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MOLECULAR MOTION-PERMEABILITY RELATIONSHIPS IN POLYCARBONATE/LIQUID CRYSTAL (EBBA) COMPOSITE MEMBRANE

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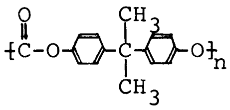
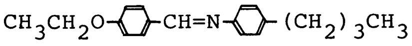
The diffusive permeability coefficient to water for the polymer/EBBA composite membrane reveals a distinct jump in the vicinity of the crystal-liquid crystal phase transition temperature of EBBA. The permeability coefficients to hydrocarbon gases increase 100∿200 times over several degrees in the phase transition temperature range.

The permeation of gas and liquid through polymer films has been studied in consideration of chemical structure, aggregated state, thermal motion of molecular chains$^{1,2)}$ and so on. The effect of the thermal molecular motion for permeation characteristics is an interesting problem from a stand point of the diffusion behaviour of permeable molecules. In the previous papers$^{3)}$, the relationship between permeability of water and the thermal molecular motion of poly(γ-methyl L-glutamate) films was reported, that is, permeability to water abruptly increased at the temperature range of the primary relaxation process of the membrane polymer. In this paper, thermal molecular motion-permeability relationship was studied for the composite membrane of the polymer/liquid crystal system. We found the discontinuous jump on permeability to water or gases in the vicinity of the transition temperature from crystalline to mesophase structure.

Polymer/liquid crystal composite membranes were cast from tetrahydrofuran or dichloroethane solutions of polycarbonate (PC) and N-(4-ethoxybenzylidene 4'-n-butylaniline)(EBBA), of which chemical structures are mentioned below.



polycarbonate (PC)



N-(4-ethoxybenzylidene-4'-n-butylaniline)
(EBBA)

The PC/EBBA composite membranes contain EBBA of 15, 30, 45 and 60 wt%. These cast films were dried in vacuo at about 333 K for 3 days. Two endothermic peaks due to crystal-nematic phase transition (304 K) and nematic-isotropic phase one (355 K) were apparently observed for the PC/EBBA composite membranes in the case of EBBA fraction above 45 and 60 wt%. On the basis of DSC and the wide angle X-ray measurements, fairly homogeneous dispersion of EBBA was confirmed for the 15 wt% EBBA blend film, while existence of EBBA crystal domains for the 45 and 60 wt% EBBA blend films$^{4)}$.

1. Water Permeation of PC/EBBA Composite Membrane

The pervaporation system reported by Hung and Lin$^{5)}$ was refered to the apparatus for the measurement of the hydraulic permeability of water. The permeation cell was maintained in a water bath regulated by a temperature controller.

Figure 1 shows the Arrhenius plot of the diffusive permeability coefficients (P) for the PC and the PC/EBBA composite membranes. The diffusive permeability coefficient was calculated from the hydraulic permeability coefficient (K) determined in a temperature range of 273-333 K. P was calculated through the equation of K=PV/RT, where V is the molar volume of water, R is the gas constant and T is absolute temperature, respectively$^{6)}$. The log P -1/T plots for the 45 and 60 wt% EBBA composite membranes reveal a distinct jump at about 304 K corresponding to the crystalline-nematic phase transition temperature. The magnitude of P increases by about two and half times within an interval of a few degrees in the vicinity of the phase transition temperature. This striking increase of P may be arised from the results that the transition of EBBA from crystal to nematic phases induces activation of the thermal molecular motion of PC and/or increase of vacancy fraction around the domain boundary of EBBA. Indeed, these behaviours make the flux of water increased remarkably. This apparently indicates that the temperature dependence of P is in close relation to the thermal molecular motion of the components composing the membrane. The thermo-mechanical measurement was carried out in a home-made water bath after the permeation tests$^{3)}$. The sharp tan δ peak appears at about 300 K for the 60 wt% EBBA composite membranes. This tan δ peak associates with the onset of the molecular motion induced by the phase transition of EBBA domain in the composite membrane. On the other hand, the tan δ peak was not observed for PC film, which is in accord with the DSC result. The PC film does not exhibit a discontinuous variation of P in the temperature range studied here. This result is in accord with the thermal behaviour detected by DSC measurement or the thermo-mechanical analysis.

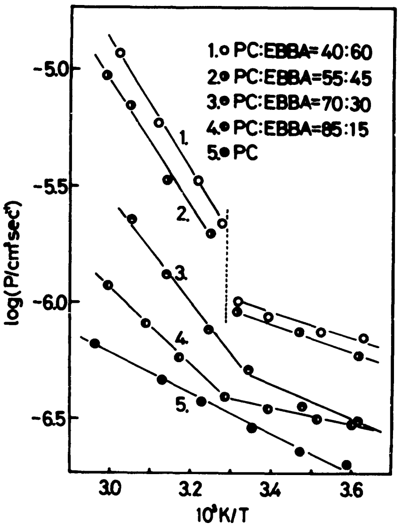


Figure 1. Arrhenius plot of diffusive permeability coefficient to water.

2. Permeability of PC/EBBA Composite Membrane to Gases

The permeability and the diffusion constants of gases were measured by the volumetric method (the high vacuum method) originally developed by Barrer$^{7)}$. Figure 2 shows the Arrhenius plot of the permeability coeffecients of methane, propane and butane for the PC/EBBA composite membrane containing EBBA of 45 wt% (the 45 wt% EBBA composite membrane). The drastic jump or the slope change on log P vs. 1/T plot for the 45 wt% EBBA composite membrane suggests a change in the mechanism of the permeation of hydrocarbon gases across the crystal-nematic liquid crystal phase

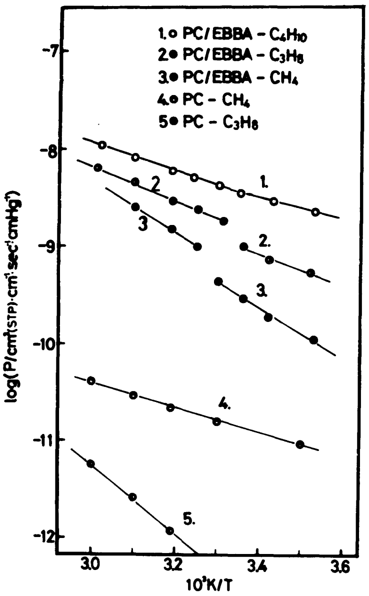


Figure 2. Arrhenius plot of P to hydrocarbon gases for 45 wt% EBBA composite membrane.

transition temperature of EBBA. The slope of log P vs. 1/T for the PC membrane remains constant in the temperature range studied here, corresponding to absence of any thermal transition. In the case of the PC membrane, the magnitude of P to CH_4 is bigger than that to C_3H_8. On the other hand, the magnitudes of P decrease in reverse order of the number of carbon atom, that is, P to C_4H_{10} is much higher than that to CH_4. These opposite tendencies on P of the PC and the PC/EBBA composite membranes should be discussed in terms of the diffusion and the solubility coefficients, D and S. If the permeation characteristics are controlled by the solubility and diffusion processes in the case of the homogeneous membrane without holes as well as validity of Fick's and Henry's laws, the following relationship among P, D and S should be hold.

$$P = SD \tag{1}$$

Figure 3 presents the Arrhenius plot of the diffusion coefficient, D to CH_4 and C_3H_8 for the PC and the PC/EBBA composite membranes. The magnitude of D is calculated by the equation.

$$D = l^2/6\tau \tag{2}$$

where τ is the time lag, i.e., the intercept on the time axis of the experimental pressure-time plot and l is the thickness of the membrane. In the case of the PC membrane, D to CH_4 shows a value two to seven times as much as that to C_3H_8. In the case of the PC/EBBA composite membrane, the log D vs. 1/T plot exhibits the discontinuous change in the vicinity of the crystal-nematic transition temperature of EBBA and also, the magnitudes of D to CH_4 and C_3H_8 are comparable each other. There have been generally recognized that the magnitude of D decreases with increase of the reduced molecular diameter of the penetrants[8]. If assumptions for equation (1) shoud be held, the solubility coefficient, S can be estimated from the results shown in figures 2 and 3 using equation (1). The magnitude of S to C_3H_8 for the 45 wt% EBBA composite membrane is about three times as large as that to CH_4, while S to CH_4 and C_3H_8 for the PC membrane are almost the same in magnitude. Therefore, it may be explained by the solubility factor that the magnitude of P for the composite membrane decreases with increase of the hydrocarbon chain length. Also, it is apparent that the crystal to nematic liquid crystal phase transition induces discontinuous increases of the permeability, diffusion and solubility coefficients. The relative magnitudes of P, D and S may indicate that the permeation of the PC membrane to hydrocarbon gases is presumably controlled by diffusion process and that of the PC/EBBA composite membrane by solubility process.

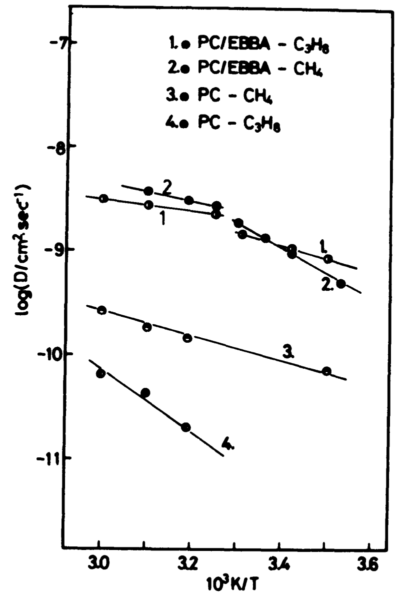


Figure 3. Arrhenius plot of D to hydrocarbon gases for 45 wt% EBBA composite membrane.

Figure 4 exhibits the Arrhenius plot of P to He gas and various hydrocarbon gases for the 60 wt% EBBA composite membrane. The prominent jumps of P to these gases were observed in the vicinity of the phase transition temperature, that is, P to hydrocarbon gases increases by approximately 100 to 200 times over several degrees in the phase transition temperature range of EBBA. Inasmuch as He gas is inert and then, the solubility property may not change over the temperature range of the phase transition, the discontinuous increase of P to He gas may be attributed to the drastic increase on the diffusion coefficient. This tendency may arise from increase of the pore formation of which probability may be enhanced by the existence of a dynamic phase equilibrium within EBBA domain going from the crystal to the liquid crystalline state or vice versa. The dynamic phase equilibrium means coexistence of solid and liquid crystalline phases with respect to time and position during the period of phase transition. The magnitudes of P increase in the order of i-C_4H_{10}, C_3H_8, n-C_4H_{10} and CH_4 in the temperature range below the phase transition of EBBA, while those do in the order of CH_4, C_3H_8, i-C_4H_{10} and n-C_4H_{10} in the temperature range above the phase transition. Except for n-C_4H_{10}, the magnitudes of P to CH_4, C_3H_8 and i-C_4H_{10} are reversed across the phase transition temperature. In other words, below the phase transition temperature, P decreases with increasing the number of carbon atom except n-C_4H_{10} and this trend suggests that the permeability is predominantly governed by the diffusion process. On the other hand, above the phase transition temperature of EBBA, P increases with increase of the number of carbon atom. Generally speaking, this tendency can not be explained by the diffusion control mechanism but it is reasonably expected that the permeability is mainly governed by the solubility process. It is very interesting that the permeability property of hydrocarbon gases changes across the temperature range of the crystal-liquid crystal phase transition of EBBA. Though there is disagreement in the results shown in figures 2 and 4 with respect to the relationship between the magnitudes of P and the number of hydrocarbon atom in the temperature range below the phase transition, it is apparent that the solubility process of hydrocarbon gases into the PC/EBBA composite membrane is one of the important factors for the permeability, especially in the temperature range above the crystal-liquid crystal phase transition temperature.

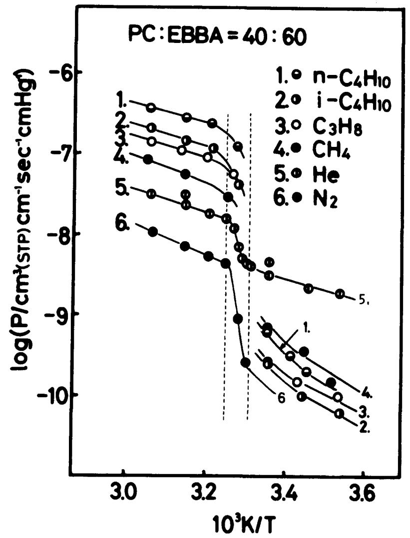


Figure 4. Arrhenius plot of P to hydrocarbon gases for 60 wt% EBBA composite membrane.

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