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Microstructure orientation and nanoporous gas transport in semicrystalline block copolymer membranes

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Abstract

Gas permeability coefficients were obtained for CO_2 and He gases at room temperature in a semicrystalline ethylene/ethylene–propylene/ethylene (E/EP/E) triblock copolymer, and a blend of polyisoprene (PI) with an E/EP diblock copolymer. It was found that the gas transport properties of these polymer systems were influenced by changes in processing conditions and solvent treatments to create nanoporous membranes. The permeability results coupled with small angle X-ray scattering (SAXS) data, provide a direct connection between changes in microstructure to the observed changes in gas transport properties. Channel die processing was used to alter the relationship of semicrystalline and microphase separated lamellar populations and produce orientation textures applicable for the construction of membranes exhibiting anisotropic gas transport properties. Depending on the processing conditions, these microstructures can be oriented normal to the plane of shear and perpendicular or transverse to the direction of shear. It was demonstrated that the transverse crystalline lamellar morphology exhibits higher gas permeability than the perpendicular microphase separated orientation morphology due to its lower crystallinity. E/EP/E triblock samples were also processed in the channel die, and then exposed to xylene or heptane to create nanoporous membranes. Depending on the choice of solvent, various degrees of porosity could be induced in the polymeric membrane. The microstructure orientation texture produced from channel die processing was not disrupted by the introduction of the pores. An E/EP randomly oriented diblock copolymer was blended with PI homopolymer and then exposed to a selective solvent to extract the homopolymer and create a porous microstructure. It was shown that the permeability of the block copolymer membrane increased due to the introduction of pores, while retaining some selectivity due to the confinement of the pores within the block copolymer self-assembled microphase separated morphology. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Microstructure orientation; Nanoporous gas transport; Block copolymer synthesis

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1. Introduction

The manipulation of polymer gas transport properties has resulted in a variety of applications for high throughput membrane materials and low permeability (barrier) uses. Polymeric membrane processes offer a number of benefits such as simple flow schemes, reliable continuous operation, low energy consumption, and competitive capital and operating costs [1–3]. Porous polymeric materials have a wide variety of applications [4–6] ranging from microfiltration, ultrafiltration, reverse osmosis and gas separations to catalyst supports, controlled release devices, microelectronic devices, and artificial cells. For example, the synthesis of nanoporous materials for the microelectronics industry will aid in the development of ultralow dielectric constant materials, since the introduction of pores lowers the dielectric constant of the polymer. Production of pores confined within microphase separated block copolymer morphologies are exciting for gas separation applications because they represent an opportunity to increase the void content of a polymeric membrane, which has been shown to increase the gas flux, while retaining gas selectivity [7]. Semicrystalline block copolymers can be used to design membranes having the structural characteristics of one component block and the permeability characteristics of another. The ability of one of the blocks to crystallize offers a much wider range of possibilities with regard to increased toughening, resistance to solvents and acids, and higher working temperature applications than in a completely amorphous polymeric membrane system. The ability to control the type and degree of microstructure orientation and porosity in a semicrystalline block copolymer nanostructure is essential for the development of polymeric materials whose gas permeability can be controlled through changes in membrane processing conditions.

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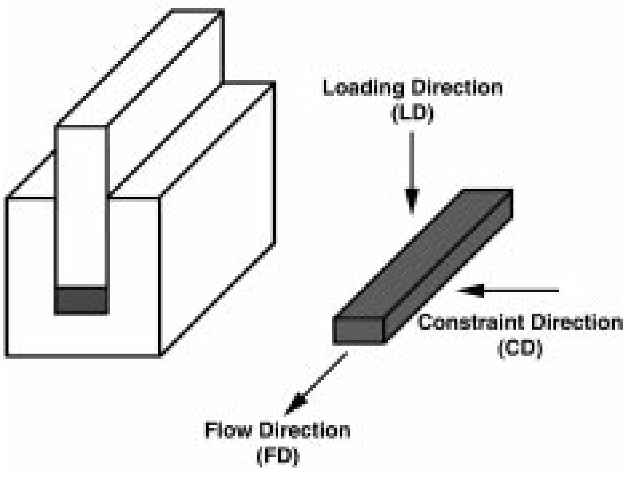

Fig. 1. A representation of the channel die and its three principal deformation directions.

Channel die processing of semicrystalline ethylene (E)/ ethylene–propylene (EP) diblock E/EP and triblock E/EP/E copolymers, can achieve orientations of the block copolymer lamellar microstructure parallel or perpendicular to the direction of shear [8,9]. Measurement of the gas permeability in these oriented block copolymer systems have resulted in a variation of the gas transport from the parallel (lower permeability) to the perpendicular (higher permeability) microstructure orientation textures [9,10]. The application of this research lies in the production of barrier or high throughput membranes from the same material, through simple changes in the processing conditions, such as a change in the applied load during plane strain compression processing.Another way to influence the permeability of gases through block copolymer systems is to create a nanoporous structure by extracting one of the components of a semicrystalline block copolymer–homopolymer blend or by selectively swelling one of the microphase separated blocks. We explored a novel technique to create nanopores in semicrystalline block copolymer and blend systems, referred to as controlled solvent crazing or solvent extraction, depending on the polymer system. This technique has been successfully applied in completely amorphous block copolymers and their blends with homopolymers [13], but has never been tried before in semicrystalline systems. Membranes having oriented nano-morphologies, produced from channel die compression of semicrystalline block copolymer and blend systems, are exposed to a selective solvent, which causes the amorphous block microphase to expand, and in addition dissolve the amorphous homopolymer in the case of the blends, while the semicrystalline block provides mechanical resistance to limit the degree of swelling and locks in the microstructure. The absorbed solvent is subsequently completely removed by exposure to vacuum, leaving behind a porous polymer film.

A transverse orientation of lamellar stacks has already been reported in plane strain compression studies of semicrystalline homopolymers [11,12], but has not yet been observed in semicrystalline block copolymer systems. We now report on the gas transport properties of a novel for block copolymers transverse to the direction and normal to the plane of shear microstructure orientation texture produced by changes in the cooling rate during channel die processing, and also on the introduction of pores confined within one of the block copolymer nanostructures. The goal is to alter the gas permeability in these semicrystalline block copolymer and blend systems due to the introduction of the pores. Careful choice of solvent systems is used to reduce the formation of regions of very high free volume, which could significantly impact selectivity. The block copolymer structure presents the opportunity to create a high flux nanoporous structure, while keeping the pores of nanometer scale, thus providing some selectivity and retaining mechanical strength.

2. Experimental

2.1. Block copolymer synthesis

The E/EP and E/EP/E triblock copolymers were synthesized by hydrogenation of 1,4-poly (butadiene) and 1,4-poly (isoprene) precursors. The butadiene block consists of 10% 1,2, 35% *trans* 1,4 and 55% *cis* 1,4 PB, while the isoprene block contains 93% *cis* 1,4 and 7% 3,4 polyisoprene (PI). Hydrogenated butadiene thus resembles low-density polyethylene (E) and hydrogenated PI is essentially perfectly alternating ethylene propylene rubber (EP). The molecular weights of each blocks of the E/EP diblock are 100,000 g/ mol, and the E/EP/E constituent blocks molecular weights are 30,000 g/mol for the E end blocks and 40,000 g/mol for the EP middle block. These values were determined from gel permeation chromatography (GPC) measurements on the polydiene precursors, from knowledge of reactor stoichiometry and conversion, and from a previous demonstration [14] that little or no degradation occurs during the hydrogenation reactions. The 1,4 polyisoprene homopolymer used in the blend samples was anionically synthesized and had a number average molecular weight (M_n) of 38,000 g/mol.

2.2. Blending

Homopolymer blending with E/EP block copolymer samples was accomplished by dissolving 5–7 g of the diblock and 10 wt% homopolymer in 200 ml of heptane in a 250 ml flask. A Teflon stir bar was added to the solvent/ polymer mixture and the flask was placed on to a heat/stir pad. The flask was then slowly heated to approximately 90°C while stirring with medium agitation for 30 min. When transparent, the solution was precipitated with a (10:1) solvent:polymer solution made up of an even mixture of acetone and methanol. The precipitated polymer was collected by vacuum filtration and air dried for 24 h. The sample was then oven dried for 24 additional hours at 70°C.

2.3. Channel die processing

Isotropic block copolymer and blend samples were heated to 150°C, above the melting point of the E block and the order–disorder temperature, to erase any thermal history, in a standard laboratory press equipped with digitally controlled heating platens. Load was applied and released to press the samples into thin sheets. The heat was turned off and the polymer sheets were allowed to cool to room temperature. Once cooled, the polymers were cut into 1/2 in. by 1/2 sq. in. The squares were stacked in the center of a channel die. The channel die was placed into the press and heated to the desired temperature, and the polymer was subjected to plane strain compression. A representation of the channel die and its principal deformation directions, the loading (LD), constraint (CD) and flow (FD) directions, are shown in Fig. 1.

The channel die was maintained at a selected constant temperature during the compression flow. An applied load of 9.2 MPa was applied continuously using the press. The compressed specimens were quenched under load to room temperature, and the load was subsequently released. The final compression ratio was determined from the reduction of the thickness of the samples. The channel die experiments were conducted at a range of compression ratios of $\lambda = 10$ to 20.

Two cooling rate protocols were employed for quenching channel die processed samples. The first method provides a cooling rate 0.27°C/s by running cold water through the cooling platens. The second method incorporates the cooling platens and a cooling system, which runs water directly through the channel die, thus cooling the sample at a rate of 3.50°C/s. The temperature data was obtained by placing a thermocouple into the polymer melt during channel die compression. Data was recorded every 5 s while the two cooling rates were applied.

2.4. Small angle X-ray scattering experiments

The change in orientation of the resulting microstructure due to deformation was studied by means of small-angle X-ray scattering (SAXS). The SAXS data were obtained using the 10 m digital camera in the National Institute of Standards and Technology (NIST) Polymers Division [15]. This SAXS instrument is modeled after the one designed by Hendricks [16] at Oak Ridge National Lab. The 2D data sets obtained in these experiments were corrected for dark current and unscattered primary beam. Depending on whether the scattering was isotropic or oriented the data was reduced to circular or sector averages by averaging over the detector picture elements within a series of annuli located at a fixed distance from the beam center. Sector averages were done at azimuthal angles of ±45° with a width of ±22.5°. All intensity values were normalized to a NIST Lupolen sample to provide absolute intensity. Uncertainties were calculated from the standard deviation of the pixel statistics in the averaged annulus and were plotted only when the uncertainty limits were larger than the size of the plotted data points [16,17]. The grid pattern seen in the 2D images is caused by the shadow of a support structure that keeps the exit window of the scattered beam path from imploding. Pixels belonging to the grid pattern are masked out of calculations on the 2D patterns.

2.5. Gas permeability measurements

Permeability measurements were taken on an ASTM Dek-Tron Scientific DCS135 Permeability cell [18]. One-inch diameter membranes were prepared from samples oriented using a channel die and processed under the desired deformation, temperature, and cooling rate conditions. Solvent swollen permeation samples were produced by exposing a permeation sample to a good solvent for the EP block and the PI homopolymer. The solvents used in this study were xylene and heptane. The sample was soaked in the solvent for 24 h at 35°C with low agitation. The samples were then removed and placed in a beaker with a perforated cover to allow the solvent to evaporate slowly over a 5 day period. The sample thickness was measured and the sample was mounted between two neoprene rubber gaskets on the permeability cell. The system was purged with the permeating gas for a period of 15 min. The apparatus was then sealed and submerged in a water bath to maintain constant temperature. The system was checked for leaks and then allowed to come to equilibrium over a minimum of 12 h at the desired gas pressure. Permeability measurements were taken over a period of 4 h for CO_2 and He gas. These values were then averaged. The estimated uncertainty associated with the measured gas permeabilities is within 10% of the reported values.

3. Results

Variations in the cooling rate of channel die processing can alter the relationship between block copolymer microphase separated and semicrystalline lamellar populations in an E/EP/E 30/40/30 sample [19]. A 0.27°C/s cooling rate and 9.2 MPa applied load during channel die processing has been shown [9] to produce microphase separated lamellar populations oriented perpendicular to the direction and normal to the plane of shear. Increasing the cooling rate from 0.27 to 3.50°C/s during plane strain compression processing above the E block melting point, while keeping the applied load constant at 9.2 MPa, produced a novel for block copolymers crystalline lamellar microstructure oriented transverse to the direction and perpendicular to the plane of shear. SAXS was used to provide quantitative information on the length scale of the lamellar periodicity of each microstructure. Two dimensional SAXS patterns are presented in Fig. 2 for: (a) the perpendicular microphase

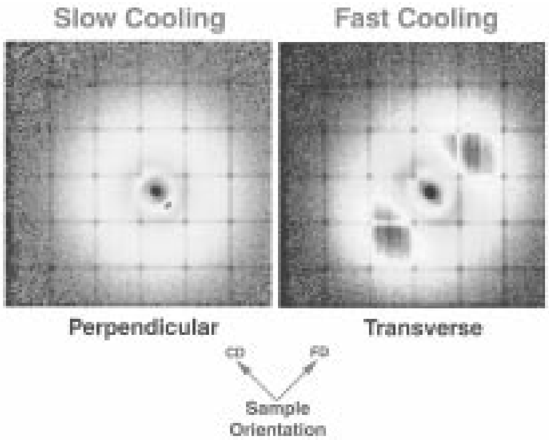

Fig. 2. SAXS patterns of E/EP/E 30/40/30 oriented via plane strain compression: (a) perpendicular; (b) transverse to the direction and normal to the plane of shear microstructure orientation textures.

Table 1
Permeability values, P_{CO_2} and P_{He} for the E/EP/E 30/40/40 microstructure orientation textures, and cooling protocols

Orientation	Cooling rate (°C/s)	P_{CO_2}	P_{He}	P_{CO_2}/P_{He}
Perpendicular	0.27	43	15	2.8
Transverse	3.50	48	27	1.7
Isotropic	0.27	39	11	3.5
Isotropic	3.50	38	10	3.8

separated block copolymer lamellar microstructure; and (b) the transverse E chain crystalline lamellar microstructure that can be obtained in a 30/40/30 E/EP/E triblock copolymer sample which has undergone plane strain compression in the channel die. The indicated scattering in Fig. 2 is from orienting the X-ray beam parallel to the LD.

Since the theoretically predicted morphology for this triblock copolymer is lamellar, the scattering intensity, I, and the scattering vector, Q, obtained from the sector average along the CD, are plotted in the form of IQ^2 vs Q, to account for the angular dependence of the form factor scattering from lamellae. Values for long period spacings, D, are calculated from the position of the peak maxima in these plots. In Fig. 2a, sharp dots are observed with a calculated long period spacing of 43.6 nm in the CD, associated with the microphase separation of the E and EP block constituents. A diffuse ring with a long period spacing of 14.5 nm is also observed for this slow cooled sample. This long period is associated with the crystallizable part of the E polymer. Fig. 2b presents the spread-out spots with a long period spacing of 13.1 nm in the flow direction (FD) for the fast cooled sample. It has been concluded [19], that the transverse orientation of semicrystalline lamellar populations in these block copolymer systems is produced from the deformation of preformed E crystallites during channel die processing. The pivotal processing parameter in forming the transverse microstructure orientation texture was the application of a 3.50°C/s cooling rate. This cooling rate protocol produced a room temperature morphology having a lower overall degree of crystallinity than the perpendicular (0.27°C/s cooling rate) microstructure. DSC experiments have determined a 19% crystallinity for the transverse lamellar orientation texture, and a 32% crystallinity for the perpendicular lamellar orientation texture [19]. Deformation of preformed crystallites produced an orientation texture of the crystalline E chain lamellae transverse to the direction of shear, and this scattering intensity is the predominant scattering feature shown in Fig. 2b.

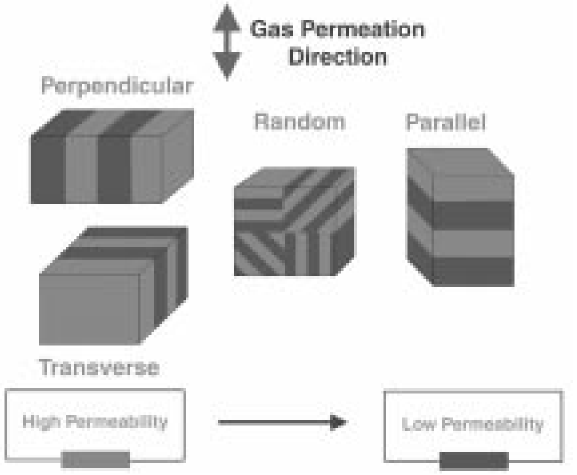

Fig. 3. Schematic of the relationship between permeation behavior and microstructure orientation texture in semicrystalline block copolymers.

Fig. 3 shows the many possible microstructure orientations that have been achieved [9,10,19] with channel die processing of semicrystalline block copolymers and their expected gas transport properties. Both the perpendicular and transverse to the direction of shear microstructures contain nanodomains oriented “in parallel” with respect to the permeation direction, which provide high throughput paths for gas transport. The permeability results obtained for the perpendicular and the novel transverse to the direction of shear microstructure orientation textures in the E/EP/E 30/40/30 triblock copolymer are presented in Table 1 for He and CO_2 gases.

The effect of cooling rate during channel die plane strain compression processing was also studied in isotropic E/EP/E 30/40/30 samples. Permeation data for isotropic slow cooled (0.27°C/s) samples and isotropic fast cooled (3.50°C/s) samples are presented in Table 1, and indicate that varying the cooling rate in channel die processing does not cause a significant change in the permeation properties of these membranes. The permeability of the isotropic samples, however, is lower than the oriented, high throughput, perpendicular and transverse microstructure orientations, as expected.

The permeability results for the porous E/EP/E 30/40/30 triblock samples, having microphase separated block copolymer domains oriented perpendicular to the direction and

Table 2
CO_2 and He permeability results for E/EP/E 30/40/30 oriented perpendicular to the direction of shear and then exposed to xylene or heptane

Solvent	P_{CO_2}	P_{He}	P_{CO_2}/P_{He}	Swell in solvent (%)
No solvent	43	15	2.8	0
Heptane	55	18	3.0	+50
Xylene	63	25	2.5	+90

normal to the plane of shear are presented in Table 2. The samples were swollen in xylene and heptane to study the effect of solvent treatment on the microstructure orientation texture and gas transport properties. Exposing the E/EP/E triblock to solvent caused swelling of the amorphous EP block while the semicrystalline E block provided mechanical resistance to limit the degree of swelling. The increase in volume (swelling) resulting from the solvent was dependent on the type of solvent used and was found to vary from 50% for heptane to 90% for xylene. SAXS was used to determine whether the solvent disrupted the channel die induced block copolymer perpendicular lamellar microstructure orientation and whether there was a change in the observed long period spacing. The 2D SAXS patterns for a "perpendicular" E/EP/E 30/40/30 sample: (a) before solvent treatment; (b) after xylene solvent treatment; and (c) the comparison of the resulting IQ^2 vs Q plots are presented in Fig. 4. A decrease of 4.3 nm in the E/EP microphase separated long period spacing and a decrease of 10 nm in the E semicrystalline long period spacing were observed as a result of the solvent treatment on the vacuum dried sample. The same sharp dots in the constraint direction are still observed, which indicates that microstructure orientation was not disrupted by the solvent treatment used to create the nanoporous membrane. In addition, the xylene treatment appears to have lowered the overall SAXS intensity by inducing partial recrystallization.

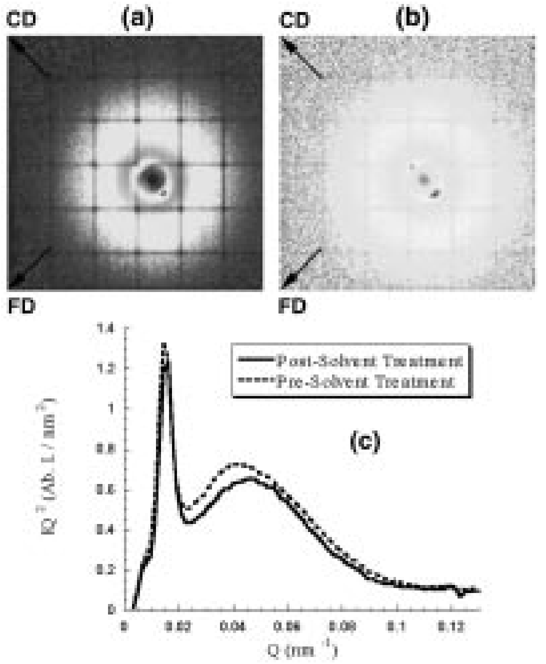

Fig. 4. SAXS patterns of a 30/40/30 "perpendicular sample": (a) before xylene solvent treatment; (b) after xylene solvent treatment; and (c) a comparison of the IQ^2 vs Q plots.

The gas permeability results (Table 2) of this perpendicular oriented solvent treated sample shows a large increase in permeability of both He and CO_2 after the solvent treatment. The xylene solvent treatment showed the largest overall increase in permeability and caused the highest degree of swelling. The xylene treatment produced a 20 barrer increase in CO_2 and a 10 barrer increase in He permeabilities. The degree of swelling with xylene was 40% greater than the degree of swelling obtained with heptane.

The room temperature gas permeability values of isotropic E/EP 100/100 diblock samples blended with 10 wt% PI, which were exposed to xylene or heptane to dissolve the PI homopolymer, are shown in Table 3. The results indicate the formation of a porous microstructure, upon the dissolution of the PI homopolymer, where the increase in permeability was dependent on the degree of swelling and type of solvent. The largest increase in permeability was observed in the xylene treated sample, which produced the largest degree of swelling. An increase of 25 barrer for CO_2, 32 barrer for He, and a decrease in the selectivity of the membrane were observed after the xylene treatment. The heptane treatment resulted in a less pronounced increase in the permeability of the membrane for both gases.

4. Discussion

Permeation of gases through membranes is usually described by the solution–diffusion model developed by van Amerongen et al. [20,21,22,23]. In this model, it is assumed that gas on the high-pressure side of the membrane dissolves in the membrane material and diffuses down a concentration gradient to the low-pressure side of the membrane, where the gas is desorbed. Gas permeation in semicrystalline polymers is essentially confined to the amorphous regions since gas molecules are generally taken to be insoluble in polymer crystallites and, therefore, are unable to permeate through them [24]. The crystallites reduce the permeability by decreasing the volume of polymer available for penetrant solution and by constraining the transport along irregular tortuous paths between them. The reduction in permeability (P), which is the product of the effective diffusion (D) and solubility (S) coefficients ($P = DS$), will be proportional to the volume fraction of the crystalline phase [25] when all samples have an isotropic morphology.

The effect of nanodomain orientation on gas permeability is significant. Permeability coefficients for a film whose nanodomains are oriented normal to the film surface (parallel to the permeation direction), are much higher than for a

Table 3
CO_2 and He permeability results for isotropic E/EP 100/100, and E/EP 100/100 blended with amorphous PI, and then exposed to xylene or heptane

Solvent	P_{CO_2}	P_{He}	P_{CO_2}/P_{He}
Homopolymer	44	19	2.3
Blend			
No solvent	47	24	1.9
Heptane	61	30	2.0
Xylene	72	56	1.2

film having its nanodomains oriented in the same plane as the film surface (in series with respect to the permeation direction) [9]. The resulting expressions for parallel and series crystalline/amorphous laminates are:

$$P_{par} = p_C v_C + p_A v_A \quad (1)$$

$$P_{ser} = \frac{p_C p_A}{p_C v_A + p_A v_C} \quad (2)$$

where p_C, p_A are the permeability coefficients for the crystalline and amorphous domains, respectively, and v_C, v_A are crystalline and amorphous volume fractions. The parallel permeation path corresponds to the high throughput perpendicular or transverse to the direction and normal to the plane of shear microstructure orientation textures in semicrystalline block copolymer channel die processing, while the series permeation path corresponds to the low permeability, parallel to the plane of shear microstructure orientation.

A study of the "parallel" microstructure orientation has been reported in Refs. [9,10]. The permeability differences between the perpendicular and transverse microstructure orientations is explored in this work. Although both lamellar orientation textures lead to high throughput materials, there are differences in permeability due to differences in the scale and composition of the two microstructures. The permeation results shown in Table 1 indicate that the transverse microstructure orientation has a higher gas permeability than the perpendicular microstructure orientation. This is expected since DSC and SAXS results [19] have indicated that the crystallinity of the transverse microstructure is lower than for the perpendicular microstructure. The lower crystallinity enables more gas flux through the membrane, and thus the transverse sample is indeed expected to show a higher gas permeability than a sample exhibiting the perpendicular orientation texture.

The permeability results obtained for samples oriented perpendicular to the direction of shear and then exposed to a selective solvent indicate an increase in the measured gas permeability. The polyethylene block is resistant to the xylene solvent, but is expected to swell to some extent and is susceptible to recrystallization. The solvent is then evaporated slowly to allow the swollen amorphous EP block to relax, creating pores throughout the material, while the semicrystalline E block crystallizes and locks in the nanoporous structure. The permeation behavior is not entirely governed by transport through a porous structure in these semicrystalline block copolymer systems. In a sample with porosity dominating the permeation mechanism, selectivity would approach unity. The SAXS results in Fig. 2 indicated the overall perpendicular microstructure orientation texture was not disrupted by the solvent treatment. However, the decrease in long period spacing for both the microphase separated and semicrystalline lamellar nanodomains suggest the solvent treatment induced a nonequilibrium packing of the block copolymer nanodomains to accommodate the pores.

This study successfully demonstrated that changes in morphology observed by SAXS in semicrystalline block copolymers can be directly related to corresponding changes in gas transport properties. Further characterization is needed to elucidate the pore size and distribution in these polymeric systems. Control over gas transport properties was achieved through variations in processing conditions, which affect the microstructure orientation texture, and solvent treatments, which create pores confined within these oriented microstructures. A novel 'transverse' microstructure orientation texture was obtained upon plane strain compression processing. This study brought to light exciting advances in the complex orientation textures exhibited by semicrystalline block copolymers and their relation to membrane gas transport properties.

Acknowledgements

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