Hydrogen Solubility in Block Copolymers of Styrene and Butadiene

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ABSTRACT: Hydrogen and deuterium gas solubilities over the temperature range 0-50 °C and up to 1 atm of pressure have been measured in block copolymers and homopolymers of butadiene and styrene. Henry's law was accurately followed in all samples. The solubility increased with temperature, demonstrating that the solution process was endothermic. The logarithm of the solubility for the hydrogen in pure polybutadiene fitted well on a linear curve of published solubilities of He, N_2, Ar, Kr, and Xe plotted as a function of the absolute temperatures of the boiling points of the gases. The solubility in the block copolymers was less than in the pure polybutadiene at 21.2 wt % polystyrene and then rose approximately linearly with increase of styrene content to that of pure polystyrene.

Introduction

Previous studies[1-4] of the solubility of hydrogen in polyethylene (PE) have been of interest for two reasons: first, the solubility was shown to vary with the physical state of the PE, and second, hydrogen was shown to act as a catalyst for the decay of the alkyl free radicals in irradiated PE samples. From the solubility studies, it was deduced that amorphous regions in the PE were structurally similar to that of liquid high molecular weight *n*-alkanes and from the catalytic studies it could be demonstrated that the free radical decay reactions occurred in the amorphous phase, at the boundary between the amorphous and crystalline regions, and in the amorphous surface layers of single-crystalline PE. Because of parallel studies now being carried out in this laboratory on the radiation chemistry of block copolymers of styrene and butadiene, it appeared to be of interest to study the solubility of hydrogen in these samples. Also, no previous measurements of the solubility of hydrogen in these block copolymers seem to have been carried out although Odani et al.[5,6] have studied the solubility of He, N_2, Ar, Kr, and Xe in pure polybutadiene (PB), pure isotactic polystyrene (PS), and block copolymers of styrene and butadiene containing 26.8 wt % styrene (Kraton 1102) and 40.8 wt % styrene (Solprene 414). Their data will be discussed and compared with our H_2 data below.

Solubility measurements of deuterium gas carried out so as to apply the theory of Frisch and Rogers[7] and Ziegel and Eirich[8] to estimates of the cavity free volume are also described.

Experimental Section

Materials. The homopolymers and block copolymers studied were the same as those previously described.[9] They were used as received from Dr. S. L. Aggarwal of the General Tire and Rubber Co. inasmuch as annealing was shown to have a practically negligible effect on the densities of the block copolymers. Annealed polystyrene was used because solubility measurements of the unannealed PS gave inordinately high results, more than 10 times greater than the solubility in the annealed samples. This was probably due to voids in the unannealed samples. The annealing was carried out by heating the PS powder between glass plates separated by metal spacers in a vacuum oven with a lead weight on top of the glass plates. On heating above the PS softening point, excess PS was squeezed out of the sandwich, and the whole system was allowed to cool slowly overnight. In this way a slab of annealed PS was prepared. The 21.2 wt % PS (type SBS) block copolymer consisted of polystyrene spheres in a polybutadiene matrix while the 61.2 wt % PS (type SB) block copolymer had polybutadiene cylinders in a polystyrene matrix. As stated by Dr. Aggarwal "these block copolymers are actually graded block copolymers in that the change from one type of monomer unit in the chain to another is not abrupt, but has a small region of alternation present". We have no information beyond that given previously[9] as to the number-average molecular weights of the different samples. Hydrogen and deuterium gases were used as received.

Solubility Measurement Techniques. The method of measuring the solubility of hydrogen and deuterium gases in the homopolymers and block copolymers of butadiene and styrene was the liquid quenching method as previously described by Kubo and Dole.[10] In this method the solid sample, usually about 0.1 g, is placed in a copper U-tube. The tube is evacuated, hydrogen admitted to a definite pressure at a selected temperature, and the gas allowed to stand in contact with the polymer for 24 h or longer in a constant-temperature bath until solubility equilibrium has been reached. The U-tube is then quickly removed from the water bath and plunged into liquid air to freeze in the dissolved hydrogen. After 15-20 min at that temperature, ambient hydrogen could be removed by evacuation; then the tube was warmed to room temperature so the dissolved hydrogen could diffuse out of the solid polymer into the gas phase. In the present experiments, this amount of hydrogen was determined by flushing it into a Varian Aerograph, Series 1400, gas chromatograph (GC). By means of data from previous calibrations, the weight of the dissolved hydrogen could be calculated after estimation of the area of the hydrogen peak in the GC recording on a Varian Model 9176 recorder. Nitrogen was the carrier gas.

The same sample of polymer was used for all of the hydrogen and deuterium solubility measurements at different temperatures for that particular polymer. In the case of the 21.2 wt % PS sample, a different sample from that used in the hydrogen experiments was used for the deuterium gas experiments. After the conclusion of the hydrogen experiments when the sample was removed from the U-tube, it had changed its appearance, so there is some question about the accuracy of the 21.2 wt % PS hydrogen experiments.

Results and Discussion

All data obtained in this research followed Henry's law as illustrated in Figure 1 for the deuterium gas solubility, *S*, measurements at 25 °C. The data in Figure 1 and Table I are in units of cm^3 of gas at STP ($\times 10^4$) dissolved at 1-cmHg pressure per cm^3 of polymer.

The Henry's law constant was calculated by a least-squares analysis of the data of Figure 1, and the solubility at 1 atm of pressure was calculated and converted into moles. It is from the latter that the data of Table I were obtained. The average deviation from the Henry's law constant of all of the measurements at 25 °C for each of the samples was 2.1, 3.4, 2.5, and 2.5% for the pure PB, 21.2 wt % PS, 61.2 wt % PS, and pure PS samples, respectively. This means that the data of Table I are reliable to only two significant figures. Because density measurements were made only at 25 °C, these values were also used in converting grams of polymer to cm^3 at 0 and 50 °C. Average values of the mole ratio of deuterium to hydrogen solubilities over the temperature range 0-50 °C are also given in Table I. One would have expected the

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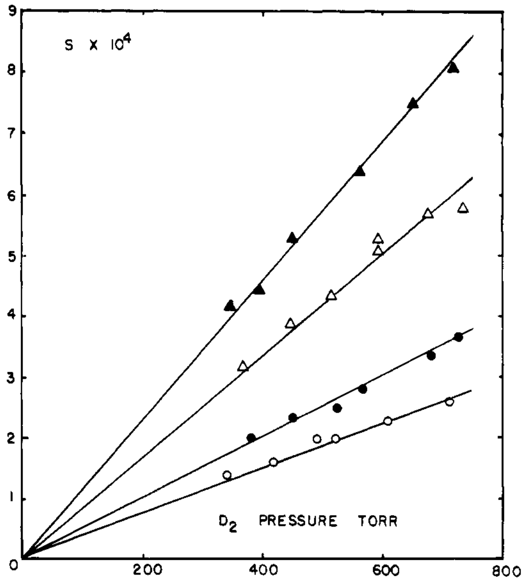

Figure 1. D_2 solubility at 25 °C in units of cm^3 (STP) of gas at 1 cmHg of pressure per cm^3 of polymer: (●) pure PB; (○) 21.2 wt % PS; (△) 61.2 wt % PS; (▲) pure PS.

Table I
Solubility of Hydrogen and Deuterium Gases at 1-cmHg Pressure in Units of cm^3 of Gas at STP per cm^3 of Polymer ($\times 10^4$)

wt % PS	solubility, *S*: H_2	solubility, *S*: D_2	D_2/H_2 ratio
	0 °C Results		
0	3.56	3.43	0.96
21.2	2.37	2.78	1.17
61.2	5.93	6.22	1.05
100.0	7.79	7.86	1.01
	25 °C Results		
0	3.77	3.72	0.99
21.2	2.48	2.97	1.20
61.2	6.28	6.51	1.04
100.0	8.38	8.88	1.06
	50 °C Results		
0	4.09	3.88	0.95
21.2	2.97	3.27	1.10
61.2	6.71	6.56	0.98
100.0	10.70	10.67	1.00

ratio to be close to unity, as it is, except in the case of the 21.2 wt % sample. The deviation in the latter case may be the result of using a different sample for the H_2 experiments from that used in the deuterium experiments.

In Figure 2, the deuterium gas solubilities are plotted as a function of the weight percent PS at 0 and 50 °C. The data for 25 °C would lie between these curves. Similar curves were obtained in the hydrogen experiments and all showed a minimum at 21.2 wt % PS, as did Odani et al.'s[5] data for N_2, Ar, and Kr (Figure 4). Note that for all four different polymer samples the solubility increased with the temperature. Odani et al.[5] also found this to be true for the solubility of helium but not for argon or xenon. Thermodynamically, one would expect the logarithm of the solubility to be a linear function of the reciprocal of the absolute temperature. Figure 3 demonstrates that this is the case for the deuterium data of Table I. The hydrogen data gave similar agreement with this relation. From the equation

$$\ln K = I - \Delta H^\circ / RT \qquad (1)$$

where *I* is an integration constant and *K* is the Henry's law constant, the heat of solution ΔH° for the reactants and products in their standard state can be calculated by determining the slopes of the lines of Figure 3. Table II gives the heat of solution values as calculated in this way for hydrogen and deuterium. It is interesting to note the decrease in the endothermic heat of solution in passing from the 21.2 to the 62.2 wt % PS sample. This may be the result of the change of the block copolymer's system from PS spheres imbedded in the PB matrix (21.2 wt % sample) to PB cylinders in the PS matrix (61.2 wt % sample). Glass and Dole[9] showed that Δv, the increase in

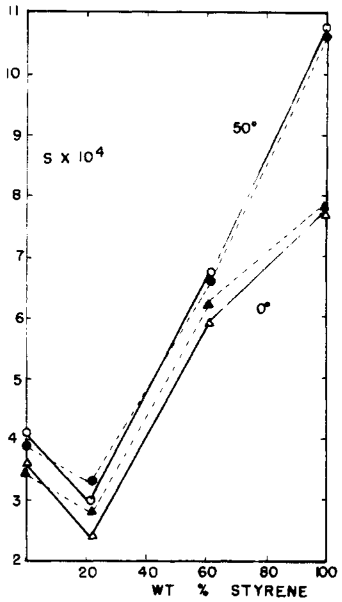

Figure 2. H_2 and D_2 solubility at 0 and 50 °C as a function of weight percent polystyrene in the polybutadiene–polystyrene samples studied. *S* units same as in Figure 1. Dotted lines represent deuterium solubility and solid lines hydrogen solubility.

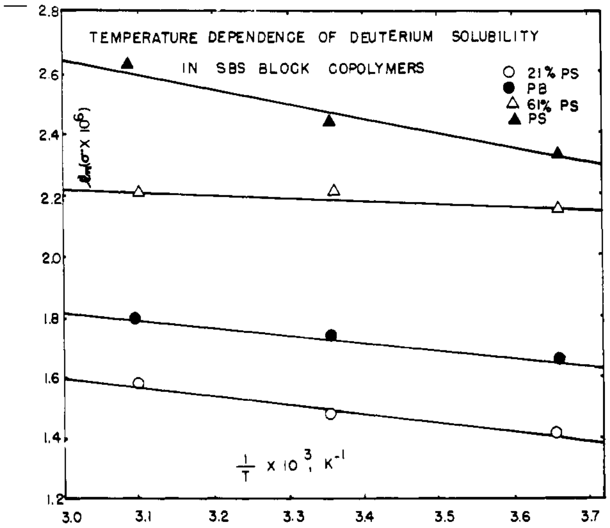

Figure 3. Natural logarithm of deuterium solubility as a function of reciprocal absolute temperature. σ in grams of D_2 dissolved per gram of sample. Percentages in weight percent.

Table II
Heats of Solution for the Styrene and Butadiene Homopolymers and Block Copolymers

wt % PS	ΔH, kcal mol^{-1}: H_2	ΔH, kcal mol^{-1}: D_2	V_f, $Å^3$
0	0.451	0.441	570
21.2	0.786	0.599	51
61.2	0.435	0.185	44
100	1.099	1.073	219

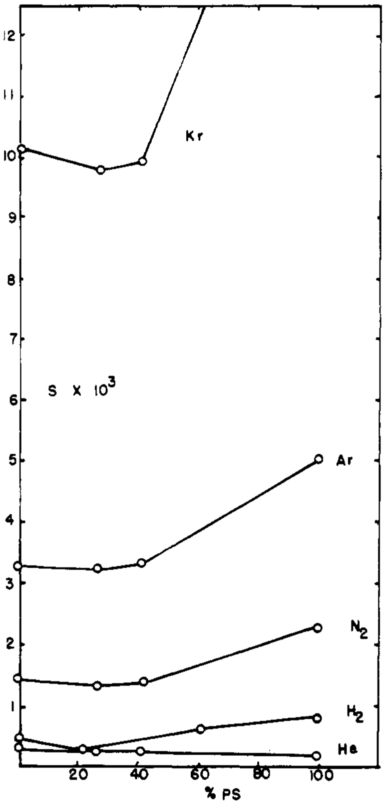

Figure 4. Comparison of the solubility, S, of H_2, N_2, and the rare gases He, Ar, and Kr in units of cm^3 of gas (STP) dissolved per cm^3 of polymer at 25 °C and 1 cmHg of pressure. Data for He, N_2, Ar, and Kr are from Odani et al.[6]

volume over that expected from the linear mixing law, was greatest in the case of the 61 wt % PS sample. With more volume available per hydrogen molecule than expected, the endothermic heat of solution should be less.

Figure 4 compares the solubility of hydrogen in the block copolymers with the solubility of He, N_2, Ar, and Kr, the data of Odani et al.[6] A decrease in the S value of 20–30 wt % PS can be seen in the H_2, N_2, Ar, and Kr data but not in the He data. The hydrogen solubility is greater than that of helium despite the lower weight of the hydrogen molecule. Another comparison of the solubility data is shown in Figure 5, where the logarithm of the solubility in pure PB is plotted as a linear function of the absolute temperature of the boiling points of the different gases. This relationship is quite accurate for all of the gases except nitrogen, which is slightly off the straight line. As pointed out by Odani et al.[6] many years ago, Gee[11] derived the following equation for the solubility of gases in polymers:

$$-\ln 76S = \frac{\Delta S_v}{R}\left(1 - \frac{T_b}{T}\right) - \ln \frac{22400}{V_0} + 1 + \chi \quad (2)$$

where S is the solubility in cm^3 (STP) of gas dissolved at 1 cmHg of pressure in 1 cm^3 of polymer, ΔS_v is the molar entropy of vaporization of the gas, T_b is the absolute temperature of the boiling point of the gas, V_0 is the molar volume of the liquefied gas at the temperature T of the experiment, which can only be estimated by extrapolation, and χ is the Flory–Huggins interaction parameter.[12] By making approximate estimates of the values of ΔS_v and V_0, Gee reduced eq 2 to

$$-\ln 76S = 4.5 - 10(T_b/T) + \chi \quad (3)$$

or

$$\ln S = -8.83 + 10(T_b/T) \quad (4)$$

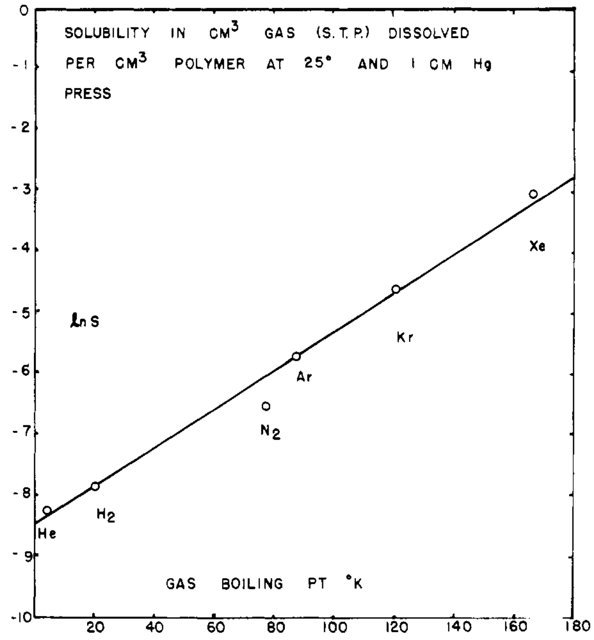

Figure 5. Logarithm of Odani et al.'s data for the solubility at 25 °C of He, N_2, Ar, Kr, and Xe in pure PB as a function of the absolute temperature of the boiling points. H_2 datum is from this research.

where χ has been neglected because according to Gee, χ is unimportant for the permanent gases considered. It is interesting that eq 4 is approximately valid for a number of polymers. As Gee has remarked "this is in accord with the observation that the solubilities of say air in a range of polymers do not differ widely". The intercept of the data for pure PB in Figure 5 at T_b equal to zero is about −8.5, which is close to Gee's value of −8.83 in eq 4. The slope of the straight line of Figure 5, d ln S/dT_b, is 0.032 (K^{-1}) while the calculated value at 25 °C from eq 4, $10/T$, is 0.034. Again, very good agreement is obtained, considering Gee's approximations made in deriving eq 3. Similar agreement results if Odani et al.'s data are tested in the case of Kraton 1102 (26.8 wt % PS) with an intercept of −8.55 and a slope of 0.033. However, the latter calculation did not include hydrogen solubility data. In both the pure PB and Kraton 1102 plots data for N_2 fell below the linear line. Nitrogen is a diatomic gas and perhaps could not be accommodated as easily into the polymer matrix as the monatomic gases He, Ar, Kr, and Xe. However, hydrogen is diatomic, yet its solubility falls on the curve of the monatomic gases in Figure 5.

Perhaps the most striking observation in this work is the pronounced drop in the solubility vs. weight percent PS curves at 21.2 wt % PS shown in Figure 2 for both H_2 and D_2 gases at 0 and 50 °C. Values at 25 °C are intermediate between the 0 and 50 °C values. This dip occurs for both the hydrogen and deuterium gases at 0, 25, and 50 °C and also for Kr, Ar, and N_2 as seen in Figure 4. Apparently, the incorporation of polystyrene spheres into the polybutadiene matrix restricts the motion of the butadiene segments required for the dissolving of the hydrogen molecules. The heat of solution data given in Table II show that the ΔH values become more positive in going from the pure PB to the 21.2 wt % PS block copolymer. This would make ΔG, the free energy of the solution process, less negative, and so decreases the Henry's law constant K. At higher PS concentrations, the solubility increases due to the greater styrene concentration. If the solubility data for hydrogen between 61.2 and 21.2 wt % polystyrene are extrapolated to 0% polystyrene, a solubility value about 1.10 ppm at 760 torr and 25 °C compared to the observed value of 2.88 ppm in pure PB is obtained. This result demonstrates vividly the effect of the polystyrene segments in reducing the ability of polybutadiene to accommodate the hydrogen molecules. Extrapolation of Odani et al.'s data[6] for N_2 gas between 40.8 and 100 wt % PS yields a similar result but the effect is much less marked for an extrapolation using their 26.8 and 40.8 wt % data. Nevertheless, it is clear that the polystyrene segments act to diminish the amount of hydrogen dissolved in the polybutadiene fraction of the block copolymers. If an extrapolation to 0% polystyrene is carried out with the hydrogen solubility data at 61.2 and 100 wt % at 0 and 25 °C, values near the solubility in pure PB are obtained, but not for the 50 °C data. If these results are correct, they would suggest that polystyrene in the bulk matrix form is less effective in modifying the PB components than PS in spheres, at least at 0 and 25 °C. As noted in Table II the heat of solution of hydrogen gas in the 61.2% PS sample is almost the same as that in the pure PB.

Thanks to our measurements of the deuterium solubility, we can apply the equation of Frisch and Rogers[7] as modified by Ziegel and Eirich,[8] namely

$$V_f = [18.8/(-\delta\Delta H) + d]^3 \qquad (5)$$

where V_f is the cavity free volume, $\delta\Delta H$ is the difference in the heat of solution in calories per mole of D_2 and H_2 $[\Delta H(D_2) - \Delta H(H_2)]$, and d is the diameter of the H_2 and D_2 molecules, 2.34 Å, to the calculation of V_f for the block copolymers and homopolymers studied in this research. These values are listed in Table II, where an enormous drop is seen between V_f for pure PB and V_f of the block copolymers containing 21.2 and 61.2 wt % polystyrene. V_f rises again in the case of pure PS. These calculations further demonstrate the reduction in the ability of the block copolymers to dissolve hydrogen as compared to the values expected on the basis of a linear additive law.

Finally, one would expect a dual mode of sorption, one mechanism in the pure PB domains and another in the glassy PS domains. All the solubility measurements were made above the glass transition temperature of pure PB, −102 °C for *cis*-1,4-polybutadiene and −48 °C for *trans*-1,4-polybutadiene.[13] The data for pure PB and pure PS show that the solubility in PS is about twice that in PB; however, the solubilities in the block copolymers are not simply the sum of the solubilities in pure PB and PS multiplied by their weight fractions. The PS segments have a marked effect on the PB domains, but the PB segments have little, if any, effect on the solubility of hydrogen in the PS blocks.

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A Study of Polyimide Properties Imparted by the Addition of Lithium Ions

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ABSTRACT: Lithium additives have been used as dopants in poly(amic acid) solutions, which, when cured by heating at 300 °C for 1 h, produce thin, flexible, and antistatic polyimide films. Polyimides derived from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride or pyromellitic dianhydride and 4,4′-oxybis[aniline], 3,3′-diaminobenzophenone, or 3,3′-diaminodiphenylcarbinol have been prepared. Thermogravimetric analysis, thermomechanical analysis, X-ray photoelectron spectroscopy, infrared spectroscopy, and elemental analysis have been used to characterize these films. Electrical conductivity has been found to increase significantly with specific polyimides upon lithium chloride addition. The lowered resistivity appears to be a function of increased moisture uptake due to the presence of surface lithium. Other lithium dopants, however, while having surface moisture, do not produce lower resistivity films.

Introduction

In recent years, research into the incorporation of metallic species into electrically neutral polymers has intensified.[1,2] The impetus is primarily directed at the enhancement of electrical, thermal, and mechanical properties of these polymers. The polymer system upon which we are focusing attention is polyimide. In our laboratory, doping with various palladium-containing compounds has been shown to lower electrical resistivity significantly for certain polyimides.[3,4]

The use of lithium dopants in this regard has only been briefly mentioned in the open literature. A polyimide

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