Modification of Polystyrene/Polybutadiene Block Copolymer Films by Chemical Reaction with Bromine and Effect on Gas Permeability

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

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received June 6, 1990; Revised Manuscript Received January 18, 1991

ABSTRACT: Permeability coefficients (*P*) for several gases were measured in heterogeneous polystyrene/polybutadiene (PS/PB) block copolymer films before and after reaction with aqueous bromine. Reacted films exhibited increased selectivity compared to the starting material. While films reacted to low and very high extents were less permeable than unmodified films, those reacted to intermediate extents displayed higher effective permeability coefficients than the original block copolymer, resulting in membranes that exhibited both selectivity and permeability enhancement relative to the starting PS/PB system. These effects are the combined result of physical and chemical changes caused by the bromination reaction.

Introduction

The gas transport properties of polymeric materials[1] can be altered by chemical modification.[2-4] Often, the goal of these modifications is to create either a material with enhanced barrier capabilities or one that exhibits a combination of high permeability and selectivity. These criteria reflect the two most prominent applications for polymers in which gas transport is crucial—packaging materials and membranes for gas separations.[5-7]

Systematic chemical modifications of polymers such as polyimides[3] and silicones[4] have demonstrated that judicious incorporation of particular segments or groups into a polymer chain can affect the material's gas permeability coefficient (*P*) through changes in either the diffusion coefficient (*D*) or the solubility coefficient (*S*). The addition of bulky segments into the polymer can result in either a decrease in *D* as a result of restricted chain mobility or an increase in *D* due to reduced segmental density. *S*, on the other hand, can be adjusted by modifying the polymer so that it contains chemical groups that present a particular thermodynamic interaction with the penetrant.

Most of the work on transport in chemically modified polymers has been conducted with homopolymers. Here, we examine gas transport in microphase-separated polystyrene/polybutadiene (PS/PB) block copolymer films that have been reacted with bromine, which is expected to add readily to the unsaturated sites of the rubbery PB—the high-permeability component of the block copolymer.[8] Changes in the diffusion and permeability coefficients in the reacted material may be expected because of bromine's large atomic size. In addition, the incorporation of the massive Br atoms may induce microstructural changes in the solid block copolymer. Of particular interest is whether the chemical modification of the block copolymer leads to effects on gas permeability markedly different from those observed in the corresponding modified homopolymers, and whether any changes offer improved characteristics for gas separations or barrier applications.

Experimental Section

The block copolymer used in this study was supplied by Phillips Petroleum Co. and has been used previously in studies relating gas permeability to block copolymer morphology.[8-10] This material contains 75 vol % PS and has a weight-average molecular weight of 180 000. Additional molecular characterization information can be found elsewhere.[8]

Sample films were prepared from an extruded sheet of this K-Resin, 0.5 mm in thickness. These samples are referred to as KR-E, for "K-Resin: extruded". Figure 1 is a transmission electron micrograph (TEM) of an osmium-stained thin section that presents a cross-sectional view of a KR-E specimen parallel to the extrusion direction. As indicated in the figure, a gas molecule permeating through these samples will travel through a random, alternating PB/PS lamellar microstructure with a PB lamellar thickness of ca. 75 Å. More detailed morphological characterization of this material has been described in an earlier publication.[8]

Polybutadiene and polystyrene homopolymers, both of nominal molecular weight 200 000, were obtained from Polysciences, Inc., and Scientific Polymer Products, Inc., respectively. Homopolymer films were cast on a flat Teflon surface from solution in toluene. PB films were mildly cross-linked (average molecular weight between cross-links of 38 000) by exposure to a 5-Mrad dose of electron beam radiation.[11]

Reaction was conducted by submerging the polymer films in a 0.1 M solution of bromine in distilled water. (There is some precedent to the reaction of solid polymers with bromine in this manner—aqueous solutions of bromine were used as an early electron microscopy stain for diene polymers[12].) Films were hung vertically from a Teflon support in a closed glass jar, which contained the solution. After remaining in the container for a given amount of time, the test films were rinsed in distilled water for 24 h and then exposed to vacuum for 4 days.

PB and PS homopolymer films were subjected to the bromine/water treatment. As anticipated, PB films experienced a weight gain after reaction and took on an orange color, which increased in intensity with greater reaction time. On the basis of published accounts of halogen reaction with diene polymers and low molecular weight alkenes,[13,14] there are several mechanisms of varying complexity that may describe the reaction of aqueous bromine with PB. In general, however, it can be expected that the reaction will result in either the addition of two Br atoms to the carbon–carbon double bond or the incorporation of a single Br atom to a double bond with the formation of a cross-link between adjacent chains.

The reacted PB films became noticeably less flexible as reaction time increased, and a sample reacted for 18.5 h exhibited a glass transition in differential thermal calorimetry at 35 °C (unreacted PB T_g = −80 °C). This indicates substantial reduction of chain mobility in the PB (a consequence of the addition of the bulky bromine atoms to the chains) along with possibly increased cross-link density.

---

* Present address: Department of Chemical Engineering, Bucknell University, Lewisburg, PA 17837.

0024-9297/91/2224-3612$02.50/0

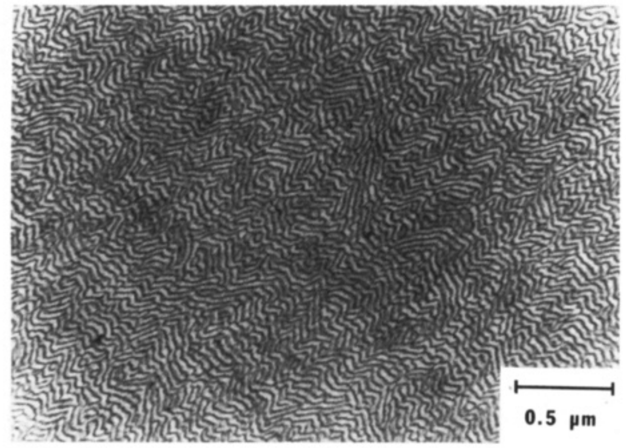

Figure 1. Transmission electron micrograph displaying cross-sectional view of KR-E film morphology.

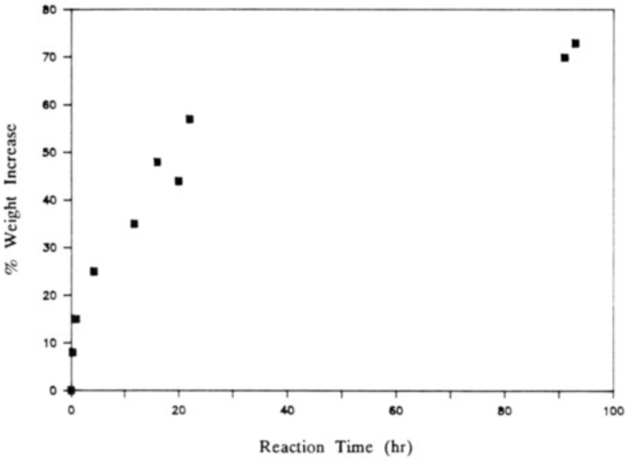

Figure 2. Weight gain of brominated KR-E films as function of reaction time.

Solid polystyrene films also exhibited a detectable increase in weight after reaction. Solution ^{13}C NMR of the brominated product indicated the presence of Br on the phenyl group. There was no evidence of bromine on the polymer backbone. Differential calorimetry detected a second glass transition (the original T_g of 100 °C was still present) at 145 °C. The existence of two transitions suggests that the reaction did not occur throughout the entire film.

A series of reactions using square 3 × 3 in. KR-E block copolymer films was conducted. Extent of reaction was characterized by the percentage change in weight of the samples (hereafter referred to as % *W*). Figure 2 is a plot of % *W* vs reaction time in hours. The curvature concave to the time axis suggests a reaction process whose rate is controlled by diffusion of the reactant into the polymer film. Sample weight gains as large as 73% (after reaction for 95 h) were achieved. The maximum possible weight increase of the block copolymer, based on addition of two Br atoms to every PB double bond (an upper limit because of the cross-linking possibility) and one to every PS phenyl group, is 108%.

Changes in the thickness of reacted block copolymer films were observed. Sample thicknesses as a function of % *W* appear in Figure 3. There is a steady increase in thickness with reaction extent, which levels at a value of 0.605 mm at % *W* = 44. Beyond this point, considerable weight increases were detected with reaction without further significant changes in sample thickness.

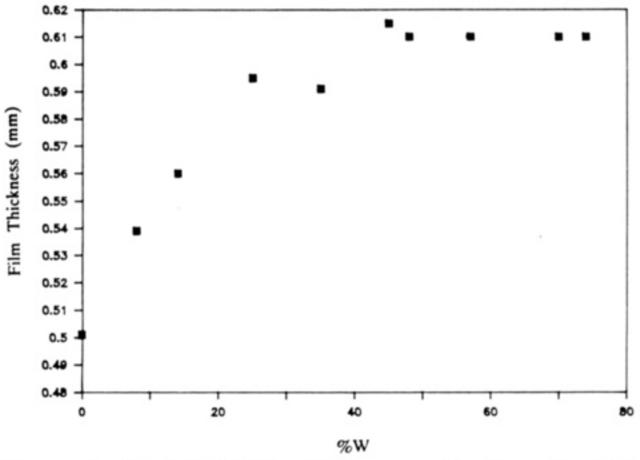

Figure 3. Final KR-E film thickness as function of weight increase.

Table I
Permeability Coefficients (*P*) in Unmodified Films[a]

	He	Ar	CO_2	CH_4
PB	47	55	435	83
PS	20	1.6	13	0.8
KR-E	21	4.2	34	6.1

[a] *P* in barrer = 10^{-10} cm^3 (STP)-cm/cm^2-s-cmHg.

Several visual observations of the originally transparent KR-E films indicated that both physical and chemical changes had occurred in the reacted material. Up to 8% *W*, the block copolymer films remained transparent, but took on an orange color similar to that observed in the reacted PB films. After 8% *W*, increasing cloudiness was observed to 35% *W*, beyond which the samples were completely opaque and gray. This opacity is a possible indication of the presence of crazes or other heterogeneities in the sample that are somewhat larger than the original 75-Å microdomain size (which does not cause appreciable scattering of visible light).

A cross-sectional view of a sample that had become visibly opaque revealed that the gray color was present only near the film surface, while the interior regions retained the orange color that was observed in the earlier stages of the reaction. This formation of a "skin layer", with a core also visibly changed from the starting material, indicates the possibility of two distinct events during the reaction process—one that results in the orange coloration and a second that causes the material near the surface to become opaque. A more detailed examination of sample cross sections using scanning electron microscopy (SEM) is presented in the following section.

Results and Discussion

Gas permeability coefficients in the homopolymers and KR-E reacted to various extents were measured at 25 °C for several gases by use of a variable-volume permeability apparatus.[15] In light of the apparent layered or composite nature of reacted block copolymer films, it should be noted that a single effective permeability coefficient, based on the actual total sample thickness, is used to describe permeation in these materials. *P*s for unreacted PB, PS, and KR-E films appear in Table I; these coefficients for materials that have not been chemically modified will be referred to as P_0.

Relative permeabilities, defined as *P* divided by P_0, for the bromine-reacted block copolymer films as a function of reaction extent to 15% *W* appear in Figure 4. Relative permeabilities are seen to decrease with extent of reaction. Note that all gases are not affected to the same degree—permeation of the larger penetrants is retarded significantly, while the transport rate of the relatively small species He is virtually unchanged from that in the starting material. The addition of the bulky halogen and resulting decrease in chain mobility causes the reacted material to selectively inhibit gas transport on the basis of size.

The result of this enhanced screening ability after reaction is a change in the selectivity or separation factor (defined as the ratio of *P* for two gases) for any gas pair considered. The largest change in selectivity is for the

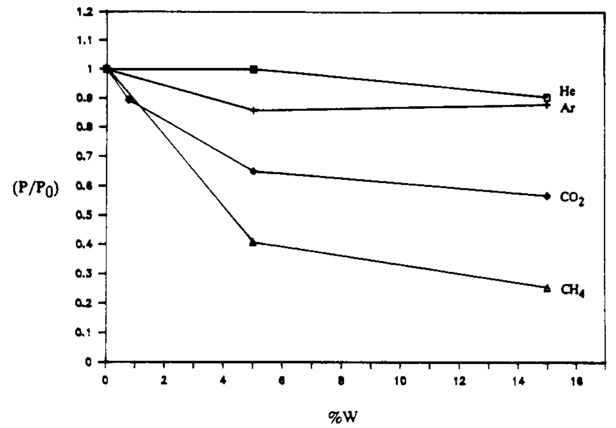

Figure 4. Relative permeabilities in brominated KR-E films reacted to 15% *W*.

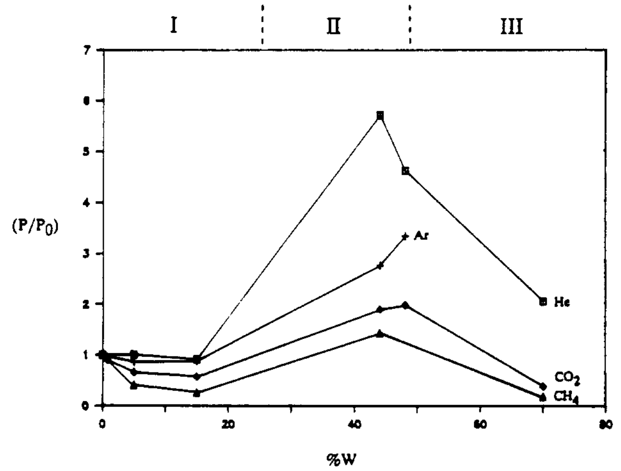

Figure 5. Relative permeabilities in brominated KR-E films reacted to 70% *W*.

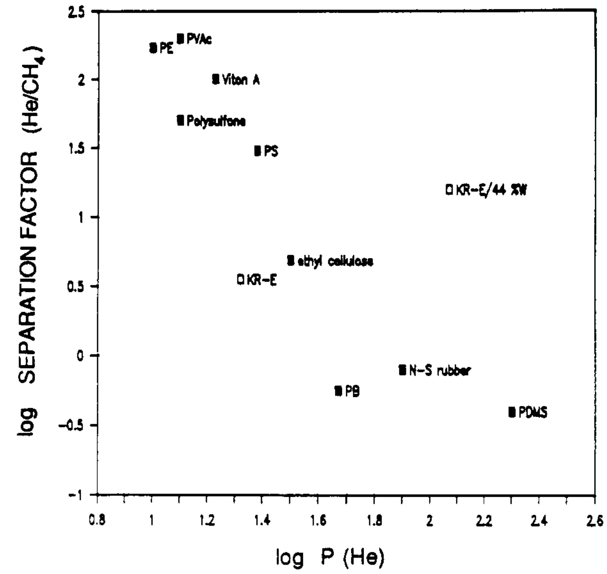

Figure 6. Separation factor vs permeability plot for helium/methane system.

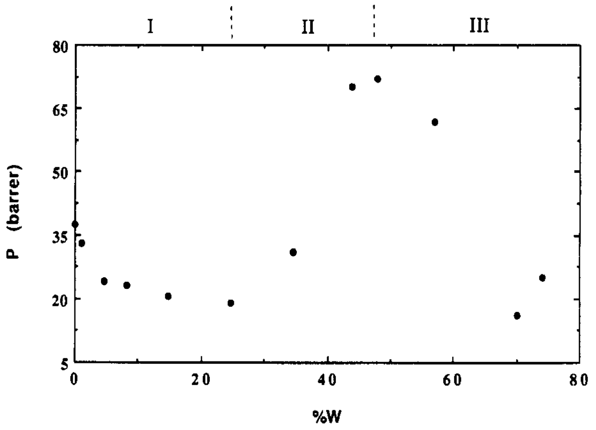

Figure 7. CO_2 permeability coefficient in brominated KR-E films as function of weight increase.

He/CH_4 pair, which is increased by a factor of 4. The fact that this is achieved with no appreciable decrease in He permeability is especially interesting from a membrane separation standpoint.

As opposed to a simple monotonic decrease in block copolymer permeability with extent of bromination, unexpected changes in permeation behavior were observed at reaction extents higher than 15% *W*. Effective permeability coefficients for all gases increased to a maximum near 45% *W*, followed by a subsequent decrease (Figure 5). P/P_0 values at some reaction extents exceed 1, indicating greater permeation rates than those in the original KR-E samples. Despite this increase, further significant changes in separation factors (beyond those achieved at 15% *W*) are not seen—the percentage change in permeation rates for each gas is similar throughout the reaction range beyond 15% *W*.

Returning to the He/CH_4 gas pair, the behavior of the brominated KR-E at 44% *W* (where it exhibits the highest effective permeability) represents an appealing property change from the starting film. It exhibits a increase in selectivity for the He/CH_4 separation by a factor of approximately 4, as well as a nearly 6-fold increase in He permeability. This combined improvement in selectivity and effective permeability is unusual and certainly desirable from a gas separation standpoint.

To gauge the significance of the property changes in the 44% *W* material, consider the separation factor vs permeability plot of Figure 6. In the figure, the He/CH_4 separation factor is plotted against the effective He permeability coefficient for a variety of polymers. Data to construct the filled squares of the plot were taken from several sources.[16-18] The nature of this plot is typical for many gas pairs. All of the polymers fall in a negatively sloping narrow band, demonstrating the commonly observed tradeoff between selectivity and permeability in polymeric materials. Because in membrane separations both high permeation rates and high selectivity are desired, a superior polymer for the separation would appear to the upper right of this band in the figure.

The open squares of the plot are experimentally determined points for the original KR-E material, and KR-E after bromination to 44% *W*. Note that the original PS/PB block copolymer lies within the zone established by the other polymers. After reaction to 44% *W*, the increases in *P* and in the ideal separation factor cause the KR-E point to be shifted well outside the range of typical behavior. Within the framework of the many polymers considered, the change in transport properties exhibited by the brominated K-Resin film does in fact represent a significant improvement and departure from the norm.

To more thoroughly characterize the permeability behavior of the block copolymer throughout the entire reaction range, effective permeability coefficients for CO_2 alone were obtained in additional samples. The resulting plot of P^{CO_2} vs % *W* appears in Figure 7. This unmistakably shows the decrease, increase, and subsequent decline of permeability throughout the reaction range and

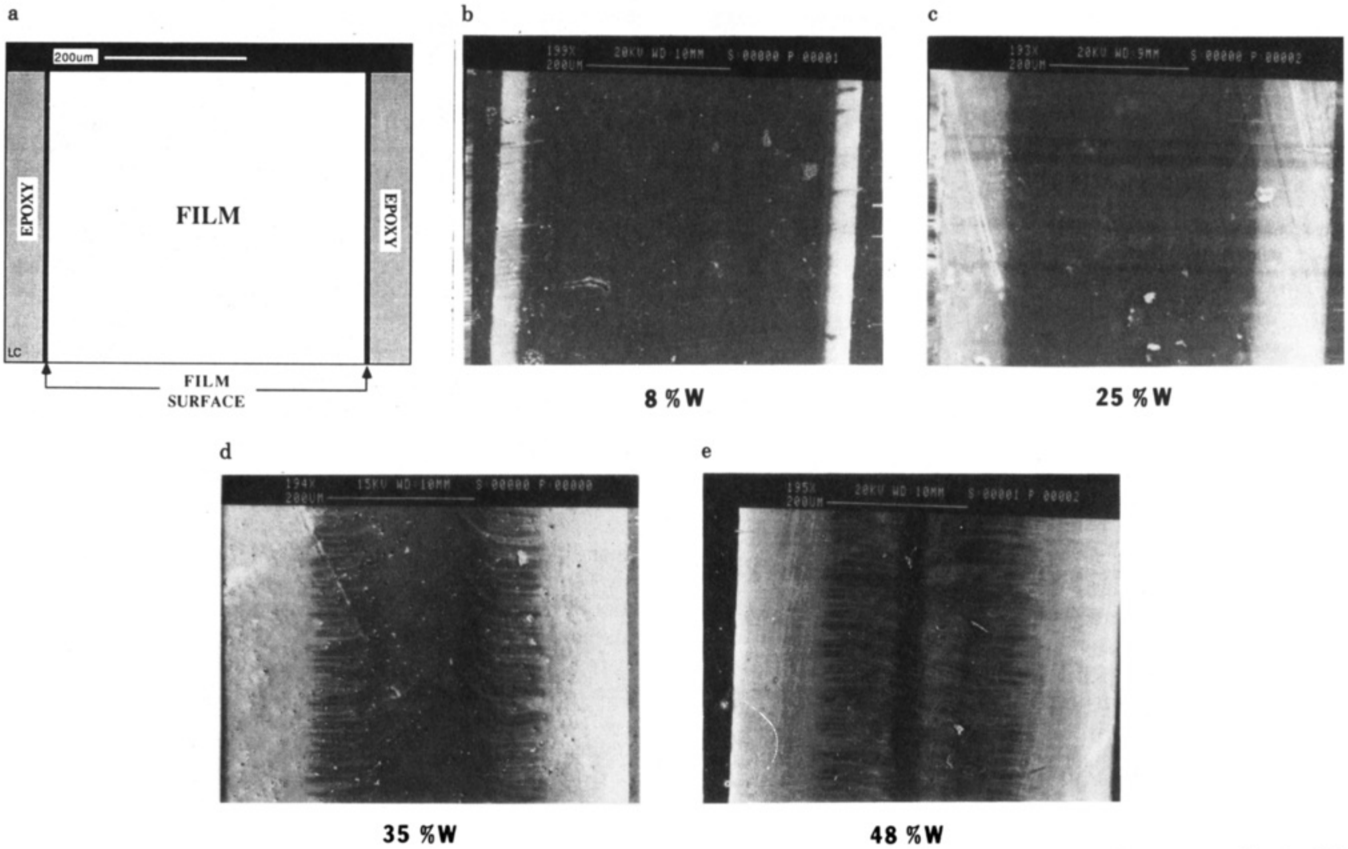

Figure 8. Scanning electron micrographs showing KR-E film cross sections at various reaction extents. (a) Schematic; (b) 8% *W*; (c) 25% *W*; (d) 35% *W*; (e) 48% *W*.

identifies a permeability minimum and maximum at 25 and 44% *W*, respectively.

Note that Figures 5 and 7 have been divided into regions I–III. While the permeability decrease and selectivity enhancement of region I can be attributed to a lowering of polymer segmental mobility caused by addition of large Br atoms, the behavior in regions II and III is more difficult to interpret. The increase in *P* of region II is indicative of an opening or expansion of the polymer structure, which is also suggested by the increase in sample thickness up to 44% *W* (Figure 3). This "opening" is then halted or reversed in region III. Note that the onset of region III corresponds to the reaction extent beyond which sample weight increases were detected without further increases in sample volume (as indicated by thickness measurements, Figure 3).

In order to gain insight into structural changes occurring in the reacted block copolymer, film cross sections were examined by SEM. Before being gold plated for SEM viewing, samples were embedded in epoxy, and a fresh surface was cut and polished by using a 0.05-μm polishing compound. The samples were cut in such a way so as to view the cross section of the sample film from the same direction as the view presented in the TEM of Figure 1.

Micrographs at various reaction extents appear in Figure 8. As reaction proceeds from 0 to 25% *W*, a discernable layer or front, indicated by a light coloration in the micrograph, is seen to grow from the film surfaces toward the center. At 35 and 48% *W*, the steady growth of this surface layer has been replaced by a more rapid development of the light-colored regions, which have extended toward the film center in thin, fingerlike regions. Recall that it is at these reaction extents where the sudden increase in permeation rates were observed (Figures 5 and 7). The fact that these growing regions appear light in color either indicates that they are porous in nature (increased electron emission would occur at the "edges" of small pores) or may be solely the result of significantly higher bromine concentrations in these areas—a fact that was determined by SEM X-ray analysis.[19]

Beyond 48% *W*, no further development of the light-colored regions was apparent. This extent of reaction corresponds to the point beyond which permeability coefficients ceased to increase, and no increases in sample thickness with further reaction time were observed. This leads to the conclusion that the material appearing white in the SEM may be a low-density material that is highly permeable to gases. The fact that an intact portion of the brominated samples near their center remains unaffected (dark in SEM) is consistent with the observation that the separating quality of these films is maintained, even though the outer portions of their cross sections may now allow rapid, nonselective gas transport.

Direct evidence that the growing surface layers observed in SEM are more permeable to gases than the film core, and in fact more permeable than the unreacted KR-E, is presented by a study of transient gas sorption.[20] Figure 9 contains a sorption curve (mass of gas uptake, M_t, divided by mass of uptake at equilibrium, M_∞, vs time $t^{1/2}$) for CO_2 into the KR-E sample brominated to 25% *W* (see SEM of Figure 8). Gas uptake into the evacuated sample was measured by monitoring pressure decay in a closed sample chamber during sorption. The initial applied CO_2 pressure was 1 atm. Details of the experimental setup are described elsewhere.[21]

For homogeneous polymer films that display a single gas diffusion coefficient, a sorption curve is typically linear to M_t/M_∞ values of 0.6 or higher, with the slope of this linear portion proportional to the square root of the diffusion coefficient.[20] The curve of Figure 9 deviates from

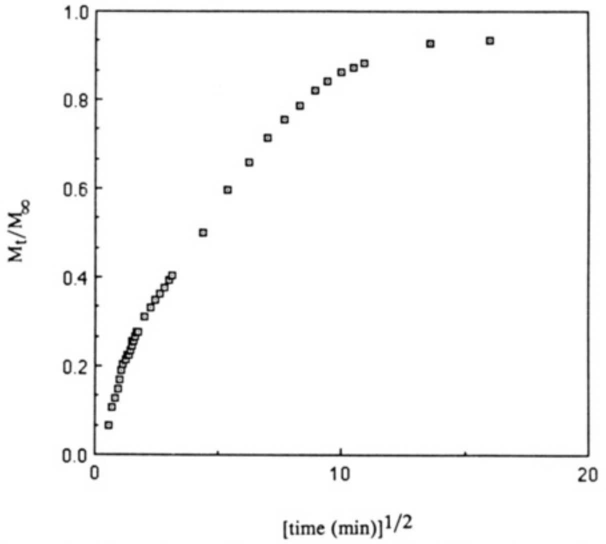

Figure 9. Experimental sorption curve for CO_2 at 1 atm into KR-E film brominated to 25% *W*.

its initially linear form at M_t/M_∞ of only 0.2, after which the rate of sorption is lower than would be expected for diffusion into a homogeneous film. This is evidence of a two-stage sorption process in which gas first diffuses quickly into the surface regions of the film and then more slowly as it sorbs into the film interior.

The CO_2 diffusion coefficient from the initial linear slope[20] of the sorption curve, which reflects uptake into the film's surface regions, was determined to be 5.0×10^{-7} cm^2/s. From transient experiments using unmodified KR-E films, which resulted in sorption curves of standard shape, *D* from the initial slope was 3.2×10^{-7} cm^2/s. The CO_2 solubility coefficient for the block copolymer films increased slightly from 1.54×10^{-2} to 1.86×10^{-2} cm^3(STP)/cm^3·cmHg after reaction to 25% *W*.

On the basis of this information from transient sorption, we conclude that the light-colored regions observed in the SEM consist of a low-density, high-permeability material, and that permeability variations in modified KR-E are primarily a reflection of changes in the diffusion coefficient.

Some information on the structure of the low-density regions is contained in transmission electron micrographs of thin sections from the 48% *W* sample (the sample that exhibited the highest CO_2 permeability). The sections were taken from the center portion of the film, where the thin, parallel extensions of light-colored regions were observed in SEM. The TEM of Figure 10 shows the presence of crazes in the sample. These crazes extend for very long distances (relative to their thickness) parallel to one another in a direction normal to the film surface. The distance between adjacent crazes is approximately 20 μm. This is similar to the measured distance between the light-colored parallel "fingers" in the corresponding SEM (Figure 8).

Permeability coefficients in reacted polystyrene and polybutadiene homopolymer films behaved differently, and more predictably, from those in the KR-E block copolymer. PS and PB films (of similar dimensions to the KR-E samples) were exposed to the bromine solution for up to 18.5 h. This final reaction time for the homopolymers corresponds roughly to the reaction time for which the block copolymer exhibited its maximum CO_2 permeability.

For PB, CO_2 permeability coefficients decreased steadily by over 3 orders of magnitude (from 435 to 0.2 barrer) through the highest reaction time of 18.5 h. What had initially been a highly permeable rubber had been transformed by the reaction into a material that is a reasonably good barrier to CO_2 transport. The helium permeability coefficient decreased only by 30% after the same extent of reaction. This disproportionate decrease in the permeability of the large CO_2 species is a result of the chain mobility reduction in the brominated rubber, which was documented by the calorimetry results described in the Experimental Section. Further studies of transport in halogenated polybutadiene are currently underway.

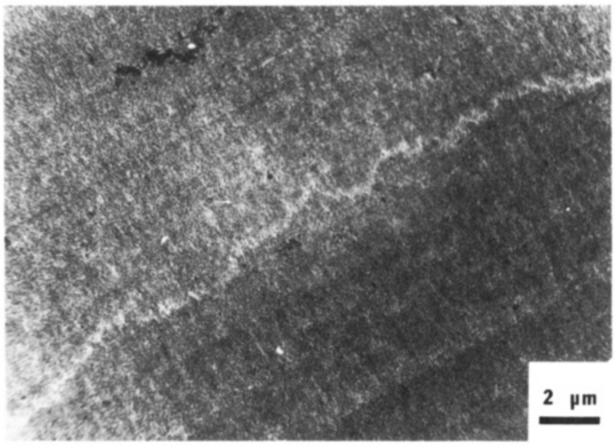

Figure 10. Cross-sectional transmission electron micrograph of KR-E brominated to 48% *W*.

The reacted PS also displayed a monotonic reduction in CO_2 permeability with reaction extent, although the decrease was modest in comparison to that of the PB—from 13 to 8.9 barrer after 18.5 h of reaction.

An important conclusion from the permeation studies of reacted homopolymers is that no increases in permeation rates with reaction were observed in either PB or PS homopolymers. This effect is unique to the microphase-separated block copolymer.

Conclusions

The sum of evidence presented above indicates that there are two distinct processes that occur during the reaction of KR-E block copolymer films with bromine, both of which affect their effective gas permeability. The first is a chemical change within the domains of the microstructure. This results in decreases in chain mobility and reduced permeability, which appears to be especially drastic in the PB. It is this mechanism which results in the increased ability to screen larger gas molecules and the enhancement of separation factors observed in the reacted block copolymer.

The second process is an opening of the block copolymer structure, at least in part through the formation of low-density craze matter. Microporous, high-permeability regions, with little if any ability to distinguish between different gas molecules, grow inward from the film surface as the reaction proceeds. Their formation is likely a result of the block copolymer's attempt to accommodate the incorporation of large Br atoms into the PS and PB microdomains.

The trends observed in the permeability plots, Figures 5 and 7, can be summarized as follows. In region I, the effects of the chemical change and the growth of a microporous surface layer compete with one another. The chemical change results in an enhancement in selectivity, but KR-E permeabilities do not fall as rapidly with % *W* as in the PB homopolymer because rapid transport is occurring near the film surface. In region II, the low-density material and resulting high-flux permeation pathways extend deep into the sample thickness. The effective thickness of the membrane is thereby greatly reduced, resulting in abrupt increases in P to above values exhibited by the unmodified material. In region III, the formation of low-density material has slowed or ceased altogether, and further chemical reaction again results in a lowering of P.

The KR-E sample reacted to 44% W displayed enhanced selectivity and permeability (Figure 6). This favorable and unusual behavior is the combined result of the concurrent processes described above. A large portion of the film structure for this sample was microporous—essentially a support material with little resistance to transport. The remaining chemically reacted dense regions, now effectively much thinner than the original sample thickness, were able to favorably separate gaseous penetrants on the basis of size. In this manner, the brominated block copolymer can be considered a new type of asymmetric gas separation membrane—the product of chemically induced changes in physical as well as chemical structure.

Acknowledgment. Financial support for this work was provided in part by the Lammot du Pont Professorship (R.F.B.), the Bayer Professorship (R.E.C.), and the Office of Naval Research.

References and Notes

(1) *Diffusion in Polymers*; Crank, J., Park, G. S. Eds.; Academic: New York, 1968.
(2) Chern, R. T.; Sheu, F. R.; Jia, L.; Stannett, V. T.; Hopfenberg, H. B. *J. Membr. Sci.* **1987**, *35*, 103.
(3) Stern, S. A.; Shah, V. M.; Hardy, B. J. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1263.
(4) Koros, W. J.; Story, B. J.; Jordan, S. M.; O'Brien, K.; Husk, G. R. *Polym. Eng. Sci.* **1987**, *27*, 603.
(5) Haggin, J. *Chem. Eng. News* **1988**, *66*(23), 7.
(6) Stookey, D. J.; Patton, C. J.; Malcolm, G. L. *Chem. Eng. Prog.* **1986**, November, 36.
(7) Ashley, R. J. In *Polymer Permeability*; Comyn, J., Ed.; Elsevier: London, 1985.
(8) Csernica, J.; Baddour, R. F.; Cohen, R. E. *Macromolecules* **1987**, *20*, 2468.
(9) Csernica, J.; Baddour, R. F.; Cohen, R. E. *Macromolecules* **1989**, *22*, 1493.
(10) Csernica, J.; Baddour, R. F.; Cohen, R. E. *Macromolecules* **1990**, *23*, 1429.
(11) *The Radiation Chemistry of Macromolecules*; Dole, M., Ed.; Academic: New York, 1972.
(12) Bradford, E. B.; Vanderhoff, J. W. *J. Colloid Sci.* **1959**, *14*, 543.
(13) Canterino, P. J. In *Chemical Reactions of Polymers*; Fettes, E. M., Ed.; Interscience: New York, 1964.
(14) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*; Allyn and Bacon: Boston, MA, 1983.
(15) ASTM D-1434, American Society for Testing and Materials, Philadelphia, PA, 1984.
(16) Stern, S. A.; Sinclair, T. F.; Gareis, P. J.; Vahldieck, N. P.; Mohr, P. H. *Ind. Eng. Chem.* **1965**, *57*(2), 49.
(17) Vatcha, S. R. M.S. Thesis, Massachusetts Institute of Technology, 1985.
(18) *The Science and Technology of Polymer Films*; Sweeting, O. J., Ed.; Interscience: New York, 1971.
(19) Thomas, E. L. In *Encyclopedia of Polymer Science and Technology*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley and Sons: New York, 1985; Vol. 4.
(20) Crank, J. *The Mathematics of Diffusion*; Oxford University: New York, 1975.
(21) Rein, D. H.; Csernica, J.; Baddour, R. F.; Cohen, R. E. *Macromolecules* **1990**, *23*, 4456.

Registry No. (PS)(PB) (block copolymer), 106107-54-4; He, 7440-59-7; Ar, 7440-37-1; CO_2, 124-38-9; CH_4, 74-82-8.