

# Heat Capacity of Some Butadiene-Styrene Copolymers from 0° to 330° K<sup>1</sup>

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The heat capacity of butadiene-styrene copolymer polymerized at 41° F (5° C) containing 22.61 weight percent of bound-styrene and of butadiene-styrene copolymer polymerized at 122° F (50° C) containing 42.98 weight percent of bound-styrene was determined in the range 15° to 330° K, and the data have been used to construct tables of smoothed values of heat capacity, enthalpy, and entropy. The glass-transformation temperature of the 41° F copolymer was estimated to be 213° K and that of the 122° F copolymer 237° K.

## 1. Introduction

The work presented in this paper is a part of the series of heat-capacity investigations being conducted at the National Bureau of Standards on rubber polymers and related substances. The results of earlier work with 41° F (5° C) and 122° F (50° C) butadiene-styrene copolymers [1]<sup>2</sup> containing 8.58 weight percent of bound-styrene and with 41° and 122° F polybutadienes [2] have shown that both polymerization temperature and composition influence the crystallizability and the glass-transformation temperature. The present two copolymers are of higher bound-styrene content than those previously studied [1]. The 41° F copolymer of 22.61 weight percentage of bound-styrene is of particular interest, inasmuch as it is similar to the "cold" rubber presently produced in large quantities. The other copolymer prepared at 122° F with the butadiene-styrene charge ratio of 50:50 by weight contained 42.98 weight percent of bound-styrene. Heat-capacity measurements were made on the two copolymers from 15° to 330° K, and the data were used to obtain a table of smoothed values of heat capacity, enthalpy, and entropy from 0° to 330° K. The glass-transformation temperature of the 41° F copolymer was estimated to be 213° K and that of the 122° F copolymer to be 237° K. Neither copolymer exhibited any crystallization effects.

## 2. Apparatus and Method

The details of the calorimetric apparatus and methods used in this investigation can be found in previous reports dealing with 1,3-butadiene [3] and diphenyl ether [4]. The various heat treatments, to which the present copolymers were subjected, were similar to those of earlier investigations [1,2]. As the copolymers described herein did not crystallize, the prolonged annealing procedures in the crystallization temperature range were not involved. However,

in several series of experiments, the copolymers were annealed just below the glass-transformation temperature; in other series, the copolymers were shock-cooled.

## 3. Samples

The copolymer sample identified as X-478 was obtained from the Copolymer Corporation, Baton Rouge, La. According to the information received from the manufacturer, this copolymer was emulsion polymerized at 41° F (5° C) with Dresinate-214 (potassium soap of disproportionated rosin) as the emulsifying agent. The initial butadiene-styrene charge ratio was 71:29 by weight, and the modifier of the polymerization reaction was Sulfole B-8 (tertiary dodecyl mercaptan). The activator was ferrous sulfate-potassium pyrophosphate, and the "short-stopping" agent was dinitrochlorobenzene. The reaction was "short-stopped" at about 60-percent conversion. No further information is known about this polymer.

The second copolymer sample was obtained through the University of Akron Government Laboratories [5] and was designated as GL-662 or 74PB1.<sup>3</sup> This copolymer was prepared at 122° F (50° C) by emulsion polymerization with an initial butadiene-styrene charge ratio of 50:50 by weight. The emulsifier was soap flakes (S. F.), and the modifier was dodecyl mercaptan (DDM). The polymerization reaction was activated by potassium persulfate and "short-stopped" by means of hydroquinone at 73.6-percent conversion.

The copolymers were purified by M. Tryon, of the Rubber Section of the Bureau, by a procedure previously outlined [1]. The analyses of the purified samples are summarized in table 1.<sup>4</sup> The styrene contents given in the table were computed from the carbon-hydrogen ratios corrected for mercaptan content (that is, Sulfole B-8 or dodecyl mercaptan).

<sup>1</sup> The work discussed herein was performed as a part of the research project sponsored by the Federal Facilities Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.

<sup>3</sup> Hereafter in this paper, the 41° F butadiene-styrene copolymer containing 22.61 weight percent bound-styrene will be identified as X-478 and the 122° F copolymer containing 42.98 weight percent bound-styrene as GL-662.

<sup>4</sup> The analyses were made by R. A. Paulson of the Analytical Chemistry Section of the Bureau.

TABLE 1. *Composition of the copolymers*<sup>a</sup>

	Percentage by weight	
	X-478	GL-662
Carbon.....	89.443	90.100
Hydrogen.....	10.4008	9.710
Sulfur.....	0.048	0.081
Oxygen.....	.15	.14
Ash.....	.098	.111
Styrene.....	22.61	42.98
Phenylbetanaphthylamine <sup>b</sup> .....	0.1	0.1

<sup>a</sup> Analysis by R. A. Paulson.<sup>b</sup> Added after the analysis.

The phenylbetanaphthylamine (stabilizer) was added after the analysis.

The samples, after being placed in the copper sample container, were further pumped on at high vacuum for several days to remove as much of the volatile impurities (moisture, air, and benzene) as possible. The mass of the X-478 copolymer investigated was 43.894 g and that of the GL-662 copolymer was 45.366 g.

## 4. Results

### 4.1. X-478 Copolymer

The heat-capacity measurements with the X-478 copolymer were carried out in a manner similar to those previously described [1,2]. In one series of experiments the measurements were made after shock-cooling the copolymer from room temperature to that of liquid nitrogen (78° C). In another series, the copolymer was cooled slowly over the same temperature range. The shock-cooling process took about 1 hour and the slow-cooling process from several days to a week or more, depending upon whether liquid

nitrogen alone was used, or dry-ice and then liquid nitrogen were used successively. The heat treatments, the temperature range of measurements, and the various observations of temperature drifts are summarized in table 2. The observed heat capacities are given in table 3 and plotted in figure 1 to show the general nature of the results. When the copolymer was shock-cooled, upward temperature drifts were observed during heat-capacity measurements from about 170° to 215° K (runs 3 and 4). When slowly cooled, downward drifts were observed from about 207° to 216° K (run 5). The copolymer exhibited no crystallization effects. The glass-transition temperature was estimated to be 213° K, the temperature at "half-height" in the upward sweep of the heat capacity.

The data were used to obtain the smoothed values of heat capacity, enthalpy, and entropy given in table 4. The details of the methods used in obtaining these quantities have been previously given [1,2]. In the temperature interval 195° to 225° K, where the heat capacity increased rapidly, the heat-capacity values of table 4 were obtained from a smooth curve drawn through the experimental results plotted on a large scale. From 225° to 330° K the heat capacity of this copolymer can be represented within 0.1 percent by the equation.

$$C = 1.396 + 2.63 \times 10^{-4} T + 4.688 \times 10^{-6} T^2$$

(abs j deg<sup>-1</sup> g<sup>-1</sup>).

Three experimental determinations of the enthalpy change were carried out for the temperature interval 195° to 225° K. In runs 3 and 4 the copolymer was previously shock-cooled. The observed changes in enthalpy for both runs were the same, 40.39 abs j g<sup>-1</sup>. The enthalpy change observed in run 5, in

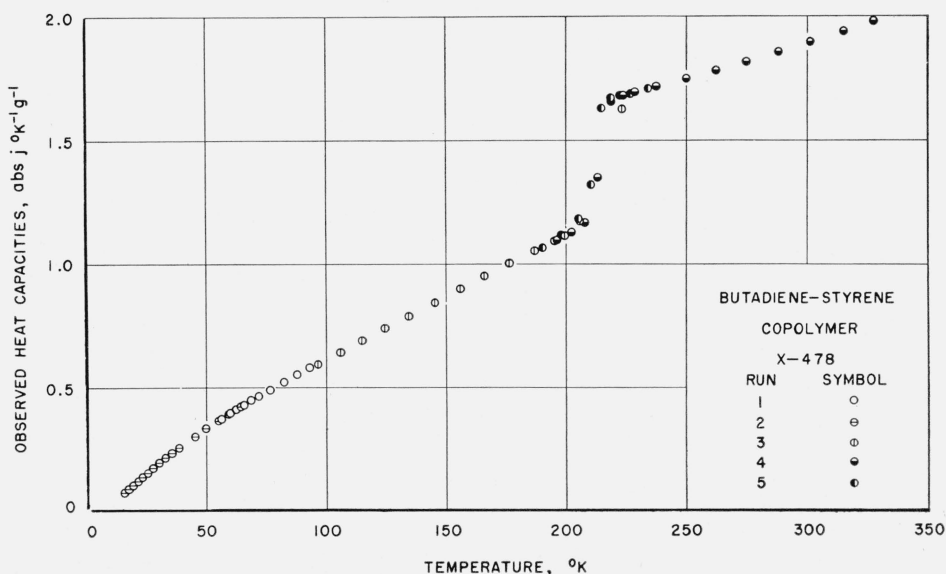
FIGURE 1. *Observed heat capacities of the butadiene-styrene copolymer X-478.*

TABLE 2. Heat treatments and observations on the butadiene-styrene copolymer X-478

(Temperatures are in °K; °K = °C + 273.16°)

Run	Treatment of sample	Temperature range of measurements	Drift observations
1----	Cooled slowly from room temperature to 90°; then rapidly to 54°.	54° to 95°----	No drift.
2----	After run 1 the sample was cooled rapidly from 95° to 15°.	15° to 66°----	Do.
3----	Cooled rapidly from room temperature to 83°.	83° to 234°...	Upward drift from 170° to 211°.
4----	Cooled rapidly from room temperature to 183° and heated to 193°	193° to 332°..	Upward drift from 193° to 215°.
5----	Cooled slowly from room temperature to 186° over 1 week.	186° to 238°..	Downward drift from 207° to 216°.

TABLE 3. Observed heat capacities of the butadiene-styrene copolymer X-478

(°K = °C + 273.16°)

T		C	T		C
Run 1			Run 3—Continued		
°K	abs j deg <sup>-1</sup> g <sup>-1</sup>		°K	abs j deg <sup>-1</sup> g <sup>-1</sup>	
55.6399 <sup>a</sup>	0.3742		155.3546	0.8998	
58.9542	.3947		165.4390	.9524	
61.9540	.4133		175.7846	1.0037	
65.1126	.4315		186.2819	1.0555	
68.3386	.4495		193.9549	1.0906	
71.4100	.4657		198.9514	1.1160	
85.9445	.4906		206.2348	1.1705	
81.8023	.5238		222.7774	1.6304	
87.2943	.5546				
92.4913	.5808				
Run 2			Run 4		
15.6156	0.0744		195.8999	1.0962	
17.2601	.0884		201.6262	1.1309	
19.0338	.1027		207.2510	1.1664	
21.0974	.1195		212.5443	1.3519	
23.0131	.1361		218.0144	1.6600	
24.9253	.1524		223.1011	1.6884	
27.3024	.1724		228.1394	1.6999	
29.9704	.1944		236.8196	1.7214	
32.4460	.2140		249.3464	1.7534	
35.1286	.2349		261.6749	1.7861	
38.3874	.2589		274.3540	1.8202	
44.9111	.3046		287.6538	1.8597	
49.2922	.3334		300.7215	1.9000	
54.5618	.3666		314.3536	1.9425	
59.3997	.3963		326.9844	1.9825	
63.9250	.4238				
Run 3			Run 5		
87.3050	0.5883		189.8650	1.0677	
96.2926	.5982		197.3133	1.1189	
105.4046	.6438		204.5483	1.1846	
114.7106	.6918		209.9087	1.3222	
124.1622	.7402		214.0593	1.6341	
134.1576	.7919		217.9034	1.6770	
144.6692	.8458		221.7021	1.6857	
			226.1066	1.6958	
			233.5882	1.7134	

<sup>a</sup> The temperatures given are accurate to ±0.01 deg K. Figures beyond the second decimal are significant only insofar as small temperature differences are concerned.

which the copolymer was previously cooled slowly, was 41.95 abs j g<sup>-1</sup>. The latter value was used in constructing the enthalpy values of table 4. The difference, 1.56 abs j g<sup>-1</sup>, indicates qualitatively the

TABLE 4. Heat capacity, enthalpy, and entropy of butadiene-styrene copolymer X-478

(°K = °C + 273.16°)

T	C	(H <sub>T</sub> - H <sub>0</sub> ) <sub>K</sub>	(S <sub>T</sub> - S <sub>0</sub> ) <sub>K</sub>
°K	abs j deg <sup>-1</sup> g <sup>-1</sup>	abs j g <sup>-1</sup>	abs j deg <sup>-1</sup> g <sup>-1</sup>
0	0	0	0
5	0.0034	0.0043	0.0011
10	.0259	.0671	.0090
15	.0674	.2967	.0270
20	.1091	.7374	.0522
25	.1530	1.393	.0812
30	.1947	2.263	.1128
35	.2339	3.335	.1458
40	.2706	4.598	.1795
45	.3052	6.038	.2133
50	.3380	7.647	.2472
55	.3694	9.416	.2809
60	.4000	11.34	.3144
65	.4304	13.42	.3476
70	.4584	15.64	.3806
75	.4853	18.00	.4131
80	.5137	20.49	.4453
85	.5419	23.13	.4773
90	.5685	25.91	.5091
95	.5930	28.82	.5405
100	.6171	31.84	.5715
105	.6421	34.99	.6022
110	.6676	38.26	.6327
115	.6932	41.66	.6629
120	.7188	45.19	.6930
125	.7445	48.85	.7229
130	.7703	52.64	.7526
135	.7960	56.56	.7821
140	.8217	60.60	.8115
145	.8474	64.77	.8408
150	.8731	69.07	.8700
155	.8987	73.50	.8990
160	.9242	78.06	.9280
165	.9497	82.74	.9568
170	.9750	87.56	.9856
175	1.000	92.49	1.014
180	1.025	97.56	1.043
85	.049	102.7	1.071
190	1.074	108.0	1.099
195	1.096	113.5	1.128
200	1.12	-----	-----
205	1.17	-----	-----
210	1.25	-----	-----
215	1.65	-----	-----
220	1.68	-----	-----
225	1.693	155.4	1.326
230	1.705	163.9	1.364
235	1.717	172.5	1.400
240	1.729	181.1	1.437
245	1.742	189.8	1.472
250	1.755	198.5	1.508
255	1.768	207.3	1.543
260	1.782	216.2	1.577
265	.795	225.1	1.611
270	1.808	234.1	1.645
273.16	1.817	239.8	1.666
275	1.822	243.2	1.678
280	1.837	252.4	1.711
285	1.852	261.6	1.744
290	1.867	270.9	1.776
295	1.882	280.2	1.808
298.16	1.892	286.2	1.828
300	1.898	289.7	1.840
305	1.913	299.2	1.871
310	1.929	308.8	1.903
315	1.944	318.5	1.934
320	1.960	328.3	1.964
325	1.976	338.1	1.995
330	1.992	348.0	2.025

extent of relaxation effects associated with glass transformation under the experimental conditions as outlined. The enthalpy values given above were obtained by summing various experimental input energies in the region of glass transformation and by correcting to the even temperature interval. The

small input energies in this range also served to establish the general shape and position of glass transformation.

The entropy change ( $0.198 \text{ abs j deg}^{-1} \text{ g}^{-1}$ ) for the temperature interval  $195^\circ$  to  $225^\circ \text{ K}$  was obtained by summing various  $\Delta H/T_m$ 's of run 5, where  $\Delta H$  is the input energy and  $T_m$  the mean temperature of the heating interval.

#### 4.2. GL-662 Copolymer

The experimental details and the results with the GL-662 copolymer are given in tables 5 and 6 and shown in figure 2. This copolymer responded to heat treatments in a fashion similar to the X-478 copolymer. When shock-cooled, upward temperature drifts were observed from about  $198^\circ$  to  $240^\circ \text{ K}$  (run 1). Also, when slowly cooled, downward drifts in temperature were observed from about  $230^\circ$  to  $240^\circ \text{ K}$  (run 3). As with the X-478 copolymer, no crystallization effects were found in this copolymer.

TABLE 5. Heat treatments and observations on the butadiene-styrene copolymer GL-662

(Temperatures are in  $^\circ\text{K}$ ;  $^\circ\text{K} = ^\circ\text{C} + 273.16^\circ$ )

Run	Treatment of sample	Temperature range of measurements	Drift observations
1----	Cooled rapidly from room temperature to $78^\circ$ .	$78^\circ$ to $240^\circ$ ---	Upward drift from $198^\circ$ to $240^\circ$ .
2----	Cooled overnight from $240^\circ$ to $223^\circ$ .	$223^\circ$ to $335^\circ$ ---	Downward drift from $231^\circ$ to $240^\circ$ .
3----	Cooled slowly from room temperature to $218^\circ$ over 3 days.	$218^\circ$ to $252^\circ$ ---	Downward drift from $232^\circ$ to $242^\circ$ .
4----	Cooled slowly from room temperature to $278^\circ$ overnight.	$278^\circ$ to $296^\circ$ ---	No drift.
5----	Cooled slowly from room temperature to $78^\circ$ over 2 days and then cooled to $15^\circ$ .	$15^\circ$ to $89^\circ$ ---	Do.

The glass-transformation temperature was estimated to be  $237^\circ \text{ K}$ .

The smoothed values of heat capacity, enthalpy, and entropy given in table 7 were obtained by procedures similar to those used with the X-478 copolymer. From  $255^\circ$  to  $330^\circ \text{ K}$  the heat capacity can be

TABLE 6. Observed heat capacities of the butadiene-styrene copolymer GL-662

( $^\circ\text{K} = ^\circ\text{C} + 273.16^\circ$ )

T		C	T		C
Run 1			Run 3		
$^\circ\text{K}$	$\text{abs j deg}^{-1} \text{ g}^{-1}$		$^\circ\text{K}$	$\text{abs j deg}^{-1} \text{ g}^{-1}$	
<sup>a</sup> 81.7399	0.4849		222.3920	1.152	
89.4599	.5220		229.2360	1.209	
96.6180	.5534		233.2240	1.272	
104.9560	.5906		235.7802	1.355	
114.3959	.6335		238.2239	1.477	
123.2797	.6742		240.5432	1.584	
131.7172	.7125		243.3349	1.650	
139.8044	.7502		248.2819	1.677	
148.2216	.7868				
157.5682	.8284		Run 4		
166.9044	.8712		280.9400		1.768
175.9899	.9120		287.1790		1.786
184.7992	.9522		293.3646		1.805
193.6374	.9940		Run 5		
202.7465	1.036		16.3153		0.0794
211.6238	1.076		18.3333		.0956
220.2657	1.124		20.4590		.1115
228.6698	1.167		22.6254		.1290
236.7170	1.292		24.8051		.1464
Run 2			Run 4		
226.8692		1.181	26.9764		.1632
235.3946		1.375	29.4574		.1822
242.0276		1.640	32.4430		.2043
246.4884		1.659	35.8330		.2284
253.0864		1.678	39.9171		.2555
263.9458		1.718	44.6071		.2849
276.8888		1.756	49.2670		.3130
288.8206		1.792	54.6340		.3437
301.2004		1.831	60.3004		.3753
313.3714		1.871	65.7303		.4041
323.5662		1.904	71.2582		.4314
331.2600		1.930	76.3689		.4572
			81.5713		.4840
			86.8869		.5109

<sup>a</sup> The temperatures given are accurate to  $\pm 0.01 \text{ deg. K}$ . Figures beyond the second decimal are significant only insofar as small temperature differences are concerned.

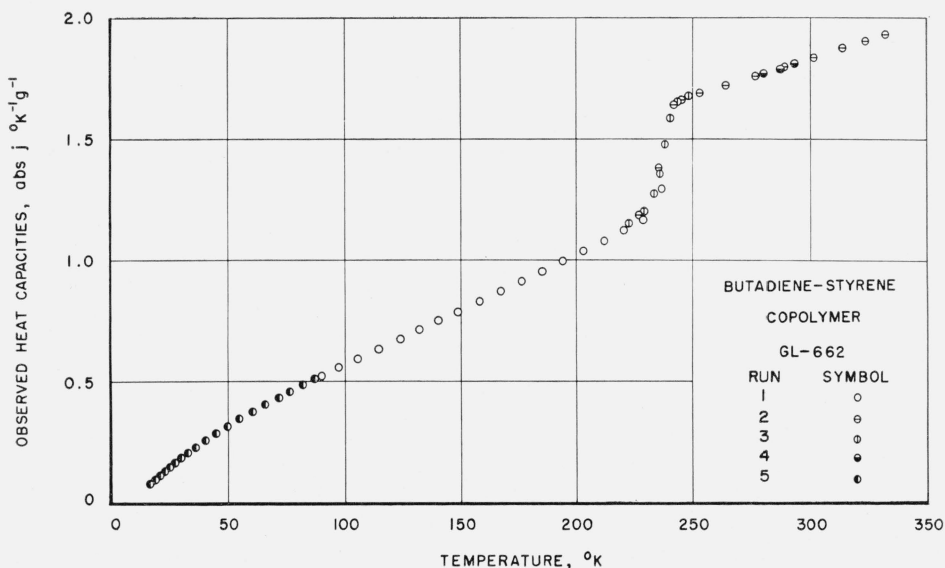


FIGURE 2. Observed heat capacities of the butadiene-styrene copolymer GL-662.

TABLE 7. Heat capacity, enthalpy, and entropy of butadiene-styrene copolymer GL-662

$$(^{\circ}\text{K} = ^{\circ}\text{C} + 273.16^{\circ})$$

<i>T</i>	<i>C</i>	( <i>H<sub>T</sub></i> - <i>H<sub>0</sub></i> )	( <i>S<sub>T</sub></i> - <i>S<sub>0</sub></i> )
$^{\circ}\text{K}$	<i>abs j deg<sup>-1</sup> g<sup>-1</sup></i>	<i>abs j g<sup>-1</sup></i>	<i>abs j deg<sup>-1</sup> g<sup>-1</sup></i>
0	0	0	0
5	0.0034	0.0043	0.0011
10	.0259	.0666	.0089
15	.0674	.2967	.0270
20	.1085	.4467	.0521
25	.1486	1.090	.0807
30	.1865	1.929	.1111
35	.2223	2.952	.1426
40	.2561	4.148	.1745
45	.2880	5.509	.2065
50	.3182	7.026	.2384
55	.3468	8.689	.2701
60	.3741	10.49	.3014
65	.4002	12.43	.3324
70	.4253	14.49	.3630
75	.4497	16.68	.3932
80	.4737	18.99	.4230
85	.4976	21.42	.4524
90	.5215	23.96	.4815
95	.5453	26.63	.5104
100	.5688	29.42	.5389
105	.5917	32.32	.5672
110	.6143	35.33	.5953
115	.6367	38.46	.6231
120	.6591	41.70	.6507
125	.6815	45.05	.6780
130	.7040	48.52	.7052
135	.7266	52.09	.7322
140	.7492	55.78	.7590
145	.7712	59.58	.7857
150	.7944	63.50	.8122
155	.8170	67.52	.8386
160	.8396	71.67	.8649
165	.8622	75.92	.8911
170	.8849	80.29	.9172
175	.9077	84.77	.9432
180	.9306	89.36	.9691
185	.9535	94.08	.9949
190	.9765	98.90	1.021
195	.9995	103.8	1.046
200	1.022	108.9	1.072
205	1.046	114.1	1.097
210	1.069	119.4	1.123
215	1.093	124.8	1.148
220	1.122	130.3	1.174
225	1.16	-----	-----
230	1.22	-----	-----
235	1.36	-----	-----
240	1.57	-----	-----
245	1.65	-----	-----
250	1.67	-----	-----
255	1.694	180.5	1.384
260	1.708	189.0	1.417
265	1.722	197.6	1.450
270	1.736	206.2	1.482
273.16	1.745	211.8	1.502
275	1.750	215.0	1.514
280	1.765	223.7	1.546
285	1.780	232.6	1.577
290	1.796	241.5	1.608
295	1.812	250.6	1.639
298.16	1.822	256.4	1.659
300	1.828	259.7	1.670
305	1.845	268.8	1.700
310	1.861	278.1	1.730
315	1.877	287.4	1.760
320	1.893	296.9	1.790
325	1.909	306.4	1.819
330	1.923	316.0	1.848

represented to within 0.1 percent by the quadratic equation

$$C = 1.322 + 1.83 \times 10^{-4} T + 5.000 \times 10^{-6} T^2$$

(abs j deg<sup>-1</sup> g<sup>-1</sup>).

In the temperature interval 220° to 255° K two determinations (runs 2 and 3) of the enthalpy were made. In run 2 (refer to table 5), the copolymer had been previously shock-cooled from room temperature, heated to 240° K, and cooled again slowly. In run 3 the copolymer was cooled slowly from room temperature. The close agreement in the enthalpy changes (50.24 and 50.21 abs j g<sup>-1</sup>, respectively) of runs 2 and 3 indicates that within the limits described in this paper the rate of cooling above the glass-transformation temperature has no appreciable effect on the enthalpy change between 220° and 255° K. The mean of the two values was used in constructing table 7.

### 4.3. Reliability of the Results

Except near the glass-transformation temperature, the results of the heat-capacity measurements in general do not scatter by more than 0.2 to 0.3 percent. In the region of the glass-transformation temperature, however, the values of heat capacity differ by as much as 1 percent. As no attempt was made to reach complete thermal equilibrium in this region of temperature drifts, the results will differ slightly from the values that would be obtained if thermal equilibrium had been reached. Previous experience [1,2] with polymers showed that temperature drifts occurred even several hours after heating. Any reasonable change in the time intervals used would certainly not alter the general nature of the results.

Upon consideration of various sources of errors, such as reproducibility of the physical state of the polymers, energy input, heat leak, and thermometry, the authors believe that the heat-capacity values given in tables 4 and 7, except near the glass-transformation temperature, are accurate to 0.3 percent. The enthalpy and entropy values, derived from the heat-capacity values, are probably accurate to 0.3 to 0.4 percent.

## 5. Discussion

Below the temperature region of glass transformation certain degrees of freedom of the polymer molecules, because of the increased relaxation times, do not have sufficient time during an ordinary course of heat-capacity experiments to come into thermodynamic equilibrium [6]. The heat capacities of the copolymers described in this paper decreased by about 30 percent on cooling through the glass-transformation temperature interval because of the "freezing-in" of these degrees of freedom. This rapid decrease in heat capacity extended over a temperature interval of about 5 to 10 deg. Previous heat-capacity investigations [1, 2] have shown similar percentage decrease in the heat capacity at the glass-transformation temperature.

In the region of the glass-transformation temperature some of the polymer molecules undergo slow transitions among the energy states of the degrees of freedom referred to in the previous paragraph.

These slow transitions are observed during heat-capacity experiments as temperature drifts, the direction depending upon whether the transitions involve liberation or absorption of energy. The relaxation time increases with decrease in temperature, and finally at sufficiently low temperatures these degrees of freedom become completely "frozen-in." When a polymer is shock-cooled from room temperature to 80° K, a large portion of the polymer molecules that would have undergone transition to lower states of energy if cooled slowly through the glass-transformation temperature remains "suspended" in states of higher energy. When the polymer is later raised to temperatures near the glass-transformation region, the polymer molecules transform from the higher states of energy to the lower, causing upward temperature drifts. When slowly cooled, the polymer molecules are given more time to transform into energy states closer to equilibrium. Subsequently, when the temperature is raised, a certain range is reached at which the equilibrium requires the molecules to transform into states of higher energy, causing downward temperature drifts. When the copolymers described in this paper were shock-cooled, upward temperature drifts started at about 40 to 45 deg below the glass-transformation temperature (see tables 2 and 5); when the copolymers were slowly cooled, downward temperature drifts were observed starting at about 6 to 7 deg below the glass-transformation temperature. The occurrence of the upward temperature drifts at much lower temperature than of the downward temperature drifts is believed to be consistent with the requirement of lower activation energy for a system in a higher energy state to transform into that of lower energy state. It is expected, on the basis of the observed results, that no temperature drifts would occur if the cooling process were sufficiently slow so that all calorimetrically detectable transformations associated with the polymer molecules took place and if the heating rate were as slow or slower than the cooling rate. Measurements of the heat capacity are generally made at a heating rate of about ¼ to 1 deg/min, which is considerably faster than the cooling rate and the time necessary for complete

transformation of the polymer molecules to higher energy states. Consequently, during the waiting period for temperature equilibrium, there are observed downward temperature drifts as the polymer molecules slowly adjust to the distribution of energy states consistent with the temperature.

Überreiter [7] and Tuckett [8] have shown that in butadiene-styrene copolymers the bound styrene hinders free rotation of polymer segments and that the increase in bound-styrene content raises the glass-transformation temperature. The results presented in this paper and those previously obtained on butadiene-styrene copolymers are consistent with their findings.

From above the glass-transformation temperature to the upper temperature limit of the measurements given in this paper, the heat capacity of the copolymers can be represented by a simple quadratic equation, of the form  $C=a+bT+cT^2$ , within 0.1 percent or better. The heat capacity of Hycar O. R.-15 [9], GR-S [10], and the butadiene-styrene copolymer containing 8.58 weight percent of bound-styrene [1] can also be represented by a similar type of equation in the region above the glass-transformation temperature.

## 6. References

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