(22) Dainton, F. S.; Ivin, K. J. *Q. Rev., Chem. Soc.* **1958**, *12*, 61.
(23) Grassie, N.; MacCallum, J. R. *J. Polym. Sci., Part B* **1963**, *1*, 551.
(24) Wellisch, E.; Gipstein, E.; Sweeting, O. J. *J. Appl. Polym. Sci.* **1964**, *8*, 1623.
(25) Grassie, N.; Melville, H. W. *Proc. R. Soc., London, Ser. A* **1949**, *199*, 24.
(26) Jellinek, H. H. G.; Luh, M. D. *Makromol. Chem.* **1968**, *115*, 89.
(27) Bowden, M. J.; Thompson, L. F. *Polym. Eng. Sci.* **1977**, *17* (4), 269.
(28) Bowmer, T. N.; O'Donnell, J. H. *J. Macromol. Sci., Chem.*, in press.
(29) Freeman, E. S.; Carroll, B. *J. Phys. Chem.* **1958**, *62*, 394.
(30) Anderson, D. A.; Freeman, E. F. *J. Polym. Sci.* **1961**, *54*, 253.

Specific Volumes of Styrene–Butadiene Block Copolymers. 2. Effect of Solvent Sorption on Density Measurements

Craig Bartels,[†] Rafil Basheer, and Malcolm Dole*

Department of Chemistry, Baylor University, Waco, Texas 76798. *Received March 29, 1982*

ABSTRACT: The slight deviations from additivity in the specific volumes of butadiene–styrene block copolymers previously reported are now shown to be smaller than the previous values when corrections are made for the extent of swelling of the samples due to sorption by the sample of the water–2-propanol in the density gradient column.

In our previous paper[1] it was shown that specific volumes of block copolymers of butadiene and styrene calculated from density measurements in a density gradient column almost exactly followed the linear additivity law

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

where 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 slight deviations from additivity, whose maximum amounted to 0.0027 cm^3 g^{-1} at 25 °C for the 61.2 wt % styrene sample, were interpreted as resulting from a lower density in the thin interfacial layers between the butadiene and styrene blocks. At that time no correction was made for a possible swelling of the polymer samples due to sorption of either water or 2-propanol while in the density gradient column.

This paper will include a brief discussion of new swelling measurements as well as of the kinetics of the sorption process and data for the sorption as a function of the 2-propanol concentration in the density gradient column.

Experimental Section

Materials. The pure polybutadiene (PB) and pure polystyrene (PS) came from General Tire and Rubber Co. as in the previous paper. Kraton 1101, kindly donated by Shell Development Co., contained 30 wt % styrene and 70 wt % butadiene segments and Kraton 1102 28 wt % styrene and 72 wt % butadiene. The microstructure of the pure PB was 38% *cis*-1,4-butadiene, 54% *trans*-1,4-butadiene, and 8% vinyl. Its weight-average molecular weight was 225 × 10^3 and its intrinsic viscosity, [η], 2.32 dL/g as measured in benzene at 25 °C. The microstructure[2] of the butadiene segments in the Kraton samples was very similar to that of the pure PB, namely, 41% *cis*-1,4-butadiene, 49% *trans*-1,4-butadiene, 2% 1,2-butadiene, and 8% vinyl. The PS was the same as that used previously.

The Kraton samples were repurified by dissolving them in toluene and reprecipitating in methanol. The precipitated polymer was then washed with methanol and dried at 80 °C for more than 2 h to constant weight in a vacuum oven. Slabs were made of the purified Kraton 1101 and 1102 by heating samples in vacuo at 120 °C between glass plates held apart by a thin spacer but with a lead weight on the top glass plate so as to squeeze out excess polymer. The thickness of the slabs was about 60 mils. The slabs of PS were transparent, indicating the absence of cavities, and the block copolymers were only slightly turbid.

Sorption. To determine the extent of sorption of the water and 2-propanol, the liquids of the density gradient column, previously weighed samples of the polymers were suspended over the water–2-propanol solution in Erlenmeyer flasks kept in a constant temperature bath at 25 °C. Eight days in the vapor phase was sufficient to reach sorption equilibrium as determined by weighing in a weighing bottle. The sorption studies were carried out with a mixture of water and 2-propanol containing 35 wt % 2-propanol. This mixture has a density of about 0.9375 g cm^{-3} at 25 °C, which is within the range of the block copolymers studied here. As shown below the weight of vapors sorbed by Kraton 1101 does not change very much over the range of solvent composition from 10 to 40 mol % 2-propanol, or from 27.3 to 69 wt %. Desorption was followed by merely measuring the decrease in weight of the sample on exposure to air.

Swelling. To measure the swelling we projected an image of a small piece of solid polymer on a long piece of chart paper affixed to a wall. The polymer image or shadow was produced by putting the piece of polymer in a 35-mm Kodak Ektagraphic slide projector, Model E-2. A brass frame, the size of a 35-mm slide, with two hook-shaped brass rods in the middle of the opening was constructed. The small rod-shaped polymer sample could be laid on the brass hooks and its shadow then projected on the chart paper about 20 feet away. The brass frame was inserted into the projector in the slot where the 35-mm slides are normally inserted. Thus the position was reproducible and the lens of the projector could be moved until the brass holder was in focus. The polymer sample could then be laid on the hooks and the length of the shadow quickly measured before the sorbed vapors had time to evaporate to any significant extent. The size of the image was about 130 cm long, resulting in a magnification of the 1.5-cm-long sample about 85-fold. Actually, in practice it turned out that the length measurements were more reproducible than the weight measurements. After the length of the polymer saturated with the vapors was measured, the sample was dried in a vacuum oven at 70 °C for 2 h, at which time the measured length became the same as that before the sorption.

To estimate the changes in density from the length changes it is necessary to assume that the swelling occurs isotropically so that the ratio of volume after swelling, v_a, to volume before swelling, v_b, can be set equal to l_a^3/l_b^3, the cube of the ratio of length after swelling to that before. In a partial test of this assumption a square piece of polymer was cut from the slabs mentioned above and the swelling measured along both the length and width axes. No difference in the l_a^3/l_b^3 ratios greater than the experimental uncertainties could be detected; see Table II. However, it was not possible with our equipment to measure accurately the thickness of the sample, so we can only state

---

[†] Present address: Department of Materials Science, Northwestern University, Evanston, IL 60201.

0024-9297/82/2215-1422$01.25/0

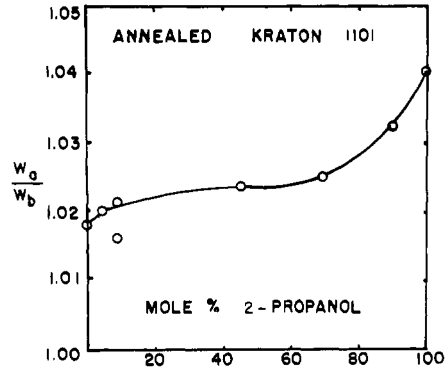

Figure 1. Ratios of weights after swelling to weights before swelling of Kraton 1101 samples on exposure to the vapor of mixtures of 2-propanol and water at 25 °C.

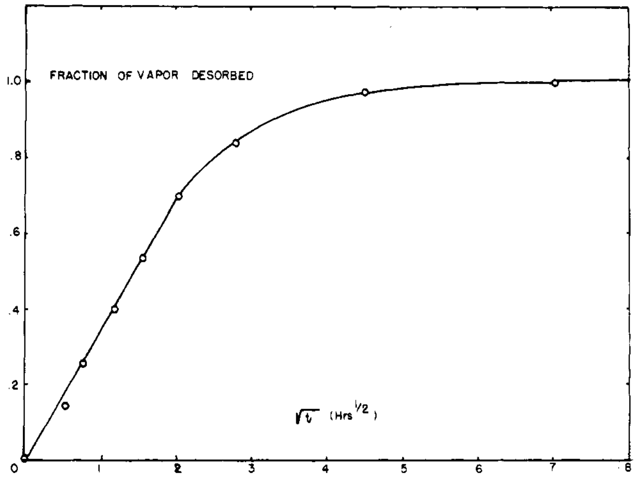

Figure 2. Fraction of vapor desorbed as a function of $t^{1/2}$ at 25 °C from Kraton 1101 after saturation of the latter with pure 2-propanol vapor.

definitely that the swelling occurred isotropically in at least two dimensions.

Results and Discussion

Sorption as a Function of Solvent Composition. In Figure 1 the sorption of vapors by Kraton 1101 (30 wt % styrene) in terms of the weight ratios after and before swelling, w_a/w_b, at 25 °C is plotted as a function of the mol % of 2-propanol in the liquid phase. It is seen that Kraton 1101 absorbs from the pure solvents more 2-propanol than water, as might be expected, but that the weight ratios are fairly constant from about 5 mol % 2-propanol to 50 mol %.

Kinetics of Sorption. Figure 2 illustrates the decrease in weight at 25 °C as a function of the square root of the time of a sample of Kraton 1101 that had previously been saturated with pure 2-propanol vapor. Because of the initial linear relation between $t^{1/2}$ and the fraction of vapor desorbed, Fick's law is applicable and from the equation given by Crank[3]

$$D = \frac{\Pi}{64} \Big/ (t/l^2)_{1/2} \qquad (2)$$

it is possible to derive the expression

$$\bar{D} = \frac{\Pi}{32}(K_s^2 + K_d^2) \qquad (3)$$

where

$$K_s^2 = l^2/(t_{1/2})_s \qquad (4)$$

$$K_d^2 = l^2/(t_{1/2})_d \qquad (5)$$

Table I
Weight and Length Changes for 38% *cis*-PB (0 wt % PS) on Sorption or Desorption

	w_b/w_a	l_b/l_a	ρ_{measd},[a] g cm^{-3}	ρ_{calcd},[a] g cm^{-3}	v_{calcd}, cm^3 g^{-1}
	0.9821	0.9978	0.8950	0.8848	1.1302
	0.9800	0.9963	0.8950	0.8869	1.1275
	0.9840	0.9982	0.8950	0.8854	1.1294
average	0.9820 ± 0.0013	0.9974 ± 0.0006	0.8950	0.8857 ± 0.0007	1.1290 ± 0.0009

[a] Density values at 25 °C.

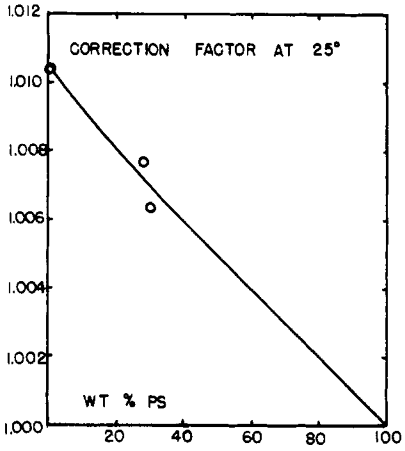

Figure 3. Correction factor as a function of weight percent styrene to correct for the swelling at 25 °C of the samples due to liquid absorption in the density gradient column.

in which l is the thickness of the sample in centimeters and $(t_{1/2})_s$ and $(t_{1/2})_d$ represent time in seconds for the sorption and desorption to attain half of the equilibrium value. In eq 3, $\bar{D}$ represents the average value of D for sorption and desorption. From the data of Figure 2 and from similar data for the sorption process, we calculated $\bar{D}$ to be 2.83 × 10^{-7} cm^2 s^{-1} for the diffusion of pure 2-propanol in Kraton 1101 at 25 °C. This is a reasonable result; for example, Fujita[4] gives a value obtained by Aitken and Barrer[5] of 2.32 × 10^{-7} cm^2 s^{-1} for the diffusion of butane in cross-linked natural rubber at 30 °C, and Odani et al.[6] give a value of 3.5 × 10^{-7} cm^2 s^{-1} for the diffusion coefficient of *n*-hexane in Kraton 1102 at 25 °C.

Weight and Length Changes on Sorption and Desorption. Table I contains data for the ratios of the sample weights, w_b/w_a, of 38% *cis*-PB before and after absorbing the vapors from an aqueous solution containing 35 wt % 2-propanol. Three different samples were studied and the uncertainty in the final average value of 0.9820 was ±0.0013 as calculated from the maximum deviation divided by the number of measurements. The length ratios, l_b/l_a, were somewhat more reproducible, uncertainty ±0.0006. The final specific volume average value was 1.1290 ± 0.0009 cm^3 g^{-1}. As Glass and Dole[1] found 1.1169 for their 40% *cis*-PB sample, correcting for swelling can be seen to amount to a correction factor of 1.0108.

Table II summarizes the swelling data for all of the samples studied here, including the square sample of Kraton 1102. The difference in the l_b/l_a ratios for sides 1 and 2 amounts to only 0.0006 or 0.06%, which is the order of magnitude of the experimental uncertainties. The correction factors by which to multiply the measured v values to obtain the values corrected for swelling are 1.0105, 1.0078, and 1.0063, respectively, for the 0, 28, and 30 wt % PS samples. These numbers are plotted as a function of the weight percent styrene in Figure 3, from which correction factors equal to 1.0080, 1.00573, and

Table II
Summary of Weight and Length Changes on Sorption or Desorption at 25 °C

sample	wt % PS	w_b/w_a	l_b/l_a	ρ_{measd}, g cm^{-3}	ρ_{calcd}, g cm^{-3}	v_{calcd}, cm^3 g^{-1}
38% *cis*-PB	0	0.9820 ± 0.0013	0.9974 ± 0.0006	0.8950	0.8857 ± 0.0007	1.1290 ± 0.0009
Kraton 1102	28	0.9760 ± 0.0005	0.9945 ± 0.0001	0.9335	0.9263 ± 0.0007	1.0795 ± 0.0005
Kraton 1101	30	0.9754 ± 0.0008	0.9938 ± 0.0004	0.9372 ± 0.0002	0.9313	1.0738 ± 0.0006

Measurements on Square Sample

sample	wt % PS	w_b/w_a	l_b/l_a
Kraton 1102	28		
measurement 1		0.9771	
side 1			0.9943
side 2			0.9949
measurement 2		0.9766	
side 1			0.9943
side 2			0.9949

Table III
Observed and Calculated Deviations of the Specific Volumes from the Additivity Relation at 25 °C[a]

wt % PS	v_{obsd}	v_{corr}	v_{calcd} (eq 1)	Δv	Δv (eq 6)
21.2	1.0834	1.0921	1.0913	0.0008	0.0010
41.8	1.0506	1.0566	1.0551	0.0015	0.0016
61.2	1.0192	1.0230	1.0210	0.0020	0.0019
		Kraton Samples			
28	1.0712	1.0794	1.0797	−0.0003	
30	1.0670	1.0745	1.0761	−0.0016	

[a] v in cm^3 g^{-1}. [b] $\Delta v = v_{corr} - v_{calcd}$.

1.00377 for the 21.2, 41.8, and 61.2 wt % PS samples previously studied[1] were read off and used to calculate the corrected v values given in Table III. The curve extrapolates to unity at 100% PS because PS does not sorb any 2-propanol or water. Correction factors equal to 1.0077 and 1.0070 for the 28 and 30 wt % samples, respectively, were read off of Figure 3 and used to calculate the v_{corr} values of Table III. From this table one can see that the deviations of v_{corr} from v calculated from the additivity eq 1, namely, 0.0008, 0.0015, and 0.0020, are slightly smaller than the values previously estimated by Glass and Dole,[3] 0.0013, 0.0023, and 0.0027 for the 21.2, 41.8, and 61.2 wt % PS samples, respectively. This means that the interface between the butadiene and styrene blocks is narrower than calculated in our first paper,[1] perhaps narrower by the ratio (0.0027–0.0020)/0.0027 or 25%.

In Table III values are given of Δv calculated from eq 2 of our previous paper,[1] namely

$$\Delta v = \frac{n_A n_B}{n_A + n_B} \rho K \qquad (6)$$

where n_A and n_B represent the number of styrene and butadiene segments per gram of polymer, ρ is the corrected density, and k is an empirical constant taken to be 0.586 in the present work as compared to 0.888 cm^6 g^{-1} used previously. Values of Δv from Table III are about two-thirds as large as in the previous work.[1] In other words, the new data fit the additive law more closely than the old data.

Kurita et al.[7] concluded from a small-angle X-ray scattering study of a styrene–butadiene–styrene block copolymer containing 26 vol % styrene and 9 vol % vinyl that "the phase boundary between PS and PB is rather sharp and the data could be analyzed by the ideal two-phase model". This agrees with our estimate, but our conclusion is based on the assumption that the specific volumes of the butadiene and styrene segments in the block copolymers are the same as in the pure polybutadiene and polystyrene. That this may not be exactly true is indicated by the rather surprising fact that the Δv values for the Kraton samples are negative. This may be the result of the butadiene and styrene phases in the Kraton samples having slightly different densities from the densities in the PB, PS, and block copolymer samples given to us from General Tire and Rubber Co.

Acknowledgment. This research was supported by income from the Chair in Chemistry established at Baylor University by a gift of The Robert A. Welch Foundation. We are greatly indebted to Drs. S. L. Aggarwal and R. A. Livigni of General Tire and Rubber Co. and to Dr. D. J. St. Clair of Shell Development Co. for the samples of the block and homopolymers used in this research.

References and Notes

(1) Glass, S. M.; Dole, M. *Macromolecules* **1979**, *12*, 965.
(2) Information received from Dr. D. J. St. Clair of the Shell Development Co.
(3) Crank, J. "The Mathematics of Diffusion"; Clarendon Press: Oxford, 1970; p 248.
(4) Fujita, H. "Diffusion in Polymers"; Crank, J., Park, G. S., Eds.; Academic Press: New York, 1968; p 87.
(5) Aitken, A.; Barrer, J. *Trans. Faraday Soc.* **1955**, *51*, 116.
(6) Odani, H.; Uchikura, M.; Taira, K.; Kurata, M. *J. Macromol. Sci., Phys.* **1980**, *B17*, 337.
(7) Kurita, K.; Miyazawa, S.; Asukabe, M.; Wade, E. *J. Macromol. Sci., Phys.* **1980**, *B17*, 375.