Volumetric Properties of Block and Random Copolymers of Butadiene and Styrene at Pressures to 1 Kilobar

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Synopsis

Densities of thermally annealed copolymers were measured at 75° and 100°C at pressures to 1 kilobar. The compositions ranged from pure polybutadiene to pure polystyrene, from completely random to completely block copolymers. The experimental results are well represented by the Tait equation. To a first approximation, specific volumes and compressibilities are linear functions of weight per cent styrene. For a fixed composition, the effect of structure on volumetric properties is small. However, it appears that, when compared at the same overall composition, the specific volume and compressibility are larger for the random copolymer; specific volume and compressibility decline slightly when the styrene is in block rather than random form.

INTRODUCTION

While volumetric properties (PVT data) have been reported for a variety of homopolymers, relatively few data have been published for random copolymers; data for block copolymers are extremely rare.[1] Here, we report experimental density measurements for copolymers of butadiene and styrene at 75° and 100°C and at pressures to 1 kilobar. Measurements have been made for various copolymers from completely random to completely block copolymers.

EXPERIMENTAL

Experimental studies were made on 12 polymers as indicated in Table I. Our measurements were conducted on the first 11 polymers; the data of Quach and Simha[2] were used for the 12th polymer.

All polymer samples were obtained from commercial sources and, therefore, they may include small amounts of impurities. We estimate that the maximum impurities are less than 1 wt-% volatile matter, less than 1 wt-% soap, and at most 0.2 wt-% ash.

Small cubic samples of copolymer (about 2 mm per edge) were degassed for at least 3 h to remove volatile impurities.

First, density measurements were made at atmospheric pressure, using a conventional glass dilatometer briefly described elsewhere.[3] The dilatometer was previously calibrated with known densities of hydrocarbons. Experimental

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TABLE I
Butadiene–Styrene Copolymers

Identification no.	Sample[a]	% Bound styrene	% Block styrene	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	Other details
1	Solprene 235	0	0	~270	~135	10% 1,2-butadiene
2	Europrene cis	0	0	327	153	100% cis-butadiene
3	Stereon 702	18–21	0.5–2.0	240	100	random copolymer
4	Europrene R130	25	0	481	239	random copolymer
5	Solprene 1206	25	0	210	120	random, 30% 1,2-butadiene
6	Solprene 1205	25	18	80	65	random with blocks 10% 1,2-butadiene
7	Europrene S140	48	15	—	—	random with blocks
8	Europrene S141	48	32	76.1	61.8	random with blocks
9	Europrene S142	70	45	126.4	97.6	random with blocks
10	TR-41-2425	25.4	all block		7–43–7	block copolymer S–B–S 40% cis-butadiene 50% trans-butadiene 10% 1,2-butadiene
11	Europrene T161	30	all block	229.6	130.5	block copolymer S–B–S
12	pure styrene	100	0			Taken from Quach and Simha[2]

[a] Solprene series from Phillips Petroleum Company; Europrene series from ANIC, Milan, Italy; Stereon from Firestone Synthetic Rubber & Latex Co.; TR from Shell Development Company.

tests with mercury at 75° and 100°C gave excellent agreement with the density data of Bigg;[4] experimental error was always less than ±0.01%.

Second, density measurements were made at high pressure. For high-pressure studies, the experimental equipment is the same as that used by Beret;[5] the central component is a high-pressure cell with a flexible bellows to contain the sample and to isolate it from the pressure-transmitting fluid.[6] The apparatus is calibrated with highly accurate PVT data for mercury and for heptane. Pressures are measured with a precision Heise gauge whose accuracy is 0.1% of full scale (±1 bar).

The high-pressure cell is located in a constant-temperature bath using silicone oil as heating fluid. The bath is controlled to ±0.01°C by a Hallikainen proportional temperature controller. Calibrated thermometers used for temperature measurements are accurate to ±0.05°C. Taking into consideration errors in temperature and pressure measurements as well as errors in calibration, the overall uncertainty of our relative volume measurements is 0.04%.

Densities of mercury at normal pressure were taken from Bigg,[4] and densities at high pressure were obtained from fitted values of Beret.[7]

After the polymer sample was weighed, it was placed inside the dilatometer or the bellows; the sample containers were then connected to the vacuum line for another 2 h of degassing and filling the empty space with previously degassified mercury.

All measurements were conducted under isothermal conditions at 75° and 100°C. In the high-pressure experiments, the pressure was always raised approximately 50 bars for each measurement. The change of volume with pressure was plotted as the data were obtained to determine possible discontinuities in slope caused by phase transitions. No discontinuities were observed.

For atmospheric-pressure measurements and for high-pressure measurements, constant temperature was maintained with a white-oil bath controlled by a Hallikainen proportional temperature controller. The temperature was measured by NBS-calibrated thermometers.

TABLE II
Specific Volumes at 1 Atmosphere

Sample no.	Specific volume, cc/g	
	75°C	100°C
1	1.1587	1.1791
2	1.1434	1.1630
3	1.1559	1.1760
4	1.1074	1.1260
5	1.1087	1.1276
6	1.1103	1.1291
7	1.0614	1.0787
8	1.0607	1.0770
9	1.0298	1.0148
10	1.0989	1.1177
11	1.0972	1.1158

While measurements reported here are at 75° and 100°C, measurements were also made at temperatures slightly lower and slightly higher than 75° or 100°C. These additional measurements were undertaken to see if there were unusual changes with temperature indicating phase transitions. No unusual changes were observed.

Early measurements indicated a lack of reproducibility, especially for those polymers containing a large amount of styrene. To obtain reproducibility, all samples were annealed prior to final experimental measurements. Annealing was done *in situ* at 120°C for 2 h, the samples were then cooled to 70°C at a rate of 2°C per hour. After annealing, measurements were always made with increasing temperature. Upon repeating the annealing cycle several times, excellent reproducibility ($\pm 10^{-4}$ cm^3/g) was obtained for all measurements.

RESULTS

Table II gives specific volumes at 1 atm and at two temperatures. Figure 1 shows these results at 75°C.
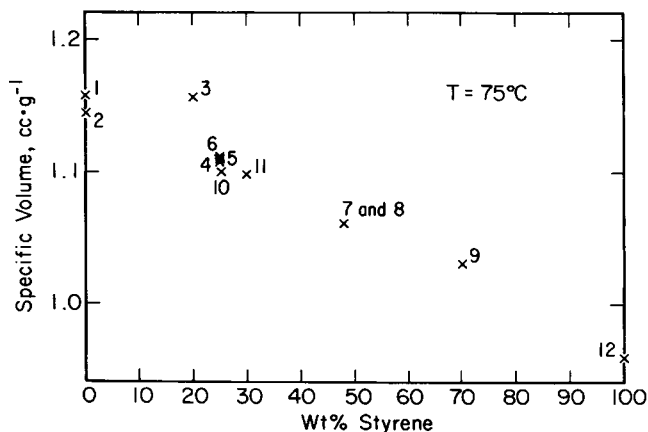

Fig. 1. Specific volumes of copolymers of butadiene and styrene at 1 atm. Samples are identified in Table I.

TABLE III
Parameters in the Tait Equation[a]

Sample no.	T = 75°C			T = 100°C		
	C	$B \times 10^{-4}$, bar^{-1}	$\sigma \times 10^4$	C	$B \times 10^{-4}$, bar^{-1}	$\sigma \times 10^4$
1	0.1221	0.1627	1.25	0.1083	0.1324	1.81
2	0.1288	0.2216	0.62	0.1228	0.1729	1.09
3	0.09695	0.1362	1.52	0.1009	0.1224	2.02
4	0.1029	0.1301	1.79	0.1182	0.1371	1.82
5	0.1147	0.1929	0.78	0.07983	0.09976	2.52
6	0.09021	0.1358	1.42	0.2500	0.3649	0.33
7	0.1344	0.2321	0.58	0.1151	0.1743	1.01
8	0.1078	0.1681	1.03	0.08794	0.1211	1.81
9	0.08723	0.1772	0.73	0.07611	0.1262	1.42
10	0.07866	0.1171	1.75	0.08936	0.1188	1.91
11	0.1303	0.2225	0.62	0.1142	0.1650	1.14

[a] σ is the standard deviation.

Specific volumes at high pressures are well represented by the Tait equation:

$$\frac{v}{v_0} = 1 - C \ln \left(1 + \frac{P}{B} \right) \qquad (1)$$

where v/v_0 is the ratio of specific volume at pressure P to that at 1 atm. Constants C and B are shown in Table III. The pressure is in bars. Detailed experimental results are available from the authors. Equation (1) represents the data within experimental error.

For our purposes here, we define the compressibility β by

$$\beta \equiv - \frac{1}{v_0} \left(\frac{\partial v}{\partial P} \right)_T \qquad (2)$$

TABLE IV
Compressibility β [See eqs. (2) and (3)]

| Sample no.	β at $T = 75°C$, bars^{-1} × 10^5				β at $T = 100°C$, bars^{-1} × 10^5			
	400 bars	600 bars	800 bars	1000 bars	400 bars	600 bars	800 bars	1000 bars
1	6.02	5.48	5.03	4.65	6.28	5.63	5.10	4.66
2	4.92	4.57	4.27	4.00	5.77	5.27	4.86	4.50
3	5.50	4.94	4.48	4.11	6.22	5.53	4.99	4.54
4	6.05	5.41	4.90	4.47	6.68	6.00	5.45	4.99
5	4.92	4.53	4.20	3.91	5.71	5.00	4.44	4.00
6	5.13	4.61	4.18	3.82	6.17	5.88	5.62	5.38
7	4.94	4.60	4.31	4.05	5.37	4.92	4.53	4.20
8	5.18	4.72	4.34	4.02	5.46	4.85	4.37	3.98
9	4.02	3.68	3.39	3.15	4.58	4.09	3.69	3.37
10	5.01	4.44	3.99	3.62	5.63	5.00	4.49	4.08
11	4.96	4.61	4.31	4.04	5.57	5.08	4.66	4.31
12[a]	2.78	2.62	2.48	2.35				

[a] From Quach and Simha.[2]
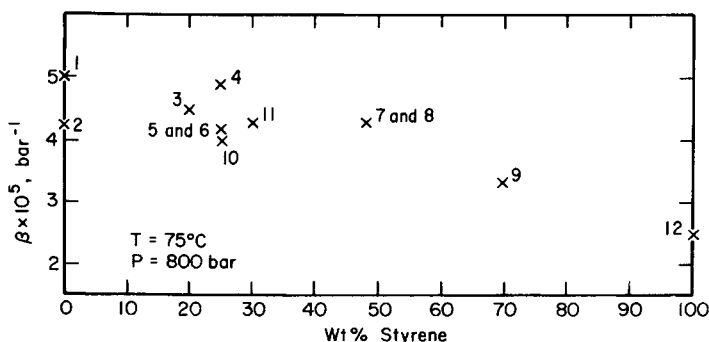
Fig. 2. Compressibilities of copolymers of butadiene and styrene at 800 bars. Samples are identified in Table I.

This compressibility is readily found from eq. (1):

$$\beta = C(B + P)^{-1} \qquad (3)$$

Table IV shows values of β at 75° and 100°C at 400, 600, 800, and 1000 bars.

When Barlow's data[8] for poly-*cis*-butadiene between 4° and 55°C are extrapolated to 75° and 100°C, the results are in good agreement with our measurements.

Figure 1 shows specific volumes at 1 atmosphere as a function of weight percent styrene. There is a clear trend indicating that the specific volume falls as the percent styrene rises; but, in addition, some structural effects are also evident. For example, sample 2 is pure poly-*cis*-butadiene, while sample 1, also pure polybutadiene, is a mixture of the cis and trans forms of polymerized 1,2-butadiene.

Samples 4, 5, 6, and 10 all have the same overall composition; but, as shown in Table I, there are differences in structure. Samples 4 and 5 are random copolymers but with different molecular weights. Sample 6 has 18% styrene in block form, and sample 10 is a radial (S-B-S) copolymer.

Figure 2 shows compressibility β at 800 bars as a function of weight percent styrene. Again, it is evident that β tends to decline as the percent styrene rises, and again some structural differences are apparent.

Unfortunately, it is not possible to draw clear quantitative conclusions from the PVT data assembled here. However, the results shown in Figures 1 and 2 at 75°C (and those at 100°C are very similar) suggest that both the specific volume and the compressibility decline when, at constant overall composition, the styrene is added to the butadiene in block rather than random form. It appears that block copolymers can pack more efficiently than random copolymers and thereby more strongly resist compression.

While the results obtained here leave many questions unanswered, they provide at least an initial view into the relatively unexplored territory of PVT properties of copolymers. The results obtained here indicate that while structure affects these properties, at any fixed overall composition, structural effects are not large in magnitude but in the direction suggested by simple geometric considerations.

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