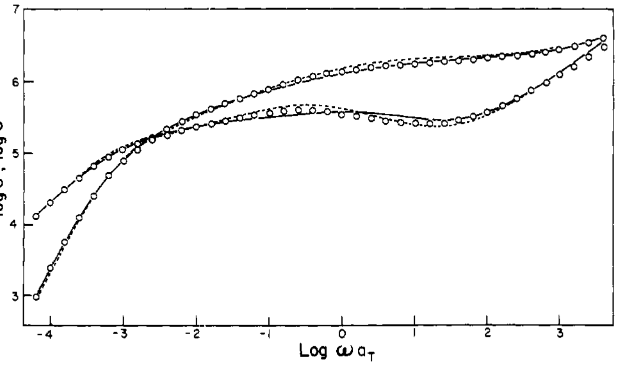

Figure 10. Comparison of experimental (circles) and calculated moduli-frequency curves of S181A: full line, model with three retardation mechanisms; dotted line, model with two retardation mechanisms.

approximate the experimental data with about equal accuracy. A similar observation was made in the analysis of G' and G'' data of comb-shaped polystyrenes whenever τ values became as close as τ_b and τ_{enh}.[28] A definitive test for an additional retardation mechanism in star polymers will apparently require higher molecular weight samples with still larger enhancement factors.

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Specific Volumes of Styrene-Butadiene Block Copolymers

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ABSTRACT: The specific volumes at 25 °C of one AB and of two ABA block copolymers of butadiene (B) and styrene (A) were measured as were also the specific volumes of the polybutadiene and polystyrene homopolymers. Although the specific volumes of the block copolymers nearly follow an ideal additive law, the slight deviations in the direction of greater volume than expected can be explained on a statistical basis.

Block copolymers have considerable theoretical interest and industrial importance. Their synthesis and properties have been extensively reviewed.[2-5] However, very little work has been devoted solely to studying the specific volumes of block copolymers. Renuncio and Prausnitz[6] recently measured the specific volumes at 75 °C of some random and some block copolymers of butadiene (B) and styrene (A) and found within the accuracy of their measurements that the specific volume was a linear function of the weight percentage of styrene. Our data given below, which were taken at 25 °C, approximately confirm the linear relation, but the deviations are systematic and can be interpreted in a significant way.

This paper represents the beginning of a series of studies on block copolymers which will include measurements of hydrogen and deuterium gas solubilities in the solid copolymers so as to determine the free volume available to these gases (research already under way) and kinetic studies of free-radical decay in irradiated samples of the block copolymers.

Table I
Properties of Butadiene and Styrene Block Copolymers and Homopolymers (Polystyrene is Atactic Polystyrene)

structural type	wt fraction of styrene	% microstructure			$M_n{}^a \times 10^{-3}$
		cis	trans	vinyl	
B	0	40.0	52.0	8.0	150
ABA	0.212	27.7	55.1	17.2	164
ABA	0.418	25.8	62.5	11.7	258
AB	0.612	29.6	54.2	16.2	606
A	1.000				193

[a] The number average molecular weights were determined by osmometry except for the AB block copolymer whose M_n value is a theoretical one calculated from the polymerization charge.

Experimental Section

Materials. The homopolymers and block copolymers studied and their properties are listed in Table I. They were prepared by R. A. Livigni of the General Tire and Rubber Co. and were sent to us along with the data of Table I courtesy of Dr. S. L.

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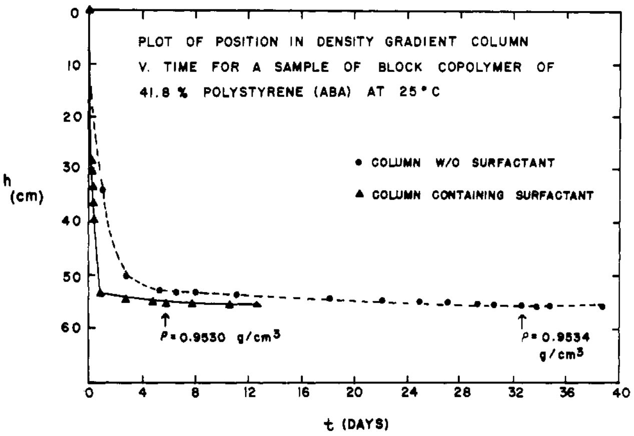

Figure 1. Time required to reach flotation equilibrium for samples of 41.8 wt % polystyrene in a density gradient column: circles, without surfactant; triangles, with surfactant.

Aggarwal. They were precipitated from solution in toluene, using methanol as the precipitant, and each polymer was stabilized with approximately 0.1% of Irganox 565, an antioxidant from Ciba-Geigy. Scanning electron microscopy of the fluffy samples by us revealed many occluded air pockets within the samples. Hence small pieces of sample were cut from the larger granules with a razor blade and then evacuated for 2 h in a water–2-propanol solution of the same approximate composition as that of the density gradient column described below. Any occluded air or adsorbed air bubbles on the samples would vitiate the density measurements. The 61.2 and 100% polystyrene (PS) samples contained air pockets that could only be removed by annealing under vacuum. They were placed in a glass tube, evacuated, and annealed in an oven at 160 °C for 4 h. This method was also tried on all of the other samples except for the pure polybutadiene, which is in the liquid state at 25 °C, and it was found that annealing did not alter their densities significantly. Folkes and Keller[7] previously showed that annealing an extruded rod of an A–B–A block copolymer of styrene and butadiene at 150 °C for 2 h did not change its birefringence. The annealing of our sample, however, failed to remove all of the occluded air pockets from the 61.2 and 100% PS samples. Accordingly, these samples were heated in an evacuated tube at 170 °C for 1 h in a sand bath with continuous evacuation during the heating. The temperature of 170 °C is well above the glass-transition temperature[8] of atactic PS. After the samples had been heated at 170 °C, they were quenched in ice water. The samples were stored in the evacuated tube until they were used in the density measurements.

Density Gradient Method. For the density measurements, the standard ASTM density gradient column method was used.[9] A 2-propanol–water system provided a density range from 0.79 to 1.00 g cm^{-3} and a water–sodium bromide solution from 1.00 to 1.41 g cm^{-3}. A separate test showed that the block copolymers did not swell in the 2-propanol–water system. The density at different heights in the columns at 25 °C was standardized by means of colored glass beads having a range of densities within the limits of the densities given above. They were obtained from the Cole-Parmer Instrument Co. In our first attempts to measure the density, we found that almost a week was required after the small granules had been introduced into the column to bring about flotation equilibrium, see Figure 1, dotted line. Following a suggestion of Dr. Aggarwal, we made the density gradient column about 0.01 wt % in the wetting agent Aerosol OT-B and found that the time to reach the flotation equilibrium was greatly reduced, Figure 1, solid line. In Figure 1, the ordinate values represent distances from the top of the column. The annealed samples reached the flotation equilibrium height much more rapidly than the unannealed samples (the data of Figure 1 are for unannealed samples), probably because of fewer air pockets that had to be displaced by the flotation liquid. The annealed samples attained flotation equilibrium within 24 h.

Once a column had been prepared, it could be used for about a month before a new column was required. With a maximum of seven granules of one sample in the column at the same time or a minimum of three (the average in eight separate experiments was five), the maximum spread in position at the flotation equilibrium of the samples in the column was 1.7 cm, corresponding to a density difference of 0.0014 g cm^{-3}, but the average spread in the eight experiments was only 0.34 cm or 0.0003 density units. In the case of the pure PS sample, only one granule was used. Its density of 1.0495 at 25 °C was intermediate between the two values, 1.047 and 1.051 g cm^{-3} quoted by Lewis.[10]

Table II
Densities at 25 °C of Block Copolymers and Homopolymers of Styrene and Butadiene

structural type	wt fraction of styrene	density as supplied, g cm^{-3}	annealed density, g cm^{-3}
B	0	0.8953	
ABA	0.212	0.9233	0.9230
ABA	0.418	0.9530	0.9518
AB	0.612		0.9812
A	1.000		1.0495

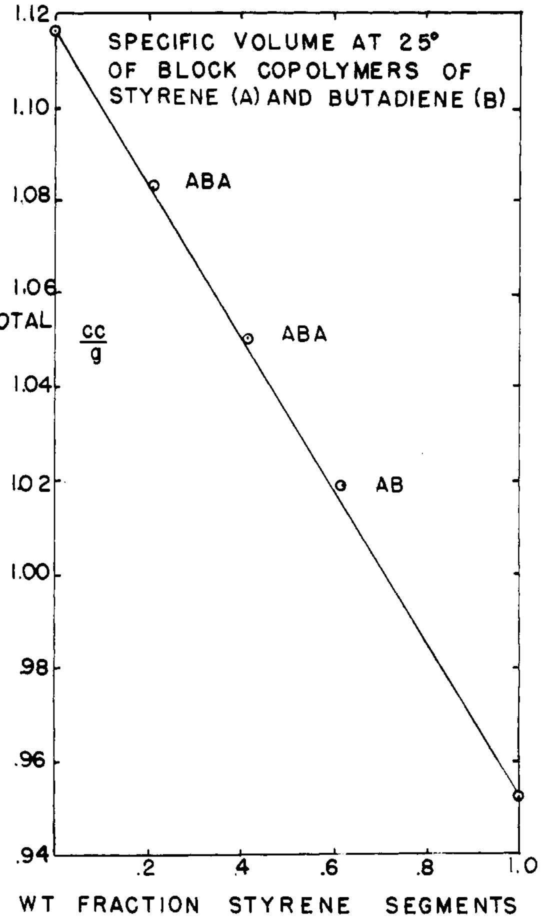

Figure 2. Specific volumes as a function of the weight fraction of styrene segments: circles, measured values; solid line from eq 1.

Results and Discussion

The density values obtained in this study are collected in Table II. Note that in the case of the 21.2 and 41.8% styrene ABA block copolymers, there was a slight decrease in density on annealing the samples. Currie and Dole[8] found that the specific heat of atactic polystyrene increased on annealing; that is, it became more liquid-like as compared to the as-received material. The decrease of density on annealing as compared to the density of the as-received samples agrees qualitatively with the observation of Currie and Dole.

The specific volumes of the annealed samples are plotted in Figure 2 as a function of the weight fraction of the

Table III
Specific Volumes (cm^3 g^{-1}) at 25 °C of the Block Copolymers as Observed and Calculated from Equation 1[a]

x_A	$\frac{n_A n_B}{n_A + n_B}$	v_{obsd}	v_{calcd} (eq 1)	$\Delta v = v_{obsd} - v_{calcd}$	Δv (eq 2)
0	0	1.1169	1.1169	0	0
0.212	0.00179	1.0834	1.0821	0.0013	0.0014
0.418	0.00293	1.0506	1.0483	0.0023	0.0023
0.612	0.00331	1.0192	1.0165	0.0027	0.0027
1.000	0	0.9528	0.9528	0	0

[a] Deviations (Δv) calculated from eq 2.

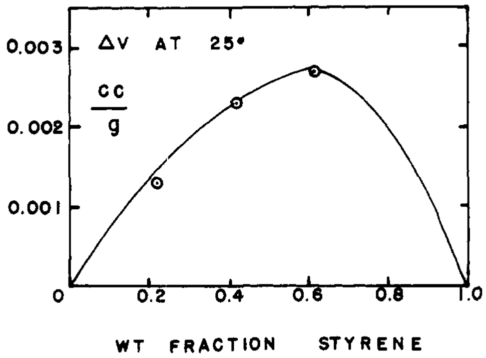

Figure 3. Deviations from specific volume additivity law, eq 1, plotted as a function of the weight fraction of styrene segments: open circles, measured values; solid line calculated from eq 2.

styrene. An approximately linear relation is seen to exist, which means that the specific volumes of the styrene and butadiene blocks are independent of composition and that the following additive relation is approximately satisfied.

$$v_t = x_A v_A + (1 - x_A) v_B \qquad (1)$$

In eq 1, v_t is the specific volume of the block copolymer, v_A and v_B are the specific volumes of the styrene and butadiene homopolymers, and x_A is the weight fraction of the styrene segments.

The deviation between the observed specific volumes of the samples listed in Table I and the values calculated on the basis of additivity, eq 1, are collected in Table III and plotted in Figure 3, open circles. The solid line of Figure 3 was calculated from

$$\Delta v = v_{obsd} - v_{cald} = \frac{n_A n_B}{n_A + n_B} \rho k \qquad (2)$$

where n_A and n_B represent the number of styrene and butadiene segments per gram of polymer, ρ is the density to convert the mole ratio to ratio per unit volume, and k is an arbitrarily chosen constant having a value of 0.833 cm^6 g^{-1} in this case. The factor $n_A n_B/(n_A + n_B)$ is proportional to the number of AB contacts[11,12] (see also Helfand[13]). The agreement between the data points and the theoretical curve of Figure 3 is remarkably good. In this connection, it should be pointed out that an expression similar to eq 2 but based on weight fractions rather than on number concentrations does not give nearly as good agreement.

The factor $\rho n_A n_B/(n_A + n_B)$ which is proportional to the free energy of mixing per unit volume was suggested by the work of Helfand and Wasserman.[11-13] These authors[12,13] postulated that at the end of each A chain, for example, where it is linked to a B chain, there is a tendency for the density to be higher near the boundaries than in the center of the domains. But as this would cause an increase in the free energy, the chains adopt conformations in which the centers of the lamellae tend to become filled. From the specific volumes plotted in Figure 2, it can be seen that the close agreement with the additivity law, eq 1, demonstrates very little change in density from that of the pure components on forming the block copolymers. This confirms the conclusion of Helfand and Wasserman[12] that "in this case the diffusion equation has an additional chemical-potential-like term which constrains the walks to occur in such a manner as to maintain uniform density on the average". The small deviations from linearity in the specific volumes which do occur are in the direction of the block copolymers being less dense than expected. The maximum deviation from strict additivity is only 0.0027 cm^3 g^{-1} at about 60 wt % PS, Figure 3. If the specific volume of the interfacial regions between the styrene and butadiene blocks were 10% greater than in the pure polymers, then 2.7% of the sample would be in the interphases. Helfand and Wasserman[12] have estimated the thickness of an AB polymer interphase at 20 °C to be 1.4 nm. In passing from the center of an A domain through a B domain to the center of the next A domain, two interphases are traversed, so that the total interphase thickness would be 2.8 nm, whereas the distance between the center of the two PS blocks is about 30 nm for an S-B-S block copolymer.[12,13] These estimates result in the interphase being about 9% of the total block copolymer, considerably greater than the value of 2.7% given above. If the specific volume of the interphase were 3% greater than that of the bulk polymer instead of 10%, then our data would agree with the estimates of Helfand and Wasserman; that is, (0.03)(0.09) equals 0.0027. A 3% difference in specific volume does not appear to be unreasonable, considering the fact that the total difference in specific volume between the pure PB and PS blocks is 16%, Table III.

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