

Oxygen enrichment properties of a family of polymer composite membranes blended with a liquid crystal with dual-mesophase

Ziyong Y. Zhang*

Department of Polymer Materials Science and Engineering, South China University of Technology, Guangzhou 510641, People's Republic of China

and Shangan A. Lin

Institute of Polymer Science, Zhongshan University, Guangzhou 510275, People's Republic of China
 (Received 12 September 1995)

A family of polymer/liquid crystal (LC) composite membranes composed of poly(*cis*-butadiene) (PB) and diethylene glycol bis(4-(4'-ethoxybenzoyloxy)benzoate) (DEBEB) with smectic and nematic phase was prepared. The oxygen enrichment properties of the composite membranes were investigated. It was found that the relationship between permeability coefficient (P) and temperature (T) was characterized by N -shape P - T curves, that is, with increasing T , P first increased, followed by a decrease, then increased again. In addition, a composite membrane with less DEBEB content, such as 10 wt%, shows better oxygen permeabilities than those with more DEBEB content as well as a PB membrane at room temperature. The oxygen enrichment properties of the composite membrane for second measurement exhibits better results than the first measurement in a temperature range of the nematic phase of DEBEB. These phenomena were interpreted as the influence of the phase behaviour of DEBEB and the morphology of the composite membranes on the gas permeabilities. Copyright © 1996 Elsevier Science Ltd.

(Keywords: gas separation membrane; oxygen enrichment membrane; polymer/liquid crystal composite membrane)

Introduction

Kajiyama *et al.* reported the preparation of a polymer/liquid crystal (LC) composite membrane for gas separation¹⁻³. This composite membrane exhibited remarkably enhanced gas permeability coefficients when heated to a temperature above the LC phase. If a fluorocarbon compound with an excellent oxygen solubility, such as perfluorotributylamine, was added to the composite membrane, a remarkable increase in both oxygen permeability coefficients and O_2/N_2 separation factors occurred simultaneously⁴⁻⁶.

In all previous reports, only one distinct jump on the P - T curves in the vicinity of the phase transition temperature of the LC was observed¹⁻⁹. This is due to the fact that the LC compounds used are all nematic LC with one mesophase and of lower viscosity and higher fluidity at the temperature of the nematic phase, and the composite membrane actually becomes an immobilized liquid membrane. Therefore, the continuous pathways of gas molecules through the polymer matrix membrane were interpenetrated.

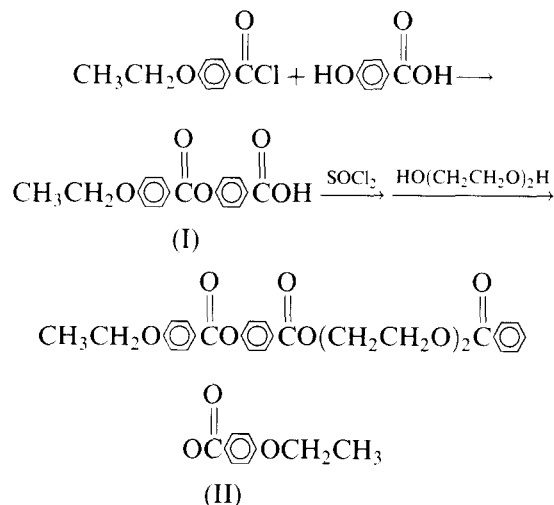
In order to evaluate the effect of the LC phase state on a permeability of a polymer/LC composite membrane, a new LC compound with smectic and nematic phases, diethylene glycol bis(4-(4'-ethoxybenzoyloxy)benzoate) (DEBEB), was synthesized and a family of composite membranes composed of poly(*cis*-butadiene) (PB) and DEBEB was prepared. The influence of temperature, the DEBEB content and a second measurement on oxygen enrichment properties of the PB/DEBEB composite membranes were investigated in this paper.

Experimental

Materials and synthesis. Poly(*cis*-butadiene) was obtained from Baling Oil Chemical Co. Its *cis*-1,4 content is 96% and the Mooney viscosity ($ML_{1+4}^{100^\circ C}$) is 45 ± 5 .

Disulfur dichloride (S_2Cl_2) was synthesized as described in the literature¹⁰.

Diethylene glycol bis(4-(4'-ethoxybenzoyloxy)benzoate) was synthesized according to the following sequence of reactions:



4-(4'-Ethoxybenzoyloxy) benzoic acid (I) was synthesized according to the method reported in the literature¹¹. Its phase transition order, $K 198^\circ C N > 300^\circ C$ (decomp.) I , is in agreement with the literature.

*To whom correspondence should be addressed

Diethylene glycol bis(4-(4'-ethoxybenzoyloxy)benzoate) (II): 0.022 mol (I) was added to ten times as much SOCl_2 . The mixture was refluxed until a clear solution was obtained. The excess SOCl_2 was removed by vacuum distillation. After cooling, the product was dissolved in dry chloroform. 0.01 mol diethylene glycol was dissolved in 0.08 mol pyridine. At room temperature the pyridine solution was added dropwise to the acid chloride solution with efficient stirring. The mixture was stirred for a further 4 h after the addition. Most solvent was removed by vacuum distillation and a small amount of THF was added. The solution formed was then poured into water with a little HCl. A white precipitate was filtered, washed with water, and dried. The product was recrystallized from toluene and washed with petroleum ether, yield 72%. Anal. Calcd.: C, 67.26; H, 5.33. Found: C, 67.18; H, 5.17. $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.47$ (m, CH_3 -), 3.97 (m, $-\text{CH}_2\text{O}-$), 4.18 (m, $\text{CH}_3\text{CH}_2\text{O}-$), 4.53 (m, COOCH_2-), 6.92, 7.30 and 8.14 (m, ArH).

The phase transition orders of (II) measured by a differential scanning calorimeter (DSC) and a polarizing light microscope are as follows:

$K 62^\circ\text{C} S 83^\circ\text{C} N 150^\circ\text{C} I$ (on first heating)

$K 50^\circ\text{C} S 80^\circ\text{C} N 150^\circ\text{C} I$ (on second heating after cooling).

Preparation of PB/DEBEB composite membranes. Several PB/DEBEB composite membranes of different weight ratio, designated 100/0, 90/10, 80/20, 60/40 and 50/50, respectively, were prepared by casting from a THF solution of PB and DEBEB on a glass plate. After solvent evaporation, the membrane coated plate was placed in a container with a small crucible of S_2Cl_2 and vulcanized at 40°C for 100 min utilizing S_2Cl_2 vapour. The resulting membrane was carefully removed from the glass plate by immersing the plate in a water bath and then drying in vacuum. A composite membrane with ca. $70 \mu\text{m}$ thickness was obtained.

Permeation and thermogram measurement. Oxygen and nitrogen permeability coefficients of the composite membranes for various temperatures were measured according to the variable-volume method of Stern *et al.*^{1,2} The permeability coefficient, P , can be calculated from the expression.

$$P = \frac{(\Delta v / \Delta t) \cdot l}{\Delta p \cdot A}$$

where Δv and Δt are the changes in volume of the permeated gas and time, A and l are the area and thickness of the membrane, respectively; Δp is the pressure difference across the membrane. P is usually corrected to standard conditions (STP) of temperature (273 K) and pressure (76 cm Hg).

The thermal behaviour of DEBEB LC, PB/DEBEB (90/10) composite membrane and PB membrane were measured by a differential scanning calorimeter (Shanghai CDR-1) at a heating rate of $10^\circ\text{C min}^{-1}$.

Results and discussion

Effect of temperature on oxygen enrichment properties. Figure 1 shows the effect of testing temperature on permeability coefficients (P_{O_2} , P_{N_2}) and separation factors ($\alpha_{\text{O}_2/\text{N}_2} = P_{\text{O}_2}/P_{\text{N}_2}$) for the PB/DEBEB (90/10) composite membrane. An examination of Figure 1 shows

that: (1) The relationship between the permeability coefficients and temperature is obviously characterized by *N*-shape curves, that is, with increasing temperature the P value first increases, followed by a decrease, and then increases again. (2) The temperatures of turning points on *N*-shape curves are the same, that is, the peak and valley values appear in the vicinity of 50°C and 70°C , respectively. (3) This composite membrane exhibits good oxygen enrichment properties at room temperature: such as P_{O_2} is about 55 barrer ($1 \text{ barrer} = 1 \times 10^{-10} \text{ cm}^3 (\text{STP}) \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$) and $\alpha_{\text{O}_2/\text{N}_2}$ is 3.22. (4) The separation factors decrease with increasing temperature. This conforms to the general rule of the influence of temperature on selectivities.

As a reference, a PB membrane without DEBEB LC was prepared and measured under the same conditions but no *N*-shape P - T curve was obtained. Its P_{O_2} and $\alpha_{\text{O}_2/\text{N}_2}$ at room temperature are 7.3 barrer and 2.81, respectively. By comparison, the P_{O_2} value of the PB/DEBEB (90/10) composite membrane is about seven times higher than that of the PB membrane. A possible cause is due to the aggregation and the dispersing state of the DEBEB molecules in the composite membrane. Figure 2 shows d.s.c. curves of the DEBEB LC, the PB/DEBEB (90/10) composite membrane and the PB membrane for the first and second heating scans. It can be seen that an endothermal peak exists, corresponding to the crystal-smectic phase transition temperature ($T_{\text{KS}} = 62^\circ\text{C}$) of the DEBEB, on the d.s.c. curve of the

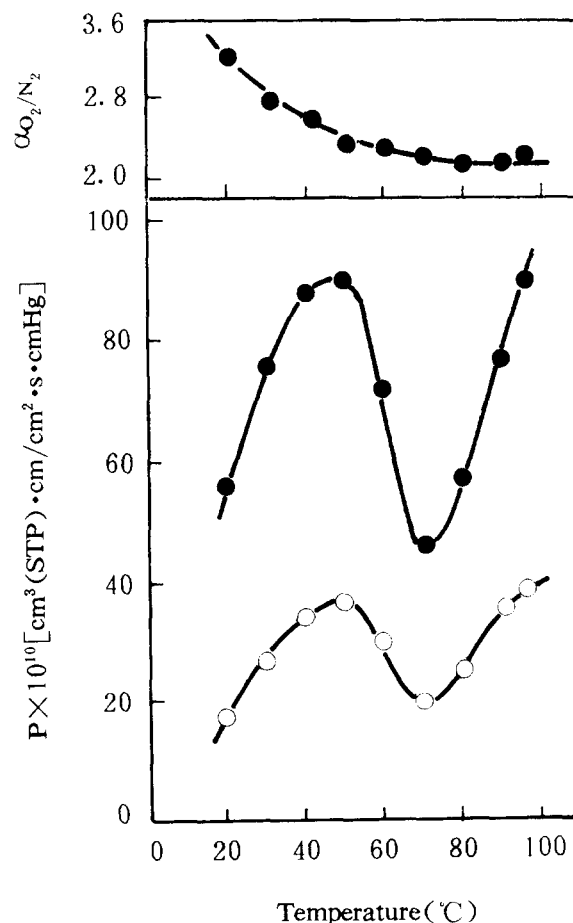


Figure 1 Effect of testing temperature on P_{O_2} (●), P_{N_2} (○) and $\alpha_{\text{O}_2/\text{N}_2}$ of PB/DEBEB (90/10) composite membrane

PB/DEBEB (90/10) composite membrane for the first heating scan. This thermal behaviour indicates that because of poor compatibility between the PB matrix and the DEBEB crystal, the DEBEB exists mainly in the composite membrane in a crystal domain state. It is suggested that microvoids possibly exist on interfaces between the PB matrix and the DEBEB crystal domains. The microvoids provide the penetration pathways of gas molecules through the composite membrane to enhance the permeability.

The cause of *N*-shape *P*-*T* curves can be explained by combination of this suggestion with the phase behaviour of the DEBEB. Because the starting temperature of T_{KS} of the DEBEB is about 50°C from the d.s.c. curve (a-1) in Figure 2, the influence of volume expansion of the DEBEB crystal domains on the microvoids is negligible below 50°C and the *P* value increases with increasing temperature. As the temperature rises to 50–70°C the DEBEB crystal domains begin to melt into the smectic phase and the expanded smectic melt also begins to plug up the microvoids. The process from the beginning melt to full transition of smectic phase is one in which the microvoids are gradually being plugged up. The temperature of the valley values, 70°C, on the curves in Figure 1 are in agreement with the end temperature of T_{KS} of the DEBEB shown in Figure 2. As a result, the *P* value decreases with increasing temperature in this temperature range. When the composite membrane is continuously heated to above 80°C the smectic phase of the DEBEB transits the nematic phase and the *P* value increases with increasing temperature again. In this range gas permeation behaviour is the same as the composite membranes containing nematic LC reported in the literature¹⁻⁹.

Effect of the DEBEB content on oxygen enrichment properties. Like the PB/DEBEB (90/10) composite

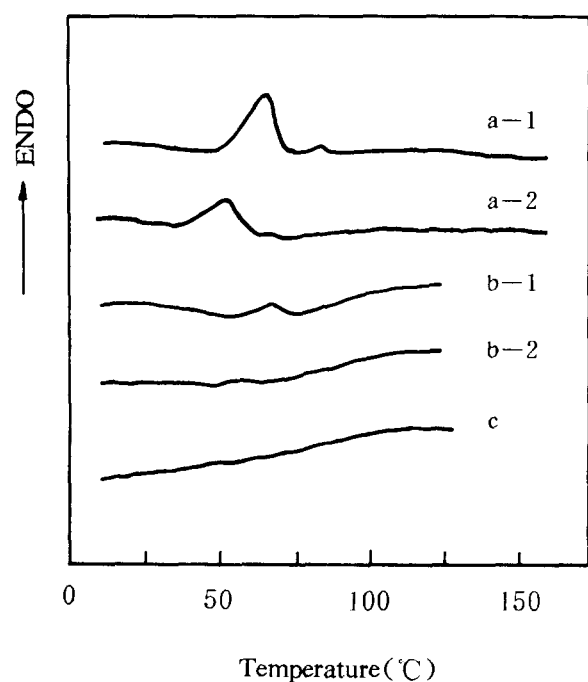


Figure 2 D.s.c. curves of (a) DEBEB, (b) PB/DEBEB (90/10) composite membrane and (c) PB membrane on the first (1) and the second (2) heating scans

membrane, the other composite membranes of different weight ratio also exhibit *N*-shape *P*-*T* curves, for example, Figure 3 shows the P_{O_2} -*T* and α_{O_2/N_2} -*T* curves of the PB/DEBEB composite membranes with three weight ratios of 80/20, 60/40 and 50/50. It is clear that all three P_{O_2} -*T* curves exhibit the characteristic *N*-shape and have the same temperatures of the peak and the valley, 50°C and 70°C, as in Figure 1. In addition, the P_{O_2} -*T* and α_{O_2/N_2} -*T* curves show inverse permeability/selectivity behaviour when changing the DEBEB content below 70°C. Figure 4 further shows the effect of the DEBEB content in the composite membranes on P_{O_2} and α_{O_2/N_2} at representative temperatures. At temperatures of 20°C and 50°C (below T_{KS}) the change of the P_{O_2} value with the DEBEB content is similar. When the DEBEB content of the composite membrane is 10 wt %, the P_{O_2} value is the highest and then decreases with an increase in the DEBEB content. The reason is possibly that more DEBEB leads to a decrease in the number of microvoids on interfaces between the PB matrix and the DEBEB crystal domains due to their connection to each other. On the other hand, crystallites reduce the volume fraction of the amorphous phase in which sorption is considered to occur. A temperature of 70°C is the temperature at which *P* values on *N*-shape *P*-*T* curves are in the valley. The influence of the DEBEB content on

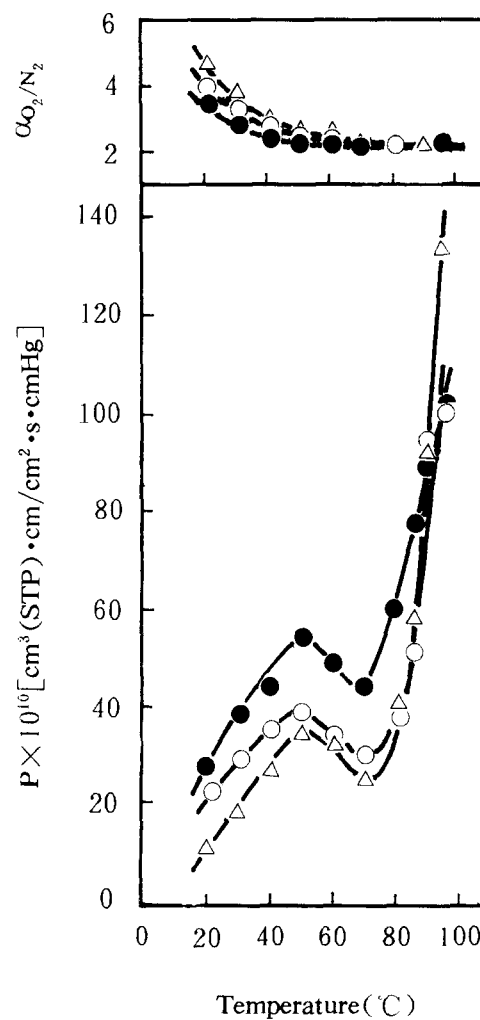


Figure 3 Effect of testing temperature on P_{O_2} and α_{O_2/N_2} of PB/DEBEB composite membranes with weight ratios of 80/20 (●), 60/40 (○) and 50/50 (△)

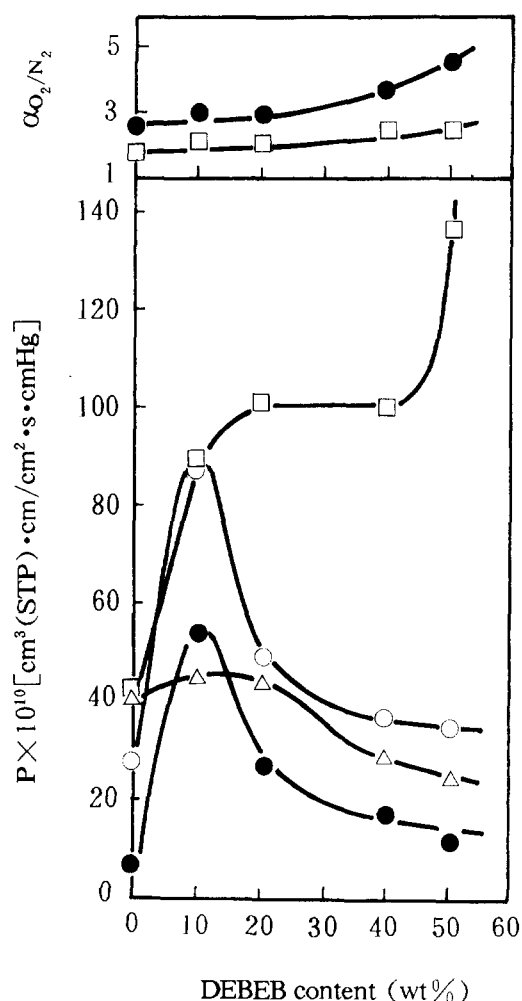


Figure 4 Effect of the DEBEB content in the PB/DEBEB composite membrane on P_{O_2} and α_{O_2/N_2} at 20°C (●), 50°C (○), 70°C (△) and 95°C (□)

the P_{O_2} value is small, but still exhibits a change like that observed at 20°C and 50°C. At a temperature of 95°C (above T_{SN}), P_{O_2} increases with increasing DEBEB content. When the composite membrane contains a DEBEB of 50 wt %, a distinct jump on the curve is observed. At this time P_{O_2} is about 136 barrer which is 100 barrer higher than the PB membrane. In addition, as shown in Figure 4, separation factors also show an enhanced trend with increasing DEBEB content at 20°C and 95°C. Especially at 20°C, α_{O_2/N_2} increases from about 3 to near 5 as the DEBEB content is increased from 10 wt % to 50 wt %.

Effect of second measurement on oxygen enrichment properties. From above discussion, the phase behaviour of the DEBEB can influence the oxygen enrichment properties of the composite membranes. Since the phase behaviour of LC is often affected by its thermal history, the DEBEB in the composite membranes which has undergone a thermal history of the first measurement must influence the oxygen enrichment properties for the second measurement. Figure 5 shows results of the first and second measurement for the PB/DEBEB (90/10) composite membrane some days after the first measurement. It can be seen that the P_{O_2} - T curves exhibit the characteristic N-shape but the appearance of the curves changed. P_{O_2} slightly decreases at room temperature but

obviously increases at higher temperatures, for example, P_{O_2} decreases from the first measurement of 54.7 to 53.4 barrer at 20°C, and increases from 88.5 to 187.7 barrer at 95°C. The peak values on the P_{O_2} - T curve of the second measurement still appear in the vicinity of 50°C, but the valley value decreases from the original value of 70°C to 60°C. This is also in agreement with the end temperature of T_{KS} of the DEBEB for the second measurement shown in Figure 2. The separation factors of the second measurement are a little higher than those of the first measurement. These results indicate that the oxygen enrichment properties of the composite membrane are affected by the thermal history of the DEBEB, especially at the high temperature of the nematic phase.

During the cooling process of the composite membrane after the first measurement, supercooling crystallization of the DEBEB in the composite membrane was carried out on the basis of its LC states and the perfect extent of newly-formed crystal must be not equal to the original DEBEB crystalline extent. However, when the DEBEB crystal domains in the composite membrane which have undergone this thermal history are reheated into LC states, order alignment of the DEBEB molecules becomes easier than the first heating process without the necessity of great realignment. In other words, under gas pressurization, the DEBEB molecules in the LC state are of greater orientational extent at this time and of great advantage to gas permeation across the composite membrane. Therefore, reduced extent of the permeability

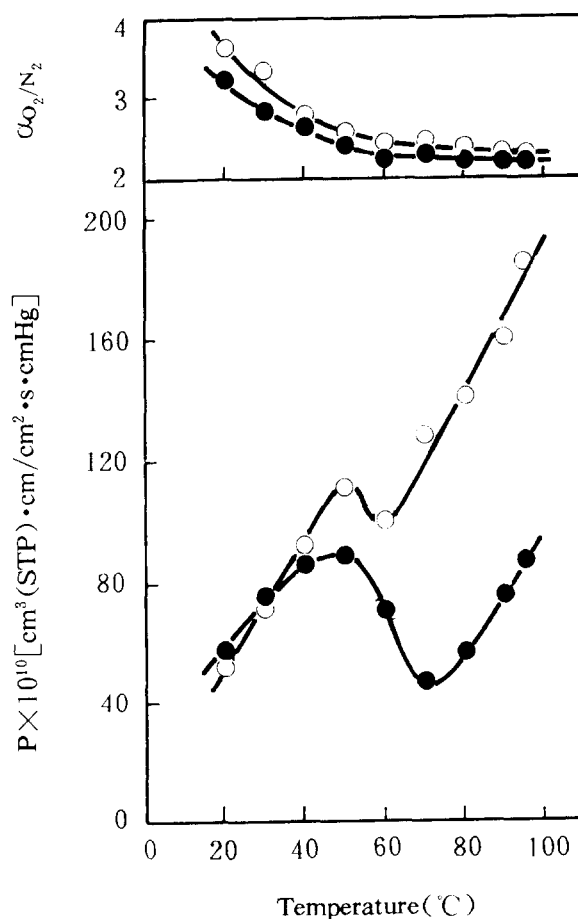


Figure 5 Effect of testing temperature on P_{O_2} and α_{O_2/N_2} of PB/DEBEB (90/10) composite membrane for the first (●) and the second (○) measurements

coefficients decreases in the temperature range of the smectic phase and better results of gas permeability are obtained above the temperature of the nematic phase transition.

It must be pointed out that the influence of the thermal history of the DEBEB on oxygen enrichment properties are not only confined to the PB/DEBEB (90/10) composite membrane. The second measurement of the PB/DEBEB (80/20) composite membrane also exhibits better results than its first measurement. Further studies on other gas permeabilities as well as morphologies for this type of composite membrane are being carried out.

Conclusions

The oxygen enriched properties of the PB/DEBEB composite membranes are affected by the phase behaviour, the thermal history and the content of the DEBEB as well as the morphology of the composite membranes. The smectic phase of the DEBEB has a disadvantageous influence on the oxygen enrichment properties of the composite membranes but the nematic phase is advantageous to gas permeation across the composite membranes. The results of the second measurement for the composite membranes demonstrate that the DEBEB in the composite membrane which has undergone a thermal history of the first measurement is enough to influence its oxygen enrichment properties of the second measurement. The composite membrane with less DEBEB content, such as 10 wt %, exhibits good oxygen enrichment properties at room temperature. At high temperature

(above K_{SN}), however, the composite membrane with a DEBEB content of 50 wt % has better oxygen permeability. This is due to the fact that in the composite membranes lower DEBEB contents may form more microvoids on the interfaces between the dipolar PB matrix and the polar DEBEB crystal domains and a adequate DEBEB content must form the continuous pathways of gas molecules through the whole membrane in this nematic phase.

References

- 1 Kajiyama, T., Nagata, Y., Maemura, E. and Takayanagi, M. *Chem. Lett.* 1979, 679
- 2 Kajiyama, T., Nagata, Y., Washizu, S. and Takayanagi, M. *J. Membr. Sci.* 1982, **11**, 39
- 3 Kajiyama, T., Washizu, S. and Takayanagi, M. *J. Appl. Polym. Sci.* 1984, **29**, 3955
- 4 Ohomori, Y. and Kajiyama, T. *Chem. Soc. Jpn.* 1985, **10**, 1893
- 5 Kajiyama, T., Washizu, S. and Ohomori, Y. *J. Membr. Sci.* 1985, **24**, 73
- 6 Kajiyama, T., Takahara, A. and Kikuchi, H. *Polym. J.* 1991, **23**(5), 347
- 7 Lin, S. A. and Sun, Q. H. CHINA-UK Bilateral Conference on Polymer Science, Beijing, China, 15-19 April, 1992
- 8 Lin, S. A. and Zhou, C. R. CHINA-UK Bilateral Conference on Polymers, Robinson College, Cambridge, 5-7 April, 1994
- 9 Wang, L. Y. and Yan, Y. F. *Membr. Sci. Technol.* (Chinese) 1988, **8**(4), 1
- 10 Brauer, G. 'Handbuch der präparativen Anorganischen Chemie', Ferdinand Enke Verlag, Stuttgart, 1, p. 287
- 11 Young, W. R., Haller, I. and Green, D. C. *J. Org. Chem.* 1972, **37**(23), 3707
- 12 Stern, S. A., Sinclair, T. F. and Gareis, P. J. *Mod. Plast.* 1964, **42**(2), 154