

Calorimetric Properties of 41° and 122° F Polybutadienes¹

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The heat capacity of 41° and 122° F polybutadienes was measured from 15° to 330° K. The 41° F polybutadiene was found to have a higher (195° K) glass-transformation temperature than the 122° F polymer (187° K). Also, the 41° F polymer exhibited a higher degree of crystallizability than the 122° F polymer. The crystallization temperature range of the 41° F polymer was found to be 200° to 295° K and that of the 122° F polymer 200° to 270° K. The data were used to construct a smoothed table of heat capacity, enthalpy, and entropy from 0° to 330° K.

1. Introduction

Calorimetric investigations of the thermal properties of 41° and 122° F butadiene-styrene copolymers containing 8.58 weight percent of bound styrene are described in a previous paper [1].² The properties studied included heat capacity, enthalpy, entropy, glass transformation, and crystallization. The two copolymers, which were prepared at two different temperatures, exhibited wide differences in thermal properties. For example, the glass-transformation temperature of the 41° F copolymer was found to be 200° K and of the 122° F copolymer, 193° K. Also, the 41° F copolymer exhibited crystallization from 210° to 285° K, whereas the 122° F copolymer showed no such crystallization effects. This paper deals with similar calorimetric studies with 41° and 122° F polybutadienes, both of which have been found to undergo crystallization. The effect of the degree of crystallinity upon the heat capacity of the two polymers was investigated, and the degrees of crystallizability of the two polymers were compared. The heat-capacity measurements were made from about 16° to 330° K. The results were used to compute a smoothed table of heat capacity, enthalpy, and entropy from 0° to 330° K.

2. Apparatus and Method

The details of the calorimetric apparatus and method used have been described [1, 2]. The polymer sample was sealed in a copper container within an adiabatic calorimetric system. The container was provided with a platinum resistance thermometer, a heater, and a vane system for rapid distribution of heat. To thermally isolate the container during the calorimetric experiments, the temperature of the shield system surrounding the container was maintained the same as that of the container surface by means of differential thermocouples and shield heaters. The space surrounding the container was evacuated, and the container and the adjacent shield surfaces were polished. The electric power input was measured by using a Wenner potentiometer, and the length of the heating periods was measured by means of a timer operated on standard 60 cycles.

¹ The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government synthetic rubber program.

² Figures in brackets indicate the literature references at the end of this paper.

The temperature measurements above 90° K are in accordance with the 1948 International Temperature Scale [3]; between 10° and 90° K they are on a provisional scale [4], which consists of a set of platinum resistance thermometers calibrated with a helium-gas thermometer.

The polymers were subjected to two generally different rates of cooling prior to the heat-capacity experiments in order to study in what way their heat capacity and crystallinity were dependent upon the thermal history. In one series of experiments, the polymers were cooled as rapidly as possible by immersing the calorimeter in liquid nitrogen with helium gas in the space surrounding the container. By this procedure the polymers were cooled to about 90° K in 30 min and to 80° K in an additional 30 min, and a portion of the polymer molecules was expected to be "frozen" in the higher energy states. In the second series of measurements, the polymers were cooled slowly in order to obtain as high a degree of crystallinity as practicable. By maintaining a high vacuum in the space surrounding the container, and by using different refrigerants successively, the cooling process was prolonged from a few days to 12 days.

3. Samples

The two polybutadiene samples were obtained through the courtesy of the University of Akron-Government Laboratories, Synthetic Rubber Research. The 41° F polybutadiene designated MS-1045 was prepared using a low-sugar cumene hydroperoxide-redox recipe [5], and the 122° F polymer designated GL-657 was prepared by using a recipe [6] generally used for GR-S type polymers. The polymerization formulas are given in table 1.

The polymers were purified by M. Tryon, of the Rubber Section of the Bureau, by a procedure previously outlined [1]. The analysis of the samples is given in table 2. The samples were pressed into sheets $\frac{1}{8}$ to $\frac{1}{4}$ in. thick and cut to fit between the vanes of the calorimeter containers. Before sealing the containers, the polymers were pumped at high vacuum for 3 days to remove moisture, air, and benzene. The mass of the MS-1045 sample investigated was 42.706 g, and that of the GL-657 was 47.081 g. A small quantity of helium gas was sealed with the polymers to enhance thermal equilibrium during heat-capacity experiments.

TABLE 1. Polymerization formulas^a

	Polymer	
	MS-1045 ^b	GL-657 ^c
Polymerization temperature.....°F	41	122
Ingredients (parts by weight):		
Butadiene.....	100	100
Dodecylmercaptan.....		1.06
Sulfolc B-8.....	0.30	
S. F. Flakes.....		4.3
Dresinate 214.....	4.5	
Na ₃ PO ₄ ·12H ₂ O.....	0.5	
NaOH.....		0.066
Daxad 11.....	0.1	
K ₂ S ₂ O ₈		0.23
Cumene hydroperoxide.....	0.10	
Water.....	168	180
Activator (parts by weight):		
FeSO ₄ ·7H ₂ O.....	0.12	
K ₄ P ₂ O ₇	0.17	
Dextrose.....	1.00	
Water.....	12.0	
Shortshopping agents (parts by weight):		
Hydroquinone.....	0.1	0.2
NaNO ₂	0.04	
Ditertiary butylhydroquinone.....	0.3	
Dresinate 214.....	0.07	
Methanol.....	3.00	
Water.....	8.0	5.0
Final conversion.....%	61.4	72.6
Viscosity, ML-4.....	36	50

^a The polymerization formulas were taken directly from the reports cited in footnotes b and c.

^b Private communication from W. K. Taft, the University of Akron-Government Laboratories, to L. A. Wood, National Bureau of Standards.

^c R. W. Laundrie, Butadiene-styrene copolymers for refractive index studies, Project P 100.74, AU-725.

TABLE 2. Composition of the polybutadienes^a

	Percentage by weight	
	MS-1045	GL-657
Carbon.....	88.47	88.66
Hydrogen.....	11.160	11.180
Sulfur.....	0.083	0.150
Oxygen.....	.12	.145
Ash.....	.34	.097
Phenylbetanaphthylamine ^b10	.12

^a Analysis by R. A. Paulson.

^b Added after the analysis.

4. Results

4.1. 41° F Polybutadiene, MS-1045

The experimental details of heat treatment, temperature range of the measurements, and temperature drifts with the 41° F polybutadiene are summarized in table 3. The observed heat capacities are given in table 4, and the general behavior of these results are shown in the plot of figure 1. The measurements of run 1 were made after shock-cooling the polymer from room temperature to 77° K. During the course of the heat-capacity measurements, upward temperature drifts were observed from 177° to 283° K as the polymer molecules slowly transformed into states of lower energy [1]. During the shock-cooling process a certain portion of the polymer molecules failed to undergo transition to states of lower energy. When the temperature was raised to a certain range during the heat-capacity

TABLE 3. Heat treatments and the observations with the 41° F polybutadiene, MS-1045

Run	Treatment of samples	Temperature range of measurements	Temperature drift observations
1	Cooled rapidly from room temperature to 77° K.	77 to 298	Upward drift from 177° to 283° K.
2	Left at room temperature for 1 day	303 to 334	No drift.
3	Cooled slowly from room temperature to 77° K over 2 days.	77 to 301	Upward drift from 180° to 280° K.
4	Cooled slowly from room temperature to 77° and then to 15° K.	15 to 88	No drift.
5	Cooled slowly from room temperature to 77° and then to 53° K.	53 to 90	Do.

TABLE 4. Observed heat capacities with 41° F polybutadiene, MS-1045

T		C	T		C
Run 1			Run 3—Continued		
°K		abs j °K ⁻¹ g ⁻¹	°K		abs j °K ⁻¹ g ⁻¹
82.40		0.5654	174.98		1.074
91.56		.6174	182.82		1.121
101.24		.6692	188.69		1.187
111.76		.7273	194.24		1.374
121.83		.7830	199.15		1.529
132.07		.8404	209.11		1.736
142.64		.8989	225.17		1.924
153.39		.9581	241.36		2.184
164.22		1.016	256.19		2.379
171.19		1.060	271.61		2.510
175.52		1.082	287.52		2.133
180.47		1.111	298.40		1.969
186.02		1.150			
191.31		1.293			
196.37		1.416			
201.41		1.397			
209.19		1.511			
219.97		1.718			
233.65		1.903			
249.20		2.200			
263.10		2.612			
276.16		2.557			
290.28		2.083			
Run 2			Run 4		
307.46		1.992	15.58		0.0707
315.26		2.017	17.51		.0872
322.98		2.043	19.88		.1068
330.62		2.069	21.79		.1240
			23.44		.1387
			25.79		.1605
			28.86		.1882
			32.18		.2188
			35.82		.2495
			39.18		.2782
			42.79		.3045
			47.02		.3380
			76.30		.5274
			81.39		.5589
			86.19		.5883
Run 3			Run 5		
80.14		0.5505	55.01		0.3910
87.24		.5928	59.00		.4182
96.11		.6409	64.54		.4547
105.52		.6918	70.06		.4882
115.73		.7479	74.35		.5145
126.23		.8056	78.86		.5422
136.90		.8641	83.11		.5687
147.71		.9226	87.55		.5958
158.70		.9821			
166.03		1.024			

experiments, these molecules acquired sufficient thermal energy for transition to lower energy states with the consequent liberation of heat. Prior to run 3, the polymer was cooled slowly from room temperature to 77° K over 2 days, and the results showed upward temperature drifts from 180° to 280° K. Below the glass-transformation temperature (195° K), the heat-capacity results of run 3 (polymer slowly cooled) were slightly lower than run

TABLE 5. Heat capacity, enthalpy, and entropy of 41° F. polybutadiene, MS-1045

T	C	(H _T -H ₀ °K)	(S _T -S ₀ °K)
°K	abs j°K ⁻¹ g ⁻¹	abs j g ⁻¹	abs j°K ⁻¹ g ⁻¹
0	0	0	0
5	0.0034	0.0042	0.0011
10	.0256	.0662	.0089
15	.0655	.2923	.0266
20	.1081	.7280	.0514
25	.1534	1.381	.0804
30	.1983	2.261	.1123
35	.2419	3.362	.1462
40	.2829	4.675	.1812
45	.3211	6.187	.2168
50	.3570	7.882	.2524
55	.3916	9.754	.2881
60	.4247	11.80	.3236
65	.4567	14.00	.3589
70	.4881	16.36	.3939
75	.5191	18.88	.4286
80	.5499	21.55	.4631
85	.5798	24.38	.4973
90	.6083	27.35	.5313
95	.6356	30.46	.5649
100	.6624	33.70	.5982
105	.6894	37.08	.6311
110	.7169	40.60	.6639
115	.7448	44.25	.6963
120	.7725	48.05	.7286
125	.8001	51.98	.7607
130	.8276	56.05	.7926
135	.8552	60.25	.8244
140	.8830	64.60	.8560
145	.9109	69.08	.8875
150	.9379	73.71	.9188
155	.9646	78.46	.9500
160	.9922	83.35	.9810
165	1.021	88.39	1.012
170	1.050	93.56	1.043
175	1.079	98.89	1.074
180	1.108	104.4	1.105
185	1.14	-----	-----
190	1.21	-----	-----
195	1.31	-----	-----
200	1.50	-----	-----
205	1.65	-----	-----
210	1.68	-----	-----
215	1.70	-----	-----
220	1.72	-----	-----
225	1.73	-----	-----
230	1.75	-----	-----
235	1.76	-----	-----
240	1.78	-----	-----
245	1.80	-----	-----
250	1.81	-----	-----
255	1.83	-----	-----
260	1.84	-----	-----
265	1.86	-----	-----
270	1.87	-----	-----
275	1.89	-----	-----
280	1.91	-----	-----
285	1.92	-----	-----
290	1.94	-----	-----
295	1.95	-----	-----
300	1.97	-----	-----
305	1.985	352.2	2.123
310	2.000	362.2	2.156
315	2.016	372.2	2.188
320	2.033	382.3	2.220
325	2.050	392.5	2.251
330	2.067	402.8	2.283

1 (polymer rapidly cooled), with the difference increasing with temperature to a maximum of about 1 percent near the glass-transformation temperature. The upward temperature drifts from about 200° to 285° K are attributed to slow crystallization of the polymer molecules. Except for a few heat-capacity points of run 1, all experimental points in the crystallization interval were above the broken line of figure

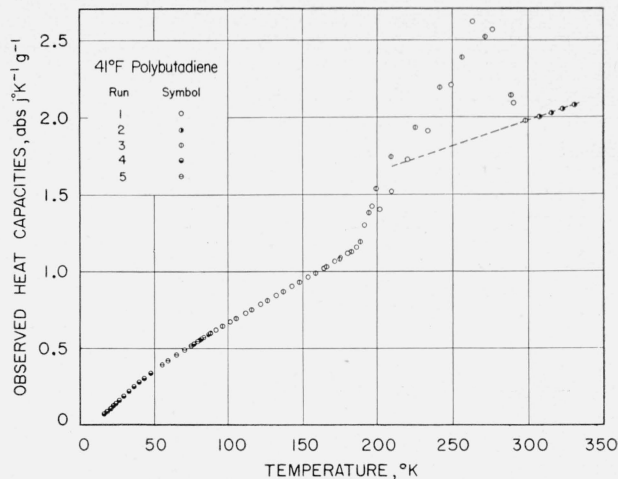


FIGURE 1. Observed heat capacities of the 41° F polybutadiene, MS-1045.

1. This indicates more melting than crystallization; consequently, the upward drifts observed are probably the result of the formation of new crystals and of the recrystallization of polymer near the heater, where the temperature was higher during the heating period. The broken line of figure 1 is the heat capacity of hypothetical amorphous polymer and was obtained by linearly extrapolating the heat capacity in the range 295° to 330° K to the glass-transformation temperature. This linear extrapolation of the amorphous portion of the heat capacity was made on consideration that the heat capacity of HyCar O. R.-15 [7], which does not crystallize, could be represented within 0.2 percent from 250° (just above the glass-transformation temperature) to 340° K by a linear equation. Similarly, in another noncrystallizing synthetic rubber, GR-S [8], the heat capacity from about 225° to 330° K could be represented by a quadratic equation to 0.1 percent or by a linear equation to about 0.3 percent or better.

The data of table 4 were used to construct the heat-capacity values of table 5, spaced at equal temperature intervals. The heat capacities given were based on the results with the polymer slowly cooled. From 180° to 305° K the heat-capacity values of table 5 were obtained from a large-scale plot of the observed heat capacities. In the crystallization interval (200° to 295° K) the results from the broken line were tabulated. Below 180° K and above 305° K the deviations of the observed heat capacities from empirical equations were first plotted, then the deviation curves and the empirical equations were used to obtain heat capacities at even temperatures. The heat capacities below the lower limit (15° K) of the measurements were obtained by fitting a Debye function to the observed values in the temperature range 15° to 30° K. The function used is³

$$C = 0.2425D(88.7/T). \quad (1)$$

³ The equation has no significance other than for extrapolation of the heat capacity.

The glass-transformation temperature of this particular sample of 41° F polybutadiene was found to be about 195° K. Above 295° K the polymer is believed to be completely amorphous.

The enthalpy and entropy of the 41° F polybutadiene were obtained by evaluating the thermodynamic relations

$$(H_T - H_{0^\circ K}) = \int_0^T C dT \quad (2)$$

and

$$(S_T - S_{0^\circ K}) = \int_0^T C dT/T, \quad (3)$$

respectively, where $(H_T - H_{0^\circ K})$ and $(S_T - S_{0^\circ K})$ are the enthalpy and entropy of the polymer relative to the absolute zero of temperature. The other symbols have their usual significance. Except below 15° K and between 180° and 305° K, eq (2) and (3) were evaluated by tabular integration, using four-point Lagrangian integration coefficients [9]. Below 15° K the Debye function (eq 1) was evaluated analytically. Between 180° and 305° K the enthalpy was obtained directly from the experimental measurements [1] by summing the energy input of run 3 (polymer was cooled slowly), in which the experiments were made continuously from 180.0093° to 301.6183° K. When corrected to the even temperature interval (180° to 305° K), the enthalpy change amounted to 247.84 abs j g⁻¹. The entropy change was obtained by summing similarly the various $C\Delta T/T_m$'s of run 3, where $C\Delta T$ is the enthalpy change of the heating interval and T_m is the midtemperature of the interval. After correcting to the temperature interval 180° to 305° K, the entropy change amounted to 1.018 abs j °K⁻¹g⁻¹.

4.2. 122° F Polybutadiene, GL-657

The experimental results with the 122° F polybutadiene are summarized in tables 6 and 7. Table 6 shows details of the heat treatments, temperature range of the measurements, and the drift observations. The observed heat-capacity values are given in table 7 and plotted in figure 2. When the polymer was cooled rapidly, the subsequent heat-capacity experiments (run 3) showed upward temperature drifts from 148° to 253° K. However, when the polymer was cooled slowly, the heat-capacity results (run 2) showed downward temperature drifts from 186° to 189° K and upward drifts from 220° to 265° K. These results show that in the experiments with the polymer rapidly cooled, the upward temperature drifts set in about 40 deg below the temperature at which the downward drifts began with the polymer slowly cooled. In the experiments with the 41° F polybutadiene slowly cooled over 2 days, no downward temperature drifts were observed below the glass-transformation temperature. Only upward temperature drifts were observed. Probably 2 days were not sufficient for much of the 41° F polymer to transform to lower energy states at temperatures below the glass-transformation temperature.

TABLE 6. Heat treatments and the observations with the 122° F polybutadiene, GL-657

Run	Treatment of sample	Temperature range of measurements	Temperature drift observations
1	Cooled slowly from room temperature to 115° K over 3 days; then rapidly to 55° K.	55 to 90.....	No drift.
2	Cooled slowly from room temperature to 78° K over 12 days.	82 to 289.....	Downward drift from 186° to 189° K; upward from 220° to 265° K.
3	Cooled rapidly from room temperature to 79° K.	79 to 292.....	Upward drift from 148° to 253° K.
4	Left at room temperature for 5 days and cooled to 273° K.	274 to 336.....	No drift.
5	Cooled slowly to 78° K; then rapidly to 15° K.	15 to 63.....	Do.
6	Cooled slowly to 150° K....	Heated continuously from 173 to 282 K.	Do.

TABLE 7. Observed heat capacities of 122° F polybutadiene, GL-657

T		C	T		C
Run 1			Run 3—Continued		
° K		abs j °K ⁻¹ g ⁻¹	° K		abs j °K ⁻¹ g ⁻¹
55.61		0.3985	164.34		1.028
57.32		.4093	175.01		1.082
59.75		.4256	181.40		1.122
62.83		.4461	185.10		1.318
65.75		.4641	189.07		1.658
68.53		.4803	192.72		1.679
72.52		.5036	196.36		1.669
77.61		.5338	200.07		1.585
82.38		.5611	211.86		1.364
87.93		.5930	229.89		1.836
			245.42		2.089
			260.48		1.973
			276.00		1.884
			287.73		1.917
Run 2			Run 4		
88.26		0.5953	277.33		1.884
99.80		.6593	282.23		1.901
116.33		.7174	287.05		1.916
120.24		.7717	291.78		1.935
130.20		.8258	296.56		1.946
140.13		.8793	301.59		1.962
150.63		.9353	306.76		1.979
161.53		.9949	312.54		1.996
171.96		1.058	318.71		2.017
180.35		1.124	324.83		2.040
185.11		1.220	331.91		2.063
188.04		1.434	Run 5		
190.94		1.567	16.70		0.0864
194.37		1.611	18.61		.1033
198.17		1.643	20.39		.1175
201.92		1.673	22.24		.1353
212.26		1.771	24.47		.1560
228.17		2.124	27.21		.1802
242.93		2.140	29.88		.2040
257.37		1.986	33.46		.2351
273.62		1.883	37.77		.2701
285.48		1.912	41.81		.3011
Run 3			46.39		.3360
83.47		0.5725	51.38		.3718
93.41		.6273	56.14		.4023
104.36		.6867	60.76		.4331
114.46		.7427			
123.90		.7963			
133.47		.8513			
143.21		.9071			
153.21		.9641			

The upward temperature drifts from 200° to 270° K are considered to arise from slow crystallization of the rubber polymer in a manner similar to the 41° F polymer described earlier. Also, the relatively high heat capacity above the broken line indicates

TABLE 8. Heat capacity, enthalpy, and entropy of 122° polybutadiene, GL-657

<i>T</i>	<i>C</i>	(<i>H_T</i> - <i>H₀</i>) _{°K}	(<i>S_T</i> - <i>S₀</i>) _{°K}
°K	abs j °K ⁻¹ g ⁻¹	abs j g ⁻¹	abs j °K ⁻¹ g ⁻¹
0	0	0	0
5	.0036	0.0045	0.0012
10	.0271	.0701	.0094
15	.0707	.3107	.0283
20	.1154	.7777	.0548
25	.1502	1.440	.0844
30	.2045	2.325	.1164
35	.2477	3.459	.1513
40	.2878	4.798	.1890
45	.3257	6.333	.2231
50	.3615	8.052	.2593
55	.3955	9.945	.2954
60	.4279	12.00	.3312
65	.4590	14.22	.3667
70	.4891	17.59	.4018
75	.5185	19.11	.4366
80	.5474	21.78	.4709
85	.5760	24.58	.5050
90	.6043	27.54	.5387
95	.6323	30.63	.5721
100	.6601	33.86	.6053
105	.6877	37.23	.6382
110	.7153	40.74	.6708
115	.7428	44.38	.7032
120	.7702	48.16	.7354
125	.7976	52.08	.7674
130	.8248	56.14	.7992
135	.8520	60.33	.8308
140	.8791	64.66	.8623
145	.9061	69.12	.8936
150	.9330	73.72	.9248
155	.9600	78.45	.9558
160	.9874	83.32	.9867
165	1.0153	88.33	1.018
170	1.0453	93.48	1.048
175	1.0798	98.79	1.079
180	1.12	-----	-----
185	1.24	-----	-----
190	1.54	-----	-----
195	1.63	-----	-----
200	1.66	-----	-----
205	1.68	-----	-----
210	1.70	-----	-----
215	1.71	-----	-----
220	1.73	-----	-----
225	1.74	-----	-----
230	1.76	-----	-----
235	1.77	-----	-----
240	1.78	-----	-----
245	1.80	-----	-----
250	1.81	-----	-----
255	1.83	-----	-----
260	1.84	-----	-----
265	1.86	-----	-----
270	1.87	-----	-----
275	1.886	280.4	1.885
280	1.900	289.8	1.919
285	1.915	299.4	1.953
290	1.929	309.0	1.986
295	1.944	318.7	2.019
298.16	1.953	324.8	2.040
300	1.958	328.4	2.052
305	1.973	338.3	2.084
310	1.987	348.2	2.117
315	2.004	358.1	2.149
320	2.021	268.2	2.180
325	2.039	378.3	2.212
330	2.058	388.6	2.243

more melting than crystallization. In the experiments with the polymer slowly cooled (run 2) all the points were above the broken line. However, with the polymer rapidly cooled (run 3) a low point was observed, which gave a γ -like shape to the heat

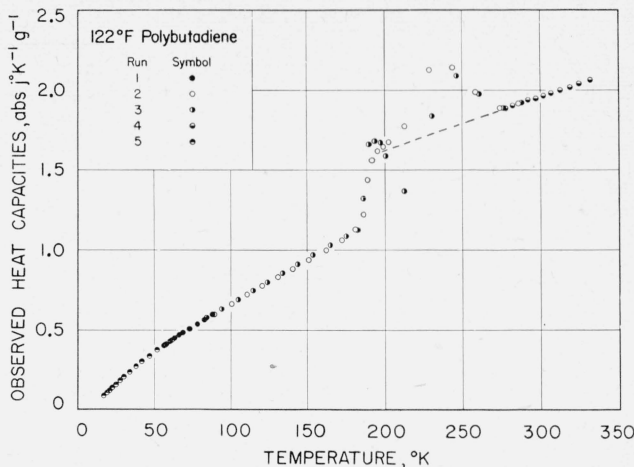


FIGURE 2. Observed heat capacities of the 122° F polybutadiene, GL-657.

capacity (see fig. 2). A large amount of crystallization has caused the apparent heat capacity to be relatively low.

The results of these measurements were used to compute a table of heat capacities at equally spaced temperature intervals (see table 8). The results used were those from the experiments with the polymer slowly cooled, and the procedure used in obtaining the smoothed heat capacities, including those in the crystallization interval, was similar to that with the 41° F polymer. The Debye function for the extrapolation of the data below 15° K was

$$C = 0.2631D(89.5/T). \quad (4)$$

The glass-transition temperature of this material was found to be 187° K. The crystallization range was 200° to 270° K, which is about 25 degrees narrower than the 41° F polybutadiene (200° to 295° K). Above 270° K, where the heat capacity is smooth, the polymer is believed to be amorphous.

The enthalpy and entropy of the 122° F polybutadiene were evaluated by a procedure similar to the 41° F polymer. The values are given in table 8.

4.3. Reliability of the Results

The reliability of the heat-capacity measurements with these polymers is difficult to evaluate because of the nonreproducibility of the physical state from experiment to experiment. The heat-capacity measurements made previously with normal materials of low molecular weight are believed to be accurate to 0.2 percent [10]. The results with these polymers show considerable scattering in the temperature range where temperature drifts occur, as the results are dependent upon how long temperature equilibrium is awaited. In the experiments where temperature drifts occurred, although no attempt was made to wait until complete temperature equilibrium was

reached, the general nature of the heat capacity is believed to be preserved. In the temperature range where no temperature drift occurred, the heat-capacity results obtained for a given heat treatment are believed to be accurate within 0.2 to 0.3 percent.

The enthalpy and entropy values given in tables 5 and 8 are believed to be generally accurate to 0.5 percent.

5. Discussion

The results of these experiments show that by changing the polymerization temperature of polybutadiene from 41° to 122° F the glass-transformation temperature was lowered from 195° to 187° K. This behavior is similar to that observed with 41° and 122° F butadiene-styrene copolymers containing 8.58 weight percent of bound-styrene [1] previously reported. Also, the temperature range of crystallization has become narrower in the 122° F polymer (200° to 270° K). The crystallization temperature range of 41° F polymer was found to be from 200° to 295° K. In the butadiene-styrene copolymers [1], crystallization took place in the 41° F copolymer but was absent in the 122° F copolymer.

In table 9 the enthalpy changes from 175° to 305° K are given for both polymers. The results listed are from experiments in which the polymers were given various prior heat treatments, as described earlier. Slight adjustments have been made in the original experimental enthalpy in order that the temperature range be the same in both polymers. In the 41° F polymer the enthalpy changes between shock-cooled and annealed differ by only 5.51 abs j g⁻¹. In the case of the 122° F polybutadiene, the difference is 12.07 abs j g⁻¹. The enthalpy changes obtained for the 41° F polybutadiene for this temperature interval are much greater than that of the 122° F polybutadiene. These results seem to indicate that the 41° F polymer has a higher crystallizability than the 122° F polymer. The integrated enthalpy change was obtained by tabular integration of the heat capacity given by the hypothetical amorphous curve. The comparison of the enthalpy change in the 122° F polymer when shock-cooled with the integrated value indicates that the amorphous condition was practically frozen-in. On the other hand, a similar comparison of the 41° F polymer would indicate that even upon shock-cooling considerable crystallization took place.

TABLE 9. Comparison of the enthalpy changes of 41° and 122° F polybutadienes from 175° to 305° K

	Polybutadiene	
	41° F	122° F
	<i>abs j g⁻¹</i>	<i>abs j g⁻¹</i>
Shock-cooled.....	247.79	227.39
Annealed.....	253.30	239.46
Integrated (amorphous).....	220.80	225.58
Annealed minus integrated.....	32.50	13.88

In the investigation of the 41° F butadiene-styrene copolymer [1] of 8.58 weight percent of bound styrene the enthalpy change difference of the annealed and integrated results amounted to about 16 to 19 abs j g⁻¹. In this investigation the 41° and 122° F polybutadienes gave 33 and 14 abs j g⁻¹, respectively. Bekkedahl and Matheson [11] reported 16.71 abs j g⁻¹ for the heat of fusion of natural rubber, which indicates that 41° F polybutadiene has a higher crystallizability than natural rubber.

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