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MOLECULAR FILTRATION OF HYDROCARBON ISOMERS THROUGH POLYMER/(LIQUID CRYSTAL) COMPOSITE MEMBRANES

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ABSTRACT

Ultrathin membranes of a polymer/(liquid crystal) mixture were prepared by spreading a single drop of a casting solution on the water surface. The thickness and the aggregation state of the water-cast membrane can be controlled by the kind of solvent and the concentration of the solution. In the case of a liquid crystalline state above the crystal-nematic phase transition temperature, T_{KN} , the polymer/(liquid crystal) composite membrane follows Henry's law for the sorption isotherm of hydrocarbon gases and, also, Fickian sorption for the sorption-desorption kinetics. These results indicate that hydrocarbon gases permeate through a homogeneous medium composed of liquid crystalline molecules. Therefore, the permeability coefficients of hydrocarbon gases can be controlled by the dimensions of the channels through which the gas molecules diffuse. The channel for diffusion is generated by thermal or fluctuating molecular motion which opens up the intermolecular distance between liquid crystalline molecules. In the case of a self-supported liquid crystalline membrane, the channel dimension can be controlled in the range of several Å by both the intermolecular distance and the degree of thermal molecular motion of the liquid crystalline molecules. Separation of hydro-

carbon isomers was investigated by use of composite membranes composed of a polymer matrix and self-supported liquid crystalline molecules.

INTRODUCTION

The permeation process of low molecular substances through a homogeneous and nonporous polymeric membrane can be explained by a solution-diffusion mechanism. The solution characteristics depend on the affinity of the membrane to the permeant molecule, which serves as the controlling factor to govern permselectivity. The diffusion process is influenced by the thermal molecular motion of the polymeric chains, that is, the amount of free volume or the size of the penetrant molecules.

Recently, functional characteristics of liquid crystals have been studied in many fields because of their unique orientations or hydrodynamic properties. The orientation of nematic liquid crystals is easily controlled by electric and magnetic fields. When liquid crystals have positive dielectric anisotropy, their molecular axes easily orient along the direction of an imposed electric field. Also, the nematic liquid crystalline phase exhibits very low viscosity, comparable to that of water or organic solvents. The unique orientation behavior and the hydrodynamic properties of nematic liquid crystals can be applied to permselectivity when the nematic liquid crystalline phase is the main phase for diffusion. The author has reported the novel polymer/(liquid crystal) composite membranes as functional permselective membranes [1-13].

When hydrocarbon gases diffuse through the membrane, their longer molecular axes align in the diffusing direction. Under such circumstances the diffusion resistance (or friction) to hydrocarbon gases is strongly influenced by the magnitude of the cross-sectional dimension normal to the main axes, as illustrated in Fig. 1 [14, 15]. Since the effective cross-sectional dimensions (diameters) of *n*-, iso-, and neo-hydrocarbon isomers are 0.49, 0.56, and 0.62 nm, respectively, it is generally difficult to separate hydrocarbon isomers by ordinary synthetic membranes, due to the inability to control the cross-sectional dimensions of the free volume or channel to within several Å.

The orientation of liquid crystalline molecules has a direct effect on the permselectivity of hydrocarbon isomers on the basis of the path length for diffusion and the distribution of molecular channel dimension, as illustrated in Fig. 2. In the case of a well-oriented state of liquid crystalline molecules, the permeant gases can diffuse along a quite straight path, resulting in a greater flux. Since hydrocarbon isomers permeate through intermolecular

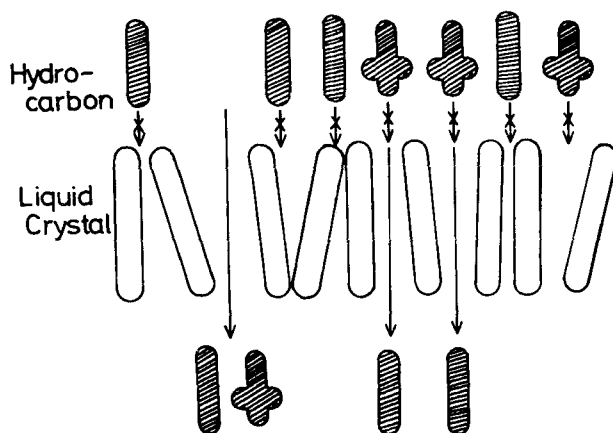


FIG. 1. Illustration of the permselectivity for isomers with different cross-sectional areas.

channels in the liquid crystalline phase for the polymer/(liquid crystal) composite membrane, it is expected that hydrocarbon isomers can be effectively separated through a liquid crystalline medium in which the intermolecular channel dimensions can be controlled within several Å with a narrow distribution. We have reported the voltage dependence of the permeation of

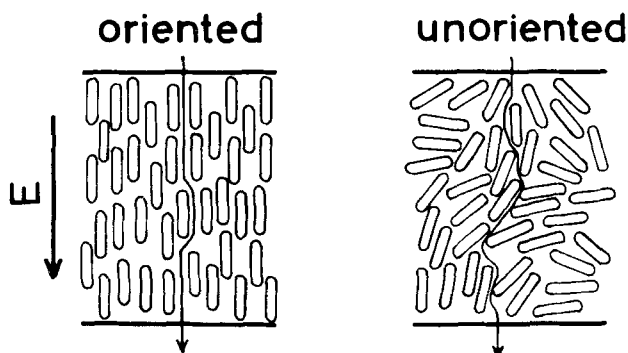


FIG. 2. Schematic representation of the path for diffusion of permeant molecules in the oriented and unoriented composite membranes.

n -C₄H₁₀ and iso-C₄H₁₀ through the polymer/(liquid crystal) composite membrane [16].

In this paper the relationship between the degree of orientation of liquid crystalline molecules or their intermolecular channel dimensions and permeation characteristics to hydrocarbon isomers is discussed for the polymer/(liquid crystal) composite membranes.

EXPERIMENTAL

Figure 3 shows the chemical structures of polycarbonate (PC) and poly(vinyl chloride) (PVC) as a matrix polymer, and *N*-(4-ethoxybenzylidene)-4'-butylaniline (EBBA), 4-cyano-4'-pentylbiphenyl (CPB), 4-cyano-4'-heptyloxybiphenyl (CHOB), and 2-sub.-1,4-bis(4-*n*-phenylbenzoyloxy)benzene (X-BPBB) as nematic liquid crystalline materials. T_{KN} for $K \rightarrow N$ and T_{NI} for $N \rightarrow I$ are the phase transition temperatures from crystal to nematic and from nematic to isotropic, respectively. The substituent X of X-BPBB was H, methyl (Me), Cl, Br, and *t*-butyl (*t*-Bu). Wide-angle x-ray diffraction (WAXD) measurements were accomplished in order to measure the average distance between liquid crystalline molecules in a nematic state and their orientations.

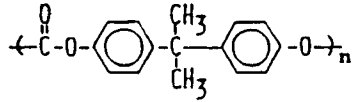
The PC/EBBA (40/60 wt/wt), and PVC/CPB (40/60) or PVC/CHOB (30/70) composite membranes were cast from a tetrahydrofuran or a 1,2-dichloroethane solution, respectively. The self-supported oriented liquid crystalline membrane was prepared from a 1,2-dichloroethane solution of the mixed phase of PVC and CHOB by using a homemade casting apparatus with a pair of attached electrodes [17]. When an electric field is applied during evaporation of solvent, CHOB molecules orient preferentially along the direction of the imposed electric field due to their positive dielectric anisotropy [14].

The PVC/X-BPBB composite thin films were prepared by carefully spreading a single drop of a solution of the mixed phase of PVC and X-BPBB on the water surface. After a considerable amount of solvent had evaporated, the composite membrane was left floating on the water surface. The weight ratios of PVC/X-BPBB and THF/toluene were 20/80 and 40/60, respectively. The thickness of the membrane spread on the water surface was about 100 nm. Ten layers of the membrane were built up to form a thin film on a porous Teflon membrane.

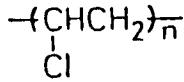
The permeabilities of butane isomers (*n*- and iso-C₄H₁₀), pentane isomers (*n*- and iso-C₅H₁₂), and hexane isomers (*n*-, iso-, and neo-C₆H₁₄) through the composite membranes were measured by a volumetric method [2-5]. A pair

(a) POLYMER

- 1) Polycarbonate(PC)

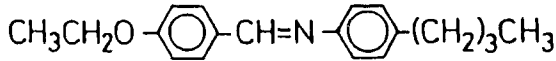


- 2) Poly(vinyl chloride)(PVC)



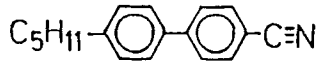
(b) LIQUID CRYSTAL

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



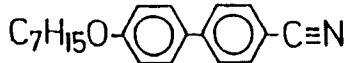
K → N 304K, N → I 355K

- 2) 4-cyano-4'-pentyl biphenyl(CPB)



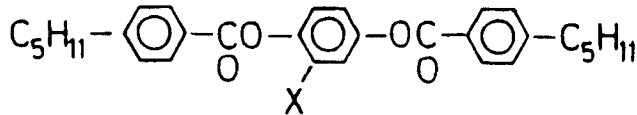
K → N 296K, N → I 308K

- 3) 4-cyano-4'-heptyloxy biphenyl(CHOB)



K → N 325K, N → I 344K, Δε = +12 (323K)

- 4) 2-Sub.-1,4-bis-(4-n-pentylbenzoyloxy)-benzene(X-BPBB)



X = H Me Cl Br t-Bu

T_{KN}/K 398 353 354 344 (316)

T_{NI}/K 459 416 415 387 (328)

FIG. 3. Chemical structures of polymers and liquid crystals.

of electrodes was placed in the permeation cell, and an electric field was applied perpendicular to the membrane surface during measurements of gas permeation in order to maintain orientation of liquid crystalline molecules above T_{KN} in the oriented PVC/CPB or PVC/CHOB composite membranes. The distance between the electrodes was 5 mm. The magnitude of the diffusion coefficient D was calculated from the time lag, as described by $D = l^2/6\tau$, where τ is the time lag and l is the thickness of the thin film.

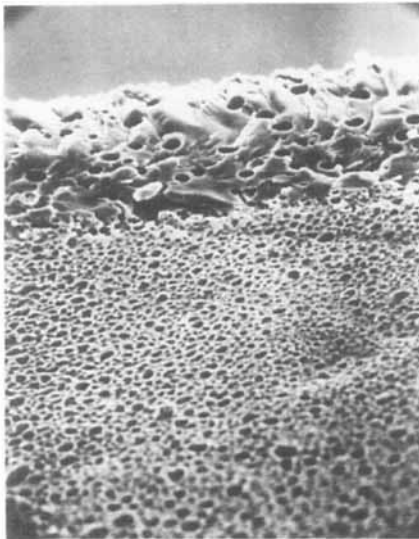
RESULTS AND DISCUSSION

Aggregation Structure of Self-Supported Liquid Crystalline Membranes

Figure 4 shows scanning electron micrographs of the fracture and the membrane surfaces for the PVC/CHOB (30/70) composite membrane which was prepared without and with an electric field after extraction of CHOB with hot ethanol. Figure 4 indicates that the PVC matrix forms spongy aggregation structures in both the random ($E = 0$ V/cm) and the oriented ($E = 2350$ V/cm) self-supported liquid crystalline membranes. Since about 95 wt% of the originally existing CHOB molecules was easily extracted from the composite membrane with hot ethanol, it is evident that the CHOB molecules form domains as an interpenetrating continuous phase within the polymer matrix. Therefore, it seems reasonable to assume that a continuous CHOB phase contributes the main diffusion region for hydrocarbon isomers, based on the sorption characteristics of gases, such as sorption isotherms or sorption-desorption experiments, which will be explained later.

Also, the aggregation state of the components in the composite membrane was investigated on the basis of the equilibrium sorption characteristics of gases. Figure 5 shows the sorption isotherms for CH_4 , C_3H_8 , and C_4H_{10} in the PC/EBBA (40/60) composite membrane above and below T_{KN} of EBBA. The validity of Henry's law with respect to the sorption isotherm of these hydrocarbon gases below T_{KN} is doubtful, but above T_{KN} it obeys the law. Calculated values of the solubility coefficients to CH_4 , C_3H_8 , and C_4H_{10} in the composite membrane are 0.0169, 0.0462, and $0.126 \text{ cm}^3 (\text{STP})/(\text{cm}^3 \cdot \text{cmHg})$, respectively. Therefore, the solubility increases with the length of the hydrocarbon chain.

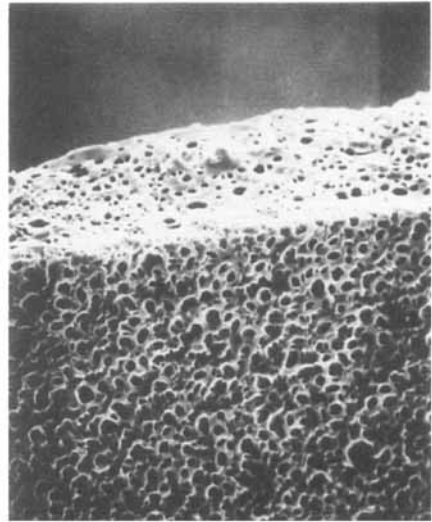
Figure 6 shows the sorption-desorption curves for CH_4 in the 40/60 composite membrane. Here, $M(t)$ is the quantity of penetrant which has entered or left the membrane in time t , and $M(\infty)$ is the corresponding quantity at infinite time, i.e., when equilibrium has been reached between sorption and de-



50 μm

$E = 0 \text{ V/cm}$

(a)



50 μm

$E = 2350 \text{ V/cm}$

(b)

FIG. 4. Scanning electron micrographs of fracture surface (upper portion) and membrane surface (lower portion) of the PVC/CHOB (30/70) composite membrane after extracting CHOB with hot ethanol. The composite membranes were prepared without an imposed electric field (a) and with a 2350 V/cm field (b).

sorption. The linear relationship between $M(t)/M(\infty)$ and $t^{1/2}$ can be recognized in the early stage of the experiment at 332 K (above T_{KN}), and the shape of the experimental curve suggests that this system follows Fickian sorption [18]. Therefore, in the temperature range above T_{KN} , it is reasonable to consider that surface equilibrium is established immediately and that the diffusion coefficient of CH_4 is a function of the concentration only. Similar behavior has been observed for the polymer-organic vapor system in the rubbery state.

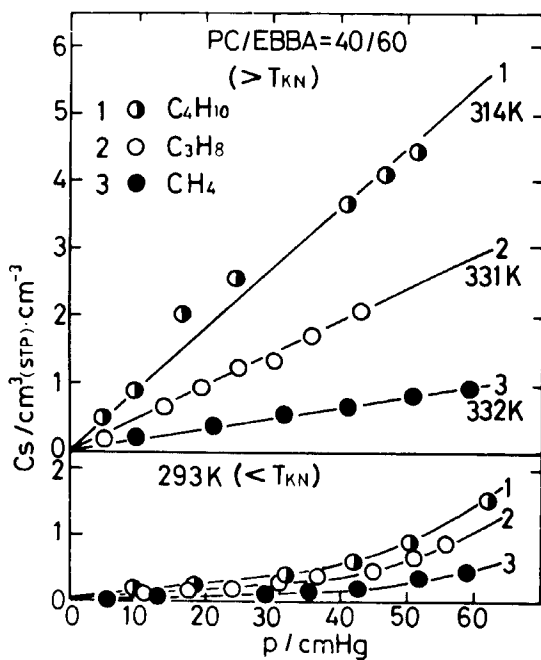


FIG. 5. Sorption isotherms for C_4H_{10} , C_3H_8 , and CH_4 in the PC/EBBA (40/60) composite membrane at 293 K (below T_{KN}) and 332 K (above T_{KN}).

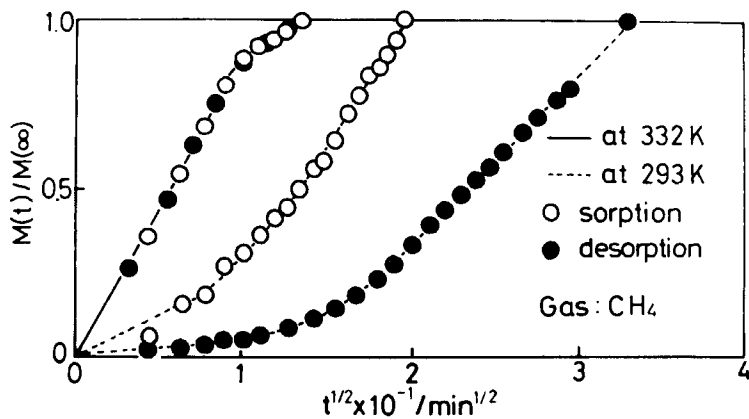


FIG. 6. Sorption-desorption curves for CH_4 in the PC/EBBA (40/60) composite membrane at 293 K (below T_{KN}) and 332 K (above T_{KN}).

These experiments apparently indicate that the polymer/(liquid crystal) (40/60) composite membrane can be considered as a homogeneous medium when considering gas permeation above T_{KN} . This means that permeating gases diffuse through the intermolecular channels between liquid crystalline molecules. Therefore, we can control the permeability for hydrocarbon isomers based on their diffusivity in passing through liquid crystalline domains. This principle can be used to design a molecular filtration membrane by using polymer/(liquid crystal) composite membranes.

Molecular Filtration through Self-Supported Liquid Crystalline Membrane Based on Orientation of Molecules

Figure 7 is wide-angle x-ray diffraction photographs of the PVC/CHOB (30/70) composite membranes prepared without and with an imposed electric field during evaporation of the solvent. When the oriented composite membrane ($E = 2350 \text{ V/cm}$) was placed as shown in Fig. 7 and an x-ray beam was passed parallel to the membrane surface (edge view), x-ray reflections corresponding to the length of a CHOB molecule or dimer were observed on the equator. The reflection at 2.16 nm corresponds to the length of a CHOB molecule and those at 3.51 and 2.94 nm to the length of the dimer. Figure 7 indicates that the CHOB molecular axes preferentially align perpendicular to the membrane surface during evaporation of solvent from a solution under an imposed electric field, in other words, parallel to the direction of an imposed electric field due to a positive dielectric anisotropy. The Fig. 7(c) photograph, taken after the permeation experiment under an imposed electric field of 50 000 V/cm perpendicular to the surface of the oriented composite membrane, demonstrates that orientation of CHOB molecules in the composite membrane was maintained even after the permeation experiment above T_{KN} .

Figure 8 shows an Arrhenius plot of the permeability coefficient P for C_5H_{12} in the oriented and the unoriented PVC/CHOB (30/70) composite membranes and also the permeability coefficient ratio, P_o/P_u of the oriented membrane to the unoriented one. It is apparent that P to C_5H_{12} for the oriented membrane is greater than that for the unoriented one. The magnitude of P increases and P_o/P_u decreases with increasing temperature. Similar tendencies were observed for iso- C_5H_{12} and neo- C_5H_{12} .

In the case of the unoriented composite membrane, the average channel dimension in the liquid crystalline domain must be greater than that for the oriented one because of a looser packing of liquid crystalline molecules, as illustrated in Fig. 2. This may lead one to expect that P for the unoriented

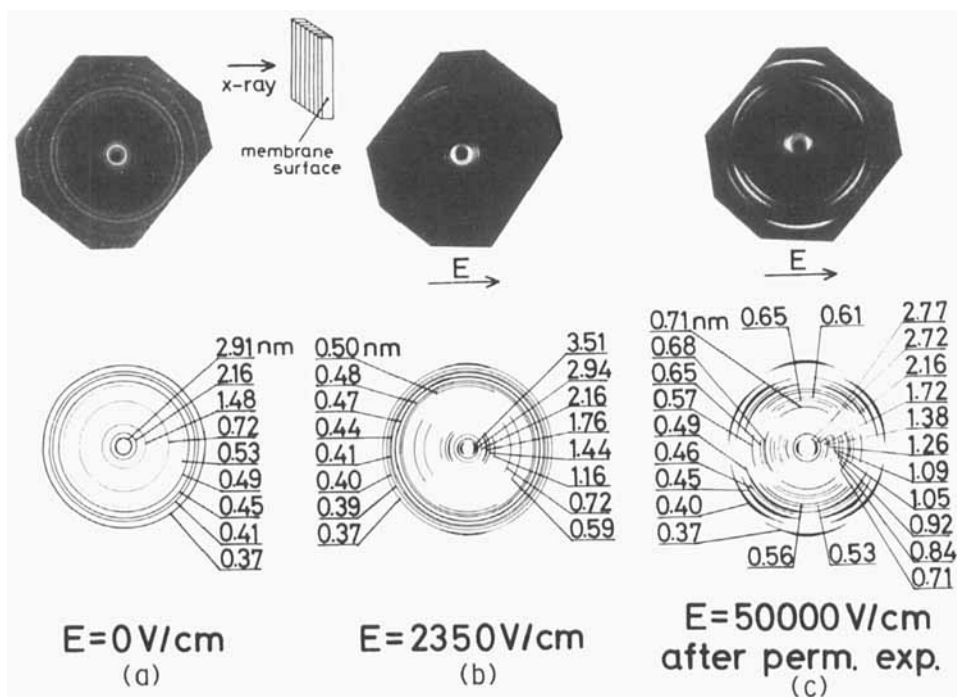


FIG. 7. Wide-angle x-ray diffraction patterns of the PVC/CHOB (30/70) composite membrane prepared without an imposed electric field (a) and with a 2350 V/cm field (b). The picture of (c) was taken after the permeation experiment under a field of 50 000 V/cm. The x-ray beam was directed along the sample surface (edge view).

membrane is greater than P for the oriented one. However, the experimental result is the reverse, as shown in Fig. 8. Consequently, the magnitude of P for the oriented and the unoriented composite membranes may be appreciably influenced by the different channel or path length required for diffusion through the composite membrane, as shown in Fig. 2. In other words, gas molecules diffuse along fairly straight paths through the oriented membrane but along tortuous paths through the unoriented one.

Since liquid crystalline molecules have a tendency to form liquid crystalline domains, molecular packing in these domains may be fairly tight even in the unoriented composite membrane. Therefore, the length of the diffusion path is more decisive for the permeability coefficient than for a loose molecular

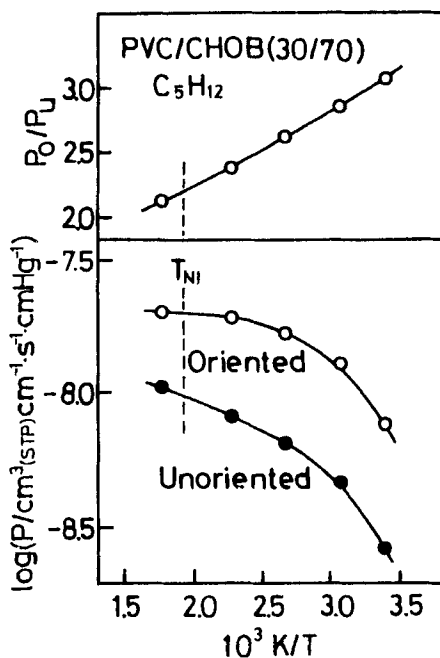


FIG. 8. Arrhenius plot of P to C_5H_{12} for the oriented and unoriented PVC/CHOB (30/70) composite membranes.

packing. The temperature dependence of P for the unoriented composite membrane is slightly more marked than that for the oriented one, as shown in Fig. 8. This may be because thermal molecular motion is more temperature-dependent in the unoriented state with looser molecular packing.

Figure 9 shows the Arrhenius plot of the permeability coefficient ratio P_o/P_u for the oriented and the unoriented composite membranes to C_5H_{12} and iso- C_5H_{12} . Since the effective cross-sectional dimension of C_5H_{12} (0.49 nm) is greater than that of iso- C_5H_{12} (0.56 nm), it is apparent that C_5H_{12} molecules can permeate faster than iso- C_5H_{12} through intermolecular channels between CHOB molecules. The effect of thermal fluctuation on the intermolecular distance of CHOB in the oriented composite membrane is less than that in the unoriented one since CHOB molecules in the former are packed more tightly or regularly than in the latter. Therefore, the distribution of the intermolecular channel dimension, as well as the intermolecular distance, must

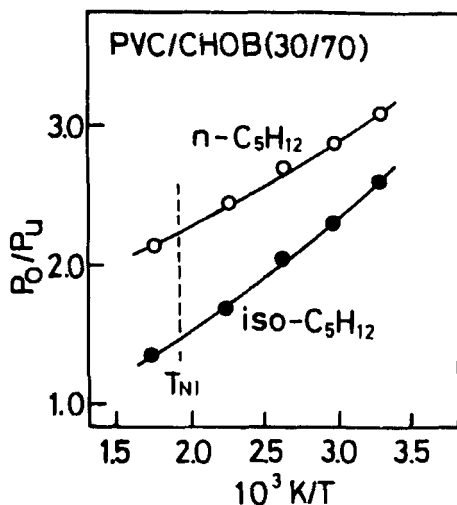


FIG. 9. Arrhenius plot of the permeability coefficient ratios of $n\text{-C}_5\text{H}_{12}$ and $iso\text{-C}_5\text{H}_{12}$ for the oriented and unoriented PVC/CHOB (30/70) composite membranes, respectively.

be narrower for the oriented composite membrane than for the unoriented one. Then, C_5H_{12} isomers can be more effectively or selectively separated by the oriented composite membrane than by the unoriented one, i.e., P_n/P_{iso} is higher for the oriented one than for the unoriented one. The inequality of P_n/P_{iso} for the oriented and the unoriented membranes suggests that P_o/P_u for $n\text{-C}_5\text{H}_{12}$ is greater than that for $iso\text{-C}_5\text{H}_{12}$, as shown in Fig. 9. Also, since the temperature dependence of P_{iso} for the unoriented composite membrane is larger than the other permeability coefficients (such as P_n , P_{iso} of the oriented one, and P_n of the unoriented one), the temperature dependence of P_o/P_u for $iso\text{-C}_5\text{H}_{12}$ is more marked than that for $n\text{-C}_5\text{H}_{12}$, as shown in Fig. 9.

We reported separation of C_4H_{10} and $iso\text{-C}_4\text{H}_{10}$ through the PVC/CPB (40/60) composite membrane. The permeation behavior on orientation of liquid crystalline molecules is similar to that of C_5H_{12} isomers mentioned above [17]. The diameters of C_4H_{10} (0.49 nm) and $iso\text{-C}_4\text{H}_{10}$ (0.56 nm) differ by only 0.07 nm. As the applied voltage was increased, the permeability to both C_4H_{10} and $iso\text{-C}_4\text{H}_{10}$ gradually increased. The permeability coefficient ratio of C_4H_{10} to $iso\text{-C}_4\text{H}_{10}$ at 0 V (unoriented aggregation of

liquid crystalline molecules) is 2 and increased to 5 at 730 V (oriented state). The increase of P with applied voltage is due to the formation of straight intermolecular paths in the oriented state. Also, the increase of P_n/P_{iso} with increasing applied voltage indicates that the size distribution of the intermolecular channel dimension becomes narrower due to more complete molecular orientation and tight packing perpendicular to the membrane surface. This result leads us to expect that a greater degree of orientation of liquid crystalline molecules promotes more effective separation of hydrocarbon isomers, even though their diameter difference is smaller than 1 Å.

Substituent Effect of Liquid Crystalline Molecules on Permeation Behavior of Hydrocarbon Isomers through Self-Supported Liquid-Crystalline Membranes

According to the WAXD pattern of X-BPBB in the liquid crystalline state, X-BPBB forms a cybotactic nematic aggregation [19]. The relationship between the transition temperatures of X-BPBB and the intermolecular distance d is shown in Fig. 10. The phase transition temperatures from crystal to ne-

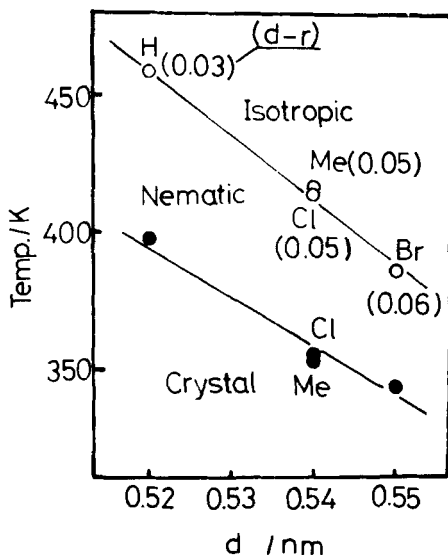


FIG. 10. Relationship between the transition temperature and the intermolecular distance, d , of X-BPBB.

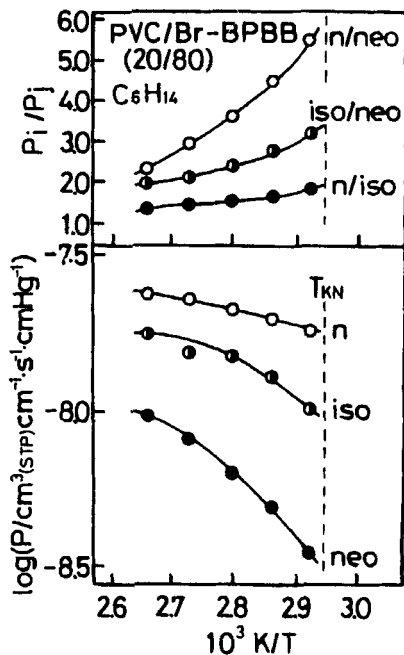


FIG. 11. Arrhenius plot of P to n -, iso-, and neo- C_6H_{14} and the permeability coefficient ratios among these isomers for the PVC/Br-BPBB (20/80) composite membrane.

matic (T_{KN}) and from nematic to isotropic (T_{NI}) decreased with increasing d due to reduction of the intermolecular interaction forces of X-BPBB.

Figure 11 is the Arrhenius plot of the permeability coefficients to n -, iso-, and neo- C_6H_{14} and the permeability coefficient ratios among these isomers through the PVC/Br-BPBB (20/80) composite thin film. Above T_{KN} of Br-BPBB P increased with decreasing cross-sectional size of the permeant molecules. This trend suggests that permeation is predominantly governed by the diffusion process. The variation of P with temperature increases in the order n -, iso-, and neo- C_6H_{14} because permeation of the larger molecule is markedly reduced at lower temperatures at which the free volume or the dimension of the channel becomes comparable to the dimensions of the permeant molecules. The permeability coefficient ratio of n - C_6H_{14} to neo- C_6H_{14} is the largest and that of n - C_6H_{14} to iso- C_6H_{14} the smallest, in correspondence to the differ-

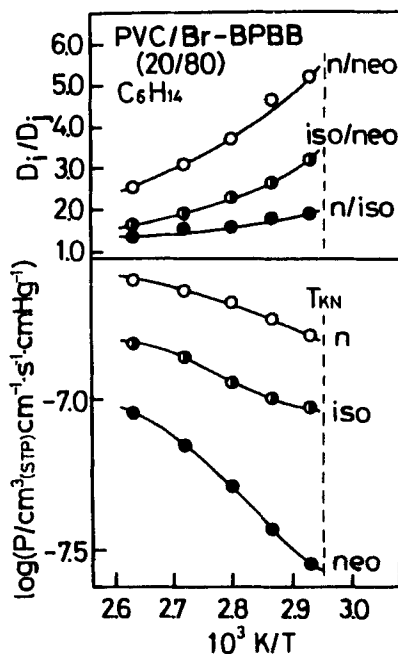


FIG. 12. Arrhenius plot of diffusivity to *n*-, iso-, and neo- C_6H_{14} and the diffusivity ratios among these isomers for the PVC/Br-BPBB (20/80) composite membrane.

ence of the cross-sectional dimensions of these two isomers. A similar permeation trend was observed for the composite thin films containing other X-BPBB's.

Figure 12 shows the Arrhenius plot of the diffusion coefficients D to *n*-, iso-, and neo- C_6H_{14} and the diffusion coefficient ratios among these isomers in the PVC/Br-BPBB (20/80) composite thin film. The temperature dependence of D for these isomers was similar to those of P . In the case of a dense membrane, P corresponds to the product of the solubility, S , and the diffusivity, D , i.e., $P = S \times D$. Therefore, S was evaluated as P/D . The solubility coefficients to *n*-, iso-, and neo- C_6H_{14} calculated from Figs. 11 and 12 are comparable to each other. This result indicates that the main contribution to separation of hydrocarbon isomers through the PVC/X-BPBB membranes arises from the diffusion process rather than from the solution characteristics. When the appropriate size of intermolecular channel for diffusion of gas is

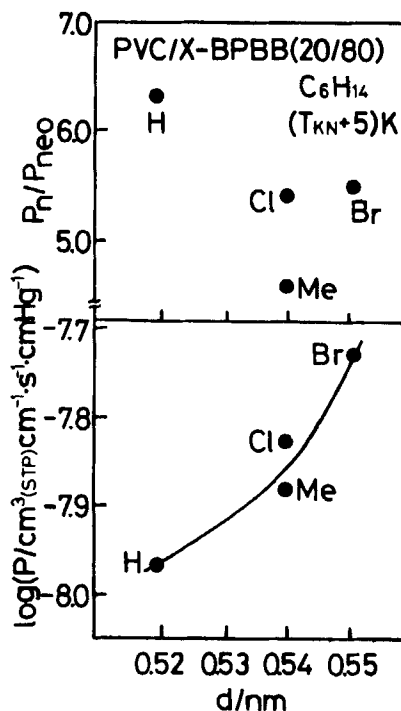


FIG. 13. A plot of P to $n\text{-C}_5\text{H}_{14}$ and the permeability coefficient ratio of $n\text{-C}_5\text{H}_{14}$ to neo- C_5H_{15} for the PVC/X-BPBB (20/80) composite membranes against the intermolecular distance on X-BPBB at $T_{KN} + 5$ K.

formed by thermal fluctuation of the liquid crystalline molecules in the composite thin film, gas molecules can diffuse in these channels. The larger penetrant isomers give a more marked temperature dependence of P and D than those for the smaller isomers since P and D for larger isomers are more strongly temperature dependent than those for smaller isomers when the molecular diameter of the permeant isomer is comparable to the size of the intermolecular channel. Figures 11 and 12 indicate that the PVC/(X-BPBB) composite thin film can be a candidate for a novel molecular filtration membrane.

Figure 13 shows the intermolecular distance dependence of P to $n\text{-C}_6\text{H}_{14}$ and the permeability coefficient ratio of n - to neo- C_6H_{14} for the PVC/X-BPBB (20/80) composite membrane at $(T_{KN} + 5)$. Since an increase in the

intermolecular distance induces an increase of the fraction of free volume or the channel dimension, both P and D of $n\text{-C}_6\text{H}_{10}$ increase with increasing intermolecular distance. However, there is no apparent correlation between the permeability coefficient ratio of $n\text{-C}_6\text{H}_{14}$ to neo- C_6H_{14} and the intermolecular distance of X-BPBB. Therefore, this is the subject for a future investigation of the relationships between permeation properties and the intermolecular distance by using liquid crystalline materials which have an intermolecular distance difference of several Å.

CONCLUSION

The permeability coefficients of hydrocarbon isomers can be controlled on the basis of the orientation of liquid crystalline molecules and the variation of the intermolecular distance. The permeability coefficient of the oriented PVC/(CHOB) composite membrane is greater than that of the un-oriented one due to the less tortuous path for diffusion in the oriented one. The PVC/X-BPBB membrane can separate hydrocarbon isomers, especially $n\text{-C}_6\text{H}_{14}$ and neo- C_6H_{14} . However, a clear correlation between the permselectivity of hydrocarbon isomers and the intermolecular distance of X-BPBB could not be found, even though the permeability coefficient ratio of $n\text{-C}_6\text{H}_{14}$ to neo- C_6H_{14} is quite large. The polymer/(liquid crystal) composite membrane is applicable for effective separation of hydrocarbon isomers as a molecular filtration membrane.

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