

on substances which are present at levels of only about 100 ppm relative to BPA.

A shortcoming of this GC/GC/MS technique involves the potential loss of trace impurities which exactly coelute with BPA and therefore are discarded before the second stage of analysis. This problem can in principle be partly overcome by performing multiple experiments using different liquid phases for the primary separation because, in theory, the same two materials are unlikely to coelute on two different liquid phases. This approach is, of course, not entirely effective. However, it should be noted that the same difficulty is inherent in all of the potentially competing approaches to this analysis such as LC/GC/MS.

## Conclusions

Use of GC/GC/high-resolution mass spectrometry to analyze the  $\text{LiAlH}_4$  and  $\text{LiAlD}_4$  reductive cleavage products from a 4-year Florida-aged sample of non-UV-stabilized bisphenol A polycarbonate has confirmed the presence of small amounts of photo-Fries and ring oxidation products along with large amounts of side-chain oxidation products. These results are consistent with a photoaging mechanism in which side-chain and ring photooxidation are initiated by a photo-Fries process and colored photoproducts are primarily derived from ring oxidation.

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**Registry No.** BPA PC (SRU), 24936-68-3; BPA PC (homopolymer), 25037-45-0.

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## Gas Permeability of a Polystyrene-Polybutadiene Block Copolymer with Oriented Lamellar Domains

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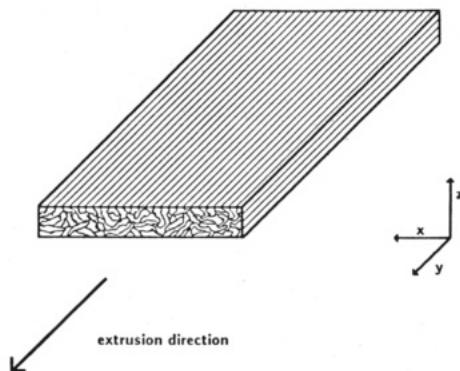
**ABSTRACT:** Permeability coefficients were measured for several gases in a polystyrene-polybutadiene block copolymer possessing a highly oriented lamellar microstructure. The effective permeability of this material was strongly dependent on the direction of domain orientation in the sample film. Permeation in samples whose lamellae were aligned parallel to the permeation direction was described in terms of a three-phase model which incorporates the permeability of the block copolymer interfacial regions.

The control of gas permeation through polymeric materials is a primary concern in the development of technology for gas separations, packagings, and coatings. New possibilities for permeability regulation are presented by block copolymers,<sup>1</sup> which can combine two (or more) polymer components with different transport properties into a microphase-separated system with advantageous morphological characteristics. Morphological features of block copolymers which may affect gas transport include the small size (ca. 10 nm) and narrow size distribution of domains, the extent and direction of orientation of the domains, a high internal surface/volume ratio, and diffuse interfacial regions which can constitute a significant volume fraction of the material. Fundamental relationships between block copolymer morphology and gas permeation are needed to indicate how changes in the size, shape, and orientation of a block copolymer's microdomains can be

utilized to alter and control its gas permeability and permselectivity.

Few studies of gas transport in block copolymers have been published, and direct measurement of permeability coefficients in these materials has been reported<sup>2,3</sup> only rarely. In addition, virtually all experimental investigations relating gas transport to block copolymer morphology have been conducted by using block copolymers whose domains were randomly oriented<sup>4</sup> or whose orientation was not known or specified.

In this study we examine the permeation of various gases through a polystyrene-polybutadiene block copolymer possessing a well-defined, highly oriented lamellar microstructure. The anisotropic nature of this material allows investigation into the dependence of permeability on the direction of domain orientation. In addition, the relatively simple, well-ordered morphology facilitates the study of



**Figure 1.** Schematic representation indicating morphology of K-Resin sheet.

transport behavior associated with the microstructure itself, since larger scale effects of unknown phase shapes and orientations are virtually eliminated.

### Experimental Section

The polymer used in this study was an experimental grade of polystyrene-polybutadiene block copolymer supplied by Phillips' Petroleum Co. (part of their K-Resin series). Routine NMR spectroscopy, UV absorption, and gel permeation chromatography methods were used for molecular characterization of this material. These measurements revealed that the block copolymer contained 75% (v/v) polystyrene and had a weight-average molecular weight of 187 000 g/mol with  $\bar{M}_w/\bar{M}_n = 1.5$ . The polybutadiene portions of the polymer chains consisted of about 90% 1,4 segments. Also utilized were polystyrene and polybutadiene homopolymers which were obtained from Polysciences, Inc., and Scientific Polymer Products, Inc., respectively. Each of these homopolymers had a nominal molecular weight of 200 000.

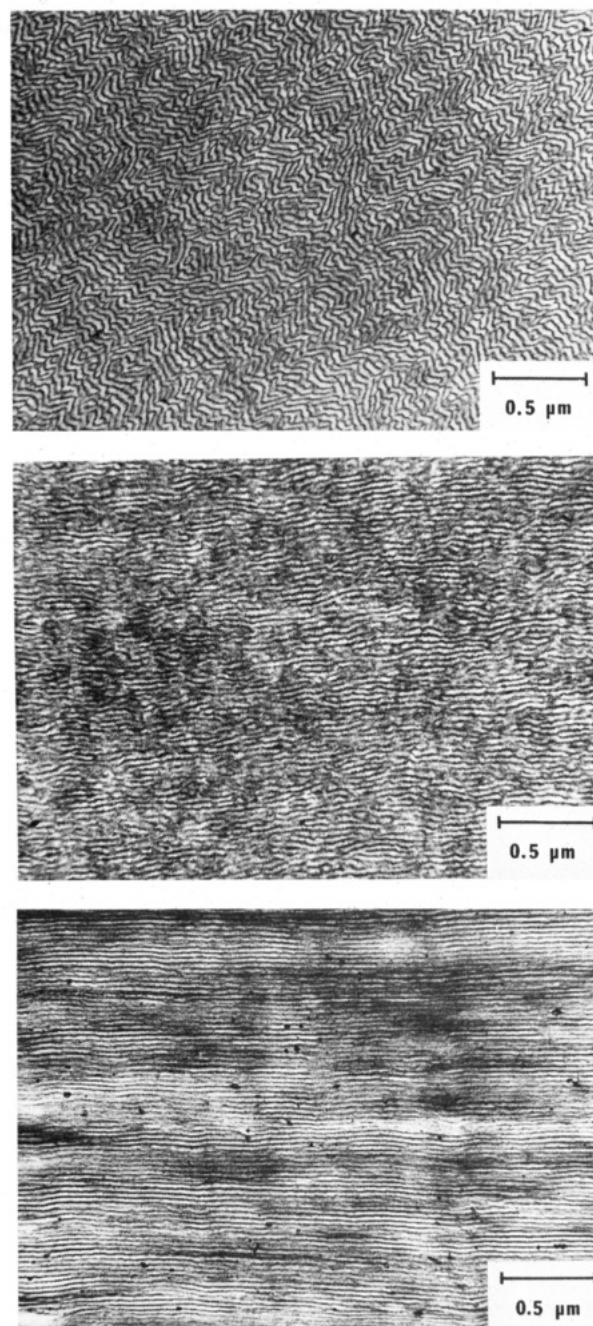
The block copolymer was provided in the form of a 0.5-mm extruded sheet. The morphology of this mechanically processed material made it especially suitable for this investigation. Transmission electron microscopy of osmium-stained sections indicated a microstructure consisting of polybutadiene lamellae which possess excellent long-range orientation in the extrusion direction. Figure 1 is a schematic diagram of the sheet's internal microstructure, with the dark regions representing polybutadiene lamellae. As indicated, very good orientation is observed when viewing the material in the *x*- or *z*-direction, while no distinguishable long-range order is seen from the *y*-direction. Figure 2 contains representative transmission electron micrographs of  $\text{OsO}_4$ -stained thin sections displaying these directional views.

In order to take advantage of the orientation in the extruded sheet, it was necessary to prepare a film in which the oriented polybutadiene lamellae were aligned normal to the film surface (i.e., parallel to the direction of permeation). To accomplish this, a number of pieces of the extruded sheet were stacked and heated to 15 °C above the  $T_g$  of polystyrene while under a small ( $\approx 1$  psi) compressive load. This produced a solid block of material from which new films (0.4–0.7 mm thick) were cut such that their faces were perpendicular to the *y*- (extrusion) direction. Transmission electron microscopy has shown that the desired microphase ordering was achieved during this annealing/cutting process. For the remainder of this paper, the as-received sheet will be designated as "film A", while samples with their microphases aligned normal to the film surface will be referred to as "film B".

The gases used in this study differed in size and shape: Ne, Ar, Kr,  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ . The purities of all gases were in excess of 99.995%, with the exception of  $\text{CH}_4$ , whose purity was listed at 99.0%. Gas permeability coefficients ( $P$ ) were determined from steady-state measurements by using a variable-volume permeation apparatus.<sup>5</sup> Pressure differences across the sample films ranged from 1 to 4 atm in these tests. (Permeability coefficients for the copolymer films showed no detectable pressure dependence in this range.)

### Results and Discussion

Values of  $P$  for copolymer films A and B, as well as for polystyrene and polybutadiene homopolymer films, appear



**Figure 2.** Transmission electron micrographs displaying views from the (top) *y*-direction, (middle) *x*-direction, and (bottom) *z*-direction.

**Table I**  
Experimental Results<sup>a</sup>

	Ne	Ar	Kr	$\text{N}_2$	$\text{CO}_2$	$\text{CH}_4$
$P_{\text{PS}}$	5.3	2.0	0.7	0.6	13	0.8
$P_{\text{PB}}$	23	55	117	21	435	83
$P_{\text{film A}}$	6.9	4.2	6.5	1.8	34	6.1
$P_{\text{film B}}$	8.7	11	19	4.3	90	14

<sup>a</sup>  $P$  in  $10^{-10}$  cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cmHg.

in Table I. Note that the rubber component always is the more conductive phase in the block copolymer—the ratio of polybutadiene permeability to polystyrene permeability ranges from about 4 to well over 150 for the gases studied.

The effect of microphase orientation on gas permeability is significant. Permeability coefficients for film B, whose microdomains are oriented normal to the film surface, were found to be higher than those measured for film A for all

**Table II**  
**Model Results and Comparison with Experiment**

	Ne <sup>a</sup>	Ar	Kr	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>
$P_2^*$	9.0	15	28	5.3	112	20
predicted $l_i$ , Å	18	27	26	23	23	26
$P_3^*$ ( $l_i = 25$ Å)	8.5	11.5	20	4.1	86	14
$P_{\text{film B}}$ (exptl)	8.7	11	19	4.3	90	14

<sup>a</sup> For the case of neon, predicted permeabilities are comparatively insensitive to model type (two- vs. three-phase) and to selection of  $l_i$  in the three-phase analysis. This results from the relatively small difference in homopolymer permeabilities for this gas (Table I).

gases studied, with the largest difference of nearly 3 times observed for krypton as the penetrant gas. This directional dependence demonstrates that morphological manipulation of block copolymers can be a useful technique for permeation control.

Obviously the ability to predict effective permeability coefficients for such oriented block copolymers would be of considerable interest. As a first attempt, the permeabilities for film B were compared with predictions made by using a parallel flux model for a two-component system:<sup>6</sup>

$$P_2 = P_B v_B + P_S v_S \quad (1)$$

where  $P_2$  = permeability coefficient of a two-phase composite;  $P_B$ ,  $P_S$  = permeability coefficients of polybutadiene, polystyrene; and  $v_B$ ,  $v_S$  = volume fraction of polybutadiene, polystyrene. Odani et al.<sup>3</sup> have previously used series and parallel models to describe permeation in block copolymers, but the models were used to relate experimental permeability with domain type, not with actual domain orientation in their samples.

The two-phase permeabilities from eq 1 were modified by a tortuosity factor  $\tau$

$$P_2^* = P_2 / \tau \quad (2)$$

which takes into account the fact that the polybutadiene domains (through which most of the permeation takes place) do not run perfectly straight through the polymer, but possess some wavy or crooked character. A tortuosity factor of 1.07 for film B was estimated by measuring contour lengths of polybutadiene domains in micrographs.

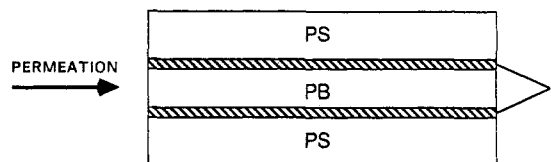
Comparison of  $P_2^*$  with measured  $P$  values for film B (Table II) reveals that the parallel model overpredicts experimental values in all cases. The magnitude of the overprediction (as high as 50%) depends on the penetrant gas used in the test. This suggests the presence of at least one other factor that affects the permeability of film B which, unlike a tortuosity, cannot be represented by a single proportionality constant for all gases.

At this point we turned our attention to the interfacial region of the copolymer<sup>7</sup>—the mixed zones that exist between the distinct pure microphases of polybutadiene and polystyrene. A model was adopted which treats the interfacial regions as a distinct third phase in the copolymer (Figure 3). Equation 1 was modified to account for this third phase:

$$P_3 = P_B \phi_B + P_S \phi_S + \bar{P}_I \phi_I \quad (3)$$

where  $P_3$  = permeability of a three-phase composite;  $\bar{P}_I$  = average permeability of the interfacial region; and  $\phi_B$ ,  $\phi_S$ ,  $\phi_I$  = volume fraction of the pure polybutadiene phase, the pure polystyrene phase, and the interface.

To obtain the average permeability of the interfacial region,  $\bar{P}_I$ , we treat this zone as a random copolymer of



**Figure 3.** Three-phase parallel model indicating the polybutadiene phase (PB), the polystyrene phase (PS), and the interface (I).

styrene and butadiene whose composition varies spatially in the interfacial zone. It is assumed that a linear concentration profile of polymer repeat units exists across the interface. The local permeability at any composition within the interface ( $P_I$ ) is estimated by using an empirical relation<sup>2</sup> which has been found to describe gas permeabilities for random copolymers (including those of polystyrene and polybutadiene):

$$\ln P_I = mx + b \quad (4)$$

where  $x$  = local volume fraction of butadiene. The parameters in eq 4 are determined from pure component permeability coefficients.  $\bar{P}_I$  is obtained by the integration of eq 4 across the interface.

Together with experimental data, the three-phase model can be used to predict the thickness of the block copolymer interface. For each gas tested, eq 3 was used to calculate the volume fractions,  $\phi_B$ ,  $\phi_S$ , and  $\phi_I$ , such that  $P_3^*$  (with the tortuosity correction of eq 2) equals the measured film B permeability. (An additional condition required for solution of eq 3 is that the interface is composed of equal volumes of polybutadiene and polystyrene.) These volume fractions in turn were used to calculate a corresponding value of interfacial thickness,  $l_i$ , by observing domain sizes in micrographs. Here it was assumed that the dark (osmium-stained) regions in micrographs ( $\approx 75$  Å) are composed of both homopolybutadiene and the interfacial material.

Interfacial thicknesses calculated in this manner for each gas tested appear in Table II. All values are in excellent agreement with previously reported<sup>8</sup> thicknesses of about 22 Å based on small-angle neutron scattering experiments on polystyrene-polybutadiene block copolymers. In addition, these predicted thicknesses appear to be independent of properties of the test gas such as molecular diameter or permeability in the homopolymers.

With a given value of interfacial thickness, the three-phase model can alternatively be used to predict effective permeabilities for the block copolymer. The use of a single interfacial thickness of 25 Å in the three-phase analysis for all gases tested yields predicted permeability values ( $P_3^*$ ) which are within 5% of measured values for film B (see Table II). This agreement is within the estimated 8–10% error associated with the experiment, and is superior to that obtained by using the simple two-phase model ( $P_2^*$ ).

The ability to attribute a permeability effect to the interface results from specific features of the block copolymer tested: its domains possessed very good parallel orientation, and the polybutadiene lamellar thickness was so small that, based on an interfacial thickness of 25 Å, the interfacial volume fraction (0.24) exceeded the volume fraction of the pure polybutadiene (the highly conductive component).

Kinning et al.<sup>4</sup> recently were unable to detect an effect of the interface on gas diffusion coefficients in polystyrene-polybutadiene block copolymers using sorption experiments and several randomly oriented lamellar copolymers of differing interfacial volume fractions. A

possible explanation is that interfacial volume fractions in their samples (again, based on a 25-Å interfacial thickness) were all lower than 20% of the pure polybutadiene fractions—perhaps too low to cause a significant effect.

In conclusion, the three-phase model, which incorporates the contribution of the interface, provides an improved ability to predict gas permeability coefficients in multiphase block copolymers. In addition, similar analyses of permeation in other well-aligned but less understood block copolymer systems may be a useful technique for estimating interfacial thicknesses.

**Registry No.** (S)(B) (block copolymer), 106107-54-4; Ne, 7440-01-9; Ar, 7440-37-1; Kr, 7439-90-9; N<sub>2</sub>, 7727-37-9; CO<sub>2</sub>, 124-38-9; CH<sub>4</sub>, 74-82-8.

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## “Thermodynamic Slowing Down” of Mutual Diffusion in Isotopic Polymer Mixtures

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**ABSTRACT:** The mutual diffusion coefficient,  $D(\Phi)$ , determined at finite blend compositions,  $\Phi$ , in blends of normal (hydrogenated) and deuterated polystyrene was found to be highly dependent on composition.  $D(\Phi)$  experiences a minimum, or “thermodynamic slowing down”, in the vicinity of the critical composition,  $\Phi_c$ . This effect increases with decreasing temperature. This result is consistent with recent small-angle neutron-scattering measurements which indicate that this system exhibits an upper critical solution temperature. The temperature dependence of the Flory interaction parameter,  $\chi$ , was extracted from the data by using a mean field prediction for the compositional dependence of  $D$ . We found that  $\chi = 0.22(\pm 0.06)/T - 3.2(\pm 1.2) \times 10^{-4}$ .

## Introduction

Evidence of nonideal mixing has been found in a number of isotopic polymer mixtures of identical structure. The small-angle neutron-scattering (SANS) measurements of Bates and Wignall<sup>1-4</sup> indicate that isotopic polymer mixtures of, 1,2-polybutadiene, 1,4-polybutadiene, polystyrene, and 1,2-polybutene are each characterized by a positive  $\chi$  and that each exhibits an upper critical solution temperature (UCST). SANS measurements of the apparent radius of gyration of a blend of normal and deuterated poly(dimethylsiloxane) by Lapp et al.<sup>5</sup> indicate that the  $\chi$  parameter is positive. However, independent SANS measurements by Yang<sup>6</sup> and collaborators on the polystyrene system have yielded contradictory results. They found that  $\chi \approx 0$  and question the existence of the UCST.

One may consider what effect a positive  $\chi$  would have on interdiffusion in binary mixtures of normal and deuterated polymers of identical structure otherwise. If  $0 < \chi < \chi_s(\Phi)$ , where  $\chi_s(\Phi) = \{[N_D\Phi]^{-1} + N_H(1 - \Phi)]^{-1}\}/2$  is the value of  $\chi$  on the spinodal,<sup>7</sup> then the mutual diffusion coefficient,  $D(\Phi)$ , should experience a minimum or a “critical slowing down” in the vicinity of the critical blend composition,  $\Phi_c$ , where

$$\Phi_c = N_H^{1/2} / [N_H^{1/2} + N_D^{1/2}] \quad (1)$$

In this equation,  $N_H$  and  $N_D$  are the degrees of polymerization of the normal and deuterated polymers, respectively. As  $\chi$  approaches  $\chi_s(\Phi)$ , or equivalently as the temperature approaches the UCST, the system experiences large fluctuations in composition. Consequently, the effect of the “thermodynamic slowing down” of mutual diffusion

should be more pronounced as the experimental temperature is lowered. In systems where  $\chi \approx 0$  or at temperatures sufficiently far from the critical point, these effects should not be observed.

Previously we published a short communication where experimental evidence of critical slowing down in binary mixtures of normal and deuterated polystyrene was presented.<sup>8</sup> The present report is concerned with the effects of temperature on thermodynamic slowing down of mutual diffusion in these systems. These measurements were performed by using elastic recoil detection (ERD). We were able to extract the segment-segment interaction parameter from measurements of  $D(\Phi)$  at different temperatures. The dependence of  $\chi$  on  $T$  is compared with that which Bates and Wignall obtained in the polystyrene system using SANS. The agreement is excellent.

## Experimental Section

The polymers used in this study were deuterated polystyrene (d-ps) of degree of polymerization  $9.8 \times 10^3$  with a polydispersity index of 1.15 and normal (hydrogenated) polystyrene (h-ps) of degree of polymerization  $8.7 \times 10^3$  with a polydispersity index of about 1.1. The d-ps and h-ps standards were purchased from the Custom Chemical and the Pressure Chemical companies, respectively.

Both mutual diffusion,  $D$ , and tracer diffusion,  $D^*$ , coefficients were determined by using ERD. In this technique, a beam of helium ions of energy 3.0 MeV is directed toward the sample at an angle 15° with respect to the sample surface. The helium ions undergo a number of collisions with target nuclei, resulting in the ejection of some of these nuclei. Of interest are the protons (H) and deuterons (D). The H and D nuclei which recoil from the surface are detected with different energies by virtue of their