

# Morphological effect of dispersed phase on gas permeation properties through heterophase polymer membrane: theoretical and experimental approaches

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## Abstract

The possibility of the continuous channel formation of the dispersed phase in immiscible polymer blends was numerically simulated by adopting the percolation concept. The numerical simulation showed that the formation probability of the continuous channels increased with the increase in the amount of the dispersed phase. Further, it increased with the decrease in the domain size of the dispersed phase at a given blend composition. The effect of the presence of the continuous channels of the dispersed phase across the membranes on gas transport properties was investigated experimentally. The domain size of the dispersed polyisoprene phase of poly(phenylene oxide)/polyisoprene (PPO/PI) blend membranes was controlled by adding the styrene–isoprene–styrene (SIS) block copolymer. When the SIS block copolymer was added at 4 wt% in PPO/PI membranes in the range of the PI content of 20–30 wt%, the domain size of the dispersed phase was reduced markedly and its permeability was consequently increased. From the theoretical and experimental results, it could be concluded that the abrupt increase in gas permeability of the blend membranes at 20–30 wt% of PI phase may result from the formation of the continuous channels of the more permeable dispersed phase when the block copolymer is added. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Immiscible polymer blend; Dispersed phase; Gas permeation

## 1. Introduction

A great portion of research effort in the membrane gas separation is still being focused on the development of membrane material. It is mainly due to the common consideration that the more wide adoption of membrane gas separation in many industrial fields can be realized with membranes of a better performance than the performance level of membranes presently used. Although there have been many different types of materials with remarkable gas separation properties have been developed, the majority of research on the material development has been directed to polymers.

Polymer blends have been attractive for a potential applicability to gas separation membranes because their gas transport properties can be rather easily controlled by adjusting the composition ratio of constituting polymers [1–7]. Pinnau et al. showed that the permselectivity of polymer blend membranes even could be reversed with

the polymer blend made of poly(1-trimethylsilyl-1-propyne) (PTMSP) and poly(1-phenyl-1-propyne) (PPP) [6,7]. PTMSP is more permeable to large organics such as *n*-butane than to small permanent gases such as hydrogen while PPP is more permeable to hydrogen than to *n*-butane. As the PTMSP composition in the blend increased from 0 to 100%, *n*-butane permeability increased by a factor of 2600, and *n*-butane/hydrogen selectivity increased from 0.4, i.e. hydrogen selective, to 24, *n*-butane selective.

Permeabilities of permanent gases like He, O<sub>2</sub>, N<sub>2</sub>, etc. in miscible polymer blends are reported to vary monotonically between those of the pure polymers [1–3]. However, the transport properties of immiscible polymer blends strongly depend upon their morphology: the volume fraction and the size and shape of dispersed phase [5–9]. The effect of the volume fraction of the dispersed phase on the transport properties of immiscible polymer blends has been widely investigated in many cases. However, the size and shape effects have not been paid much attention.

In an immiscible blend of two polymers, its morphology strongly depends upon their composition. At a given composition, the size of the dispersed phase can also be varied by

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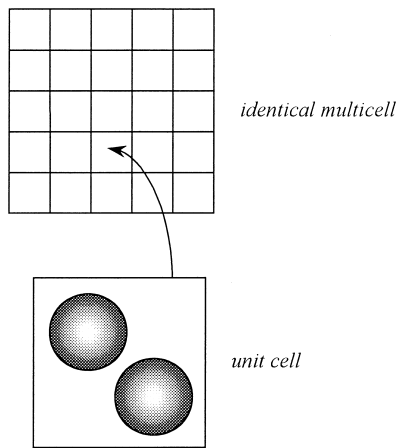


Fig. 1. Representation of the unit square model.

adding a compatibilizer. For example, a block copolymer has been commonly employed as a compatibilizer to control the size of the dispersed phase where each block is miscible with one or the other phase of the polymer blends. Such block copolymer in a polymer blend tends to migrate and to be located in the interphase between two phases if its concentration is lower than its critical micelle concentration [10]. The migration of the block copolymer is due to the thermodynamic energy balance by enthalpic gain and entropic loss. When the block copolymer stays in the

interphase, their interfacial tension will be reduced, and consequently its dispersed phase becomes finer. Therefore, the final morphology of the blend membrane: in particular, the size of the dispersed phase at a fixed composition can, then, be varied by adding a block copolymer [11].

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polyisoprene (PI) will be used as an immiscible pair, and styrene–isoprene–styrene block copolymer (SIS) as a morphology controller because of the miscibility of polystyrene with PPO [12,13]. In this work, the morphology of the membranes made of PPO/PI blends will be varied by adding SIS block copolymer, and their gas transport properties will be measured. The effect of the volume fraction and the size of the PI phase on gas permeation properties will be investigated theoretically and experimentally.

## 2. Computer simulation

In order to simulate the effect of the morphology of immiscible polymer blends on transport properties, the basic concept of percolation theory was adopted. The percolation theory has been applied to interpret gas permeation properties of immiscible blend or block copolymer membranes [14,15]. A drastic increase in the permeability through heterophase membranes has been observed at a certain blend composition, termed the percolation threshold, where a minor component starts to make continuous channels across the membrane. The possibility of the formation of the continuous diffusion paths of the dispersed phase will be investigated by varying the domain size at a fixed composition.

Fig. 1 shows the lattice model employed here to simulate the size effect of the dispersed phase on gas permeation properties. A membrane is assumed to comprise many identical square cells, which is analogous to the thermal conduction treatment through a composite medium by Jefferson et al. [16] Each square cell consists of spherical domains, dispersed in a continuous matrix. For mathematical simplicity, the 3-dimensional volume fraction is assumed to be equal to the 2-dimensional areal fraction.

For numerical calculation, the number of the dispersed phase, called particle hereafter, and its corresponding size can be calculated first at a given volume fraction of the particle. Afterward the position of each particle is determined by generating random number. When all particles are positioned, the number of continuous paths is calculated. This procedure is repeated 5000 times. The schematic flow chart for this procedure is shown in Fig. 2. The number of the particles will be consecutively increased for the next step and the number of the continuous paths is calculated. As a result, the number of continuous paths can be obtained as a function of the number of particles.

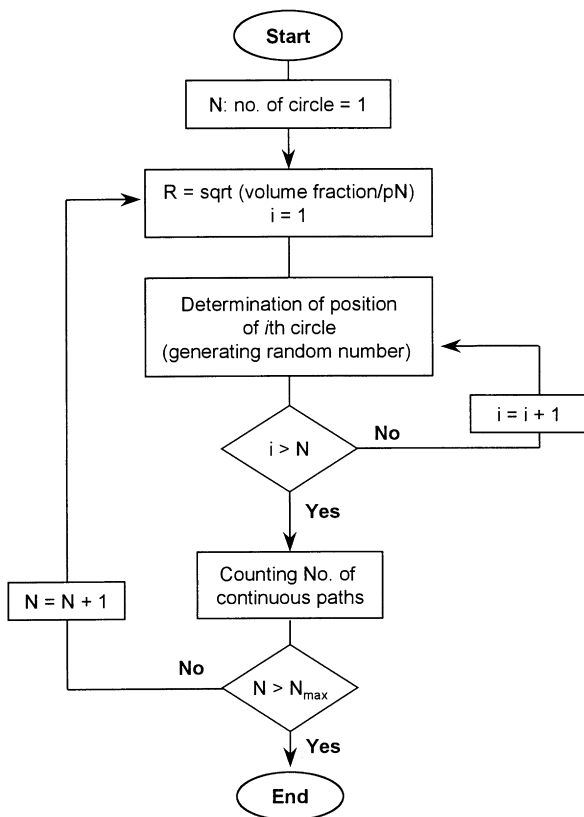


Fig. 2. Flow chart for the computer simulation.

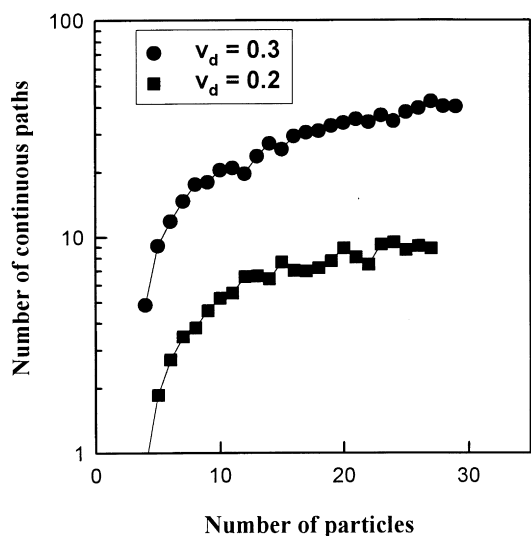


Fig. 3. Calculated number of continuous paths as a function of the number of particles at fixed fractions of the dispersed phase:  $v_d = 0.2$  and  $0.3$ .

### 3. Experimental

#### 3.1. Materials

PPO ( $M_w$  4.5 kg/mol) and PI ( $M_w$  80 kg/mol) used were obtained from Asahi Chemical Co., Japan and Japan Synthetic Rubber Co. They were used as received without further purification. Styrene–isoprene–styrene triblock copolymer (SIS) was obtained from Japan Synthetic Rubber Co. Its molecular weight and block ratio of PS/PI are 140 kg/mol and 15/85, respectively.

#### 3.2. Membrane preparation

Casting solutions were prepared from the above polymers in mono-chlorobenzene at a total polymer concentration of 5 wt%. Membranes were prepared by casting the polymer solution on a glass plate. After the solvent was removed by evaporation at 70°C for one day, the membranes were dried at 60°C in a vacuum oven for two days. The thickness of the obtained membranes was in the range of 40–50  $\mu\text{m}$ .

#### 3.3. Morphological observation

Cross-sectional morphology of membranes was investigated with a scanning electron microscope (SEM, JEOL JSM-35) and energy dispersive X-ray microscope (EDX). Membranes were fractured at liquid nitrogen temperature, and subsequently coated with gold for SEM and with carbon for EDX. In order to stain the double bonds of PI block specifically, a membrane for an EDX analysis was exposed to the  $\text{OsO}_4$  vapor for two days at room temperature.

#### 3.4. Gas permeation

The permeabilities for oxygen and nitrogen were

measured at 35°C by the ‘constant volume method’ and the effective membrane area was 13.59  $\text{cm}^2$ . All the experiments were performed at least twice. Differences in permeability between samples of the same material were all within 3–6% error.

## 4. Results and discussion

### 4.1. Model simulation

Fig. 3 shows the number of the continuous paths detected as a function of the number of particles at fixed fractions of the dispersed phase:  $v_d = 0.2$  and  $0.3$ . No path is detected until the number of particles reaches four for both cases, above which the number of continuous paths increases abruptly up to 10 particles, followed by a slow increase beyond 10. Both cases for  $v_d = 0.2$  and  $0.3$  show similar trend in general. However, the number of the continuous paths is much higher for  $v_d = 0.3$  than that for  $v_d = 0.2$ . It has been also found that the continuous channels can be formed even at the low content of dispersed phase of 20% and their number increases with the decrease in the domain size of dispersed phase, i.e. the increase in the number of particles. The result of model simulation demonstrates that the permeability can strongly depend upon the volume fraction of the dispersed phase as well as its domain size when the permeabilities through both phases are different from each other. The increased number of continuous paths is expected to promote permeability when the dispersed phase is more permeable. The theoretical domain size effect on permeation properties will be experimentally verified here by controlling the domain size through the addition of a block copolymer in immiscible polymer blend membranes.

### 4.2. Morphology of polymer blends

Most of two-phase blends consist of a continuous phase of one component into which second component is dispersed. Depending on the composition of blends and on the viscosity ratio of the two-component polymers, the continuous phase and the consequent dispersed phase is determined [17].

Fig. 4 shows SEM images of cross-section of PPO/PI (9/1 by wt) blend membranes containing the SIS block copolymer at various contents (0, 2 and 4 wt%). As expected, the domain size of the dispersed PI phase is reduced with the increase in the block copolymer content. When the block copolymer content reaches 4 wt%, their size reduction becomes significant.

Fig. 5 shows the EDX micrographs of cross-section of the blend membranes of the PPO/PI (9/1) and PPO/PI (9/1) containing 4 wt% of the block copolymer. The black spots represent the PI phase stained with  $\text{OsO}_4$ . It can be clearly seen that the domain size of the dispersed phase is reduced by adding the block copolymer.

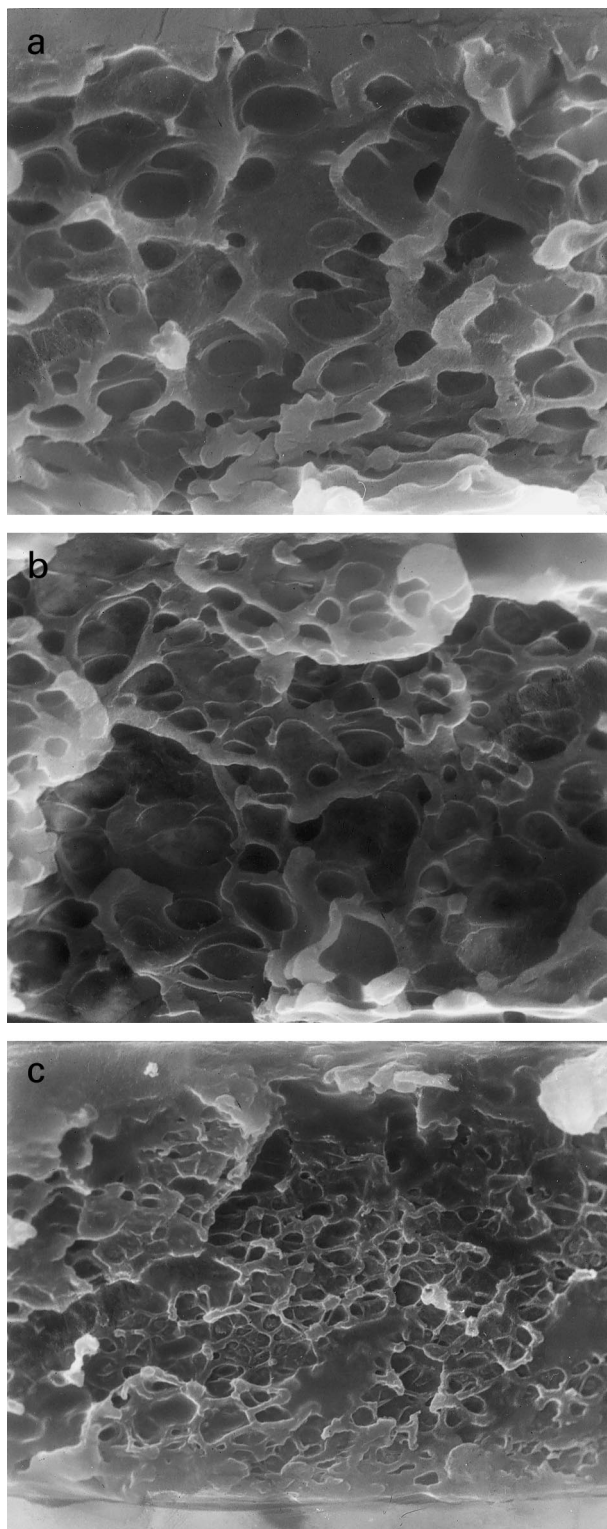


Fig. 4. Scanning electron microscopy images of the cross-section of PPO/PI (9/1 by wt) blend membranes: (a) 0; (b) 2; and (c) 4 wt% of the SIS block copolymer (2000 $\times$ ).

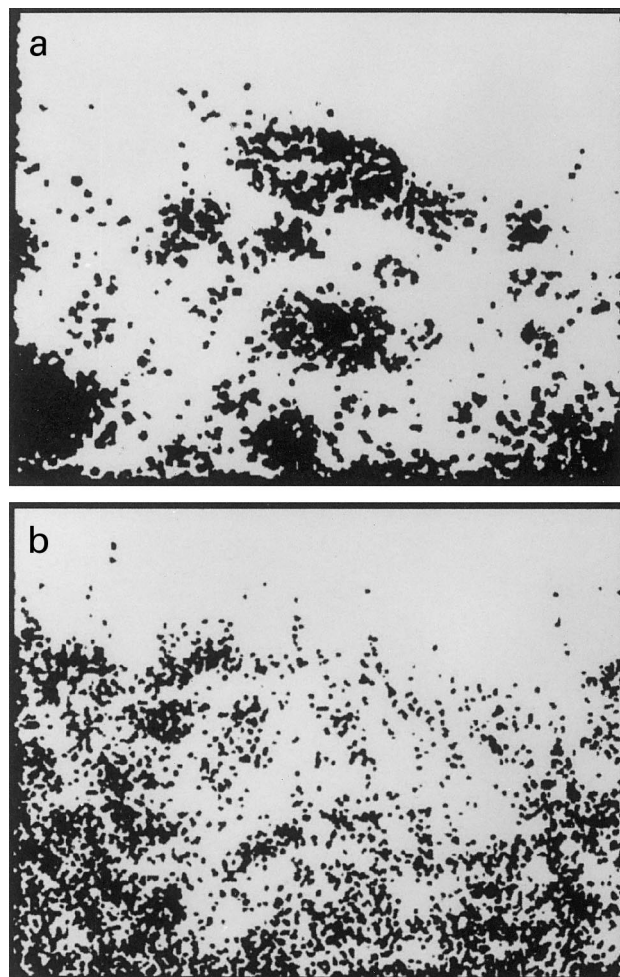


Fig. 5. Energy-dispersive X-ray micrographs of the cross-section of PPO/PI (9/1 by wt) blend membranes: (a) 0; and (b) 4 wt% of the SIS block copolymer.

In Fig. 6 are shown the SEM images of the cross-section of the PPO/PI (8/2) and PPO/PI (5/5) membranes together with the membranes containing the block copolymer. When the block copolymer is added at 4 wt% in the PPO/PI (8/2) blend, the domain size of the dispersed PI phase is reduced and consequently their number is increased (Fig. 6(a) and (b)). In the case of PPO/PI (5/5) where phase inversion occurred, the addition of the block copolymer also causes the reduction in the domain size of the dispersed PPO phase (Fig. 6(c) and (d)).

From these experimental observations, it is concluded that the possibility of forming continuous PI paths will be increased with the decrease in the domain size of the dispersed PI phase at a fixed composition, which gives rise to the enhanced permeability. The effect of domain size on gas permeability will be discussed in following sections.

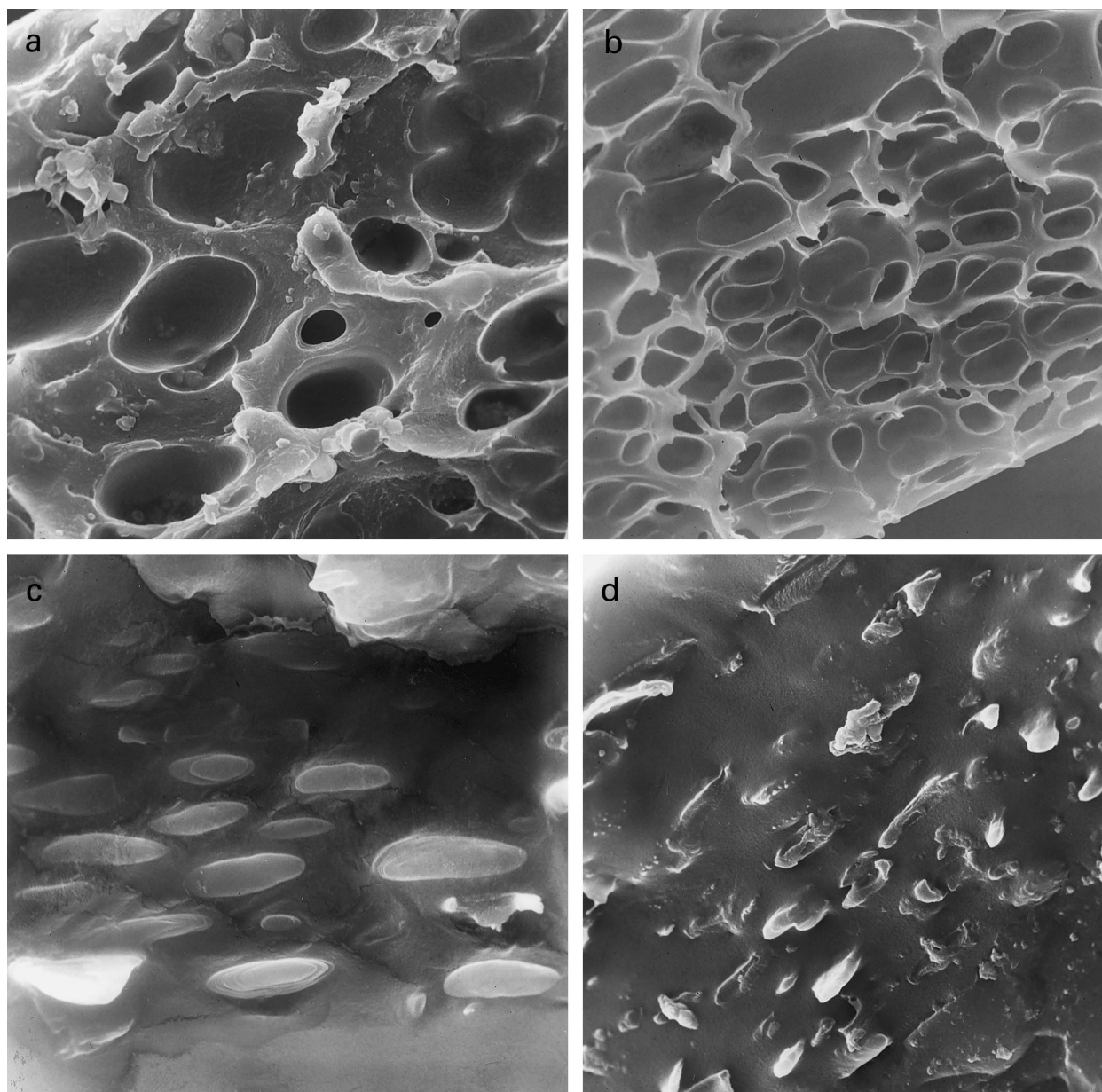


Fig. 6. Scanning electron microscopy images of the cross-section of PPO/PI blend membranes: (a) 8/2 (0 wt%); (b) 8/2 (4 wt%); (c) 5/5 (0 wt%) and (d) 5/5 (4 wt%). The number in the parenthesis denotes the content of the SIS block copolymer (2000 $\times$ ).

#### 4.3. Effect of PPO/PI blend composition on gas permeation properties

The permeabilities ( $P$ ) of oxygen and nitrogen as a function of blend composition are shown in Fig. 7. Both oxygen and nitrogen permeabilities increased sigmoidally with the content of PI phase. The oxygen permeability increased abruptly near the PI content of 20–30 wt%. In this range, the nitrogen permeability also increased. This result is consistent with the continuous path formation predicted by the model simulation. The leveling-off of permeability above 30 wt% of the dispersed PI phase is also consistent with the simulation result by the numerical model as shown in Fig. 3.

There have been proposed numerous models to treat the permeation behavior through heterogeneous binary polymer blends, whose validity has been rigorously evaluated by Petropoulos [18]. At this moment, as pointed out by Petropoulos, all of the proposed models have some shortages in explaining the drastic increase in the gas permeability through a heterogeneous polymer blend when the dispersed phase forms continuous channels above the ‘percolation threshold’ concentration.

The oxygen selectivity over nitrogen is plotted as a function of the PI content in Fig. 8. The selectivity changed insignificantly from 4.4 to 3.4 with the PI content. The decrease in the selectivity at the range of 20–30 wt% may be due to the formation of the continuous channels. Note

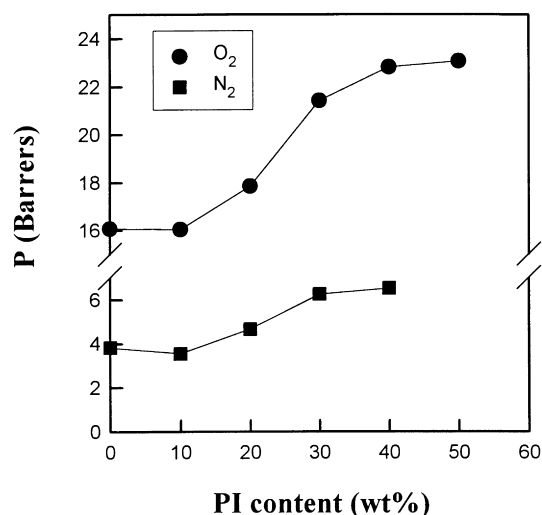


Fig. 7. Oxygen and nitrogen permeabilities as a function of the PI content in PPO/PI blend membranes.

that the oxygen selectivity over nitrogen is 4.2 for pure PPO and 2.7 for pure PI. The selectivity of the membranes having the PI contents higher than 30 wt% is still higher than that of pure PI membranes. This represents that gas molecules permeate competitively through the bicontinuous PPO and PI phases.

#### 4.4. Effects of block copolymers on gas permeation properties

The permeabilities of oxygen and nitrogen through PPO/PI (9/1) blend membranes are shown as a function of the SIS block copolymer content in Fig. 9. The oxygen permeability does not change up to the block copolymer content of 2 wt%, whereas it increased from 15.8 to 18.6 Barrer

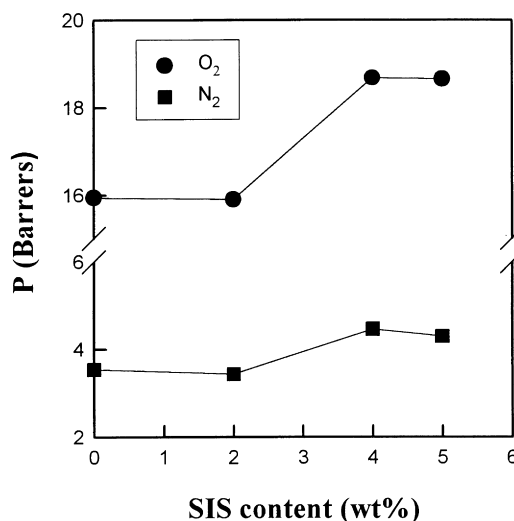


Fig. 9. Oxygen and nitrogen permeabilities as a function of the SIS block copolymer content in PPO/PI (9/1 by wt) blend membranes.

when the block copolymer was added at 4 wt%. Above 4 wt%, it almost levels off. The nitrogen permeability shows almost identical behavior with the oxygen permeability, but is lower than the oxygen permeability. The increase in both oxygen and nitrogen permeabilities manifests the possible formation of the continuous PI channels when the block copolymer was added at 4 wt%, which was evidenced in Figs. 4 and 5.

The permeability change in PPO/PI membranes with and without the block copolymers is compared in Fig. 10. In the range of the PI contents of 10–20 wt%, the block copolymer help increase the permeability significantly whereas its effect becomes insignificant above the PI contents of 30 wt%. When the PI content is lower than 30 wt%, the block copolymer help to form the continuous PI paths by

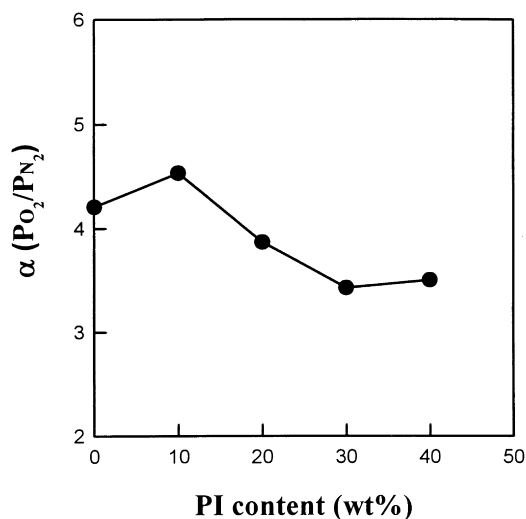


Fig. 8. Oxygen selectivity over nitrogen as a function of the PI content in PPO/PI blend membranes.

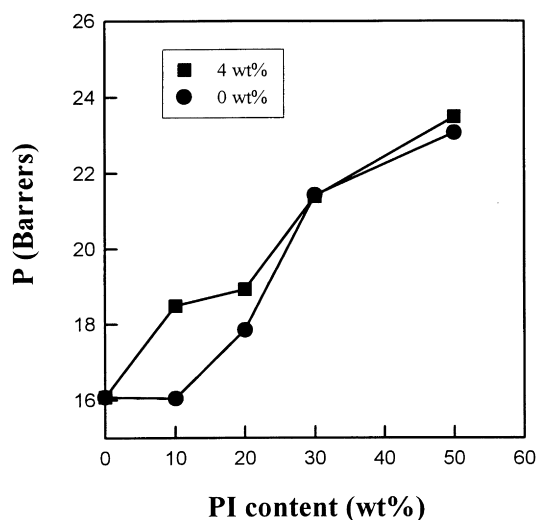


Fig. 10. Oxygen permeabilities as a function of the PI content in PPO/PI blend membranes: (a) with 4 wt% SIS block copolymer; and (b) without block copolymer.

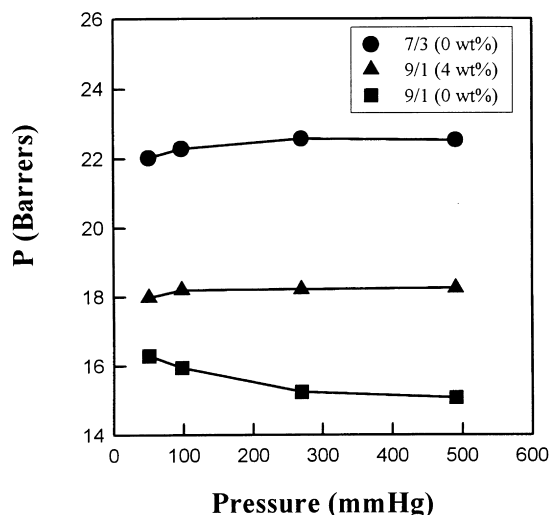


Fig. 11. Oxygen permeabilities as a function of up-stream pressure in PPO/PI blend membranes: (a) 7/3 (0 wt%); (b) 9/1 (4 wt%); and (c) 9/1 (0 wt%). The number in the parenthesis denotes the content of the SIS block copolymer.

decreasing the domain size of the dispersed phase as demonstrated previously. The increased possibility of formation of the continuous paths gives rise to the increased permeability. When the PI content is more than 30 wt%, the continuous PI channels seem to be already formed in PPO/PI (7/3) membrane even without the block copolymer, and therefore the effect of the block copolymer can be hardly seen.

#### 4.5. Effects of upstream pressure on gas permeation properties

Fig. 11 shows the oxygen permeability through PPO/PI (9/1), PPO/PI (9/1) containing 4 wt% block copolymer, and PPO/PI (7/3) blend membranes as a function of upstream pressure. As shown in Fig. 13(c), the permeability through PPO/PI (9/1) blend membrane decreases with increasing upstream pressure demonstrating typical dual mode transport behavior in common glassy polymers [19,20].

The dual mode transport was also observed for the CO<sub>2</sub> permeation through a miscible glassy polymer blend made of poly(butylene terephthalate) and a random copolyester of bisphenol-A and iso/terephthalate acids [21].

The dual mode transport suggests that the gas permeation behavior through the PPO/PI (9/1) blend membrane may be determined mostly by the glassy PPO phase of the blend membrane. In other words, the continuous PI paths may not be formed at this composition or may insignificantly contribute to the permeability due to the limited number for the continuous PI channels formed. Increasing the PI contents or adding the block copolymer help to form the continuous rubbery PI channels. When a gas penetrates through a rubbery polymer, the permeability maintains almost constant irrespective of upstream pressure. As can be seen

in Fig. 11, both the PPO/PI (7/3) (a) and PPO/PI (9/1) with 4 wt% copolymer membranes (b) give almost constant permeabilities, demonstrating the formation of rubbery channels. This is also consistent with the possible formation of continuous channels at the PI contents of about 30 wt%.

## 5. Conclusions

The gas transport properties of PPO/PI immiscible blend membranes were studied and, in particular, the relationship between morphology and gas transport properties was investigated by controlling the morphology with the aid of the styrene–isoprene–styrene (SIS) block copolymer. The computer simulation using the concept of the percolation theory showed that the formation probability of continuous paths of the dispersed phase in heterophase polymer blend membranes increased with the decrease in the domain size of the dispersed phase at a fixed composition. This theoretical result was verified experimentally with PPO/PI blend membranes. The domain size of the dispersed PI phase has been controlled by the SIS block copolymer. The addition of the block copolymer into the blend membranes reduced the domain size of the dispersed phase, which resulted in the increase in gas permeability through the formation of continuous channels of dispersed, more permeable phase.

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