일반강연 I -6

Percolation Approach to the Morphology of Rigid-Flexible Block Copolymer on Gas Permeability

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Polyimides and related polymers, when synthesized from aromatic monomers, have generally rigid chain structures resulting in a low gas permeability. The rigidity of polymer chains reduces the segmental motion of chains and works as a good barrier against gas transport. To overcome the limit of use as materials of gas separation membranes due to low gas permeability, block copolymers with the incorporation of flexible segments like siloxane linkage and ether linkage have been studied. These block copolymers have microphase-separated structures composed of microdomains of flexible poly(dimethylsiloxane) or polyether segments and of rigid polyimides segments. In case of rigid-flexible block copolymers, the characteristics of both phases for gas permeation are of great difference. The permeation of gas molecules occurs favorably through microdomains of flexible segments, whereas those of rigid segments hinder the permeation of gas molecules. Accordingly the increase of content of flexible segments in a rigid polymer matrix will increase the gas permeability of the membrane linearly. However, this prediction does not satisfy enough many experimental results and in particular the drastic increase of the permeability is observed in a certain volume fraction. It was proposed that the gas transport mechanism is dominated by diffusion rather than gas solubility in a certain content of flexible phase if solution-diffusion mechanism is adopted. However, the transition from solubility-dependent to diffusion-dependent cannot be explained by the understanding of mechanism itself. Therefore, we consider an effective chemical path which permeable phase can form in a microheterogenous medium, and percolation concept is introduced to describe the permeability transition at near threshold where for the first time a percolation path occurs.

The volume fraction of both phases is defined as V_α and V_β in block copolymers, and the volume of β phase in the threshold forming geometrically a traversing channel is defined as $V_{\beta c}$. The formation mechanism of shortest chemical channel is schematically depicted in Fig. 1. At the volume fraction lower than threshold, the system is a stable state as α rich phase and thus the existence of dispersed β phase cannot give significant changes to the total system. In above case where α phase is a continuous phase and permeable β phase is a dispersed phase, the effective permeability coefficient of block copolymers depends on only the magnitude of mean cluster size or correlation length of β phase. At near the volume fraction of threshold, the connectivity of β phase can be effectively achieved and at the same time the system exists as intermediate state. Hence gas molecules permeate along with a favorable channel of β phase. At near threshold, the permeability coefficient of block copolymers P is expressed as a function of V_β and it obey a power law as follows

$$P(V_\beta) \propto (V_\beta - V_{\beta c})^t$$

where the critical exponent t is univeral value and depends only dimension, and threshold value $V_{\beta c}$ depends on both dimension of system and its morphologies. Above threshold, the system is stable as β rich phase and gas permeability is proportional to percolation probability that permeable phase belongs to a spanning β phase.

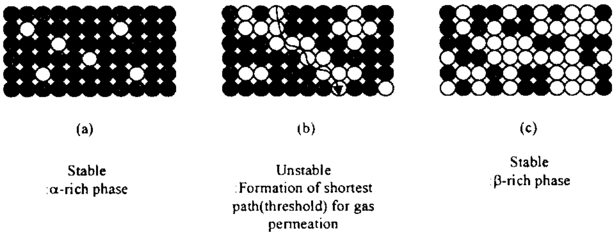

Fig. 1

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