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Gas Transport in Polybutadiene Treated with Aqueous Bromine

by

D.H. Rein, R.F. Baddour and R.E. Cohen
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139-4307

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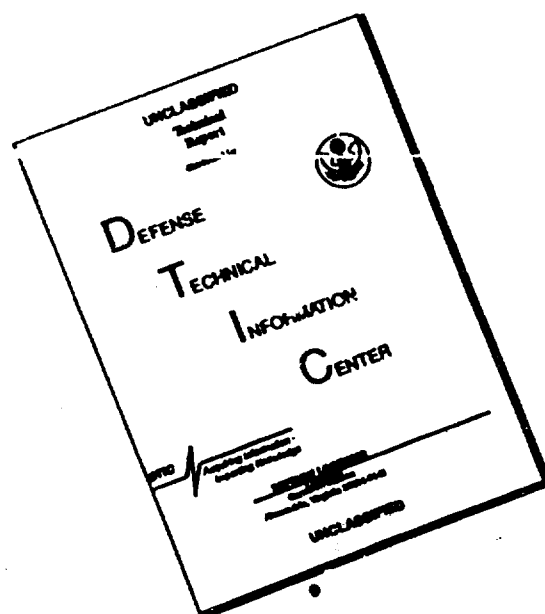
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D. H. Rein, R. F. Baddour, and R. E. Cohen*

Department of Chemical Engineering

Massachusetts Institute of Technology

Cambridge, MA 02139

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Abstract

Diffusion, solubility and permeability coefficients were measured for He, CO₂, Ar and CH₄ in polybutadiene (PB) and in polybutadiene reacted in the solid state to various extents with aqueous bromine. Analysis of the sorption curves and x-ray emission spectra showed that the bromination created a heterogeneous membrane with an outer brominated skin and an unreacted core. At relatively low extent of bromination, the diffusion and permeability coefficients for CO₂, Ar and CH₄ decreased by two orders of magnitude, while the transport coefficients for He were virtually unchanged. The permeability coefficients for CO₂, Ar and CH₄ became immeasurably small after about 3% bromination. The ideal separation factor for gas pairs with different molecular size increased with bromination, suggesting applications in gas separation processes.

Introduction

Tailoring the structure of existing commodity polymers through chemical modification is an attractive approach to improving the properties of membranes for gas separation and barrier applications. Systematic alterations of the polymer structure also provide a convenient route for studying the effects of molecular architecture on the permeability. Substitutions to the backbone or side chains affect the intrasegmental mobility and intersegmental chain packing, resulting in changes in gas diffusivity, solubility and permeability coefficients. A more complete understanding of the role of molecular architecture and supermolecular structure on the gas transport properties will help to explain

the extraordinary behavior of polymers such as poly(1-(trimethylsilyl)-1-propyne), a glassy polymer that exhibits gas permeabilities a factor of ten higher than any other polymer studied [1], and speed the development of others.

Changes in gas transport with chemical modifications have been studied in silicones [2], polycarbonates [3], polyimides [4,5], polystyrenes [6] and poly(phenylene oxides) [7,8]; it has been observed in these studies that decreasing the chain packing density increases the diffusion and permeability coefficients, while decreasing the segmental mobility decreases the diffusion and permeability coefficients. Often, the effects of chemical modification are mutually compensating, so the net change on gas transport is difficult to predict. For example, in the aryl bromination of 2,6-dimethyl-1,4-poly(phenylene oxide) the observed minimum in gas diffusivity with extent of bromination was thought to be caused by the competition between reduced packing and reduced chain mobility [8]. In general, chemical substitutions which inhibit both the chain packing and the segmental mobility were found to increase permeability and have little effect on the selectivity, while those substitutions which decrease the segmental mobility without affecting the chain packing tended to increase selectivity with little effect on the permeability [4].

This paper will focus on the changes in gas solubility, diffusivity and permeability in polybutadiene brominated in the solid state. Most of the previous work on the systematic modification of homopolymers has involved reaction in solution or synthesis from substituted monomers to create homogeneous membranes. Chemically modified skinned membranes have been made by *in situ* fluorination of polyethylene and dramatically reduced the permeability to CO₂ and CH₄ while not affecting the permeability to He [9]; the fluorinated skin layer thickness, however, was not reported. In this work, the effect on gas transport of bromine substitution to the main chain unsaturation in PB will be examined. It is anticipated that reaction in the solid state will create a skinned membrane with well controlled thickness, so that the effect of heterogeneous chemical modification will be considered.

Experimental Section

The polybutadiene homopolymer (PB) used in this study was obtained from Polysciences, Inc. and has a molecular weight of 200,000 g/mole with 90% 1,4 addition. Films (about 0.2 mm thick) were made by static casting a 5% toluene solution onto a flat Teflon surface. The cast films were lightly crosslinked with a 5 Mrad dose of electron beam radiation before removal from the casting surface.

The conditions used to brominate the PB films have already been described in detail elsewhere [10]. The films were submerged in a 0.1 M aqueous bromine solution at room temperature for various reaction times. After the reaction, the films were rinsed in distilled water for 24 hours and placed in a vacuum oven at room temperature until there was no weight loss.

As the bromination reaction proceeded, the PB films became orange and increased in weight and size. At complete reaction, the final weight uptake, W_{∞} , of a polybutadiene specimen was a factor of three greater than the original weight, W_0 ; this amount of weight gain corresponds to the incorporation of two bromine atoms for each double bond in the polybutadiene [11,12]. The extent of reaction will hereafter be referred to as a fraction of the maximum achievable weight increase, i.e. $W(t)/W_{\infty}$ or $W(t)/(3 W_0)$. The glass transition temperature (T_g), determined by differential scanning calorimetry, increased as the bromination reaction proceeded. The T_g increased from -80°C for the unreacted PB to 35°C for a film reacted to 2.7 % extent of reaction.

Results

Permeability Coefficient

The gas permeability coefficients for He, CO_2 , CH_4 and Ar at 35°C were measured for the untreated PB and the bromine modified PB films in a variable volume permeability apparatus [13]. The permeability coefficients are shown in Figure 1 as a function of

percent of reaction. The permeability coefficients for CH_4 , Ar and CO_2 decreased dramatically as the bromination reaction proceeded; with extent of bromination of only 0.5% the permeabilities of CO_2 , CH_4 and Ar dropped by over an order of magnitude and at 2.7% extent of reaction the CO_2 permeability coefficient dropped by almost three orders of magnitude and those for Ar and CH_4 were too low to measure in the present apparatus. The permeability coefficient of He, however, remained relatively unaffected up to 2.7 % bromination.

The changes in permeability with bromination were accompanied by changes in the gas selectivity. The selectivity characteristics can be evaluated by comparing the ratio of the permeability coefficients for a gas pair (ideal separation factor, α) in the reacted and unreacted films. The values of α for the gas pairs He/ CH_4 , He/ CO_2 and CO_2 / CH_4 increased from 0.74, 0.16 and 4.5, respectively, in the original PB to 14, 1.7 and 8.3, respectively, in the 0.5 % brominated film. For He/ CO_2 , α further increased to 56 in the film reacted to 2.7 %. Brominating PB creates a membrane which greatly increases the ideal separation factor for separations involving He; furthermore, the brominated PB is a good barrier material for relatively large gas molecules such as CH_4 , Ar and CO_2 .

Solubility Coefficient

The permeability coefficient of a penetrant in a homogeneous material can be broken down into a product of the diffusion (D) and solubility (S) coefficients [14]. It is of interest to determine whether the large decrease in P with bromination was caused by decreases in D or S. The D and S coefficients for CO_2 , Ar and CH_4 were measured at 35 °C in a pressure decay sorption apparatus to explore the source of the permeability decrease. The details of the experimental apparatus and analysis technique are described elsewhere [15].

The equilibrium solubility of CO_2 at 35 °C as a function of extent of bromination is shown in Figure 2. Up to 14.3 % bromination the CO_2 solubility decreased by 35% of its original value. Ar and CH_4 displayed similar decreases in solubility with bromination.

Although there are measurable decreases in the gas solubility coefficients with reaction, these are insufficient to account for the orders of magnitude decreases in the permeability coefficient.

Diffusion Coefficient

The diffusion coefficients for CO₂, Ar and CH₄ at 35 °C were determined from the half-times of the sorption curves [15]. The results for CO₂ are shown in Figure 3. The diffusion coefficients decreased monotonically with increasing bromination. For 2.7 % reacted films, the diffusion coefficients for Ar, CO₂ and CH₄ decreased by two orders of magnitude from their original values. By 14.3 % extent of reaction, the diffusion coefficient for CO₂ had decreased by over three orders of magnitude.

Discussion

The large decreases in the permeability coefficient are attributable primarily to changes in the diffusion coefficient. However, assuming the bromine reacted uniformly throughout the PB film to give a homogeneous material, the measured decreases in the diffusion and solubility coefficients do not sufficiently account for the decreases in the permeability coefficient. At 2.7 % bromination, the permeability coefficient for CO₂ decreased by a factor of 690 while the combined change in the diffusion and solubility coefficients account for a decrease of only a factor of 90 in permeability (assuming $P = DS$).

Insight to this apparent inconsistency is obtained by considering the shapes of the sorption curve. The sorption curve for CO₂ in the film reacted to 2.7 % is shown in Figure 4; it has a sigmoidal shape with a slow initial gas uptake rate. This curve is indicative of a composite material with an outside skin layer of much lower diffusion coefficient than the bulk material [16]. For this type of composite, the gas permeability coefficient will not be a simple product of the half-time diffusion coefficient and solubility coefficient. This complication occurs in composite membranes because the diffusion coefficient calculated from the half time of the sorption curve is not equal to the steady state effective diffusion coefficient. Evidently, the bromine did not react homogeneously throughout the material,

and therefore agreement between the observed changes in the permeability coefficient and the product of the solubility and diffusion coefficients should not be expected.

Direct evidence for the formation of a skin layer during the bromination reaction was obtained using SEM. A film brominated to 14.3 % extent was frozen in liquid nitrogen and fractured. Specimens for SEM were prepared from the fractured sample by mounting at two different orientations and gold coating. Figure 5a shows an example of the roughened surface texture (observed to various extents for all the brominated materials) when viewed normal to the film surfaces. Figure 5b shows a SEM micrograph of the fractured edge viewed almost parallel to the film surface; this micrograph clearly reveals an outer skin layer which is brighter than the inner core. The image in this micrograph was formed using the secondary electron detector with an accelerating voltage of 25 kV. The contrast seen can be identified with differences in the atomic number of the species in the material. Species with higher atomic numbers (Br atom vs C atom) yield a higher concentration of backscattered electrons and appear brighter [17]. Since the skin layer is brighter than the core, it clearly contains a higher bromine concentration.

The energy dispersive x-ray analyzer in the SEM was used to quantitatively characterize the brominated skin layer [18]. The relative bromine concentration as a function of distance from the film edge was determined from the x-ray emission spectrum (xes) and is displayed in Figure 6. Using the data from Figure 6, it is straightforward to estimate that bromination to 14.3 % yields a membrane with an outer shell which is completely brominated (100 % reacted) and which has a thickness of approximately 15 % of the bulk thickness.

The CO_2 diffusion coefficient in this fully brominated PB skin can be estimated once the thickness is known. This calculation involves simulating the experimental sorption curve using a finite difference method for modeling gas uptake in a composite [16]. In the simulation, gas first diffuses through the outer skin then into the central core. There is no net flux through the membrane in a sorption experiment since the penetrant gas enters from all sides. The composite was assumed to consist of a skin layer (the 100 % brominated

PB comprising 15% of the total thickness) with a low diffusion coefficient and a central core of pure PB. Although bromine was detected to a small extent into the core region, this was ignored to simplify the simulation.

The diffusion coefficients from the simulated and the measured sorption curves were calculated from the half times. The diffusion coefficient of the pure PB core was fixed based on the measured value of $5.0 \times 10^{-6} \text{ cm}^2/\text{sec}$ determined in our laboratory while the diffusion coefficient in the brominated skin was adjusted to create a match between the measured and simulated D. The CO_2 diffusion coefficient in the brominated PB skin was determined from the simulation to be $1.0 \times 10^{-9} \text{ cm}^2/\text{sec}$ with an error of 30% assuming an error of 25% in determining the skin thickness. Thus, the solid state bromination of PB to full conversion decreases the diffusion coefficient by 3.5 orders of magnitude.

We suggest that the decrease in gas diffusion with bromination in PB is brought about by three factors. First of all, the removal of unsaturation in PB could decrease the diffusion coefficient by decreasing the ease of hole formation for a diffusional jump in the polymer; evidence for this effect was seen by the decrease in the diffusion coefficient of octadecane in PB by a factor of two upon hydrogenation [19]. Secondly, the addition of bulky Br decreases the diffusion coefficient by decreasing the chain flexibility, similar to the decrease of the N_2 diffusion coefficient in PB by a factor of 10 upon methyl substitution to yield poly(2,3-dimethyl butadiene) [20]. Finally, the addition of the polar Br side group increases the chain cohesive energy, decreasing the diffusion coefficient; halogen-substituted polycarbonates have lower gas diffusion coefficients than methyl-substituted polycarbonates [21]. Thus, the structural changes in brominated PB responsible for the lowering of the gas diffusion coefficient include both decreasing the chain flexibility and increasing the chain cohesive energy.

The CO_2 permeability coefficient for brominated PB can be estimated from the skin layer thickness data. As indicated by the xes analysis of the 14.3 % brominated sample, the skin thickness (as a percent of the total thickness) is essentially equal to the extent of

bromination. The skinned brominated PB is a composite laminate arranged in series with respect to the direction of gas transport, and the permeability coefficient for such a laminate can be expressed as:

$$1/P_{\text{par}} = v_1/P_1 + v_2/P_2$$

where P_{par} is the composite permeability coefficient, P_1 is the permeability in the skin layer with volume fraction v_1 and P_2 is the permeability of the bulk material with volume fraction v_2 . For the 2.7 % brominated film, P_1 (the skin layer permeability) was calculated to be 0.021 barrer assuming that P_2 was pure PB and P_{par} was the measured value of 0.75 barrer.

Given the estimated permeability and diffusion coefficients for CO_2 in the brominated skin layer, the solubility coefficient of the skin can be estimated assuming the P in the homogeneous skin layer can be expressed as a product of D and S . Using this relation, the solubility coefficient for CO_2 in the fully brominated PB was estimated as .0021 cc(STP)/cc/cm Hg, a factor of 5 lower than the CO_2 solubility in unmodified PB.

Conclusions

Gas permeation, diffusion and solubility have been measured for He, CO_2 , Ar and CH_4 for polybutadiene films exposed to an aqueous bromine solution at room temperature for various reaction times. The bromination created a film with a skin layer of brominated PB and a virtually unreacted core. The skin layer dramatically reduced the permeation to Ar, CO_2 and CH_4 , while decreasing only slightly the permeation to He. The bromination reaction produces a material which selectively permeates gases based on size with the cutoff size larger than He and smaller than Ar.

Sorption curves and xes measurements allowed the estimation of the gas transport parameters of the fully brominated layer. The CO_2 diffusion coefficient was estimated to decrease by a factor of 5000, the permeability coefficient by a factor of 25,000 and the solubility coefficient by a factor of 5 upon aqueous bromination in the solid state.

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Figure 1. Permeability of gases at 35 °C in PB films reacted to various extents in aqueous bromine

Figure 2. Solubility coefficient of CO₂ at 35° C in brominated PB films

Figure 3. Diffusion coefficient of CO₂ at 35 °C in brominated PB films

Figure 4. Sorption uptake curve for CO₂ at 35 °C in a PB film brominated to 2.7 %. Sigmoidal shape indicates presence of skin layer.

Figure 5a. SEM top view of PB film brominated to 14.3 %. Roughness was observed to some extent for all brominated samples

Figure 5b. SEM edge view of PB film brominated to 14.3 %.
Bright outside edge is brominated skin layer and
total film thickness is 200 μ.

Figure 6. Relative Br concentration as a function of distance from outer edge determined from xes. Film center is at 100 μ.

