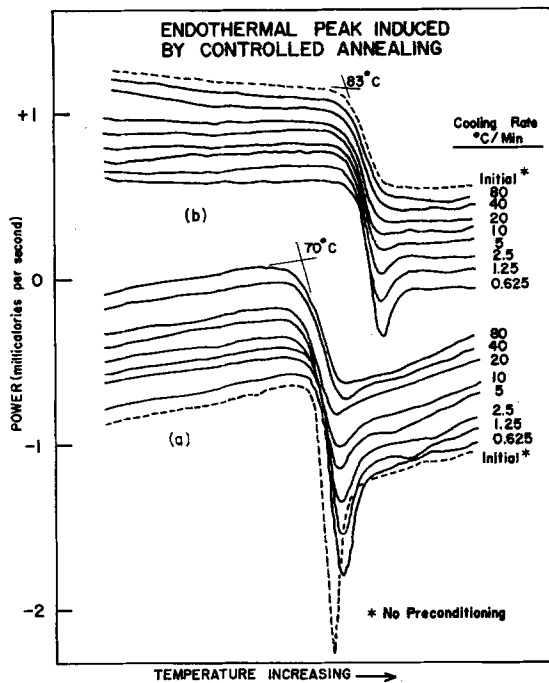
Fig. 4. DSC curves for (a) PVC copolymer (Exon 487) and (b) PVC (Opalon 630), showing effect of cooling rate on formation of endothermal peak at the glass transition. Sample weight 27 mg.

endothermal peak is smaller. In both cases the endothermal drop is sharper as the annealing time is increased (cooling rate decreased). This results in an increasingly higher indicated glass transition temperature as obtained by the extended-line-intercept technique. The magnitude of this increase in apparent T_g is approximately 5°C. for the copolymer Exon 487 and 3.5°C. for the homopolymer Opalon 630.

Constant-Temperature Annealing of PVC

In order to examine in more detail this process occurring on slow cooling and to determine the rate of the process, the DSC equipment was programmed to permit extended annealing times at specific temperatures below T_g. In each case the sample (10 mg.) was first heated above the glass transition to 120°C. to obtain the amorphous state, quenched to 0°C., and then brought to the specific temperature, thus maintaining the amorphous state at the start of each annealing cycle. After a given length of annealing time at this temperature the sample was again quenched, presumably preserving whatever state of crystallinity or physical orientation had been achieved. This sample was then scanned at the constant rate of 20°C./ min. to obtain the DSC curve. The procedure yields a family of curves at each temperature very similar to those of Figure 4.

Selection of data from the DSC curves involves choice. It is assumed that the physical orientation process involved is separate from and added to the glass transition process. Also it is assumed that in the nature of both DTA and DSC procedures, the energy state of the sample from experiment to experiment is more nearly identical following the glass transition (that is, in the rubbery state of the polymer) than in the glassy state in which the total energy includes that due to the variable amount of physically oriented material. Measurement of the area of the peak was rejected, since it involves both the selection of a baseline and the problem of the changing slope of the T_g endotherm. Consequently the added height of the peak measured from the baseline following the glass transition has been selected as a measure of this physical orientation process. These measurements of the height of the added peak above the final baseline are presented in Table I for both homopolymer and copolymer.

TABLE I
Height of Additional Peak on DSC Curve of Glass Transition for Annealed PVC

Time, hr.	Peak height, mm., at various annealing temperatures									
	Homopolymer Opalon 630						Copolymer Exon 487			
	55°C.	60°C.	65°C.	70°C.	75°C.	80°C.	50°C.	55°C.	60°C.	65°C.
1				3.6	12.6	12.4	1.4	2.2	12.9	17.9
2			1.0	8.9	16.0		1.9	6.4		23.1
4			4.7	16.0			2.0	14.0	25.0	28.9
12	2.6	9.2	19.4	27.1	30.6	9.0	20.1	32.7	42.4	28.7
24		15.0	29.2							
64	12.5				32.0			51.8		

These values of peak height plotted against time yield reasonably smooth curves apparently originating at zero time with no indication of an induction period. In the early portion of the process, the rate appears constant and can be represented by a straight line but soon drops off, perhaps due to exhaustion of available reaction species in the orientation area. Values of the peak height at 1 hr. were read from the straight-line portion of the curves and are used in the construction of Figure 5 plotted as log peak height versus $1/T$. The lines drawn through each set of values are nearly parallel. Calculation of the activation energy for this process of peak development from the data of Figure 5 at 1 hr. annealing time yields 43.6 kcal./mole for the copolymer and 47.8 kcal./mole for the homopolymer.

Initial inspection of the data of Table I indicates that the time to reach a given peak height is much longer at each temperature for the homopolymer than for the copolymer. However, the glass temperature of the homopolymer Opalon 630 is 82°C. and that of the copolymer Exon 487 is 67°C., a difference of 15°C. Assuming that the process involved is the same in each type of polymer and is characteristic of the PVC chain segments the time–temperature superposition principle should be applicable.

TABLE II
Application of Superposition Principle to Data for Rate of Peak Height Formation
During Annealing of PVC
(T_g Homopolymer 82°C., T_g Copolymer 67°C.)

Superposition temperature, °C.	Temperature of annealing, °C.		Measured peak heights (1 hr. annealing), mm.	
	Homopolymer	Copolymer	Homopolymer	Copolymer
$T_g - 17$	65	50	(1.1)[a]	1.4
$T_g - 12$	70	55	3.6	2.2
$T_g - 7$	75	60	12.6	12.9
$T_g - 2$	80	65	12.4	17.9

[a] Extrapolated.

The data of Table I for the peak height after 1 hr. annealing have been reassembled in accord with this principle in Table II. Thus at equal temperatures below the glass temperature of the polymer the rate of the process
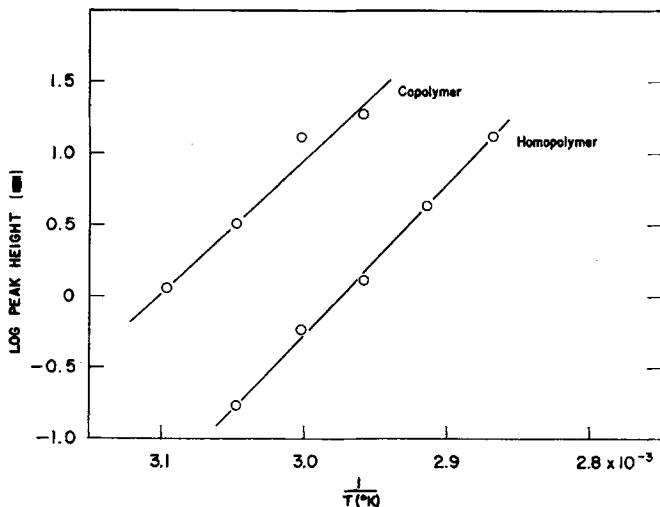

Fig. 5. Temperature dependence of the orientation process during annealing of PVC. DSC values of peak height at 1 hr.; copolymer Exon 487, Homopolymer Opalon 630.

that produces the endothermic peak is the same in homopolymer and copolymer.

DISCUSSION

The DTA curves for the annealed samples include the following differences from the DTA curves for the quenched samples: (*1*) there is greater energy absorption at the glass transition for the annealed sample; (*2*) the extra energy involved appears as an added peak more similar to first-order transitions than to the inflection type transition associated with the normal

glass transition; (3) if there is any change in location of the endotherm it moves to a higher temperature, generally by 2–5°C., with prolonged annealing times and higher annealing temperatures. These changes brought about by slow annealing are consistent with the concept of an increase in crystallinity. The amount of increase is extremely small, as indicated qualitatively in the DTA and DSC data and by the lack of x-ray evidence for crystallinity.

One structural arrangement consistent with the experimental evidence would be a local alignment of segments of chains similar to the suggestion by Reding et al.[8] On slow cooling (annealing) from the amorphous state, sections of the random chains slip into alignment with adjacent chains wherever there is a regular sequence of syndiotactic units on each of the adjacent chains. This represents the preferred equilibrium arrangement, but only those portions of the chains which have matching stereoregularity can align in such a manner as to form a crystalline orientation. In this view then, segments of many different chains having similar stereoregularity form areas of crystallinity in the solid, which, however, remains chiefly amorphous. In no case is a whole polymer molecule considered to be included in one area of regular chain segment alignment. On heating such a polymer, as the glass temperature is approached, more energy is required to release these aligned segments of each polymer chain from their regular and close orientation with respect to similar segments of unaligned polymer chains. This agrees with both the slightly higher T_g observed and the increased depth of the endotherm. The strong and alternate polarity of the stereoregular PVC chain supports this view and is probably the cause for the positioning of adjacent chain segments, with the repulsion of the atactic chlorine atoms interrupting the chain alignment. In the case of the copolymer the bulk of the acetate unit effectively interrupts the spatial alignment of the PVC chain units. Sabia and Eirich,[10] in discussing their analysis of the viscoelastic behavior of plasticized PVC as determined by stress relaxation and creep measurements, have used a similar picture of the participation of the individual chains in several crystalline areas which act as crosslinking points, and further state the "crystallites" are "obviously of very low order, and represent presumably areas of aligned chains."

The conclusion that the orientation process measured by DTA and DSC procedures is identical in homopolymer and copolymer is based on the similarity in development of the annealing peak on the T_g endotherm, the near equality of the activation energy calculated from the rates of the annealing process, and finally from the fact that application of the time–temperature-superposition principle yields identical rates at equal temperatures below the glass transition. It is assumed that the process involves stereoregular chain sequences of the PVC backbone, and it is deduced that the average length of segment in the oriented area is less than the average chain length separating acetate units in the 13% acetate copolymer.

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Résumé

On a observé une différence dans les courbes DTA et DSC de la transition vitreuse à la fois d'un homopolymère de chlorure de polyvinyle et d'un copolymère d'acétate dépendant de la vitesse de refroidissement ou de recuit en-dessous de la température de transition vitreuse. La différence apparaît comme un pic endotherme additionnel à la courbe de transition vitreuse et elle est attribuée à l'alignement des segments de chaînes stéréoréguliers des molécules polymériques adjacentes. Les longueurs des segments de chaîne sont supposées être tellement courtes qu'il n'y a pas eu moyen d'obtenir d'évidence cristalline par rayons-X. Le processus d'orientation comportait une énergie d'activation de 47.8 Kcal/mole dans l'homopolymère et de 43.6 Kcal/mole dans le copolymère. La vitesse mesurée de ce processus est en accord avec le principe de superposition temps–température avec des vitesses devenant égales pour l'homopolymère et le copolymère à des températures équivalentes en-dessous des températures de transition vitreuse des substances considérées.

Zusammenfassung

Ein von der Abschreckgeschwindigkeit oder der Temperung unterhalb der Glasumwandlungstemperatur abhängiger Unterschied in den DTA- und DSC-Kurven für die Glasumwandlung von PVC und PVC-Acetatcopolymeren wurde festgestellt. Dieser Unterschied tritt als endothermes Maximum zusätzlich zur Glasumwandlungskurve in Erscheinung und wird auf eine Parallellagerung stereoregulärer Kettensegmente von benachbarten Polymermolekülen zurückgeführt. Es wird angenommen, dass die Länge der Kettensegmente so gering ist, dass kein Röntgennachweis einer Kristallinität erhalten wurde. Der auftretende Orientierungsprozess besitzt eine Aktivierungsenergie von 47,8 kcal/Mol im Homopolymeren und von 43,6 kcal/Mol im Copolymeren. Die gemessene Geschwindigkeit des Prozesses stimmt mit dem Zeit–Temperatur-Superpositionsprinzip überein, wobei die Geschwindigkeiten für Homopolymeres und Copolymeres bei Temperaturen gleich weit unterhalb ihrer Glasumwandlungstemperatur gleich werden.