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Percolational Effect of Siloxane Content in Poly(amideimide siloxane) on the Gas Permeation Behavior

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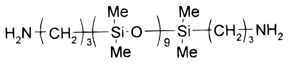
Introduction. Percolation theory[1−5] provides moderate models for the diffusion in random heterogeneous media and for the ionic transport in polyelectrolytes. In the present study, the percolation approach was attempted to explain the gas permeation behavior of a block copolymer composed of rigid polyamideimide block and a flexible siloxane block.

Permeability of oxygen through poly(amideimide siloxane) (SPAI) membranes containing different siloxane contents showed a peculiar exponential permeation behavior, indicating there existed a threshold of gas permeation at around 0.2 volume fraction of SPAI. SPAI with high siloxane contents forms a connected siloxane path in SPAI from top to bottom, resulting in an increase of flexibility and free volume in polymer and thus of gas permeability. A number of approaches failed to explain the peculiar permeation behavior of block copolymers. Siloxane-containing block copolymers exhibit microphase-separated structures[6,7] composed of microdomains of flexible siloxane segments and of rigid polyimide segments, though diblock copolymers in general do not undergo a macroscopic phase separation since two homopolymers are chemically combined in a diblock system. In the case of rigid−flexible block copolymers, the characteristics of both domains for gas permeation are of great difference. The permeation of gas molecules occurs favorably through microdomains of flexible segments, whereas rigid segments provide an obstacle to the permeation of gas molecules.

As yet, such transition behavior cannot be explained only by adopting diffusion mechanism in a heterogeneous media. Hence the effect of the morphology of two microphase-separated domains should be considered. Gas transport in block copolymer systems consisting of two or more phases would primarily depend on the type of each component and the magnitude of interactions within or between components, on the extent of incompatibility between chemical units in a mixture of homopolymers, and on the size of interphase regions. Although multiphase systems are commonly used as gas separation membranes, it is essential to the problem that the mechanisms of gas transport through multiphase copolymers are unsatisfactory and thus need more rigorous theories.

In applying the percolation theory to the present gas separation system, we assumed that a microphase-separated block randomly distributed in the matrix and could form a path with adjacent blocks. Therefore poly(amideimide) as a hard segment is less permeable to gases than silicone polymer as a soft segment, meaning that poly(amideimide) blocks could be assumed as impermeable sites. In the present study, a percolational approach was used to study the gas permeation behavior in block copolymers having very different permeabilities.

Experimental Section. Silicone-containing poly(amideimide)s (SPAI) used in the present study are a family of compounds that possess both a rubbery component and a glassy one. SPAI based on oligomeric dimethylsiloxane (ODMS, $M_n = 900$), **1**, 4,4′-oxydianiline (ODA), **2**, and trimellitic anhydride chloride (TMAC), **3**, was synthesized as previously reported.[8] The volume fraction of siloxane moiety was controlled to be less than 0.85, because SPAI having a siloxane content of greater than 0.85 could not form a film due to its intrinsically sticky property.



$H_2N\text{-}(CH_2)_3\text{-}(Si(Me)_2\text{-}O)_9\text{-}Si(Me)_2\text{-}(CH_2)_3\text{-}NH_2$

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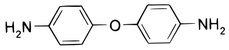

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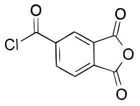

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Gas permeation behavior of SPAI obtained was studied in the present work. Gas permeabilities of oxygen and nitrogen were measured at room temperature by the vacuum method[9] using a membrane mount cell with an effective membrane area of 13.42 cm^2. A pressure transducer (Baratron 127AA10000B, 626A02-TBE, MKS Instrument Inc.) was employed to measure the change of pressures upstream and downstream as a function of time. A vacuum gauge with a type 146 controller (MKS Instrument Inc.) was used to control the pressure transducer. At a downstream position having constant volume V (78.27 cm^3), the time vs the increase of pressure at the permeating side was monitored every 3 s by a personnel computer through an RS-232 serial cable. When Fick's law is still valid, the diffusivity is

$$D = \frac{l^2}{6\theta} \qquad (1)$$

When a mixture of gases (1 and 2) is separated, the ideal separation factor (gas selectivity) for components 1 and 2 is defined as the ratio of permeability of each component as follows:

$$\alpha_{12} = \frac{P_1}{P_2} \qquad (2)$$

All the gas permeation experiments were performed more than three times and the reported values were the mean of at least three experiments. The standard deviation was within ca. ±5%.

Results and Discussion. The results of oxygen and nitrogen permeation through SPAI series membranes are shown in Figure 1. The volume fraction of siloxane was calculated by using the UNIFAC−FV method.[10] As expected, the permeability tended to increase with the volume fraction of siloxane in the poly(amideimide) matrix. This might be due to the fact that the flexibility of siloxane chains induces the increase in the gas permeability of the membrane. For all the samples

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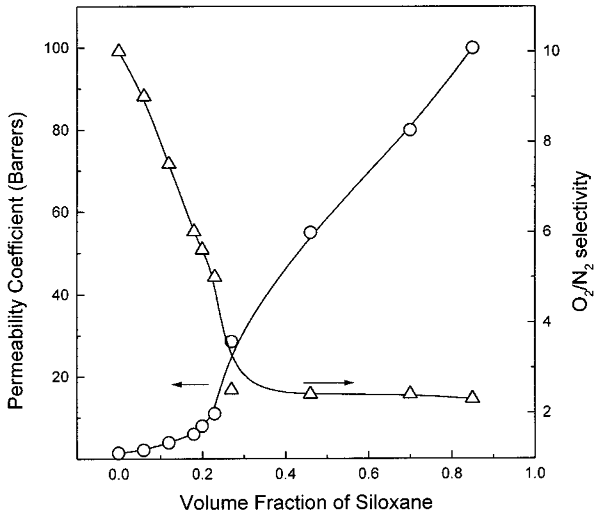

Figure 1. Gas permeability and oxygen/nitrogen selectivity vs volume fraction of siloxane.

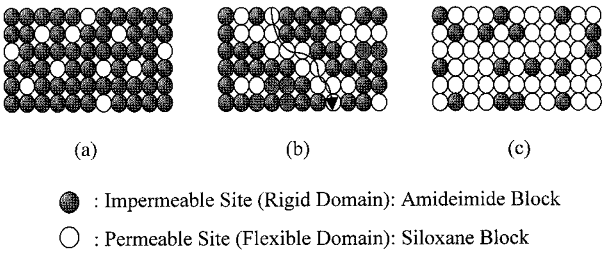

Figure 2. Ideal scheme of present percolating system: three categories of SPAI matrixes.

where siloxane was introduced, the selectivity decreased with an increase in the siloxane content as shown in Figure 1.

The addition of the siloxane moiety in the poly(amideimide) matrix probably increased the polymer free volume and disrupted its packing. This result can also be attributed to the flexibility of the introduced siloxane linkage, which affects the packing of the polymer chain. The flexibility tended to enlarge the gas pathway in a membrane and therefore resulted in a decrease of the oxygen/nitrogen selectivity (permeability ratio). As can be also seen in Figure 1, the oxygen permeability drastically increases at around 0.2 volume fraction of siloxane in a copolymer matrix.

SPAI matrixes can be divided into three categories as depicted in an ideal scheme of SPAI matrixes shown in Figure 2. The matrix in Figure 2a is mainly formed from the less permeable domain of a rigid amide–imide block. A small amount of a microphase-separated siloxane block also existed in this matrix. Since the volume fraction of the siloxane block is rather small, siloxane blocks could not be connected to each other. Therefore, permeability of matrix in this category is similar to that of the poly(amideimide). As the volume fraction of siloxane block in a matrix increases, the probability of block connection from top to bottom increases. In the case of the percolation model, fluids or currents cannot flow through the media until permeable or conductive clusters form an effective channel.[11] However, a small amount of gas permeates through poly(amideimide) domains before siloxane spanning. Most copolymers have $D_A/D_B \neq 0$,[12] where, D_A and D_B are the diffusivities of impermeable phase and permeable phase, respectively. However, the increase of gas permeability through the poly(amideimide) domain can be relatively negligible when compared with the increase of the gas permeability of flexible domains such as spanned siloxane.

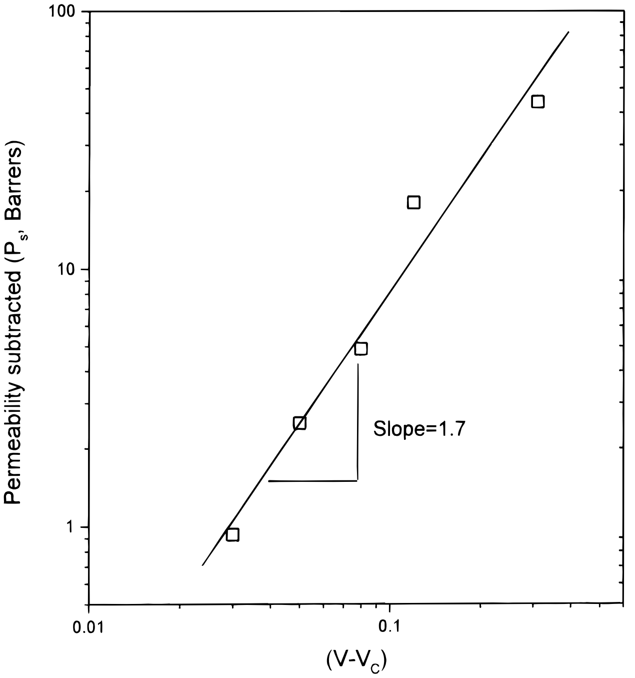

Figure 3. A log–log plot of permeability subtracted linear background vs the excess volume fraction of SPAI.

A matrix at threshold volume fraction started to form a connected path of siloxane block as shown in Figure 2b. Connected paths of the siloxane block caused a drastic enhancement of the permeability of the SPAI matrix. The gas permeability of SPAI increased exponentially with the volume fraction of siloxane block up to around the threshold content of siloxane. That is, the gas permeability is proportional to the probability that gas transport occurs through the spanning siloxane phase. Above the threshold volume fraction of siloxane, an increase in permeability is dominated by the contribution from the siloxane-rich phase.

An addition of flexible domains in the rigid matrix slightly increases the amounts of permeating gas, and thus the permeability of SPAI is proportional to the excess volume fraction ($V - V_c$) of siloxane moiety, where V is the siloxane volume fraction and V_c is the percolation threshold. To characterize the percolational factors of V_c and τ,[13] we subtracted a linear background term, P_b, extrapolated from the first three data point in Figure 1, from the measured permeability. The subtracted permeability ($P_s = P - P_b$) was fitted to the power law in the critical region, between 0.18 and 0.46 volume fraction of siloxane moiety, as follows:

$$P_s = P_0(V - V_c)^{\tau} \qquad (3)$$

Here P_s is the subtracted permeability of SPAI, P_0 is a constant prefactor and τ is a critical exponent. The exponent τ is a universal constant that depends on the dimensions only and is applicable to any percolation system regardless of its chemical, structural, and morphological properties. For a three-dimensional system, τ was reported to range between 1.5 and 2.0.[14] On the contrary, the percolation threshold depends on both dimensionality and the manner in which the two components are dispersed. Figure 3 plots the perme-

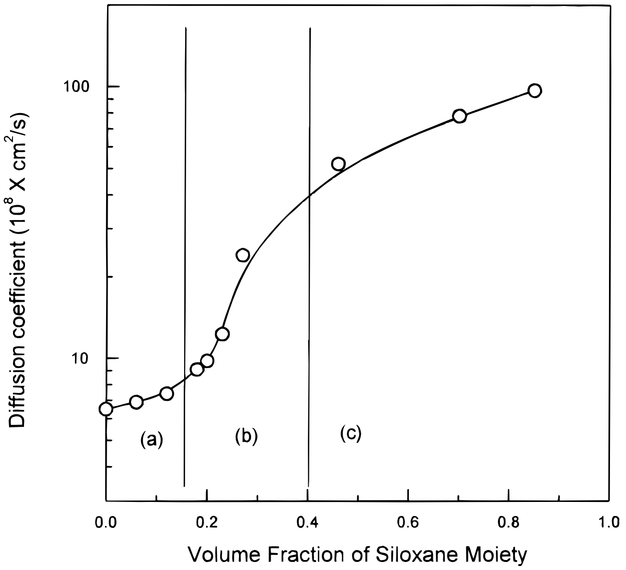

Figure 4. Change of diffusion coefficient with varying volume fraction of siloxane.

ability subtracted vs the excess volume fraction on a log−log scale. The slope was determined from a fit of eq 3 to our data points. When we determined these three parameters, the R value of result was 0.983. Least-squared regression yielded $V_c = 0.15$, $\tau = 1.7$, and $P_0 = 408.6$ Barrers, respectively. These percolation threshold and critical exponent is fairly consistent with the result reported.[15] For a three-dimensional random system, the theoretical value of percolation threshold (V_c) is reported as 0.15. The critical exponent for rubber to glassy transition of permeability ranges within the result reported.[15] This consistency indicates that the state of dispersion and particle shape for SPAI are similar to observations for ideal random dispersion of spheres in three dimensions.[16]

The percolation behavior of diffusion coefficient with varying the volume fraction of siloxane is shown in Figure 4. There are three regimes of interest in Figure 4. First, regime a does not show the transition of the diffusion coefficient. The siloxane block does not possess sufficient connection to propagate connectivity. In regime b, the transition of the diffusion coefficient could be observed. The origin of the transition is due to the increase of correlation length or cluster size of siloxane block. The connectivity of permeable domain is related to the diffusion coefficient of a random media composed of permeable domain and impermeable domain. Finally, there exist connected domains that traverse across the system in regime c. Because the composition of the main matrix changes to a siloxane block, we can see that the gas transport around this composition is dominated by the siloxane phase (flexible domain). On the other hand, the poly(amideimide) phase (rigid domain) will affect the flow line of gas permeation.

Our results show that the percolation model can elucidate the permeability transition phenomenon in a block copolymer. The percolative nature of the gas permeation through a siloxane-containing block copolymer was identified in the present study. The permeability of SPAI obeys a simple power law above and near the percolation threshold.

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References and Notes

(1) Yilgor, I.; Riffle, J. S.; McGrath, J. E. *In Reactive Oligomers*; Harris, F. W., Spinelli, H. J., Eds.; Acs Symposium Series 282; American Chemical Society: Washington, DC, 1985.
(2) Noshay, A.; McGrath, J. E. *In Block Copolymers: Overview and Critical Survey*, Academic Press: New York, 1977.
(3) Ibemesi, J.; Grozdic, N.; Keumin, M.; Lynch, M. J.; Meier, D. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26* (2), 18.
(4) Manson, J. A.; Sperling, L. H. *In Polymer Blends and Composites*; Plenum: New York, 1976.
(5) Stauffer, D.; Aharony, A. *In Introduction to Percolation Theory*; Taylor & Francis: London, Washington, DC, 1992.
(6) Arnold, C. A.; Summers, J. D.; Chen, Y. P.; Bott, R. H.; Chen. D.; McGrath, J. E. *Polymer* **1989**, *30*, 986.
(7) Spontak, R. J.; Sameseth, J. E. *Polym. J.* **1991**, *27*, 109.
(8) Ha, S. Y.; Oh, B.-K.; Lee, Y. M. *Polymer* **1995**, *36*, 3549.
(9) Choi, M. J.; Park, C. K.; Lee, Y. M. *J. Appl. Polym. Sci.* **1995**, *58*, 2373.
(10) Van Krevelen, D. W. *In Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1990.
(11) Kirkpatrick, S. *Rev. Mod. Phys.* **1973**, *45*, 574.
(12) Ferdinand, A.; Springer, J. *Morphology of Polymers, Proceedings of the 17th Europhysics Conference on Macromolecular Physics, Prague, Czechoslovakia, July 15−18, 1985*; Water de Gruyter: Berlin, New York, 1986.
(13) Hsu, W. Y.; Wu, S. *Polym. Eng. Sci.* **1993**, *33*, 293.
(14) Hsu, W. Y.; Barkely, J. R.; Meakin, P *Macromolecules* **1980**, *13*, 198.
(15) Webman, I.; Jortner, J.; Cohen, M. H. *Phys. Rev. B* **1977**, *16*, 2593.
(16) Cohen, M. H.; Jortner, J.; Webman, I. *Phys. Rev. B* **1978**, *17*, 4555.

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