Heat Capacity and Thermodynamic Properties of Poly(Vinyl Chloride)

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Heat capacities, C_p, of three different samples of poly(vinyl chloride), PVC, have been determined from 6 to 375 K by adiabatic calorimetry. These three samples were derived from either bulk- or suspension-polymerization processes and were measured either as received or after pelleting under pressure. The heat capacities of the samples are almost identical if the thermal and pressure histories are the same. Below the glass transition temperature, T_g, of about 355 K, C_p of PVC was found to be exceptionally linear over a wide temperature range. C_p of annealed PVC may be represented by $(10 + 0.166\,T)$ J K^{-1} mol^{-1} to within 1 percent of the measured values from 80 to 340 K. Approximately 200 J mol^{-1} of energy were stored in the samples by the pelleting processes. The stored energies begin to release at about 30 to 40 K below the glass transition temperature. T_g for powdery or relaxed samples occurs around 352 to 356 K for the suspension-polymerized PVC sample and 348 to 351 K for bulk-polymerized sample.

Key words: Calorimetry; enthalpy relaxation; glass transition; heat capacity; polymer; poly(vinyl chloride); pressure effects; thermodynamic properties.

1. Introduction

Poly(vinyl chloride), PVC, is one of the most important and widely used polymers. Of all the thermoplastics, its production is second only to that of polyethylene. Heat capacity behaviors of PVC have been reported in more than twenty papers. Most of the papers prior to 1968 were collected in a review article [1],[1] others may be found among references [2–22]. Except references [2–5], all others reported their results in graphical representation only. Reference [2] gave a table of smoothed values at 25 K intervals derived from measurements conducted between 60 and 300 K. Reference [3] used linear equations for the temperature range between 250 and 330 K. References [4–5] reported mean values over wide temperature regions.

The agreement among different investigations is usually very poor. This poor agreement is often attributed to the differences in the samples studied rather than the differences in the experimental techniques and practices employed by different laboratories. It is the purpose of this work to establish more representative thermodynamic properties on this industrially important polymeric material.

Three PVC samples were studied in this work by precision adiabatic calorimetry. These samples include one sample consisting of suspension polymerized PVC and two samples consisting of bulk-polymerized PVC.

The suspension polymerized PVC sample contained a small amount of poly(vinyl alcohol) as the suspension agent, which was incorporated on the surface of the PVC granules. A chemically purer PVC sample made by bulk-polymerization process was also studied. Both samples were pressed into pellets before the measurement. The heat capacity behaviors

of these two samples are essentially the same if their thermal and mechanical histories are similar. Both pelleted samples showed phenomena associated with the release of the stored mechanical energy when compared with a third sample which consisted of unpelleted bulk-polymerized PVC powder.

2. Experimental Detail

2.1. Calorimetric Technique

Heat capacities of PVC samples were measured in a vacuum adiabatic calorimeter described previously [23]. The heat capacity of the suspension polymerized sample was measured manually, whereas those of the two bulk-polymerized samples were measured automatically. A minicomputer was used for both data acquisition and experimental control. Both temperature and energy were measured using a double six-dial potentiometer, which had been converted from manual into programmable mode of operation [24]. Although the intermittent heating method is used, continuous calorimetric measurements over a prolonged period may be made without being interrupted thus avoiding modification of sample thermal history. The minicomputer was also used to decide when a steady state of temperature uniformity throughout the sample was reached, and then to adjust and apply a measured amount of energy to the sample as required. Detailed description of the automated calorimeter measurement system and the measuring procedures is given elsewhere [25].

2.2. Materials

Three calorimetric samples of PVC have been studied in this work.

Sample S:—This sample consisted of pellets made by pressing a commercially available suspension-polymerized

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[1] Figures in brackets indicate the literature references at the end of this paper.

powder. The powder was supplied to us by Edward A. Collins of the B. F. Goodrich Chemical Corporation with the designation Geon 103EP.[2] Its number-, viscosity-, weight- and z-average molecular weights M_n: M_v: M_w: M_z = 64300: 129000: 142000: 254000 were obtained by gel-permeation chromatography in tetrahydrofuran at 40 °C. The intrinsic viscosity $[\eta]$ is 0.91 dL g^{-1} in cyclohexane at 30 °C. The sample has been used for the ASTM D20-70-04 round robin program. The pellets, about 1.27 cm diam and 1 cm height, were produced in a pellet-mold in a hydraulic press at room temperature with a pressure of about 500 MPa. This sample contained about 0.03 percent of poly(vinyl alcohol).

Sample B:— This sample was obtained by pelleting a powder bulk-polymerized sample. The powder was supplied to us by Marvin R. Frederick of the B. F. Goodrich Company. It bears the designation Geon 80X5 and has an intrinsic viscosity of about 0.75 dL g^{-1} and M_w of 80,500 measured by gel-permeation chromatography. A pelleting pressure, just enough to press the powder into pellet, of about 140 MPa was used.

Pelleting of powdery samples is often employed in calorimetry to facilitate the thermal conduction through contacts and to reduce the adsorption of heat conducting helium gas at lower temperatures, thereby reducing the time required for the establishment of thermal equilibrium.

Sample P:— This is the starting material for sample B, the original bulk-polymerized sample in the powder form as received.

Neither bulk- and suspension-polymerized samples contain additives other than that mentioned for sample S and have been pumped in vacuum to remove unreacted monomers.

In each of the sample loadings, the sample container was cooled with a water jacket while the top was sealed with 50:50 indium-tin solder, so that the thermal history of the samples would not be altered before the calorimetric measurement. Helium gas, at a pressure of about 4 kPa and a mass equal to that used when the heat capacity of the empty sample container was measured, was sealed with the pelleted samples S and B. Approximately 50 kPa pressure of helium gas was sealed with the powder sample P. Summary of the calorimetric samples is listed in table 1.

TABLE 1. *Summary of PVC samples*

Designa-tion	Polymeriza-tion	Form	Pelleting pressure, MPa	Sample mass, g	P_{He} at 295 K kPa
S	Suspension	Pellet	500	66.337	3.8
B	Bulk	Pellet	140	55.659	4.0
P	Bulk	Powder	—	75.59	49.3

3. Results and Discussion

Heat capacity data for PVC suspension-polymerized pellet (S), bulk-polymerized pellet (B) and bulk-polymerized powder (P) are listed chronologically in table 2 and shown in figure 1. The second character of the two-character code

denotes the history of the sample, i.e., 1, 2, A, and Q represent first heating, second heating, annealed and quenched, respectively. The quenching rate applied was about 5 K min^{-1}. Annealing was accomplished either by slow cooling (rate annealing) or by holding the sample at a temperature (soak annealing) about 10 to 20 K below the glass transition temperature of the quenched sample.

Interruptions in the manual heat capacity measurement process are noted by the blanks which separate the data for sample S in table 2. Heat capacities of both bulk-polymerized samples B and P were measured with an automated measurement system controlled by a minicomputer. Thus continuous measurements on samples B and P were extended over a wide temperature range and for a prolonged period.

In determining the temperature increment due to an energy input, the drift due to non-adiabaticity of the calorimetric system and that due to the configurational relaxation in the glass transition region are combined. Therefore, the heat capacity values listed in table 2 represent that of a glass with its configurations fixed at mid-point of the energy input period and do not contain the long term time effects such as the relaxation process of the glass transition phenomena.

The thermodynamic properties of PVC from 10 to 380 K are presented in table 3. These are calculated from the data of BA as listed in table 2. Throughout this paper, the superscripts for the symbols denote the states of the material, e.g., A and L represent annealed glass and liquid respectively. Specific temperatures are denoted by the subscripts.

Gibbs free energies, $G - H_0$, are not listed in table 3. Since the residual entropies of these glassy PVC samples are not determined, the combination of the enthalpy and entropy increments from $T = 0$ K could only yield

$$G - H_0 + TS_0 = H - H_0 - T(S - S_0).$$

However, approximate values of $G - H_0$ may be estimated by assuming a residual entropy of R ln 2 for PVC [26]. At 298.15 K the term TS_0 is more than 10 percent of either quantity, $G - H_0$ or experimentally determinable $H - H_0 - T(S - S_0)$.

Heat capacity data of all three samples in the glassy state are compared against the smoothed values of annealed bulk-polymerized pellet, BA, in figure 2. Between 50 and 250 K, regardless of the differences in the origins of the samples and their thermal histories, heat capacity values are within 0.2 percent of each other. Above 250 K the heat capacities of quenched samples begin to deviate from that of the annealed samples, increasing to about 1·percent higher at 340 K. However, heat capacities of different samples with similar thermal history remain within an envelope of about 0.2 percent.

It has been noted that heat capacities in the glassy state are relatively insensitive to physical, chemical and configurational changes [26]. In general these changes produce less than 1 percent change in the heat capacity. Typical examples may be found by comparing the results from polystyrene samples of different tacticities and sources [27], and cis-1,4-polyisoprene samples containing varied amounts of antioxidant and stabilizer [28] and from different sources [29].

Greater differences are to be expected from highly plasticized samples and crystallizable samples, especially if there is a large change in the densities of the samples, such as polyethylene [30] and polytrichlorofluoroethylene [30a]. Near T_g, the relative percentage change in the heat capacity is
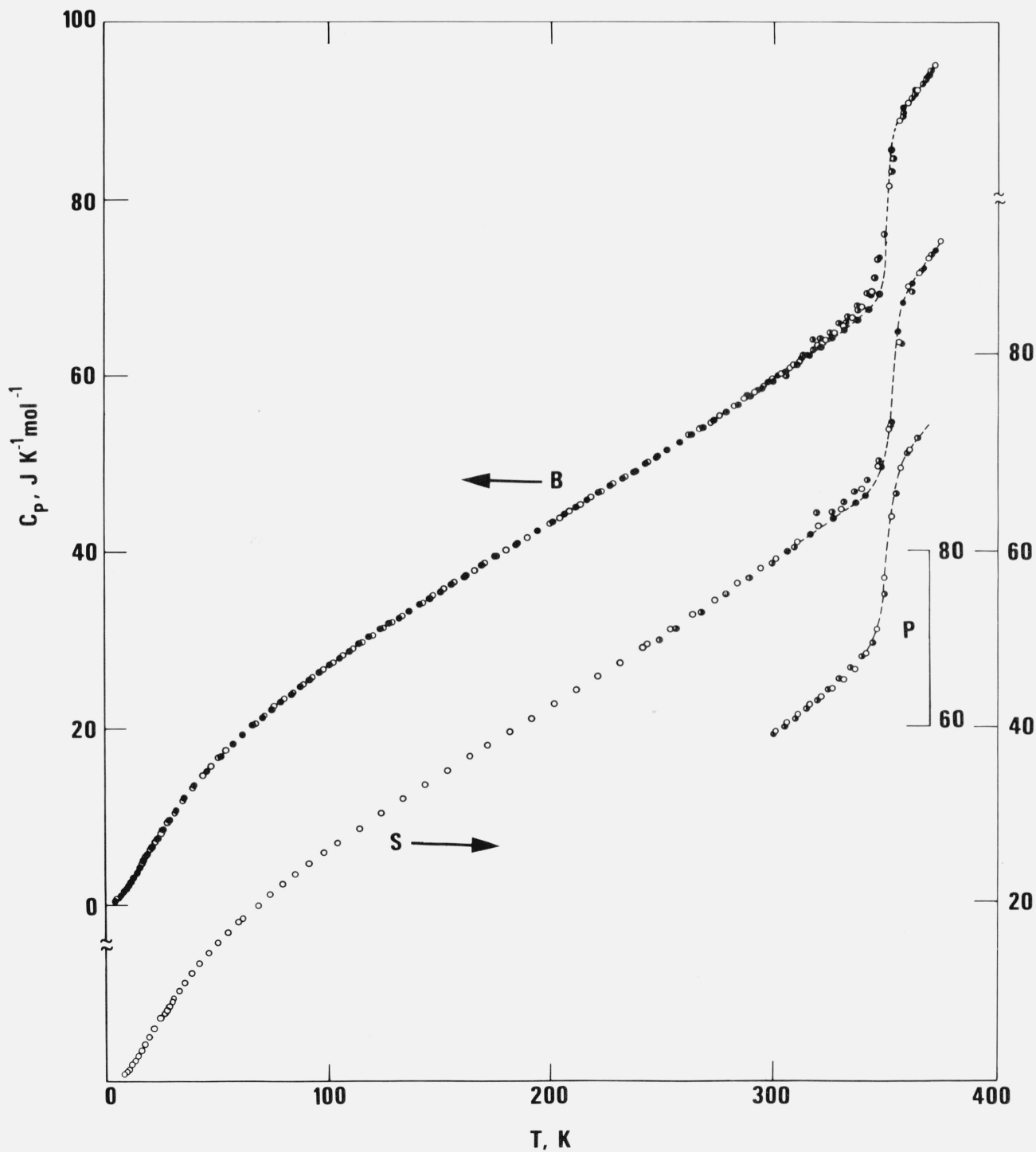
FIGURE 1. *Heat capacities of poly(vinyl chloride).*
◑ First heating (1), ○ Quenched (Q), ● Annealed (A), B Bulk-polymerized, pelleted; P Bulk-polymerized, powder; S suspension-polymerized, pelleted. Inserted C_p scale applied to P only.

TABLE 2. *Heat capacity data of poly(vinyl chloride)*

(—CH$_2$CHCl— = 62.499)

T, K	C$_P$, J K^{-1}mol^{-1}	T, K	C$_p$, J K^{-1}mol^{-1}
A. Suspension polymerized, pellet (S)			
Series I.	As Received (S1)		
248.82	50.43	41.53	13.833
256.02	51.60	45.57	15.020
267.83	53.57	49.70	16.171
278.81	55.51	54.02	17.304
289.22	57.28	58.94	18.511
299.68	59.17		
		8.00	1.148
309.48	60.98	9.12	1.500
319.38	64.78	10.18	1.874
326.85	64.95	11.24	2.268
331.79	66.19	12.54	2.778
336.83	67.33	13.95	3.337
342.01	68.73	15.44	3.962
347.28	70.97	17.11	4.675
352.46	74.79	19.03	5.501
357.47	84.21	21.28	6.453
362.14	90.05	23.82	7.528
366.63	92.43	26.40	8.559
371.03	94.07	28.88	9.502
Series II.	Quenched (SQ)		
		243.02	49.85
60.76	18.937	253.60	51.62
67.58	20.461	263.74	53.27
73.29	21.667	273.94	54.99
78.81	22.768	283.96	56.73
84.58	23.921	293.93	58.45
90.76	25.102		
97.36	26.315	301.06	59.66
		310.74	61.53
103.49	27.408	320.48	63.32
113.51	29.159	330.16	65.32
123.29	30.83	339.69	67.60
133.17	32.39	346.86	70.21
143.19	34.06	351.65	74.50
153.39	35.67	356.31	84.26
163.53	37.28	360.87	90.60
171.07	38.47	365.39	92.21
		369.95	93.88
181.24	40.05	374.74	95.76
191.16	41.62	Series III.	Annealed (SA)
201.12	43.12	306.46	60.45
211.10	44.69	316.84	62.30
221.01	46.25	327.04	64.20
230.96	47.85	337.05	66.29
241.06	49.53		
24.28	7.700	341.49	67.23
25.59	8.231	348.91	70.12
27.36	8.926	352.84	75.06
29.54	9.755	355.50	86.55
32.09	10.704	358.13	88.75
34.95	11.717	362.08	91.04
38.07	12.753	367.27	92.71
		372.40	94.62

TABLE 2. *Heat capacity data of poly(vinyl chloride)* — Continued

(—CH$_2$CHCl— = 64.299)

T, K	C$_p$, J K^{-1}mol^{-1}	T, K	C$_p$, J K^{-1}mol^{-1}
B. Bulk-polymerized, pellet (B)			
Series I.	First Heating (B1)	Series II.	Quenched (BQ)
305.07	60.17	271.83	54.64
309.01	61.07	275.77	55.29
313.03	62.28	278.89	55.90
317.10	64.08	282.89	56.55
321.19	64.15	286.98	57.30
325.32	64.86	291.04	58.01
329.46	65.77	295.08	58.69
333.56	66.72	299.09	59.94
337.62	68.02	303.08	60.13
341.69	69.35	307.04	60.83
345.71	71.18	311.08	61.63
349.69	76.13	315.21	62.35
353.59	84.62	319.31	63.30
357.55	89.45	323.39	63.98
361.58	91.52	327.44	64.90
365.64	93.09	331.46	65.70
369.76	94.56	335.47	66.69
		339.55	67.89
		343.71	69.68
		347.81	73.24
		351.76	81.57
		355.52	88.82
		359.42	90.85
		363.58	92.37
		367.69	93.79
		371.76	95.18

TABLE 2. *Heat capacity data of poly(vinyl chloride)* — Continued

(—CH$_2$CHCl— = 62.499)

T, K	C$_p$, J K^{-1} mol^{-1}	T, K	C$_p$, J K^{-1} mol^{-1}
Series III.	Annealed (BA)		
6.21	0.643	155.51	36.02
7.12	0.896	162.51	37.12
8.20	1.203	169.42	38.21
9.37	1.597	176.17	39.29
10.57	2.013	185.29	40.71
11.76	2.466	194.48	42.19
12.96	2.946	201.40	43.21
14.28	3.471	206.39	44.04
15.75	4.100	211.59	44.86
17.34	4.778	216.74	45.70
19.10	5.549	221.84	46.54
21.06	6.368	226.89	47.28
23.26	7.295	232.03	48.14
25.73	8.298	237.25	48.85
28.53	9.388	247.52	50.56
31.76	10.596	252.73	51.42
35.52	11.920	258.03	52.33
39.92	13.355	263.27	53.19
45.18	14.916	268.47	54.08
51.56	16.690	273.63	54.83
57.24	18.117	278.88	55.77
61.59	19.145	284.21	56.65
65.97	20.121	289.50	57.57
70.38	21.082	294.74	58.42
74.69	21.972	299.94	59.33
78.93	22.857	305.23	60.28
83.28	23.679	310.60	61.21
87.60	24.541	315.91	62.25
91.90	25.349	321.19	63.17
96.35	26.176	326.43	64.14
100.81	27.003	331.74	65.18
105.27	27.788	337.13	66.36
109.76	28.596	342.47	67.50
132.38	32.33	347.73	69.34
136.87	33.03	352.63	85.65
141.43	33.82	357.75	90.31
146.05	34.51	363.09	92.45
150.74	35.26	368.48	94.08

TABLE 2. *Heat capacity data of poly(vinyl chloride)* — Continued

(—CH₂CHCl— = 62.499)

T, K	C_p, J K^{-1} mol^{-1}	T, K	C_p, J K^{-1} mol^{-1}
	Series IV. Quenched (BQ)		
6.89	0.826	147.50	34.78
7.93	1.118	152.16	35.60
9.08	1.491	156.90	36.26
10.25	1.908	161.58	37.06
11.43	2.336	166.19	37.72
12.64	2.811	170.88	38.50
13.97	3.335	175.65	39.25
15.41	3.954	180.37	40.03
16.99	4.622	185.03	40.71
18.69	5.353	189.78	41.48
20.58	6.164	194.61	42.21
22.72	7.064	199.40	43.00
25.12	8.060	204.14	43.70
27.86	9.127	208.96	44.43
31.00	10.311	213.87	45.22
34.65	11.619	218.73	46.04
38.92	13.048	223.54	46.79
43.36	14.401	228.32	47.54
47.34	15.543	233.17	48.32
50.88	16.507	238.12	49.06
54.11	17.337	262.62	53.13
57.10	18.095	267.68	54.03
61.77	19.183	272.57	54.85
67.17	20.370	282.38	56.50
71.52	21.318	287.42	57.43
75.94	22.216	292.43	58.26
80.28	23.111	297.39	59.18
84.58	23.946	302.32	60.02
89.00	24.792	307.33	60.94
93.41	25.624	312.43	61.91
97.82	26.416	317.49	62.88
102.23	27.219	322.50	63.83
106.66	28.020	327.48	64.89
111.12	28.789	332.53	65.97
115.62	29.547	337.67	67.34
120.15	30.31	342.76	69.21
124.73	31.13	347.77	73.26
129.36	31.81	352.68	83.22
133.91	32.61	357.54	89.70
143.04	34.03	362.46	91.92
		367.53	93.60

C. Bulk-polymerized, powder (P)

Series I.	First Heating (P1)	Series II.	Second Heating (P2)
304.29	60.06	300.52	59.50
299.73	59.18	305.75	60.52
304.68	60.10	310.94	61.46
309.75	60.97	316.08	62.49
314.62	62.01	321.17	63.39
319.42	63.07	326.22	64.35
324.34	64.24	331.22	65.38
329.34	65.59	336.18	66.52
334.47	66.68	341.08	68.27
339.57	67.92		
344.64	69.71		

TABLE 3. *Thermodynamic functions of poly(vinyl chloride)*

(—CH₂CHCl— = 62.499)

T K	C_p J K^{-1} mol^{-1}	$H-H_0^A$ J mol^{-1}	$S-S_0^A$ J K^{-1} mol^{-1}
10	1.81	5.54	0.75
15	3.78	19.4	1.84
20	5.92	43.6	3.22
25	8.01	78.5	4.79
30	9.95	123.4	6.40
35	11.73	177.7	8.07
40	13.38	240.5	9.75
45	14.89	311.3	11.41
50	16.28	389.2	13.05
60	18.77	564.7	16.25
70	20.99	763.7	19.31
80	23.05	984.0	22.25
90	24.98	1224.	25.08
100	26.82	1483.	27.81
110	28.59	1761.	30.45
120	30.29	2055.	33.01
130	31.94	2366.	35.50
140	33.56	2694.	37.92
150	35.15	3037.	40.29
160	36.73	3397.	42.61
170	38.31	3772.	44.88
180	39.88	4163.	47.12
190	41.45	4569.	49.32
200	43.03	4992.	51.48
210	44.61	5430.	53.62
220	46.21	5884.	55.73
230	47.79	6354.	57.82
240	49.37	6840.	59.89
250	50.99	7342.	61.94
260	52.63	7860.	63.97
270	54.29	8394.	65.99
273.15	54.81	8566.	66.62
280	55.95	8945.	67.99
290	57.64	9513.	69.98
298.15	59.03	9989.	71.60
300	59.35	10098.	71.97
310	61.11	10700.	73.94
320	62.94	11321.	75.91
330	64.88	11960.	77.88
340	66.96	12619.	79.84
350	87.59	13317.	81.86
360	91.08	14110.	84.38
370	94.56	15138.	86.93
380	98.05	16101.	89.49

approximately that of the density changes. At liquid helium temperatures, the heat capacity difference between glass and crystal could be relatively very large. The heat capacity of the glass may be 2 to 4 times higher than that of its crystalline counterpart [26].

The rapid rise in C_p/T^3 as temperature is lowered in the liquid helium temperature region, figure 3, has commonly been observed in all amorphous materials studied [26]. The behavior of all three PVC samples is quite similar in this aspect. A maximum in C_p/T^3 generally occurs in the temperature range between 2 and 7 K for amorphous materials [26].

The observations on PVC indicate that the maxima would occur at temperatures below 6 K.

Heat capacity measurements on PVC have not been extended to temperatures below 6 K. Excessively long equilibration times were experienced below 6 K, due probably to the adsorption of the helium heat exchange gas by the powdery samples.

3.1. Linear C_p in the Glassy State

Below the glass transition temperature the C_p of PVC is highly linear over a wide temperature range. The following simple expressions, eqs (1) to (3), may be used to describe the observed C_p behavior of annealed PVC, depending upon the precision and the temperature range as stated below for the individual expressions:

$$C_p = 11.45 + 0.158\,T \qquad 0.1\%,\ 140-240\ \text{K} \qquad (1)$$

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$$C_p = 10.95 + 0.162\,T \qquad 0.5\%,\ 100 - 320\ \text{K} \qquad (2)$$

$$C_p = 10 + 0.166\,T \qquad 1\%,\ 80 - 340\ \text{K} \qquad (3)$$

where C_p is in J K^{-1} mol^{-1} and T in K. The simple expression of eq (3) represents the C_p of annealed, bulk-polymerized PVC to about 1 percent of the observed values over the entire temperature range from liquid nitrogen temperatures to just below the glass transition region. Equation (1) gives C_p values within 0.1 percent, about the experimental precision, of the observed C_p values for annealed PVC for a narrower temperature range.
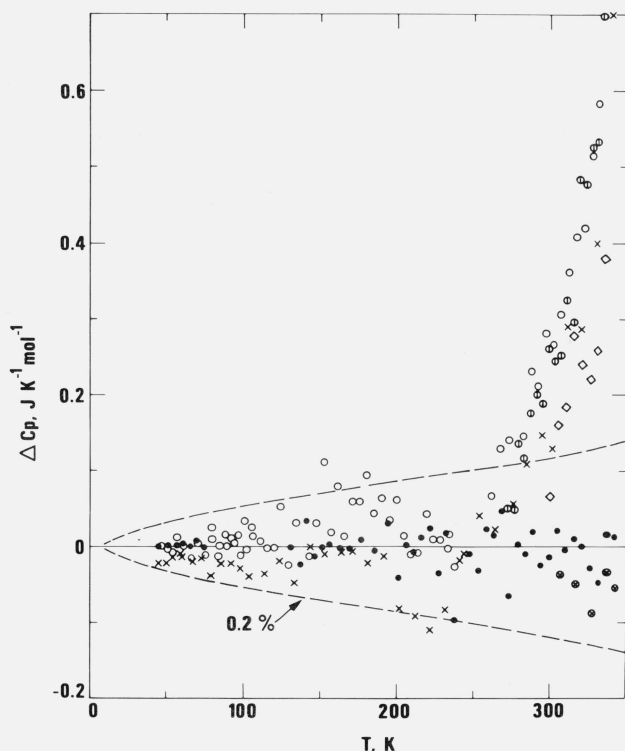
FIGURE 2. *Comparison of heat capacities of poly(vinyl chloride).*
Baseline ($\Delta C_p = 0$) — Smoothed C_p of BA. × SQ, ⊗ SA, ○ and ① BQ, ● BA, ◇ P2.
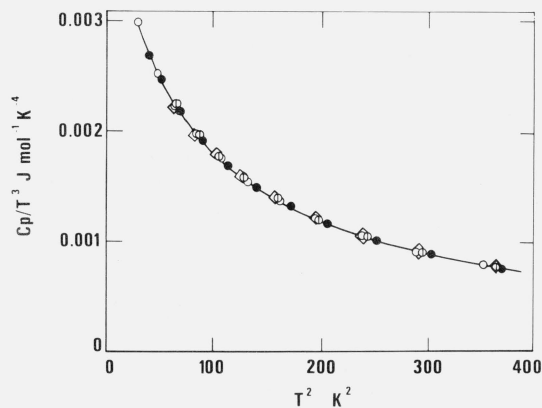
FIGURE 3. *Low temperature heat capacities of poly(vinyl chloride).*
◇ SQ, ○ and ① BQ, ● BA.

3.2. Comparison With Literature Values Below T_g

Measurements by Lebedev et al. [2] cover the temperature range from 60 to 300 K. From 75 to 150 K, their reported values agree well within 1 percent of ours. From 175 to 275 K their values are about 2 percent lower and at 300 K about 1 percent higher than ours. Their extrapolated values for 25 and 50 K deviate significantly from our measured values.

Alford and Dole's measurement [3] covered the temperature range from 250 to 390 K. Between 300 and 390 K their data were shown graphically. Two linear equations were given to represent the C_p behavior of their original polymer and their annealed sample. The temperature ranges of applicability for the two expressions were not given explicitly. Both their dC_p/dT values of 0.191 J K^{-2} mol^{-1} for the original PVC sample and 0.221 J K^{-2} mol^{-1} for the annealed sample are higher than our mean dC_p/dT value of 0.176 J K^{-2} mol^{-1} for the temperature range from 250 to 340 K. Their C_p values intersect ours at around 280 to 300 K. At either end of their temperature range of measurement in the glassy state, their values deviate from ours about 1 to 5 percent.

3.3. Glass Transformation

The enthalpy changes in the glass transition region for sample S are shown in figure 4. In order to obtain the precision required, these changes are not computed as the integral of the heat capacity values reported in table 2, which do not contain the configurational contribution. Instead the enthalpy increments in table 4 are calculated as the sum of the energy inputs, ΣQ, applied to the calorimeter between a temperature, T, and the final temperature, f, in the supercooled liquid state, L, minus the enthalpy increment of the
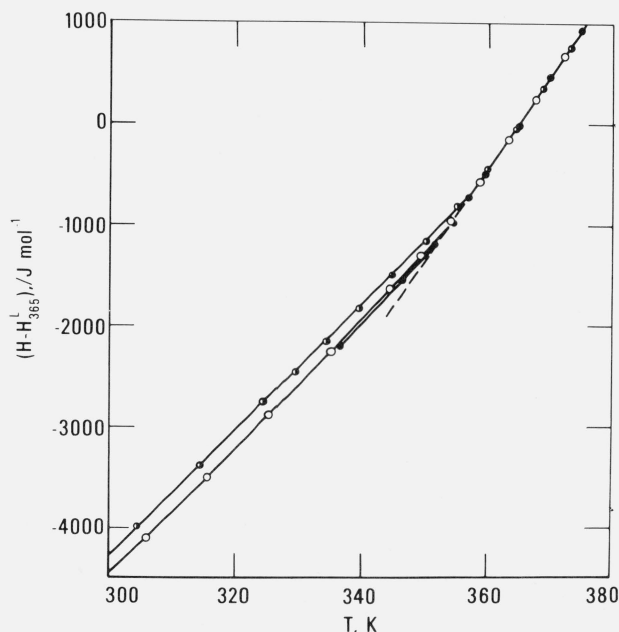

FIGURE 4. *Enthalpy changes of poly(vinyl chloride) in the glass transition region.*
◑ S1, ○ SQ, ● SA.

TABLE 4. *Enthalpy and entropy changes of poly(vinyl chloride) in the glass transition region*

(—CH$_2$CHCl— = 62.499)

Sample Designation	No. of runs	T_i K	T_f K	$H_{365}^L - H_{300}$ J mol^{-1}	S_{365}^L S_{300} J K^{-1} mol^{-1}
S1	11	304.5	364.4	4261.	12.80
SA	11	301.2	364.7	4495.	13.47
SQ	11	296.2	367.7	4456.	13.36
B1	16	303.1	363.6	4371.	13.11
BQ	16	301.1	365.6	4522.	13.55
BA	13	302.5	365.8	4571.	13.69
BQ	13	299.9	360.0	4525.	13.56
P1	14	302.1	361.5	4543.	13.61
P2	14	297.9	358.3	4546.	13.61

FIGURE 5. *Enthalpy changes of poly(vinyl chloride) in the glass transition region.*
$H - H^B = H - H_{365}^L - 10(T - 365) - 0.083(T^2 - 365^2)$ J mol^{-1}
◑ S1, ○ SQ, ● SA.

empty sample container, MT, for the same temperature interval:

$$H_f^L - H_T = [\Sigma Q - (H_T^{MT} - H^{MT})]/n \qquad (4)$$

where n is the number of moles of the sample. This enthalpy increment between temperatures T and f is then adjusted to a common reference temperature, r, in the supercooled liquid, L, thus:

$$H_T - H_r^L = \int_r^f C_p^L \, dT - (H_f^L - H_T) \qquad (5)$$

where C_p^L is the heat capacity of the sample in the supercooled liquid state. A reference temperature of 365 K was chosen. The energy applied to the calorimeter should be corrected for any non-adiabatic condition that existed between the sample container and its surroundings. In the present instrument, the typical temperature drift due to non-adiabaticity is less than ±0.1 mK min^{-1}. Therefore for an experiment lasting about 10 hours and covering some 60 K range, the non-adiabatic contribution is less than 0.1 percent of the total energy applied and may be neglected.

In order to show the enthalpy changes in the glass transition region in greater detail than that in figure 4, a base enthalpy increment between the reference temperature 365 K and the temperature of observation as calculated from eq (3) for annealed PVC was subtracted from the observed enthalpy increment. The results are shown in figure 5, where

$$H - H^B = H - H_{365}^L - 10(T - 365)$$
$$- 0.083(T^2 - 365^2) \text{ J mol}^{-1} \qquad (6)$$
$$= H - H^A - (H_{365}^L - H_{365}^A).$$

The heavy solid lines in figure 5 connect the initial temperatures after each electrical energy input to the calorimeter. The double points or the thin lines linking each of the double points denote the extent of enthalpy relaxation which occurred during the temperature drift observation period of about one half to one hour. The sample container and, its contents were in adiabatic condition with the surroundings. When the sample temperature was raised or lowered spontaneously due to the enthalpy relaxation, the sample enthalpy was decreased or increased due to the corresponding temperature changes of the sample container with that of the sample.
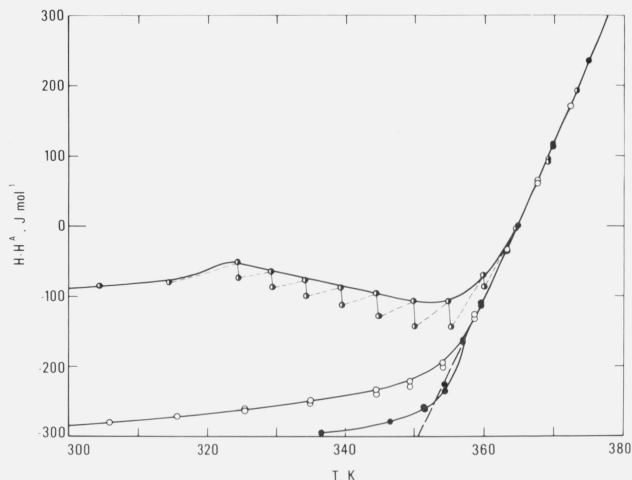
The exchange of enthalpy between the sample and its container causes the effect of spontaneous enthalpy relaxation of the sample to appear more isothermal than adiabatic.

3.4. Glass Transition Temperature

The glass transition temperature, T_g, is defined here as the temperature of intersection of the enthalpy curves (sometimes extrapolated) for the glass and for the supercooled liquid. The T_g so defined is determined by the history by which the glass was formed on cooling but it is independent of the rate of observation during the heating in the glass transition region. This definition is analogous to that used in dilatometric studies where the break in the volume versus temperature curve is defined as the glass transition temperature. For the suspension polymerized sample, T_g for SQ occurred at 355 K and for SA at 352 K. For the bulk-polymerized samples, T_g for BQ, BA, P1 and P2 are 351, 348, 351, and 350 K, respectively. Although the heat capacities of the bulk- and suspension-polymerized samples are almost identical below the glass transition region, the glass transition temperature of the bulk-polymerized sample is about 4 K lower than that of the suspension-polymerized sample with similar history. The lowering of T_g perhaps reflects the fact that the bulk-polymerized sample has a lower molecular weight. Differences in the molecular weight distribution and/or the residual monomer content may also play a part.

3.5. Enthalpy Relaxation and Adiabatic Temperature Drift

Large spontaneous temperature drifts have been observed in the glass transition region for either quenched or annealed glasses, due to the configurations relaxing toward the supercooled liquid under adiabatic conditions [32]. An exothermic peak is generally observed to occur just below the glass transition temperature for the quenched glass, while an endothermic peak may be seen above the T_g for the annealed glass.

Figure 6 shows the spontaneous drifts observed for sample S at different times after the termination of electrical energy input to the calorimeter heater. Due to the axial configuration of the heater and the thermometer in the calorimeter, the temperature of the central heater-thermometer assembly is a few kelvins higher than that of the sample at the end of the heating period. When the electrical energy to the heater is turned off, a near exponential decay of the temperature of the thermometer is observed for the establishment of a uniform temperature throughout the sample container. The time constant is in the order of 50–100 s at temperatures around 300 K. In figure 6A, the influence of the above mentioned effect may still be observed, at 10 min after the termination of the electrical energy input to the calorimeter.

The usual exothermic and endothermic behaviors for quenched and annealed glasses are observed for SQ and SA. For S1, an additional amount of positive drift due to the release of stored pelleting energy appears in the temperature range 320 to 350 K. Similar behavior has also been observed for B1. For P1, the initial drift is slightly negative and reaches about -0.3 mK min^{-1} at about 330 K where exothermic behavior begins to be noticed. Therefore the initial slight negative drift near room temperature for both S1 and B1 may also be associated with the original samples, although such a behavior is soon masked by the release of pelleting energy. Above 360 K, all observed drifts remain slightly positive. This is probably associated with the onset of thermal degradation of the material [33].

In general the relaxation time constant becomes shorter as the temperature is increased. This behavior is readily observable by examining the changes in the drift with time for SA at two temperatures, 356.9 and 354.2 K (fig. 6), before and after the heat capacity measurement at a mean temperature of 355.55 K (table 1). The drift at 356.9 K is much greater than that at 354.2 K at 10 min after the energy input. At 20 min after the energy input, the drift at 356.9 K is already less than that at 354.2 K.

Longer observations have been made on P1. The relaxation time constants τ were estimated to be 42.5 min at 350.5 K and 126.5 min at 335 K. It is possible to construct an Arrhenius-type plot, which yields an apparent activation energy for the relaxation process in the glass transition region as 69 kJ mol^{-1}. However, as the glass transition process cannot be described by a single relaxation time and the relaxation times are estimated for a glass with progressively changing configurations, and with the further complication that the observations on PVC may include the effects of thermal degradation in and above the glass transition region, such an estimation of activation energy is at best a rough approximation.

Straff and Uhlmann [34] reported recently that the enthalpy of PVC decreases by 150 to 170 J mol^{-1} after annealing for 50 to 250 hours near T_g. In our experiment the decrease in the enthalpy is about 20 to 40 J mol^{-1}. They also reported an activation energy spectrum with a peak around 78 kJ mol^{-1} for the enthalpy relaxation process of PVC.

3.6. Stored Energy from Pelleting Process

This subject has been dealt with in detail elsewhere [31]. When the pelleted, suspension-polymerized PVC, S1, was being heated from room temperature for the first time, spontaneous energy release began to be observable at about 320 K and lasted through the entire glass transition region (fig. 6).
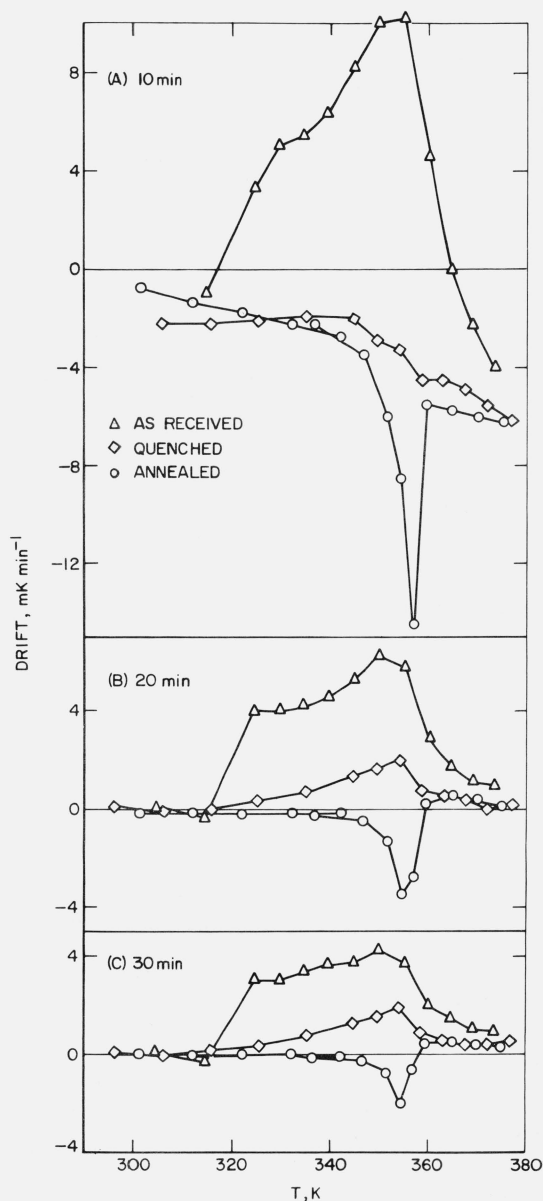

FIGURE 6. *Spontaneous temperature drifts of poly(vinyl chloride) in the glass transition region.*
Δ S1, ◇ SQ, ○ SA.

Similar findings were observed for B1 [31]. The onset of the release of the stored energy from the pelleting process also caused small anomalies in the heat capacity behavior for S1 and B1 (fig. 1).

Around room temperature, the enthalpies of S1 and B1 are substantially higher than that of the corresponding samples which received subsequent quenching and annealing treatments, figures 4 and 5. By combining the results of the two bulk-polymerized samples, B and P, it was found that the enthalpy increments for P1 and P2 lie between those of BQ and BA [31]. Hence the enthalpy of the original material is approximately midway between that of the material after quenching and annealing. The difference in enthalpy be-

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tween B1 and P1 is about 175 J mol^{-1}. The differences in enthalpy between S1 and the mean value of SQ and SA is about 215 J mol^{-1}.

3.7. Effect of Pressure Densification on T_g

The glass transition phenomenon may occur over a wide temperature region depending upon different physical properties being observed and the criteria chosen as the indication for the transition. It is generally believed that the breaks in the extensive thermodynamic properties, such as the volume, enthalpy and entropy, would occur at the same temperature for a configurationally fixed glass formed by a particular history. This view is supported by most dilatometric and calorimetric observations on glasses normally formed under atmosphere pressure, and by the observations that, upon annealing, all the extensive thermodynamic properties relax to lower values, i.e., toward that of an equilibrium supercooled liquid state.

It is also possible to reduce the volume of a glass by permanent pressure-densification [35, 36], either by compressing in the glassy state or by vitrification from the liquid state under pressure and followed by the release of pressure around room temperature. The pressure-densified glasses, though having lower volumes, may contain higher enthalpies and entropies than that of a normally formed glass, and are actually further removed from the equilibrium supercooled liquid state at normal pressure, as observed in the present and other works [37, 38]. In contrast to most observations [37–41] that the enthalpies of pressure-densified glasses are either essentially unchanged if formed at low pressures (less than 100 MPa) or higher than that of normal glasses if formed at high pressures, references [42, 43] reported lowering of enthalpy for pressure-densified glasses. Hence for most systems observed, the dilatometry may show a depression of the glass transition temperature, whereas the calorimetric observation may show an elevation of the glass transition temperature, as compared with that of a normally formed glass. Observations on the same pressure-densified glasses indicate that the volumetric and the enthalpic relaxations do not necessarily occur simultaneously or relax with the same time constant [38].

Hence, the dilatometric and calorimetric glass transition, defined as a break in the volumetric or enthalpic curves, may not necessarily occur at the same time nor at the same temperature for pressure-densified glasses. Thermodynamic studies lead to a conclusion that more than one ordering parameter is required to describe the glassy state [44, 45]. It is possible that some of these parameters appear to be more active dilatometrically and others to be more active calorimetrically. Further thermodynamic studies are underway to clarify this apparent distinction [46].

3.8. C_p of Liquid

Around 360 K and above, all the PVC samples studied reach equilibrium supercooled liquid state within the normal drift observation period of one-half to one hour. Although the temperature range of measurement for the supercooled liquid region is relatively narrow, the heat capacity values of PVC liquid are reproducible to within 0.1 percent for each of the three samples.

For each sample, no progressive change in the heat capacity with time may be detected beyond the experimental

uncertainties. After the calorimetric measurement, these samples appear slightly tinted with uneven purplish color. The intensity and the spread of discoloration in the sample seem to increase as the duration and the highest temperature at which the sample have been subjected to are increased. Apparently the slight discoloration or decomposition does not affect the C_p significantly. Discoloration of PVC has also been observed in other calorimetric measurements [3]. More detail about the early stage of thermal decomposition of PVC has been reported elsewhere [33]. The heat capacity values of different liquid PVC samples differ slightly, but the slopes dC_p/dT are almost identical. C_p of the liquid of sample B is 0.9 percent higher than that of sample S, and that of sample P is 0.4 percent higher than that of sample B. Since the only difference between samples P and B is the mechanical treatment of the pelleting process, the lowering of C_p of sample B may be attributed to some residual effect from the pelleting process or stress-induced crystallization. However, the low crystallinity of PVC [47] indicates that induced crystallization is not likely to cause these effects. Similar argument may be used for sample S because of its higher pelleting pressure. However, the difference in C_p between S and B or P may be due to the differences in the sample condition and preparation.

The rate of change of C_p with respect to temperature for liquid PVC, dC_p/dT, is about 0.355 J K^{-2} mol^{-1} for all three samples. This value is higher than that of the glasses at about 0.16 J K^{-2} mol^{-1} just below T_g. This phenomenon of higher dC_p/dT for liquid than that of glass just across the T_g is not very common. Normally dC_p/dT of liquid is observed to be less than that of the glass. Often dC_p/dT of liquid is negative just above the T_g.

Higher dC_p/dT values above T_g have also been observed in highly crystalline polymers, such as polyethylene [30] and polytrifluoroethylene [30a]. This behavior is probably due to the wide distribution of crystallite sizes and crystalline perfection, and hence the extension of premelting phenomena to temperature near T_g. It is less plausible to assume that the high dC_p/dT of supercooled PVC liquid, containing about 1 percent of crystal, may be caused by similar mechanisms as that observed in highly crystalline polymers. The dehydrochlorination reaction at temperatures above T_g may cause a higher dC_p/dT than usual.

Alford and Dole's work [3] on PVC liquid covers a similar temperature range of 360 to 390 K. Judging from their graph, their C_p values at 360 and 380 K differ about +0.6 percent and −0.6 percent from our values at corresponding temperatures. Although their dC_p/dT value for liquid PVC of 0.29 J K^{-2} mol^{-1} is less than ours, it is nevertheless also higher than their dC_p/dT values for the glasses at 0.19 to 0.22 J K^{-2} mol^{-1}.

4. Summary

Heat capacities of poly(vinyl chloride) samples, from two different polymerization processes (suspension and bulk) and in either the original powder form or after pelleting were determined from 6 to 375 K by precision adiabatic calorimetry. Below 250 K C_p of PVC is essentially independent of sample origin and previous histories. Between 250 K and T_g, C_p is a function of thermal and pressure histories rather than a function of sample origin. C_p of glassy PVC is linear with temperature for an exceptionally wide temperature range. From liquid nitrogen temperatures to T_g, C_p of annealed PVC

may be represented by $(10 + 0.166\ T)$ J K^{-1} mol^{-1} to 1 percent of the observed values.

The pelleting process contributes 175 to 215 J mol^{-1} of energy to be stored in the sample. The stored energies begin to release at about 30 to 40 K below T_g. Thus in calorimetric work, especially in enthalpic measurements in reaction calorimetry, where samples are customarily pelleted care must be taken to eliminate the stored energies due to pelleting in order to achieve highest reliability.

T_g of PVC is however more sensitive than C_p to both the histories and sample origin. The higher enthalpy of the pelleted sample raises the T_g as observed calorimetrically. However, the pressure-pelleting process may cause a permanent pressure-densification of the sample. A sample so-treated would show a lowering of T_g dilatometrically. Therefore the glass transition as observed calorimetrically is not necessarily identical to that observed dilatometrically, even though it is observed on the same material.

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