Heat Capacities of cis-1,4-Polyisoprene from 2 to 360 K

S. S. Chang and A. B. Bestul*

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

Heat capacities of amorphous synthetic cis-1,4-polyisoprene have been determined for the quenched and annealed glasses from 2 to T_g (around 200 K) and for the liquid from T_g to 360 K, with a precision of better than 0.05 percent above 15 K. T_g, as determined from H versus T plots, is 203 K for the quenched glass and 198 K for the annealed glass. For the glasses the heat capacity values from this research are about 1 percent higher than that reported in 1935 for natural rubber hydrocarbon. For the liquid the result from this research agrees better (within 1 percent) with recently (1967) proposed values than those from the earlier experiment cited. Effects of crystallization and melting, stark rubber crystals, and additives (antioxidants and stabilizers) were also studied.

Key words: Annealed and quenched glass; calorimetry; glass transformation; heat capacity; natural rubber; normal and supercooled liquid; cis-1,4-polyisoprene; rubber, natural; thermal diffusivity; thermodynamic properties.

1. Introduction

Heat capacities of natural rubber hydrocarbon from 14 to 320 K were reported by Bekkedahl and Matheson in 1935 [1].[1] After several decades, a review by Gehman [2] on the thermal diffusivity of natural rubber showed discrepancies which Wood and Bekkedahl [3] explained by the suggestion that Bekkedahl and Matheson's values for the temperature dependence of the heat capacity were too high around room temperature, and too low at lower temperatures. They proposed that the 1935 heat capacity results had been affected by undetected crystallization effects, which were little understood at the time of those measurements. On the basis of more recent knowledge of crystallization in natural rubber, they proposed adjustments to the 1935 data to bring it into greater consistency with current thermal diffusivity values.

To provide a new experimental basis for these heat capacities, the present paper reports new determinations for cis-1,4-polyisoprene from 2 to 360 K with a precision of about 0.05 percent of the values over most of that range. The effects of quenching and annealing on the heat capacity of the glass and on the glass transformation temperature were also studied.

The cis-1,4-polyisoprene sample investigated was the synthetic product rather than the natural product. Although the synthetic polymer contains about 3 percent of the 3,4-adduct as compared with a typical value of 2 percent for the natural polymer, the synthetic sample was chosen for the two following reasons. The

natural product requires a much more complicated and uncertain purification process. Also the synthetic polymer crystallized much more slowly than the natural polymer [4], thus making it much easier to avoid the crystallization effects which are thought to have affected the 1935 measurements [1].

2. Experimental Detail

2.1. Apparatus

The heat capacity measurements reported here were performed in the vacuum adiabatic calorimeter described previously [5]. The measuring procedures and methods of data treatment, especially for the glass transformation region, were discussed in more detail in a previous paper [6], where several modifications on the instruments were also described.

The following additional modifications have now been made in the apparatus:

By pumping on the liquid helium reservoir, the calorimeter can now be cooled to 1.8 K and maintained there for 5 to 6 hours. The mechanical choppers of the adiabatic shield control system are replaced by photochoppers, and the outputs from the power amplifiers are rectified and filtered before being fed to the shield heater.

Constant current supplies, capable of supplying 1 to 10 mA with stabilities in the order of 1 ppm, are used instead of batteries to energize the platinum resistance thermometer and its measuring potentiometer. This eliminates the necessity of readjusting the potentiometer and the thermometer currents during a day of measurements. The drift in the thermometer

---

potential now reflects only the change in the temperature of the thermometer element, without any additional change in the thermometer current. A nanovolt null detector is used instead of the photoelectric galvanometer. This detector recovers from a large overvoltage at its input in a few seconds, whereas a galvanometer coil sticks off scale. Connections between circuit modules are made with barrier-type terminal strips. In critical circuits, gold-plated copper shorting links and washers are used on the terminal strips to avoid the generation of thermal emf's. Multiple-gang low thermal emf silver-alloy wafer switches are used as the master selector switch, the range switch, and the reversing switch. The master selector switch controls the application of electrical energy to the calorimeter heater, turns the heater timer on and off synchronously with the energy, and selects either the heater or the thermometer for the potentiometer input. The range switch adjusts the heater circuit voltage divider network, composed of calibrated standard resistors, to maintain the signal near the 0.1-V full-scale reading of the potentiometer. The reversing switch is used to reverse the polarities of all power supplies at their terminals. Thus the residual emf in a circuit can be checked without disturbing the connections for emf input to, and for detector output from, the potentiometer. With room temperature maintained within 1 °C and potentiometer corrections applied from inter-dial comparisons, the accuracy for the entire potentiometric system is better than 2 ppm for the ratio of potentials involved in the resistance ratio measurement, and better than 10 ppm for an individual potential measurement. As the thermometric potentiometer system measures liquid helium temperatures, the null detector can resolve 5 nV, and around room temperature the resolution is about 10 nV. The resistance of the platinum resistance thermometer, including that of the leads, varies from 3 to 50 Ω over the temperature range of the measurements. Thus the 25-Ω (at 0 °C) platinum resistance thermometer, excited by a 2 mA current above 40 K, and below this by higher currents up to 10 mA at 2 K, yields a resolution in temperature better than 5×10^{-3} K at 2 K, 5×10^{-4} K, at 10 K, and 5×10^{-5} K above 40 K. The output of the nanovoltmeter is recorded on a strip chart. A full scale of $\pm 1\mu V$ is normally used, which is equivalent to a 0.01 K span above 40 K.

A constant current supply, with high power rating and 10 ppm stability, was used as the energy source for the calorimeter heater.

The platinum resistance thermometer was originally calibrated in accordance with the International Practical Temperature Scale (IPTS) of 1948 and the NBS–1955 provisional scale. This calibration has been adjusted so it conforms with the IPTS–1968 [7, 8] above 13.81 K. Between 2 to 20 K, this platinum thermometer was compared against germanium thermometer S/N 1466 which has been calibrated through the same range by the Temperature Section of NBS in accordance with the NBS–1965 (2 to 20 K) provisional scale [9]. The result of the comparison

was fitted to a fifth-degree polynomial [10] which was then used to calculate temperatures of the platinum thermometer between 2 to 14 K. The use of the new temperature scale eliminates the mini-maximum in the heat capacities around 70 and 90 K which was caused by the old temperature scales in some previous data [6, 11, 12].

The heat capacities used for the empty calorimeter have been redetermined experimentally based on the new temperature scale.

2.2. Sample

The sample of synthetic cis-1,4-polyisoprene was supplied by the Goodyear Tire and Rubber Co. through the courtesy of S. D. Gehman and E. Schoenberg. The sample was in the form of a rough sheet about $1/2$ in thick. It was translucent, having pale yellow color. The ash content of the sample was determined from spectroscopic analysis of the ashes by the Analytical Chemistry Division of NBS as 0.11 percent, with titanium and aluminum as the major components. The following information about the sample was given by the supplier: The dilute solution viscosity was 6.4 dl/g in toluene at 30 °C. The polymer was composed of 97.0 percent cis-1,4 adducts and 3.0 percent 3,4 adducts. To 100 parts of polymer, 0.93 parts of antioxidant and 0.20 parts of stabilizer were added. These additives were of cresol and amine types with overall weight ratio C:N:H:O = 77:7:10:6.

The calorimetric sample consisted of four annuli, weighing 68.608 g in vacuo. The weighings were carried out on a single-pan balance, designated NBS 166591, with a capacity of 1 kg and a sensitivity of 0.1 mg. The annuli, 2 in in o.d. and $1/2$ in i.d., were punched from the sheet. The sample container was surrounded by a water-cooled jacket while the cover was soldered to the container with low melting In-Sn solder, so the sample would not heat up and would remain as closely as possible to "as received" condition. Helium gas at 10 cm Hg pressure at room temperature was sealed into the container to increase thermal conduction within it.

The heat capacity of the sample was first determined in the as received condition. When the sample was subjected to a temperature above room temperature for the first time, the heat capacities showed a broad peak, about 1.5 percent higher than the base observed later, centering around 315 K. The height of the peak diminished as the sample was recycled to successively higher temperatures up to 330 K. After the sample had been heated above 330 K, the heat capacity in the region between 290 and 330 K remained constant within 0.05 percent upon further thermal treatment. X-ray powder patterns indicated the existence of small amounts of stark rubber [13] at a barely detectable level in the original sample. Thus this initial peak was probably due to the melting of these stark rubber crystals [14]. The amount of heat represented by the peak is about 60 J/mol. This amount of heat corresponds to an estimated content of stark rubber around 1.5 percent if the heat of fusion for stark rubber is as-

sumed to be equal to that for ordinary rubber crystal [15].

After the heat capacity had been measured for the sample in the as received condition, most of the additives were removed by vacuum distillation. The calorimetric sample, while still in the sample container, was maintained at 80 °C in high vacuum for 24 days. The collected distillate was a mixture composed mainly of transparent crystals and of some yellow liquid. The total weight loss was 0.726 g or 1.06 percent. The weight of the additives in the sample, calculated from the information given by the supplier, was 0.77 g or 1.12 percent of the sample. Hence the weight loss on pumping the sample amounted to 95 percent of the weight of the additives. 1,2-dichloroethane solutions containing from 0.1 to 1 percent of the sample, before and after the pumping process, were centrifuged, filtered, and analyzed by UV spectrometry. The spectra indicated approximately a ten-fold diminishing in the absorption at 270 to 280 nm, probably due to alkylated phenols. Naphthyl group absorption in the region of 309 nm was not observed either before or after pumping on the sample. Helium gas at 10 cm Hg pressure at room temperature was again sealed in with the sample to provide good thermal contact.

Heat capacity measurements reported here in detail were made on this purified sample. These results differed very slightly from the values obtained from the sample in as received condition. The difference in heat capacity per unit weight was less than 0.1 percent over most of the temperature range investigated, except below 10 K. No shift in glass transformation temperature was detected. Hence the effective heat capacity of the additives was within 10 percent of the heat capacity of the samples, and apparently the additives did not act as plasticizers.

The quenched glass was produced by cooling at a rate of about 5 K/min through the glass transformation range. The annealed glass was produced by first cooling at a rate of about 1 K/hr (rate annealing) through the glass transformation range, and then holding at 195 K (soak annealing) for two days, when thermal drift became negligible.

3. Results

Heat capacity data for *cis*-1,4-polyisoprene are listed in table 1 and shown graphically in figure 1. The table is divided into sections for annealed glass, quenched glass, and liquid. Each section is composed of several series of continuous determinations, and is arranged in the order of increasing initial temperature of each series. These series are numbered chronologically so that the thermal history of the sample may be followed. More than one physical state may be involved in a series. The approximate temperature increment for each determination may be inferred from the temperature differences between the adjacent determinations. The temperature rise for each determination is generally 1 degree below 10 K, 10 percent of the tempera-

ture up to 100 K, and 10 degrees above 100 K. Deviations of individual values from the smoothed curves for the respective physical forms are shown in figure 2. The precision of measurement is better than 0.05 percent above 15 K and gradually changes to 1 to 2 percent at 2 K. Although the accuracy of the measurement was shown to be comparable with the precision [5], estimated error for this sample is probably greater than the precision because of the remaining additives and the content of 3,4-adducts.

TABLE 1. *Heat capacity data for* cis-1,4-polyisoprene

(base mole $[-C_5H_8-] = 68.119$)

ANNEALED GLASS					
T	C_p	T	C_p	T	C_p
SERIES X		SERIES IX		SERIES XII	
K	$J/K/mol$	K	$J/K/mol$	K	$J/K/mol$
2.50	.046	30.81	14.67	157.09	63.53
2.99	.086	34.01	16.88	167.15	66.70
3.61	.161	37.55	18.29	177.33	69.92
4.32	.281	41.50	20.30	187.42	73.16
5.05	.444	45.84	22.34	194.81	76.41
5.79	.644	50.42	24.53	199.60	78.62
6.53	.887	55.41	26.81	203.44	133.50
7.27	1.156	60.95	29.23		
8.01	1.456	67.11	31.82		
8.79	1.807	73.94	34.62		
9.64	2.207	SERIES XI			
10.56	2.672				
11.65	3.257	79.40	36.78		
12.91	3.975	87.64	39.98		
14.13	4.618	98.47	43.98		
		107.77	47.28		
15.37	5.429	117.36	50.59		
16.89	6.355				
18.58	7.409	127.04	53.83		
20.33	8.491	136.99	57.07		
22.27	9.688	147.10	60.33		
24.46	11.02				
26.85	12.43				
29.52	13.94				
32.64	15.67				
35.98	17.47				

QUENCHED GLASS					
SERIES V		SERIES VI		SERIES VIII	
2.22	.032	27.72	12.95	153.81	62.72
2.63	.057	30.72	14.63	163.51	65.83
3.21	.112	33.65	16.25	173.46	69.02
3.91	.210	SERIES III		183.58	72.16
4.65	.355			193.47	76.65
5.39	.540	68.01	32.24	200.68	85.68
6.13	.762	73.46	34.46	204.84	109.05
6.89	1.026	79.28	36.77		
7.67	1.332	85.48	39.19		
8.47	1.674	92.06	41.68		
9.26	2.045	100.00	44.58		
10.06	2.438	109.31	47.89		

TABLE 1. *Heat capacity data for* cis-*1,4-polyiso-prene*—Continued

(base mole $[-C_5H_8-] = 68.119$)

QUENCHED GLASS—Continued

T	C_p	T	C_p	T	C_p
SERIES VII		SERIES IV			
4.64	.354	119.83	51.54		
5.40	.545	129.27	54.69		
6.17	.775	138.76	57.80		
6.96	1.057	148.44	60.94		
7.79	1.381				
8.66	1.766				
9.63	2.226				
10.67	2.755				
11.78	3.356				
12.97	4.040				
14.24	4.766				
15.62	5.618				
17.18	6.570				
18.89	7.632				
20.69	8.741				
22.71	9.977				
25.02	11.38				
27.78	13.02				
30.79	14.67				
34.07	16.48				
37.77	18.41				
41.69	20.38				
45.83	22.38				
50.32	24.50				
55.49	26.86				
61.20	29.36				
67.16	31.87				
73.31	34.40				

LIQUID

T	C_p	T	C_p
SERIES XII		SERIES II	
209.03	110.85	276.18	124.50
214.82	111.85	286.07	126.82
SERIES VIII		295.82	129.17
		305.44	131.46
210.53	111.05	314.92	133.87
SERIES XIII		SERIES XIV	
		317.22	134.32
221.18	112.99	326.56	136.63
230.50	114.77	335.78	138.91
240.08	116.65	345.48	141.32
249.90	118.87[a]	355.24	143.73
259.78	121.10[a]	SERIES I	
269.70	123.73[b]		
279.65	125.43	344.83	141.03
289.47	127.69	354.17	143.36
299.17	130.00		
308.73	132.32		

[a] less accurate assignment of quasi-adiabatic drift due to crystallization.
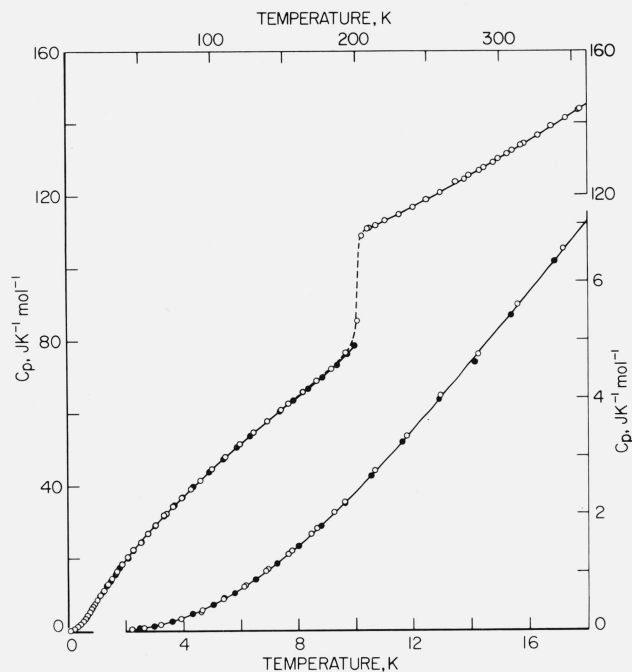
[b] fusion included.

FIGURE 1. *Heat capacities of* cis-*1,4-polyisoprene.*
• annealed glass, ∘ quenched glass and liquid.

Smoothed heat capacity values at rounded temperatures are listed in table 2, along with enthalpy and entropy integrals referenced to the annealed glass at 0 K. The values for the quenched glass are placed on this reference by first integrating and summing the data for the annealed glass from 0 K up to 210 K, where the sample is in the equilibrium liquid state and has thermodynamic properties independent of thermal history. From this point, the data for the quenched glass are then summed and integrated back down to the temperatures listed in table 2. The glasses are expected to have undetermined residual entropies at 0 K; hence the entropy and enthalpy increments listed in table 2 cannot be combined to give a Gibbs free energy.

Plots of C_p/T^3 versus T^2 for both glasses below 15 K are shown in figure 3. They show pronounced peaks between 4 and 5 K for both glasses. Clearly the glasses have not yet reached the Debye T^3 region even at 2 K. Entropy and enthalpy increments between 0 and 2 K are however estimated by means of a T^3 dependence of the heat capacity. These estimates, which amount to 0.011 J/mol for the enthalpy and 0.008 J/K/mol for the entropy, should not introduce any significant error in the respective integrals.

The heat capacity of the quenched glass is higher than that of the annealed glass throughout the entire temperature range of measurement. The difference is about 1 to 2 percent below 15 K; it decreases to 0.1 percent between 35 to 100 K and then increases to 1 percent at 190 K. The heat capacities of the glasses from this research are about 1 percent higher than those from reference [1] between 70 and 200 K and increase to 4 percent higher at 15 K.
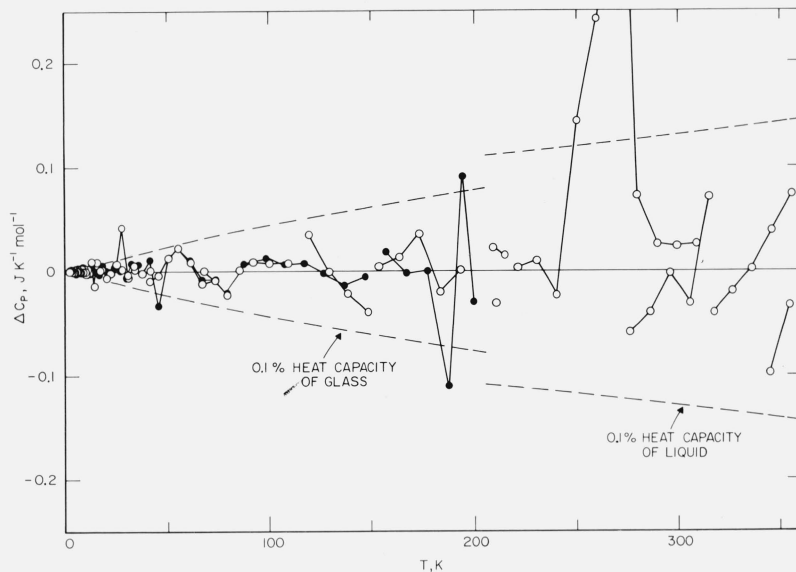
FIGURE 2. *Deviations of individual heat capacity determinations for cis-1,4-polyiso-prene from smoothed curves.*

• annealed glass, ○ quenched glass and liquid.

TABLE 2. *Thermodynamic functions of cis-1,4-poly-isoprene*

(Units in K, J and mol; $[-C_5H_8-] = 68.119$)

	ANNEALED GLASS		
T	C_p	$H - H_0^{AG}$	$S - S_0^{AG}$
0		[0]	[0]
2	0.023	0.011	0.008
5	0.43	0.53	0.14
10	2.39	7.03	0.96
15	5.21	25.82	2.45
20	8.29	59.52	4.37
25	11.34	108.65	6.55
30	14.22	172.62	8.87
35	16.94	250.6	11.27
40	19.56	341.9	13.70
45	21.98	445.8	16.15
50	24.33	561.6	18.59
60	28.81	827.5	23.42
70	33.03	1136.8	28.18
80	37.03	1487.3	32.86
90	40.86	1876.9	37.44
100	44.52	2304.	41.94
110	48.05	2767.	46.35
120	51.48	3265.	50.67
130	54.81	3796.	54.93
140	58.06	4361.	59.11
150	61.27	4957.	63.22
160	64.44	5586.	67.28
170	67.60	6246.	71.28
180	70.68	6937.	75.23
190	74.27	7661.	79.14
200	78.85	8426.	83.07
210 (liq.)		[9595.]	[88.77]

TABLE 2. *Thermodynamic functions of cis-1,4-poly-isoprene* — Continued

(Units in K, J and mol; $[-C_5H_8-] = 68.119$)

	QUENCHED GLASS		
T	C_p	$H - H_0^{AG}$	$S - S_0^{AG}$
0		[171.7]	[0.77]
2	0.023	171.7	0.78
5	0.44	172.2	0.92
10	2.41	178.8	1.75
15	5.23	197.7	3.25
20	8.32	231.6	5.17
25	11.36	280.8	7.36
30	14.24	344.9	9.69
35	16.97	423.0	12.09
40	19.54	514.3	14.52
45	21.99	618.2	16.97
50	24.34	734.1	19.41
60	28.83	1000.	24.25
70	33.06	1310.	29.01
80	37.07	1660.	33.69
90	40.90	2050.	38.28
100	44.58	2478.	42.78
110	48.12	2941.	47.19
120	51.57	3440.	51.53
130	54.93	3973.	55.79
140	58.23	4538.	59.98
150	61.48	5137.	64.11
160	64.70	5768.	68.18
170	67.89	6431.	72.20
180	71.06	7126.	76.17
190	74.85	7855.	80.11
210 (liq.)		[9595.]	[88.77]
	LIQUID		
210	110.99	9595.	88.77
220	112.77	10715.	93.97

117

TABLE 2. *Thermodynamic functions of* cis-1,4-poly-
isoprene—Continued

(Units in K, J and mol; $[-C_5H_8-]=68.119$)

	LIQUID—Continued		
T	C_p	$H-H_0^{AG}$	$S-S_0^{AG}$
230	114.67	11851.	99.03
240	116.66	13008.	103.95
250	118.74	14184.	108.76
260	120.91	15383.	113.45
270	123.15	16603.	118.06
280	125.44	17846.	122.58
290	127.79	19112.	127.02
300	130.18	20402.	131.39
310	132.60	21716.	135.70
320	135.04	23054.	139.87
330	137.49	24416.	144.14
340	139.94	25803.	148.28
350	142.38	27215.	152.38
360	144.81	28651.	156.42
273.15	123.86	16992.	119.49
298.15	129.74	20161.	130.59

3.1. Glass Transformation

Enthalpy changes as functions of temperature through the glass transformation range are shown in figure 4. The enthalpy of the quenched glass is about 195 J/mol higher than that of the annealed glass at 200 K and about 172 J/mol at 0 K. The corresponding entropy differences are 1.04 and 0.77 J/K/mol, respectively.

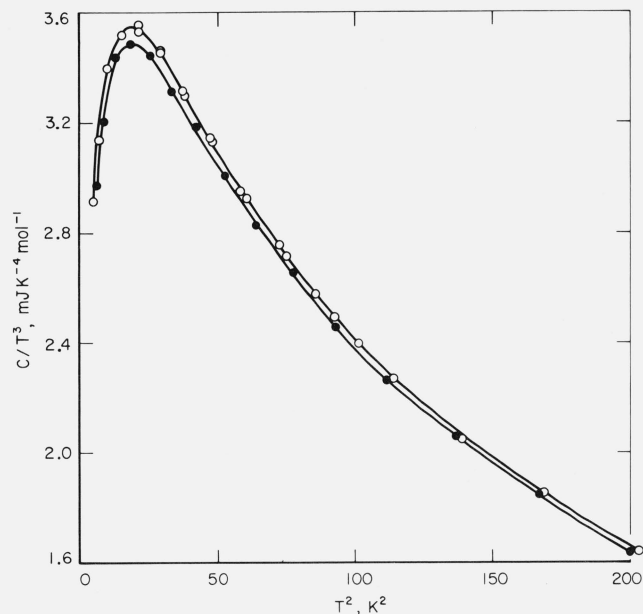The glass transformation temperature T_g, defined as the temperature of intersection of the extrapolated enthalpy versus temperature curves from the equilibrium supercooled liquid and the configurationally fixed glasses, is 203 K for the quenched glass and 198 K for the annealed glass. The extrapolation of the well-behaved liquid curve should not introduce appreciable error. During the normal measuring process a well-annealed glass tends to maintain fixed configurations up through its T_g. Hence the T_g of annealed glass can easily be so determined. For the quenched glass, energy releases due to configurational change can be detected as far as 40 deg below the T_g. Hence in constructing the enthalpy curve for the quenched glass at such temperatures for a configurationally fixed state, preference is given to the initial enthalpy-temperature relation of the sample immediately after an energy input. Also the slope of the enthalpy curve for the annealed glass is taken as a lower limit for that of the quenched. The elongated data points in figure 4 indicate the extent of temperature change occurring during a typical drift period of about 1 hr. The combined enthalpy of the sample and of the sample container remains fixed during the drift period. However, the enthalpy of the sample shows either a loss or gain due to the corresponding gain or loss in the enthalpy of the sample container with changing temperature for quenched or annealed glasses, respectively. Although T_g so defined is dependent on the thermal history by which the particular glass was produced, it is independent of the rate of observation. This method corresponds to the dilatometric method in which T_g is taken as the intercept in the volume-temperature diagram. If the inflection points or the onset of the rise in the C_p versus T curves were used as T_g, the hysteresis effect could cause an apparently higher T_g for the annealed glass than for the quenched glass.

Spontaneous adiabatic temperature drifts in the glass transformation range are shown in figure 5. Drift observations for the sample in the as received condition are also included. Positive drift, or energy release, for the quenched glass may be detected from
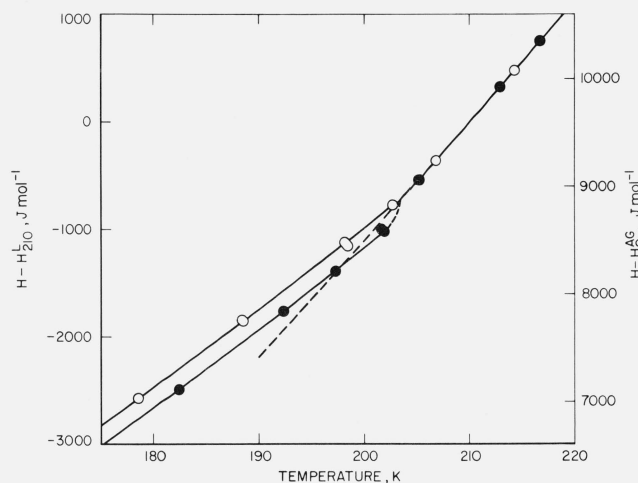
FIGURE 3. C_p/T^3 *versus* T^2 *plot for* cis-1,4-polyisoprene below 15 K.

• annealed glass, ○ quenched glass.

FIGURE 4. *Enthalpy changes of amorphous* cis-1,4-polyisoprene near glass transformation region.

• annealed glass and liquid, ○ quenched glass and liquid.

temperatures 40 deg below T_g. Negative drift, or energy absorption, for the annealed glass started to show up just about at its T_g. These drifts indicate the directions in which the glasses tend to move themselves toward the equilibrium configurations of the supercooled liquid. The minimum in the drift at temperatures above the T_g of a annealed glass shows that the heat capacity measurement was carried out at a faster rate than the relaxation rates governing configurational changes below and at T_g. At higher temperatures the relaxation time decreases to the order of the experimental time scale. The maximum in the drift at temperatures below the T_g of a quenched glass is produced because the experimental time is long in comparison to the relaxation time for many of the configurational changes in the quenched glass. The minimum and the maximum in the drift plot correspond roughly to the inflection points in the heat capacity curves. Above 205 K an equilibrium liquid is produced within the normal experimental time irrespective of the previous history.

The difference in the heat capacities between the liquid and the glass at 200 K is 30.5 ± 0.5 J/K/mol.

3.2. Crystallization

Crystallization of the sample may be detected by warming drifts in the temperature range from 235 to 270 K. If the sample has been cooled to temperatures below T_g since its last melting, the maximum rate of energy release from the sample is about 1 mW/mol at 250 K. If the sample has not been cooled below 240 K since its last melting, the rate of energy release is much smaller, presumably due to fewer nuclei being formed. It takes about 4 hr to measure heat capacities through the crystallization region. The total energy released by the sample in this time is in the order of 10 J/mol. This energy corresponds to a degree of crystallinity of about 0.25 percent, based on a heat of fusion of 4360 J/mol obtained from the melting points of a polymer-diluent system [15].

3.3. Liquid

Except for the results of a few determinations where crystallization and fusion occurred, the heat capacity of the liquid above 205 K can be fitted by least squares to a cubic expression in T with a standard deviation of 0.035 percent. In the crystallization range of 235 to 270 K, the rate of spontaneous energy release passes through a maximum as a function of temperature. At the maximum the half-time for the crystallization is in excess of 25 hr [4]. The rate of crystallization appears to be constant at fixed temperature. The observed calorimetric drift includes both the heat release from crystallization as well as the heat leak in the calorimetric system. By extrapolating the combined drifts to the midpoint of a heating period, the heat capacity of the sample is determined with minimal effect from the crystallization process. The heat capacity so determined in the crystallization range shows a deviation on the order of 0.1 to 0.2 percent, from values interpolated from higher and lower temperatures. This is probably due to the nonlinear change in the combined drift during the heating period and to the uncertainties in determining the linear region for relatively large drifts. The small amount of crystals, produced during the heat capacity measurements in the crystallization range, can be observed to melt around 270 K. The melting process sometimes introduces a somewhat longer time constant than normal for the system to reach a steady state. However, it does not introduce an additional contribution to the quasi-adiabatic temperature drift beyond that due to the heat leak of the calorimetric system. Hence the energy required to melt the crystal cannot be eliminated from the determination of the apparent heat capacity by extrapolation of drifts. The deviation at 270 K, about 0.5 percent higher than the base, is probably due to the inclusion of the heat for melting.

A comparison of literature values [1, 3] with the result from this research as the base line is shown in
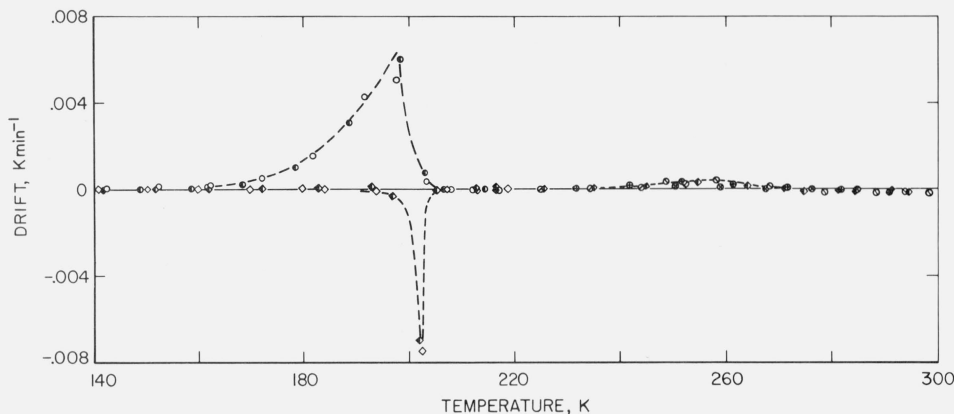

FIGURE 5. *Calorimetric temperature drifts for cis-1,4-polyisoprene near the glass transformation and the crystallization regions.*

◆ annealed glass and liquid, ● quenched glass. All other unfilled circles and diamonds, observations from sample before purification.
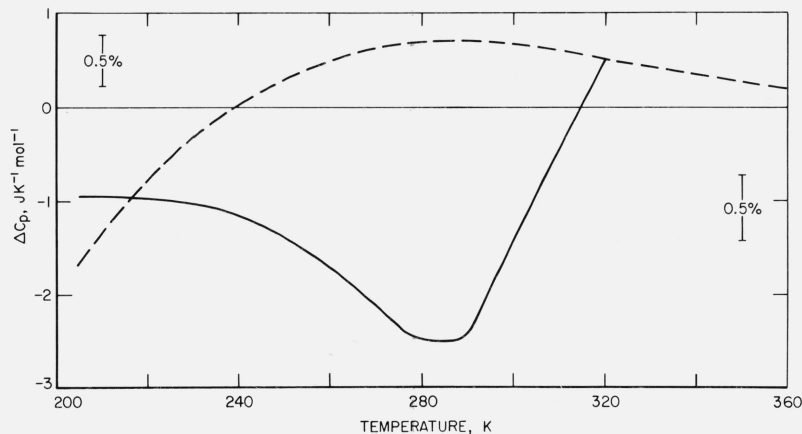
FIGURE 6. *Differences between literature values for heat capacities of cis-1,4-polyiso-prene from smoothed values reported in this research.*

————— Bekkedahl and Matheson (1935);
· · · · · · Wood and Bekkedahl (1967).

figure 6. The solid line represents the deviation of the earlier work on natural rubber hydrocarbon [1] from ours. The deviation ranges from 1 to 2.5 percent. The dashed line represents the deviation of Wood and Bekkedahl's [3] proposed behavior for liquid natural rubber from ours. This behavior was proposed after examining heat capacities of many other liquid elastomers. It is represented by a straight line linking two points—the heat capacity at the highest temperature, 320 K, of Bekkedahl and Matheson's measurement [1], and a mean value at 100 °C over a 150-deg interval reported by McPherson and Bekkedahl [16]. Except at temperatures below 220 K, the proposed behavior is within 1 percent of the experimental values from this research.

Gehman [2] calculated the temperature coefficient of thermal diffusivity $d\alpha/dt$ of rubber at 25 °C, in 10^{-6} $cm^2/s/K$, as -1.9 using data from reference [1] and -1.15 using the proposed value from reference [3]. If the result of this research is used to estimate $d\alpha/dt$, a value of -1.18 is obtained. Results obtained both from this research and from the proposed value give closer agreement with the experimental value of -0.9 [17].

4. References

[1] Bekkedahl, N., and Matheson, H., J. Res. Nat. Bur. Stand. (U.S.), **15**, 503 (1935).

[2] Gehman, S. D., Rubber Chem. Tech. **40**, 36 (1967).

[3] Wood, L. A., and Bekkedahl, N., J. Polymer Sci. **B5**, 169 (1967).

[4] Scott, K. W., Trick, G. S., Mayor, R. H., Saltman, W. M., and Pierson, R. M., Rubber and Plastic Age **42**, 175 (1961).

[5] Sterrett, K. F., Blackburn, D. H., Bestul, A. B., Chang, S. S., and Horman, J., J. Res. Nat. Bur. Stand. (U.S.), **69C** (Eng. and Instr.), 19 (1965).

[6] Chang, S. S., Horman, J. A., and Bestul, A. B., J. Res. Nat. Bur. Stand. (U.S.), **71A** (Phys. and Chem.), 293 (1967).

[7] Comité International des Poids et Mesures, Metrologia **5**, 35 (1969).

[8] Bedford, R. E., Durieux, M., Muijlwijk, R., and Barber, C. R., Metrologia **5**, 47 (1969).

[9] Cataland, G., and Plumb, H. H., J. Res. Nat. Bur. Stand. (U.S.), **70A** (Phys. and Chem.), 243 (1966).

[10] Berry, R. J., Can. J. Phys. **45**, 1963 (1967).

[11] Furukawa, G. T., and Reilly, M., J. Res. Nat. Bur. Stand. (U.S.), **69A** (Phys. and Chem.), 5 (1965).

[12] Roder, H. M., J. Res. Nat. Bur. Stand. (U.S.), **69A** (Phys. and Chem.) 527 (1965).

[13] Roberts, D. E., and Mandelkern, L., J. Res. Nat. Bur. Stand. (U.S.), **54**, 167 (1955).

[14] Roberts, D. E., J. Res. Nat. Bur. Stand. (U.S.), **71A** (Phys. and Chem.), 225 (1967).

[15] Roberts, D. E., and Mandelkern, L., J. Am. Chem. Soc. **77**, 781 (1955).

[16] McPherson, A. T., and Bekkedahl, N., J. Res. Nat. Bur. Stand. (U.S.), **14**, 601 (1935).

[17] Frensdorff, H. H., J. Appl. Polymer Sci. **6**, 828 (1962).

(Paper No. 75A2–654)

120