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Morphological Arrangements of Block Copolymers That Result in Low Gas Permeability

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ABSTRACT: Gas permeability coefficients for several gases (Ar, N_2, CO_2, CH_4) were measured at 25 °C in two polystyrene/polybutadiene block copolymer systems. One possesses a morphology of alternating lamellae that are highly oriented and perpendicular to the permeation direction; the second contains spheres of polybutadiene in a polystyrene matrix. The measured permeabilities of these two materials are dominated by the behavior of the low permeability polystyrene component. Models are presented to describe transport in these microphase-separated systems and to facilitate comparisons with the transport behavior of other two-component polymer systems.

Introduction

The use of polymers in applications that require control of gas transport is increasing rapidly.[1,2] Prominent examples include polymer membranes for gas separations, where low-energy requirements make such processes extremely attractive to industry, and plastic containers and packages, which are currently being used to hold items from foodstuffs to industrial solvents. For many applications, it may be desirable to utilize heterogeneous polymer blends or block copolymers in which one component provides desired permeability characteristics, while the other improves material properties such as modulus or impact strength. If the final application requires that a low-permeability component provide a barrier quality or an enhanced selectivity, it will be desirable (and probably necessary) to have the individual components of the heterogeneous material arranged in series with respect to the permeation direction. In this manner, the diffusing species will not be able to circumvent the low permeability phase via high-conductivity pathways.

In previous investigations from this laboratory[3,4] on the gas permeability of a polystyrene/polybutadiene block copolymer with a lamellar morphology, alternating lamellae of polystyrene and polybutadiene were either misordered[3] or aligned in parallel with the permeation direction.[4] Here we report the behavior of two polystyrene/polybutadiene block copolymer samples whose morphological arrangements allow the low-permeability polystyrene to exert a greater influence on the overall transport properties, causing them to be considerably less permeable than these earlier cases. One is a lamellar system in which the platelike microdomains are oriented in the same plane as the film surface, in series with respect to permeation. The second system exhibits a morphology of discrete polybutadiene spheres contained in a polystyrene matrix.

Experimental Section

The lamellar block copolymer used in this investigation was the same K-Resin polymer used previously.[4] This material contains 75% by volume polystyrene; detailed characterizations have been described earlier.[4] In order to obtain sample films in which lamellae exist parallel to the film surface, the material was exposed to a melt flow technique similar to those employed by earlier investigators[5,6] to yield highly ordered block copolymer morphologies. Well-controlled solvent-casting techniques have also been described, which result in thin block copolymer films that possess alignment parallel to the film surface,[7,8] but these were not employed here.

The production of ordered lamellar films consisted of a two-stage process. First, films of 1.6-mm thickness were made by compression molding in a hot press at 160 °C. Morphological characterization of the resulting 5 × 5 cm square films using small-angle X-ray scattering (SAXS) indicated that there was some lamellar orientation near the film perimeter. However, considerably poorer alignment existed near the center of these samples, where presumably less flow occurred during the first-stage molding procedure. The second step consisted of squeezing the molded film between two parallel Teflon-coated steel plates (of the same surface dimensions as the molded film), again at 160 °C, to a final thickness of 0.25 mm (compression ratio ≈ 6). The gap between the plates was closed at a rate of approximately 0.3 mm/s. As opposed to being confined by a mold, during this compression step excess material was permitted to flow out from between the plates. Two-dimensional SAXS patterns from these squeezed samples with the beam parallel to the film surface (Figure 1a) show first- and second-order maxima, which indicate excellent long-range microphase orientation parallel to the film surface in regions both near the film perimeter as well as near its center. The virtual absence of scattering when the incident beam is perpendicular to the film surface (Figure 1b) lends strong support to the view that the platelike lamellar domains are indeed aligned with the plane of the film. Transmission electron microscopy (TEM) of osmium-stained thin sections from these films also indicates long-range lamellar orientation parallel to the film surface (Figure 2). It is concluded that a permeating species will encounter polybutadiene and polystyrene lamellae in series in these films, and

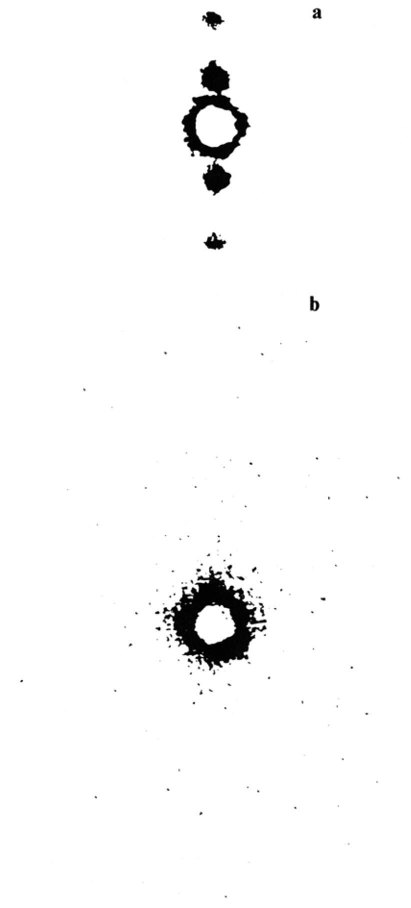

Figure 1. SAXS patterns for KR-S samples with incident beam (a) parallel and (b) perpendicular to the film surface. First- and second-order maxima occur at $Q = 0.015$ and 0.032 Å^{-1}, respectively.

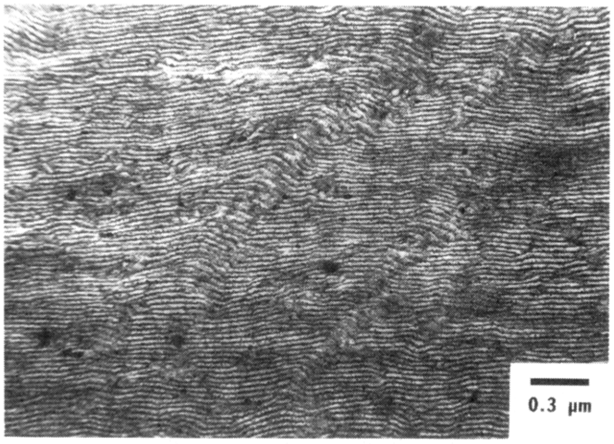

Figure 2. Transmission electron micrograph displaying cross-sectional view of KR-S film morphology.

such samples are designated KR-S (for K-Resin series).

The second polymer used in this study is designated SB10 and was synthesized in this laboratory[9] via anionic polymerization methods. It is a diblock copolymer with a polystyrene content of 74 vol %, a number-average molecular weight of 860 000, and a polydispersity of 1.2. The polybutadiene microstructure is 90% 1,4, with approximately equal amounts of cis and trans adduct. Sample films (0.4–0.5 mm thick) for permeation tests were cast from a 5% (w/w) solution in toluene by solvent evaporation on a stationary, flat, Teflon surface. TEM (Figure 3) indicates a morphology consisting of uniformly sized polybutadiene spheres contained in a polystyrene continuum. The average sphere diameter taken from micrographs is about 1000 Å.

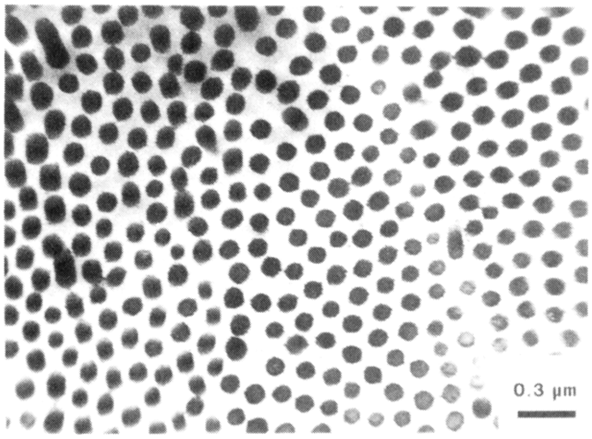

Figure 3. Transmission electron micrograph displaying SB10 film morphology.

Table I
Experimental and Model Permeability Coefficients[a]

	Ar	N_2	CO_2	CH_4
	Homopolymers			
PB	55	21	435	83
PS	1.6	0.6	13	0.8
	Lamellar System			
KR-P	11	4.3	90	14
KR-ST	5.4	2.1	44	5.9
KR-S	2.8	1.0	20	2.0
P_{ser}	2.1	0.8	18	1.1
P_{ser3}	2.3	0.9	20	1.2
	Spherical System			
SB10	2.8	1.0	18	1.6
unit cube	2.7	1.0	21	1.4
P_{ser}	2.1	0.8	18	1.1

[a] Units: (10^{-10} cm^3 (STP) cm)/(cm^2 s cmHg).

Gas permeability coefficients (P) for various gases in these films were measured at 25 °C by using a variable-volume permeability apparatus.[10] Values presented here are averages of at least two separate runs. Differences in permeability between samples of the same material were all within the precision of the experimental technique (8–10%).

Results and Discussion

Permeability coefficients for KR-S appear in Table I along with values for polystyrene and polybutadiene homopolymers, which were also determined in this laboratory.[4] Also appearing are coefficients for the previously studied K-Resin samples with different morphological orientations: KR-P refers to the samples with alignment parallel to the permeation direction and KR-ST to the samples with a misordered, isotropic, lamellar microstructure. As expected, the KR-S series samples are considerably less permeable than the samples with the different microphase orientations. Note the wide range of permeabilities that can be displayed by the same block copolymer as a result of these morphological changes. This demonstrates the important role of microphase arrangement in these materials.

On the basis of the characterization results from TEM and SAXS, it is anticipated that the permeability of the KR-S samples will be described by a series model:

$$1/P_{ser} = v_S/P_S + v_B/P_B \qquad (1)$$

where v_S and v_B are volume fractions of polystyrene and polybutadiene, and P_S and P_B are permeabilities for polystyrene and polybutadiene. We further anticipate that it may be necessary to take into account the contribution of block copolymer interfacial regions to gas permeability, as was demonstrated in earlier studies.[3,4] This would lead to a three-component series model:

$$1/P_{\mathrm{ser3}} = \Phi_{\mathrm{S}}/P_{\mathrm{S}} + \Phi_{\mathrm{B}}/P_{\mathrm{B}} + \Phi_{\mathrm{I}}/\bar{P}_{\mathrm{I}} \quad (2)$$

where the subscript I refers to the interfacial region, Φ's are volume fractions, and $\bar{P}_{\mathrm{I}}$ is the average permeability of the interphase. Values for these parameters have been determined for this block copolymer in an earlier investigation,[4] where it was concluded that the interfacial volume fraction is comparable to those of the pure components, in part as a result of the copolymer's small (≈75 Å) domain size.

Permeability coefficients from the series models P_{ser} and P_{ser3} appear below experimental values in Table I. We see that the behavior of the KR-S samples does indeed approach the predictions from the series models, which indicates a lower limit for flux in multicomponent systems. As opposed to the earlier cases,[3,4] incorporation of the interfacial region into the model leads to only a small change in permeability predictions. In this series situation, permeability is dominated by the low-conductivity polystyrene phase, regardless of whether we consider the overall system to consist of two or three regions. Even though the difference in predictions is small, the three-component model does more closely approximate the experimental KR-S behavior.

The positive deviations of the experiment from the model are an indication that the KR-S samples are not perfect series materials. Although good series organization is indicated by TEM and SAXS, it is likely that there exist some defects or connections between domains that serve to short circuit the series arrangement in these samples. Only a small amount of such parallel defects would be required to raise the permeability above the series model to that exhibited by the KR-S samples. Despite these imperfections, the relatively simple film fabrication process does a remarkably good job in producing samples whose properties indicate a contribution from the low-permeability polystyrene that is near its theoretical limit. As indicated earlier, this is vital in applications where the low-permeability component is expected to provide transport characteristics to the final material.

Permeability coefficients for the spherical morphology SB10 system are located in the lower section of Table I. Like the KR-S permeabilities, the tabulated values are much closer to those of polystyrene than to those of polybutadiene. This is to be anticipated, since the high-permeability spherical rubber domains have no continuity from one side of the film to the other.

On the basis of the morphology of SB10, we can develop a simple permeability model, similar to a development by Jefferson et al.,[11] which describes thermal conductivity in a composite medium. We consider the sample to be composed of many identical cubes. Each cube represents a single microstructural repeat unit and consists of a polystyrene matrix with a polybutadiene sphere in its center. (It is known that under equilibrium conditions, spherical domains in diblock copolymers tend to arrange in a body-centered cubic lattice,[12] and we recognize that it is not possible to construct such a lattice from the identical cubes considered here.) Because all cubes are the same and therefore have equal permeabilities, the permeability of one cube will be equal to that of the entire sample. The permeability of such a "unit cube" is estimated in the following manner.

Figure 4 is a cross-sectional view of the unit cube—polystyrene surrounding a polybutadiene sphere of radius r_0. With the length of a cube side equal to one, r_0 is set so that the component volume fractions in the cube are equivalent to the material's overall composition. Figure 4 is a "side view", that is, the direction of permeation is from top to bottom. If we assume that flux occurs only in this direction (probably not strictly true), then we can express the permeability for any straight line path through the cube as a function of r. For $r < r_0$ (case A in Figure 4), transport occurs in series, encountering first polystyrene and then polybutadiene, followed by polystyrene again. The permeability P_{i}, for this path can be expressed by the series model

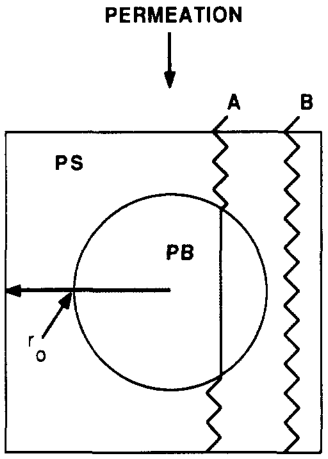

Figure 4. "Unit cube" model representation.

$$1/P_{\mathrm{i}} = d_{\mathrm{S}}/P_{\mathrm{S}} + d_{\mathrm{B}}/P_{\mathrm{B}} \quad (3)$$

where d_{S} and d_{B} are fractions of the path length through polystyrene and polybutadiene. On the other hand, for situations where $r > r_0$ (case B in Figure 4) transport occurs through the polystyrene only, and the permeability for such a path is simply that for pure polystyrene.

To arrive at the permeability for the entire cube, we sum all possible straight line permeation paths over the entire cross-sectional area available for permeation. This corresponds to parallel addition of the contributions from such paths. The solution to this integration problem is given by

$$P(\text{unit cube}) = P_{\mathrm{S}}(1 - \pi r_0^2) + \left[\frac{\pi P_{\mathrm{S}} P_{\mathrm{B}} r_0}{P_{\mathrm{S}} - P_{\mathrm{B}}}\right] + \left[\frac{\pi P_{\mathrm{S}} P_{\mathrm{B}}^2}{2(P_{\mathrm{S}} - P_{\mathrm{B}})^2}\right] \ln\left[\frac{P_{\mathrm{B}}}{P_{\mathrm{B}} + 2(P_{\mathrm{S}} - P_{\mathrm{B}}) r_0}\right] \quad (4)$$

In addition to providing a somewhat simpler final expression, the approach and solution described here are slightly different from those of Jefferson et al.[11] Here, in our final step we sum paths that traverse the length of the cube, whereas the other treatment carries out the integration earlier in the formulation, using a summation result from the vicinity of the sphere in subsequent series and parallel formulas.[11]

Permeability predictions from our unit cube model appear in Table I. SB10 experimental results are seen to be in excellent agreement with the model (within 10%) for all gases except CO_2, where the model prediction is about 15% too high.

In addition to the unit cube model predictions, permeabilities given by the simple series law (eq 1) based on overall volume fractions of the SB10 copolymer appear in Table I. While predictions from the two models are close to one another (which is expected, since transport through the spherical morphology is a type of series process), the unit cube model is superior in its prediction of SB10 permeabilities. It is interesting to note that unit cube permeability predictions are always slightly higher than those from the series law. This results from the concentrations to flux from those gas molecules that pass through the cube near its center. These encounter an amount of polybutadiene that is considerably higher than the overall volume fraction.

As opposed to the lamellar block copolymers discussed earlier, an effect on permeability of a third interfacial region is not apparent in the SB10 samples. While an interfacial region undoubtedly exists in the SB10 material, its failure to be detected by the permeation tests can be explained in two ways. First, the domain size in SB10 is large in comparison to the system's interfacial thickness—1000-Å sphere diameter versus an interfacial thickness of around 22 Å.[13] As a result, the volume fraction of interfacial material in SB10 is nearly an order of magnitude lower than in the K-Resin, for which the interfacial zones had a measurable effect on permeation.[3,4] Second, as mentioned earlier, the addition of a third component into the series formulation does not cause a particularly large effect, and transport through SB10 is basically a series process.

It is interesting to compare the behavior of SB10 and KR-S samples. While their overall compositions are virtually identical (75% polystyrene in the K-Resin and 74% in SB10) these block copolymers represent two entirely different morphologies. Despite this, both SB10 and KR-S display the potentially desirable characteristic described at the outset of having their transport behavior dominated by the low-permeability phase.

For the gases studied, measured permeabilities of SB10 are equal to or lower than those of KR-S (Table I). This is in spite of the fact that the series model, used to describe the permeability of KR-S, predicts slightly lower permeabilities than the unit cube model. Recall that it was concluded that the KR-S samples were not perfect series materials but possessed a small number of defects, which raised their permeabilities. The spherical morphology in the SB10, however, ensures that there is no connectivity of high-permeability polybutadiene domains. So while in principle the lamellar system arranged in series should display a lower permeability, in practice producing such a sample without defects may be virtually impossible. In contrast, the low-permeability spherical system requires no special mechanical manipulations at all.

Both systems offer improved mechanical properties as compared to polystyrene homopolymers. There has been considerable work which shows that the microphase separated spherical morphology at a volume fraction of 0.25 polybutadiene leads to enhanced toughness.[14] Likewise, the K-Resin materials have also been shown to have higher impact strengths than unmodified polystyrene,[15] and the lamellar morphology would provide the optimal use of the polybutadiene for film flexibility. All of these considerations need to be taken into account when choosing the best system morphology for a given application.

A more general picture of the permeation behavior of these heterogeneous block copolymers can be obtained by viewing the systems on a separation factor versus permeability plot. This type of representation is commonly used to assess relative transport performances of different polymeric materials and is constructed for a single gas pair by plotting, for a variety of polymers, the ideal separation factor α (defined as the ratio of permeabilities for the two gases) versus the logarithm of the permeability for the more permeable gas. For many gas pairs, such plots have a negative slope, indicating the commonly observed tradeoff between high permeability and high selectivity in polymers.

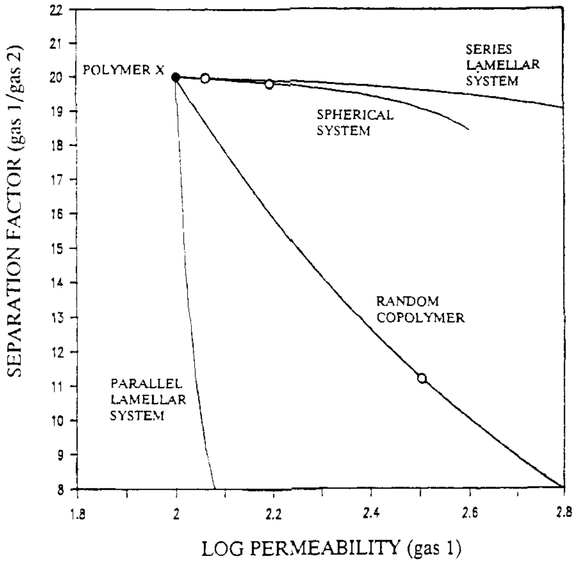

Figure 5. Expanded region of ideal separation factor versus permeability plot for a model system. Open circles correspond to individual systems containing 75 vol % polymer X.

Here we will generate such a plot for a model system consisting of two polymers (X and Y) and two gases (1 and 2). For this example we assign polymer X an α_X ($=P_X{}^1/P_X{}^2$) of 20 and a permeability $P_X{}^1$ of 100 and for polymer Y an α_Y of 2 and $P_Y{}^1 = 10\,000$. Note that the relative behavior of these polymers conforms to the situation mentioned above, where the polymer with low permeability (X) possesses a high selectivity. We can use the models described earlier to place curves on the plot for a hypothetical block copolymer of X and Y with (1) a lamellar morphology arranged in series, (2) a lamellar morphology arranged in parallel,[4] and (3) spheres of polymer Y in a matrix of polymer X (unit cube model). Also of interest is the expected behavior of a random copolymer of X and Y. This represents a homogeneous combination of the two components in the absence of microphase separation and will serve as a useful basis for comparison. Permeabilities for random copolymers (P_r) can be expressed by[16,17]

$$\ln P_r = v_X \ln P_X + v_Y \ln P_Y \qquad (5)$$

where v's and P's are component volume fractions and pure component permeabilities, respectively.

The region near pure polymer X of the resulting separation factor versus permeability plot appears in Figure 5. Because in this discussion we have been concerned primarily with block copolymers that have their permeability dominated by the low-conductivity component, we focus our attention on this area only. In the figure, the curve describing the behavior of the spherical system ends at the volume fraction where the spheres within the unit cubes begin to impinge on one another; the other curves would continue to a common point far off the figure to the lower right where the behavior is that of pure polymer Y. Indicated by open circles are points that correspond to systems containing component Y at a volume fraction of 0.25. This point for the lowest curve (lamellar system arranged in parallel) occurs at log $P^1 = 3.1$ and $\alpha = 2.1$ and falls well outside the region presented in Figure 5.

Starting from the polymer X end point, moving along any curve indicates addition of Y to the system. As seen in the figure, the existence of heterogeneity in a material gives rise to behavior quite different from that of the random copolymer of X and Y. Addition of polymer Y in the series and the spherical block copolymer systems leads to some increase in permeability without considerable loss of selectivity; more enhancement of permeability is obtained at 25% Y in the spherical system than in the series system, with little selectivity difference for these two cases. In contrast to these situations, when lamellar domains are arranged in parallel, drastic permeability increases and selectivity reductions result upon addition of component Y (recall the point for 25% Y at log $P^1 = 3.1$, $\alpha = 2.1$).

It is clear from this analysis that both the series lamellar and spherical block copolymer systems essentially maintain the permeation characteristics of their low-permeability component, even though they contain significant amounts of highly conductive material. In contrast, at 25% Y, the random copolymer shows a considerable permeability increase and selectivity decrease compared to polymer X, while the parallel lamellar system has lost virtually all resemblance to polymer X behavior. These latter cases would obviously be inadequate if polymer X transport qualities were important.

Conclusions

The use of heterogeneous block copolymers for gas permeation applications offers a wide range of opportunities in membrane and packaging design. Here we have demonstrated morphological arrangements of block copolymers in which transport characteristics of a low-permeability component can be incorporated into the system without being significantly compromised by the presence of an additional material, which in this case, has a beneficial influence on mechanical properties. Such concepts of morphological engineering can have important implications in situations where a high selectivity or barrier quality is a necessity.

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