Quantitative Study of the Annealing of Poly(vinyl Chloride) near the Glass Transition

CARL R. FOLTZ and PAUL V. McKINNEY,* *Armstrong Cork Company, Lancaster, Pennsylvania 17604*

Synopsis

Poly(vinyl chloride) displays a normal DSC or DTA curve for the glass transition when quenched from above its T_g. However if cooled slowly or annealed near the glass transition temperature, a peak appears on the DSC or DTA curve at the T_g. In this paper quantitative studies of the time and temperature effects on the production of this endothermal peak during the annealing of PVC homopolymer and an acetate copolymer are presented. The phenomenon conforms to the Williams, Landell, and Ferry equation for the relaxation of polymer chains, the rate of the peak formation becoming negligible at more than 50°C below T_g. The energy difference between the quenched and annealed forms is small. For a PVC homopolymer annealed 2 hr at 68°C, which is $T_g - 10$°C, the difference is 0.25 cal/g. For a 13% acetate copolymer of PVC similarly annealed, the difference is 0.36 cal/g. The measured rates of the process give a calculated activation energy of 13–14 kcal/mole for PVC homopolymer and copolymer. This appearance of a peak on the T_g curve for a polymer when annealed near the glass temperature appears to be a general phenomenon.

INTRODUCTION

In an earlier publication[1] it was noted that commercial poly(vinyl chloride) homopolymers have normal glass transition curves but that the T_g curves for commercial acetate–PVC copolymers were irregular, having an additional endothermal peak at the end of the transition. It was also noted that by proper conditioning both homopolymer and copolymer could be made to exhibit either type of glass transition curve. In these early studies, variations in conditioning were made by changing the rate of cooling from the amorphous rubbery state through the glass transition to room temperature. Wunderlich et al.[2] made such a cooling rate study of the glass transition of polystyrene and include an extensive analysis of theory. In a more detailed study of the PVC glass transition,[3] the time duration of annealing at selected temperatures near T_g was varied and it was concluded that the difference between the behavior of the homopolymer and copolymer was related to their glass temperatures. It was noted that at equal temperatures below T_g the initial rates of the production of the endothermal peak on the T_g transition curves were approximately equal. In the present study this annealing process near the glass transition temperature has been examined quantitatively employing a modified DSC procedure.[4]

* Present address: 620 Great Road, Princeton, New Jersey 08540.

EQUIPMENT AND PROCEDURE

The equipment used in the annealing study is the Perkin-Elmer Differential Scanning Calorimeter (DSC-1) described by Watson and others[5] and O'Neill.[6] The procedure has been modified as previously noted[4] by using the amorphous quenched state of the polymer as the reference material and the annealed specimen as the sample.   Thus difference in energy absorption between the annealed and amorphous phases during scanning is transcribed directly by the instrument.   All scanning rates were 20°C per min and the DSC instrument was calibrated with indium and with the recrystallization transition of NH_4SCN for the temperature scale and for peak area measurement.[7] Specimen containers, pans, and lids were matched by weight to achieve the proper heat capacity balance.   Specimens were weighed to 20.00 ± 0.01 mg.   Quenching was achieved by application of an air stream onto the specimen containers.   In each individual run, both sample and reference specimens were heated above the T_g to 120°C and quenched to "freeze in" as nearly identical molecular configuration as possible prior to each investigation.   Presumably this represents the completely amorphous phase of the PVC polymer.   The quenched reference material was removed from the DSC instrument and maintained at room temperature while the test specimen was annealed.   Such annealing was initiated by bringing the test specimen rapidly to the desired annealing temperature where it was maintained for a selected annealing time.   At the end of this annealing period the test specimen was quenched to room temperature, the quenched reference was reinstalled in the reference holder, and the scanning thermogram was obtained.   Annealing temperatures ranged from 10°C above the polymer T_g to approximately room temperature in 5°C intervals.   Annealing times ranged from 1 min to 16 hr with a few longer studies.   Following each test scan, both reference and test specimens were quenched to room temperature and rescanned to 120°C.   This produced the nearly straight quench-versus-quench thermogram which provided the baseline for determination of peak area.

The materials investigated included a commercial PVC homopolymer (Opalon 630, Monsanto Chemical Company) and a 13% acetate copolymer (Exon 487, Firestone Plastics Company).   (Opalon 630: $\eta_{sp} = 0.38$, $[\eta] = 0.84$; $\bar{M}_w = 75{,}900$, $\bar{M}_w/\bar{M}_n = 2.02$; Exon 487: $\eta_{sp} = 0.21$, $[\eta] = 0.50$; $\bar{M}_w = 41{,}400$, $\bar{M}_w/\bar{M}_n = 2.75$ [η_{sp} at 30°C, 0.4 g/100 ml, cyclohexanone]).   These materials were investigated in the original powder form as received from the manufacturer.   Infrared analysis confirmed the absence of plasticizer or other additives.

EXPERIMENTAL RESULTS

The effect of time on the rate of transformation for the homopolymer annealed at 73°C, which is 5°C below its T_g, is illustrated in Figure 1 and that for the copolymer annealed at 53°C, 15°C below T_g, is shown in Figure 2.   The energy value equivalent to the peak area is shown with each
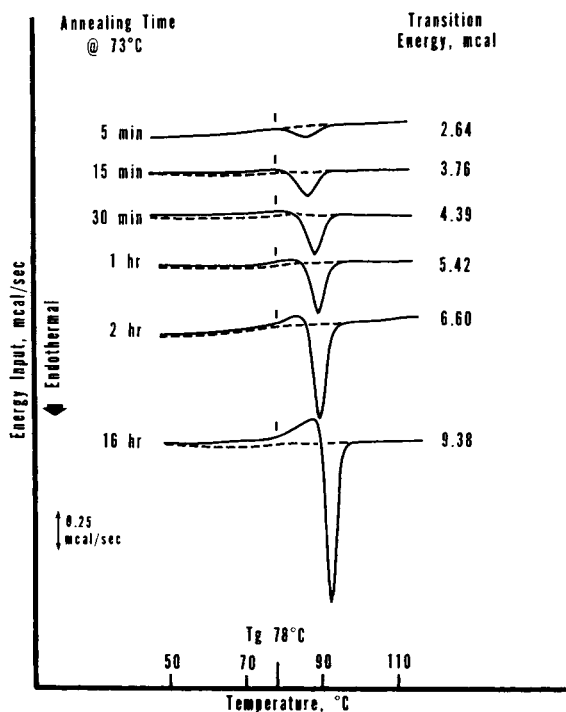
PVC HOMOPOLYMER

Fig. 1. Effect of annealing time on peak formation at 5°C below T_g for PVC homopolymer (Opalon 630): modified DSC procedure; scanning at 20°C/min, 20-mg sample; - - - baseline from quench-vs.-quench specimens.

TABLE I
Annealing Study of PVC[a]

Annealing time	Peak area, mcal[b]								
	48°C	53°C	58°C	63°C	68°C	73°C	78°C	83°C	88°C
2 min						1.75	1.57		
5					1.59	2.64	2.25		
10				1.48	1.96	3.32	2.76	1.44	
15			1.31	1.66	2.58	3.76			
30		1.42	1.83	2.15	3.36	4.39	4.18		0
1 hr	1.25	1.72	2.15	2.76	4.39	5.42	4.95	3.60	
2	1.81	2.15	2.84	3.52	5.01	6.60	5.35		
4	1.92								
7.3		2.88							
14					6.34				
16	2.88						9.38		
2.7 days					9.97				

[a] Opalon 630, T_g 78°C, 20-mg sample.
[b] At specified annealing temperatures.

thermogram. In each case the measured area of the peak increased with increased annealing time. Data at other temperatures from room temperature to 10° above T_g are listed in Tables I and II, along with the specific data used in the figures. At equal temperatures below the T_g, the peak area is greater for the copolymer than for the homopolymer for corresponding periods of annealing.

The effect of temperature on the rate of transformation after 2 hr of annealing is shown for a PVC homopolymer in Figure 3 and for the copolymer after 15.5 hr of annealing in Figure 4. The area of the peak increased
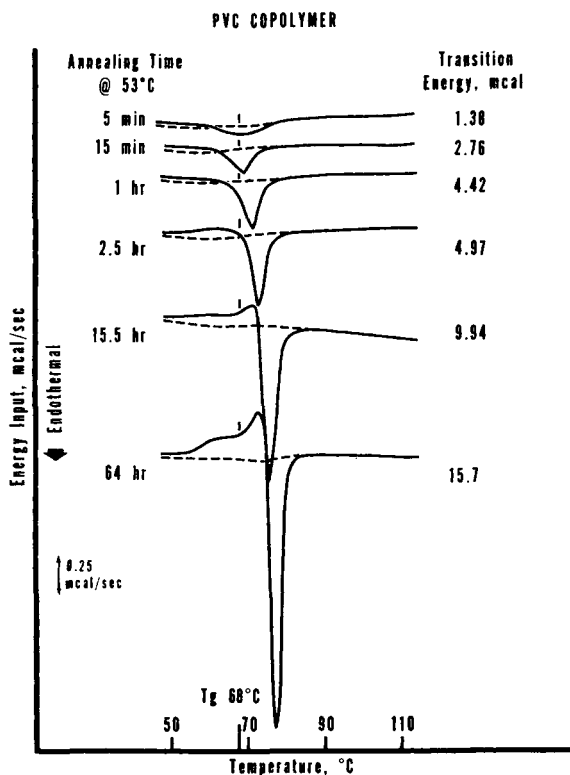

Fig. 2. Effect of annealing time on peak formation at 15° below T_g for PVC copolymer (Exon 487): modified DSC procedure; scanning at 20°C/min, 20-mg sample; - - - baseline from quench-vs.-quench specimens.

with the temperature from the lowest temperature investigated through 5° below T_g but decreased at T_g and above. With each resin annealed at the T_g temperature, there was an appreciable peak area indicating that all of the polymer does not remain amorphous at the conventionally designated T_g. The decrease in peak area continued above T_g, and at 10° above no peak area was measured for either polymer after 30 min annealing. Similar data can be obtained from conventional DSC thermograms by superimposing thermograms for quenched and annealed specimens.
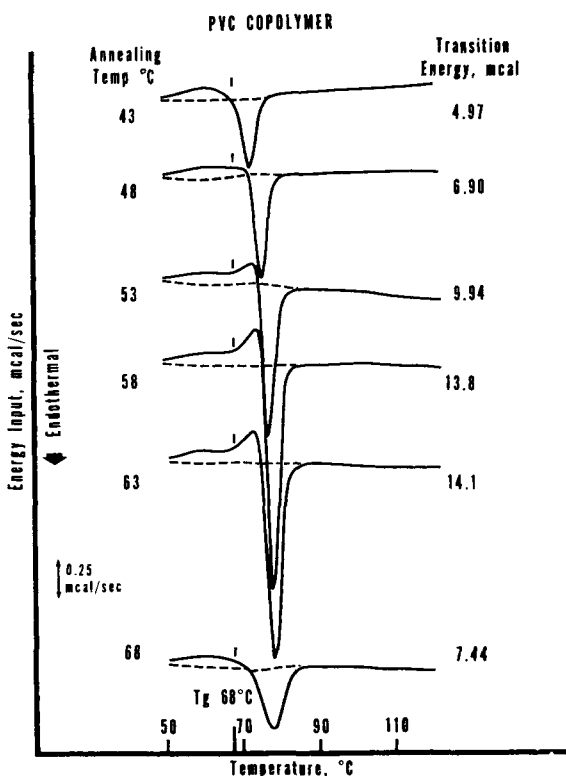
Fig. 3. Temperature effect on 2 hr annealing of PVC homopolymer (Opalon 630): modified DSC procedure; scanning at 20°C/min, 20-mg sample; - - -baseline from quench-vs.-quench specimens.

TABLE II
Annealing Study of PVC Copolymer[a]

Annealing time	Peak area, mcal[b]								
	24°C	43°C	48°C	53°C	58°C	63°C	68°C	73°C	78°C
1 min						1.38	1.65	1.38	
2					1.38	2.48	3.04		
5			1.38	1.38	2.76	3.58	4.14		
10			1.66	2.48	3.30	4.42	4.97		
15			1.95	2.76	3.86	5.24	5.24		
30		1.36	2.48	3.31	5.24	6.90	5.52		0
1 hr		1.93	3.04	4.42	6.07	7.73	6.21		
2		2.48	3.86	4.98	7.17	9.10	6.68		
2.5		3.32		4.97	7.73		6.90		
15.5		4.97	6.90	9.94	13.8	14.1	7.44	2.21	
2.7 days				15.7					
3.6		8.27							
8.9	3.68								
74.3	6.04								

[a] Exon 487, T_g 68°C, 20-mg sample.
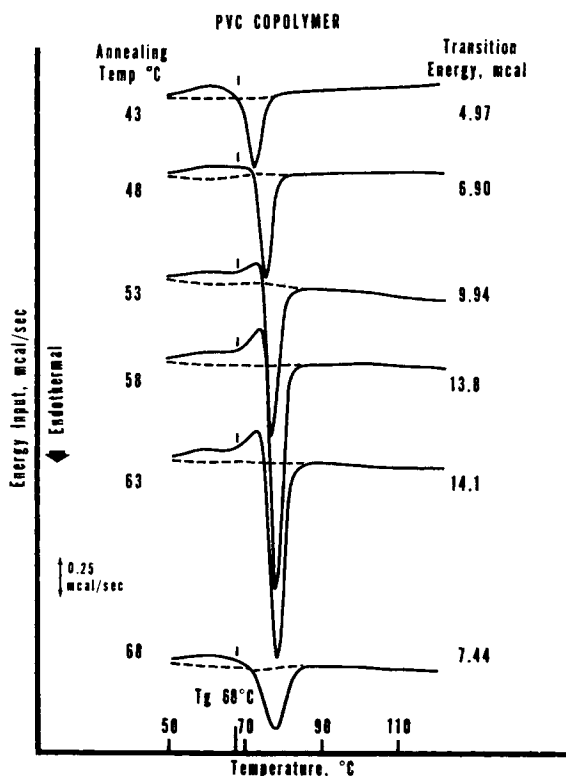[b] At specified annealing temperatures.

Fig. 4. Temperature effect on 15.5 hr annealing of PVC copolymer (Exon 487): modified DSC procedure; scanning at 20°C/min, 20-mg sample; - - - baseline from quench-vs.-quench specimens.

However, at the short time periods there is only an inflection on the T_g curve and no peaks are indicated.

DISCUSSION

The glass transition temperature usually is determined arbitrarily as the temperature at the intersection of straight lines defining the measured function below the transition and the line of greatest change at the transition. As a point of reference, the T_g for each *quenched* PVC polymer is shown on the scanning curves in Figures 1 to 4. From inspection it is obvious that the "transition temperature" for the annealed specimens, determined in the same manner or determined as the location of the peak as is done for first-order transitions, increased as the extent of annealing increased either by longer time or increased temperature. At short annealing times and lower temperatures, these "transition temperatures" are well below the T_g of the polymer. Such a variation would seem to indicate differences in the nature of the molecular structure or aggregates involved in

the annealing process, probably a great variety of chance groupings of chain ends and lengths of chains between entanglements.   Wunderlich et al.,[2] in a study of polystyrene by "Dynamic" DTA in which annealing was achieved by a controlled rate of cooling, concluded that "there exists a hole-size distribution characterized by different activation energies and relaxation-time spectra."

Quantitatively, the degree of annealing which has occurred in any time period at T_g and at equal temperatures below T_g as measured by the transition energy is greater in the case of the copolymer than for the homopolymer.   This suggests a less compacted entanglement structure with more
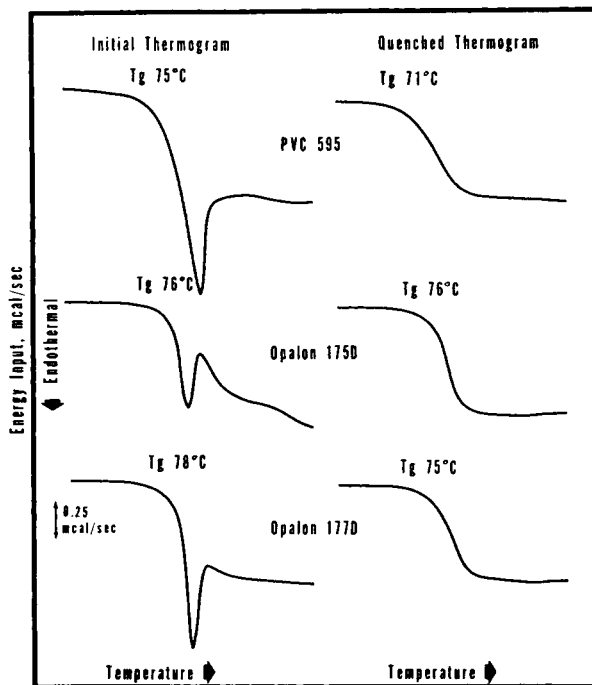

Fig. 5. Experimental low molecular weight PVC homopolymers.   PVC-595 is recent preparation.   Opalon 175D and 177D in storage since 1958:   thermograms are conventional DSC scans at 20°C/min on 20-mg specimens.

freedom of movement of polymer chains or segments of chains in the copolymer.   Since the DSC values with a calibrated instrument are proportional to specimen heat capacity, the specific heat differences between the annealed and quenched polymers have been calculated.   They will be reported separately.   In the present connection it is sufficient to note that a small difference in specific heat exists between the two forms below T_g in both PVC and the copolymer, the specific heat of the annealed specimen being less than that of the quenched specimen.   One would expect similar differences in all other physical properties affected by change in free volume.

A recent reference[8] reports such measurements on annealed forms of rigid PVC.

A small but consistent irregularity related to this difference in specific heat appears as a slight exothermic rise prior to each peak in the thermograms of Figures 1 to 4. In conventional DTA or DSC scanning procedures, the T_g inflection occurs at a temperature a few degrees higher in the annealed form than in the quenched form, as may be seen in Figure 5 and in references 3 and 4. Consequently, in the present modified DSC procedure, at each temperature just prior to the T_g the quenched specimen in the reference position absorbs more energy than the annealed specimen and the resulting thermogram indicates that the annealed specimen is apparently exothermic by that amount.

Relation of Annealing to Stress Relaxation Time

The rapid decrease in the rate of annealing below T_g for both homopolymer and copolymer suggested a parallel to the phenomenon of molecular relaxation of polymer chains expressed in the Williams, Landel, and Ferry equation. According to the analysis of this equation by Gordon,[9] all appreciable change should have disappeared at approximately 50°C below the glass transition. For the polymers under examination, $T_g - 50°C$ becomes 28°C for the homopolymer and 18°C for the copolymer. Since room temperature is about 24°C, it is evident that after manufacture the homopolymer can be expected to remain stable in the amorphous form. On the other hand, during room temperature storage the copolymer would slowly anneal to the more stable form even though completely amorphous at the time of manufacture, since the storage temperature is only 45°C below the glass temperature. This is the result obtained experimentally with commercial PVC polymers and copolymers.

On this basis attempts were made to obtain samples of homopolymer with T_g less than 50°C above room temperature. An experimental sample of low molecular weight PVC homopolymer, PVC-595, was prepared for us by R. A. Park of the Firestone Plastics Company, Chemical Division (Pottstown, Pennsylvania).

Also two samples of experimental low molecular weight PVC homopolymer, X61-175D and X61-177D, which had been retained in storage since

TABLE III
Physical Properties of Experimental Materials

Material[a]	η_{sp} (30°C, c = 0.4) cyclohexanone	$[\eta]$	T_g, °C initial	quenched
PVC-595	0.167	0.395	75	71
X61-175D	0.235	0.540	76	76
X61-177D	0.233	0.540	78	75

[a] Experimental samples.

1958, were made available by C. W. Bulkley of the Monsanto Company Technical Service, Plastics Division (Springfield, Mass.).   Physical properties of all three are listed in Table III.   The experimental homopolymer PVC-595, with a T_g of 71°C, had an initial DSC scanning curve with an endothermal peak as predicted (Fig. 5).   The quenched scanning curve is normal with no such peak.   The two PVC polymers X61-175D and X61-177D, which have a T_g very close to that of the homopolymer used in the present investigation, also have initial scanning thermograms with an endothermal peak.   These samples have had ten years of "annealing" during room temperature storage, giving a remarkable demonstration that stress relaxation of the polymer molecule and the annealing process are continuous phenomena with no time limit.   The fact that these aged samples display normal "no peak" T_g thermograms after heating above the glass temperature and quenching appears to rule out oxidation or other chemical changes as factors in the formation of the endothermal peak.

Activation Energy

The temperature dependence of the rate of the annealing process near the glass transition has been determined by calculation of the Arrhenius-type activation energy of the annealing process from the data of Tables I and II. In both homopolymer and copolymer, the slope of the lines for all times from 10 min to 2 hr were nearly parallel.   The charts for the 1-hr values are
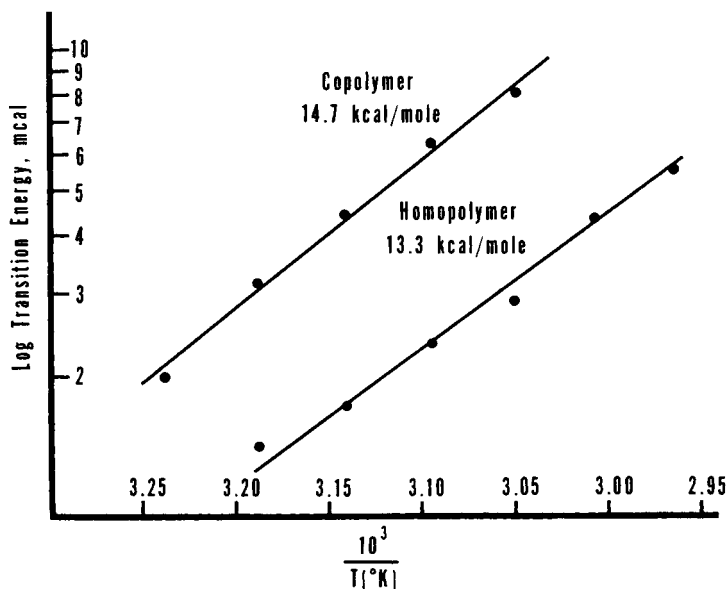

Fig. 6. Transition energy (peak area) after 1 hr annealing for PVC homopolymer (Opalon 630) and PVC copolymer (Exon 487):   Activation energy calculated from slope of line.

shown in Figure 6. The activation energies for the several annealing periods are tabulated in Table IV.

The activation energy appears essentially independent of annealing time and approximately equal for homopolymer and copolymer within the probable accuracy of the method. This equality of activation energies suggests that the same process occurs in the two polymers during annealing. Perhaps the temperature-dependent step is the rotation of the carbon-to-carbon bond in the chain backbone which allows coiling, chain slippage, and other molecular orientation during annealing.

All the amorphous and semicrystalline polymers that have been examined in this laboratory after annealing near the glass temperature have shown this phenomenon of a peak on the T_g curve measured either by DTA or DSC. These include, in addition to PVC, polystyrene,[7,8] polycarbonate,[10] polymethyl methacrylate, polyethylene terephthalate,[11] and polyvinyl acetate. The reference numbers in this paragraph designate

TABLE IV
Calculated Activation Energy for Several Periods of Annealing Time

Annealing time, min	Activation energy, kcal/mole	
	homopolymer	copolymer
10	14.1	15.4
15	13.7	15.4
30	13.5	14.8
60	13.3	14.7
120	13.5	13.4
150	—	13.4

those polymers for which published data found in the literature also show such an endothermal peak on the T_g curve. Similar inflections on the T_g curves for natural and synthetic rubbers are discussed by Mauer.[12] It is concluded that this is a general phenomenon. Polymers, when cooled from the rubbery state above the glass transition, do not have sufficient time to coil, physically orient, or simply untangle to reach an equilibrium condition. They exist in a state in which there is an excess of free volume. If these polymers are maintained at a temperature less than 50°C below their T_g, an orientation (relaxation) occurs which is temperature and time dependent and results in a polymer of slightly changed physical properties, such as lower specific heat and greater specific gravity.

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