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ABSTRACT

The miscibility of poly(methyl methacrylate) (PMMA) with polycarbonate (PC) polymer has been extensively studied, and emphasis was placed on the preparation conditions and the composition effects. The effect of added metal salt on the miscibility and the gas permeability of the PMMA/PC blend membrane was investigated. Trends of gas permeabilities and selectivities for PMMA/PC-rich blend membranes are similar to the miscible blend membranes, although the former membranes are translucent. The added metal salt complex modification effectively improved the miscibility of the PMMA/PC-rich blend membrane as evidenced from dynamic mechanical analysis and differential scanning calorimetry studies. The gas permeabilities of the added metal salt complexes of PMMA/PC-rich and PMMA-rich/PC blend membranes are higher than those of the corresponding non-complexing blend membranes. Wide-angle x-ray diffraction analysis was made to study the difference of crystallinity for the effect of blend miscibility and salt additivity on PMMA/PC blend membranes.

INTRODUCTION

A number of papers (1, 2) have reported that the miscibility of poly-(methyl methacrylate) (PMMA) and polycarbonate (PC) blend systems is

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related to the methods used for preparing blends and the solvent for casting and precipitation. Recently, Nishimoto et al. (3) reported slow-phase separation in assessing the equilibrium phase behavior of the PMMA/PC blend system.

In polymer blend membranes, the major composition consists of two phases, and the boundaries between different phase are affected by the interaction of polymers influencing the gas permeation process (4, 5). Moreover, the transport behavior of penetrant across the polymer blend membrane is affected by interpolymer interactions. The segmental mobility decreased, and the miscibility increased. These changes contributed to lower gas permeability (6, 7). In earlier work (8) a higher milling temperature and the addition of grafted copolymer were used to improve the miscibility of blend membranes. In a previous paper we observed that transition metal salt additives in PC and PMMA casting solution are capable of improving the oxygen fluxes (9, 10). In this study the salt solution ($CuCl_2 \cdot 2H_2O$/DMF) is added to improve the miscibility, the performance of gas permeation, and the crystallinity of (PMMA/PC)/($CuCl_2 \cdot 2H_2O$/DMF) blend membranes.

By dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) measurements, the miscibility was analyzed. Thermogravimetric analysis (TGA) and microscopic observations of PMMA/PC blend membranes were utilized to measure the thermal stability and membrane morphology to assist in understanding the gas permeation properties. Furthermore, DMA and DSC studies were conducted to measure the improvement of miscibility of a salt additive complexing PMMA/PC-rich blend membrane. In addition, the effects of the miscibility and the salt additivity on the crystallinity of the prepared membranes were studied by wide-angle x-ray diffraction (WAXD) scan measurements.

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EXPERIMENTAL

Membrane Preparation

The PMMA and PC used in this study were chemical reagents from Aldrich Chemical Company with molecular weights of 92,000 and 25,000, respectively. The blend membranes were prepared by using a casting-air drying method on a glass plate with dichloromethane as the cast solvent. The maturation time was 24 hours for all casting solutions in this study. The membrane formation on the glass plate was slowly evaporated for 40 minutes at room temperature and gelled in a refrigerator at $-10°C$ for 40 minutes. Then the membrane was peeled off and dried in vacuum for 24 hours. The salt additive complexing blend membranes were prepared by adding various concentration of $CuCl_2 \cdot 2H_2O$/DMF salt solution into the

PMMA/PC blend casting solution. The concentration of salt solution is defined as the S value, that is, the molar ratio of $CuCl_2 \cdot 2H_2O$ to DMF.

Gas Permeation Measurement

Oxygen and nitrogen permeabilities of membranes were determined by using the Yanaco GTR-10 gas permeability analyzer. The gas permeability was determined by the following equation:

$$P = \frac{ql}{(P_1 - P_2)At}$$

where P is the gas permeability [cm^3(STP)·cm/cm^2·s·cmHg], q is the volumetric flow rate of gas permeation [cm^3(STP)/s], l is the membrane thickness (cm), P_1 and P_2 are the pressures (cmHg) on the high and low pressure side of the membrane, respectively, and A is the effective membrane area (cm^2). The experimental procedure employed in this study for the permeability measurements was similar to that described in a previous paper (9).

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Microscopic Observation

The microstructures of the prepared membranes were examined with a Hitachi S-570 scanning electron microscope (SEM). The samples were mounted on cylindrical brass, freeze-dried under vacuum, and rendered electrically conductive with a coating of gold. Then they were viewed in a scanning electron microscope operating at an accelerating voltage of 20 kV.

Thermal Properties

Differential scanning calorimetry (DSC) measurements were conducted with a DuPont 9900 in aluminum pans at a heating rate of 10°C/min, and the temperature ranged from 0 to 300°C. Thermogravimetric analysis (TGA) was carried out with a DuPont TGA-951 at a heating rate of 10°C/min under a nitrogen atmosphere. Dynamic mechanical properties were obtained using a Perkin-Elmer 7 series thermal analysis system at a frequency of 1.0 Hz and a heating rate of 5°C/min.

Crystallinity

Wide-angle x-ray diffraction (WAXD) scans were generated by a Shimadzu XD-5 diffractometer operating with monochromatized copper radiation.

RESULTS AND DISCUSSION

Performance of PMMA/PC Blend Membrane

The effect of the PC weight fraction in the PMMA/PC blend membrane on the gas separation performance is shown in Fig. 1. The PMMA/PC = 9/1 (wt%) blend membranes were transparent, and the others were translucent. The gas permeabilities for the PMMA/PC blend membranes are lower than those calculated from logarithmic additivity rule represented by the dashed lines in Fig. 1. In addition, the O_2/N_2 selectivity for the PMMA/PC blend membrane is higher than that represented by the logarithmic additivity rule. Similar results have been reported for several other miscible blend systems, e.g., poly(methyl methacrylate) with bisphenol chloral polycarbonate (11) and polystyrene with tetramethyl bisphenol-A polycarbonate (12).

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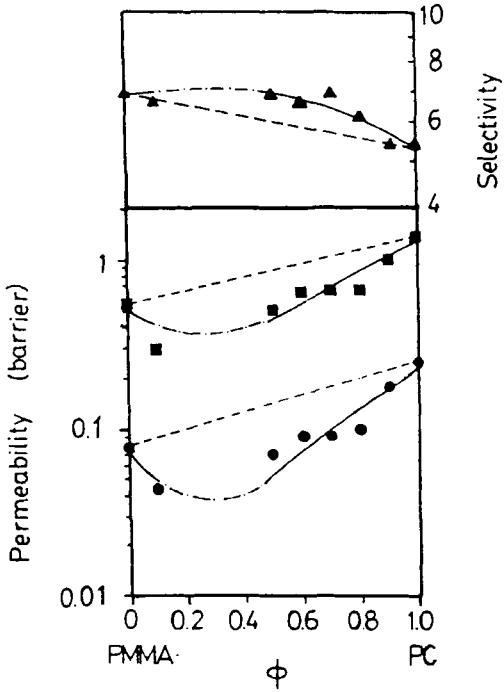

FIG. 1 Semilogarithmic plots of permeabilities and O_2/N_2 selectivity versus weight fraction of PC in blend. Operation temperature: 35°C; operation pressure: 0.1 MPa. (■) O_2, (●) N_2, (▲) O_2/N_2 selectivity.

On the other hand, the gas separation performance is a function of the blend composition for the PMMA/PC blend membrane. This result may be related to the microstructure of the blend membranes. The microphases of the PMMA/PC blend membranes observed in SEM are shown in Figs. 2 and 3. Figure 2(B) presents a very dense cross section for the PMMA/PC = 9/1 (wt%) blend membrane. Chiou et al. (1). indicated that some PC polymer could be dissolved into the PMMA matrix and used dichloro-

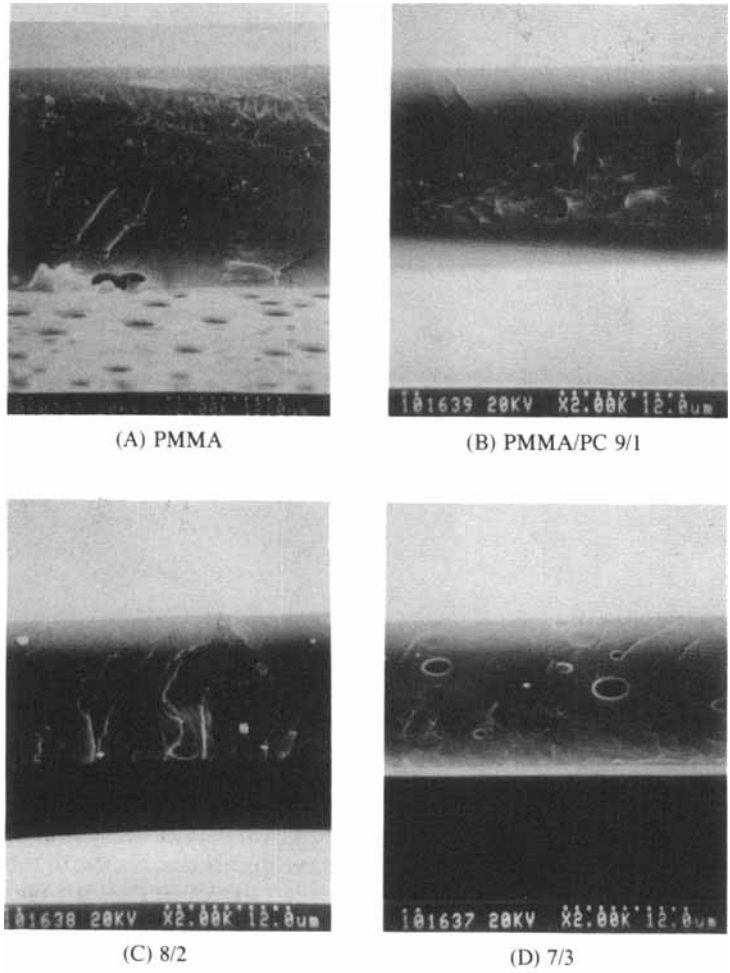

FIG. 2 Cross-sectional view of PMMA/PC blend membranes in SEM (×2000), PMMA-rich blend.

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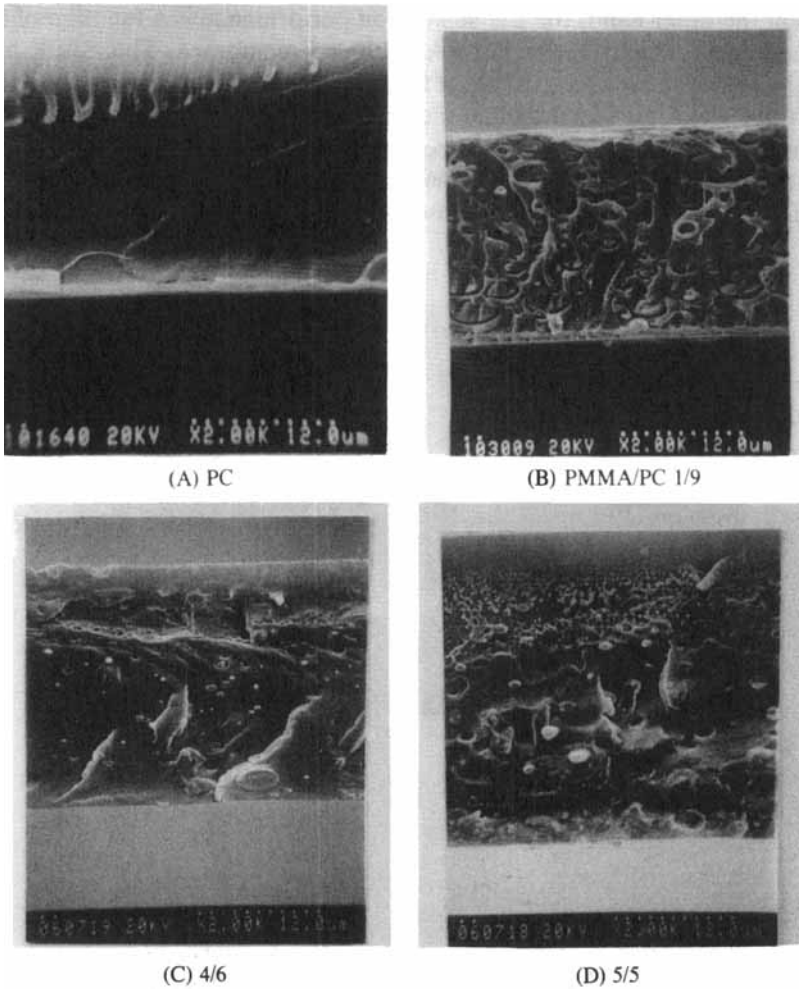

(A) PC (B) PMMA/PC 1/9

(C) 4/6 (D) 5/5

FIG. 3 Cross-sectional view of PC-rich blend membranes in SEM (×2000).

methane as a cast solvent. Thus, in the PMMA-rich/PC blend membrane system, the additive PC polymer may have good adhesion with the PMMA matrix. This confirms the miscibility for the PMMA/PC = 9/1 blend membrane. Concerning other compositions, 20–40 wt% PC in the blend was poorly mixed and displayed phase separation in the SEM [as shown in Fig. 2(C) and (D)]. As a result, those membranes did not have good selectivities for oxygen to nitrogen. When the PC polymer contained over 50

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wt% in the blend system, the PC continuous phase was formed in the membrane. Then the PMMA polymer dispersed in the continuous phase of the PC domain, as shown in Fig. 3(B)–(D). This shows that the PMMA polymer chain extends into the PC matrix. Nagase et al. (13) reported on poly(dimethylsiloxane) (PDMS)-*grafted*-poly(1-trimethylsilyl-1-propyne) (PTMSP) gas separation membranes and noted that PDMS chain might fill the microvoids of the PTMSP matrix and reduce the free volume. For this reason, oxygen permeability decreases and O_2/N_2 selectivity increases.

Miscibility of PMMA/PC Blend Membrane

The secondary transition temperature (T_g) of PMMA/PC blend membranes were measured by DSC first and second runs shown in Fig. 4 and Table 1. The PMMA-rich/PC = 9/1 blend membrane presents a single T_g because the PC polymer dissolves in the PMMA matrix to form a miscible blend membrane. The single T_g reveals that the blend may be miscible between PMMA and PC polymer at the PMMA-rich composition. On the other hand, two distinct T_gs appeared, illustrating the phase separation

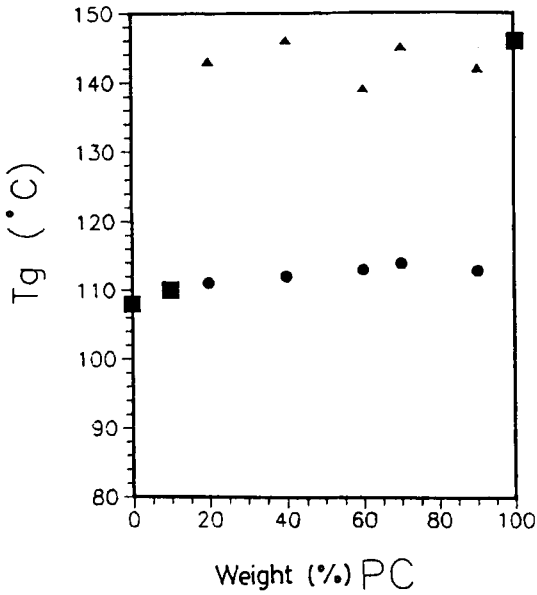

FIG. 4 T_g–composition curve for PMMA/PC blends (DSC second run). (■) Single T_g, (●) lower T_g near the T_g of PMMA, (▲) higher T_g near the T_g of PC.

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TABLE 1
Thermal Properties of PMMA/PC Blend Membrane at Various Compositions in Nitrogen Atmosphere with a 20°C/min Heat Rate

PMMA/PC composition	T_g (°C) 1st	T_g (°C) 2nd	T_{start}[a] (°C)	$T_{50\%}$[b] (°C)	Selectivity, PO_2/PN_2
10/0	108	108	278	370	7.02
9/1	111	110	318	375	6.67
8/2	111 144	111 143	325	380	—
5/5	112 140		335	417	6.81
4/6	112 139	113 139	343	435	6.60
2/8	112 140		360	467	6.15
1/9	112 146	113 142	375	478	5.40
0/10	144	146	440	493	5.34

[a] T_{start}: Temperature of the start of intense degradation.
[b] $T_{50\%}$: Temperature corresponding to a 50% weight loss.

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phenomena for PMMA/PC = 8/2–1/9 (wt%) blend system, which is an immiscible blend membrane.

Chiou and Kyu et al. (1, 2) extensively studied the PMMA/PC blend system and its miscibility, e.g., solvent system, casting conditions. Recently, Kyu et al. (14) reported that PMMA/PC blend in THF had an immiscibility loop phase diagram, and Nishimoto et al. (3) reported a slow phase separation in assessing the equilibrium phase behavior. In this study it was found that the miscibility of PMMA/PC blend in dichloromethane is a function of blend composition. The gas permeabilities for PMMA/PC-rich blend membranes present similar trends as misible blend membranes (Fig. 1), although the PMMA and PC-rich polymers are not miscible.

Thermal Stability of PMMA/PC Blend Membrane

Figure 5 shows the TGA curves of the PMMA/PC blend system in comparison with those of the pure components. The temperature of the start of intense degradation (T_{start}) and the temperature corresponding to a 50% weight loss ($T_{50\%}$) at various blend compositions were higher than that of pure PMMA, as shown in Table 1. This result implies that the thermal stability of PMMA/PC membranes can be increased by increasing the PC content in these blend polymers. These phenomena might be due to the PC chain being in close proximity to the PMMA end-group, with consequent suppression of PMMA degradation (14). Thus, PMMA/PC blend membranes not only have a microphase separation phenomenon but also have high selectivity for oxygen to nitrogen and high thermal stability.

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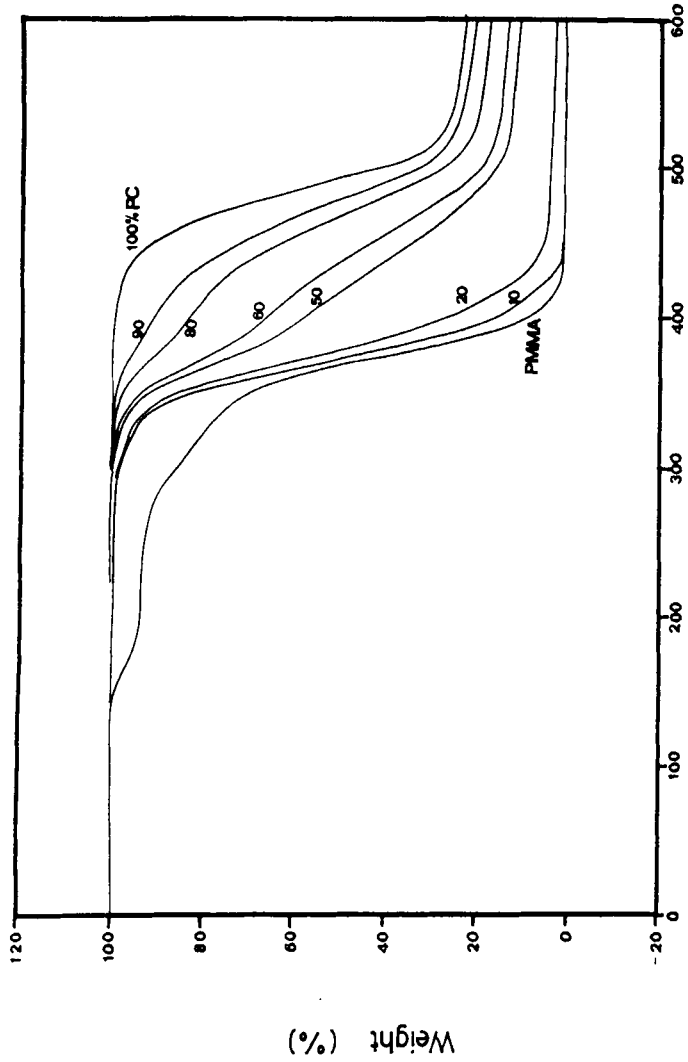

FIG. 5 Thermal stability of PMMA/PC blend membranes analyzed by a thermogravimetric weight loss of 50%.

Miscibility of Salt Additive Complexing PMMA/PC-Rich Blend Membrane

It has been reported that the miscibility of blend membranes was improved with a higher milling temperature and the addition of copolymer (8). In this study a salt solution of $CuCl_2 \cdot 2H_2O$/DMF was used to improve the miscibility of PMMA/PC blend membranes. Figure 6 plots the loss modulus (DMA) with rising temperature and the DSC second run traces for blend and complexing blend membranes. From the solid lines, the

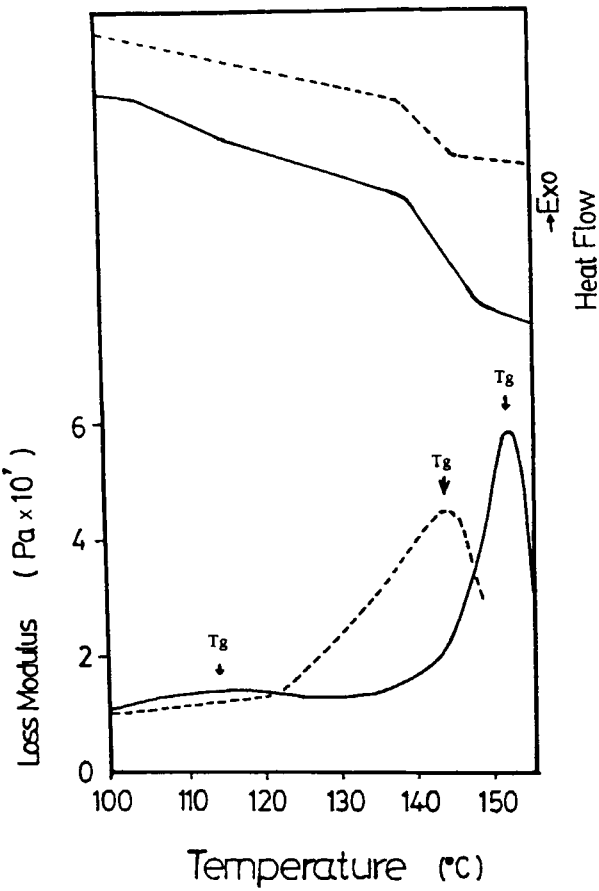

FIG. 6 Temperature dependence of E'' (loss modulus) and glass transition temperature (T_g) of PMMA/PC = 1/9 blend membrane (——) and salt additive complexing PMMA/PC = 1/9 blend membrane with S = 0.045 (---).

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PMMA/PC = 1/9 (wt%) blend membrane has two distinct T_gs: 114°C for PMMA and 150°C for PC, but the salt additive complexing PMMA/PC = 1/9 (wt%) blend membrane only presents a single T_g, the peak being shifted to 143°C (dashed lines). DMA and DSC studies show that the additive salt could improve the miscibility of this blend membrane. This improvement may be caused by a complex formed between the PMMA and PC with the DMF/$CuCl_2 \cdot 2H_2O$ salt solution. It suggested that the complex structure could improve the miscibility of a PMMA/PC blend membrane.

Performance of Salt Additive Complexing PMMA-Rich/PC Blend Membrane

Figure 7 presents the O_2 and N_2 gas permeability and O_2/N_2 selectivity for the salt additive complexing PMMA/PC = 9/1 blend membrane with different S values (the molar ratio of $CuCl_2 \cdot 2H_2O$ to DMF). The O_2/N_2 selectivity increases and the gas permeability decreases with increasing S value from 0.045 to 0.135. These phenomena might be due to the swelling effect of nonvolatile solvent DMF and the complex structure caused by the DMF/$CuCl_2 \cdot 2H_2O$ salt solution. This trend is similar to that seen in PMMA/$CuCl_2 \cdot 2H_2O$/DMF complex membranes (10). To further investigate the effect of additive salt content on membrane morphology, the

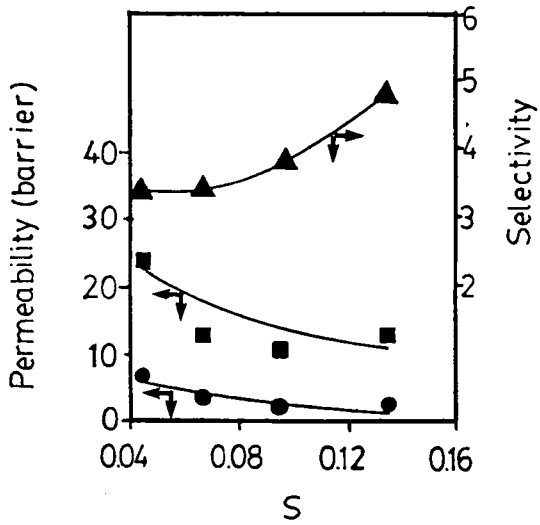

FIG. 7 The effect of S (molar ratio of $CuCl_2 \cdot H_2O$/DMF) on gas permeability and separation factor of modified PMMA/PC = 9/1 blend membranes. Operation temperature: 35°C; operation pressure: 0.1 MPa. (■) O_2, (●) N_2, (▲) O_2/N_2 selectivity.

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same membranes were studied with scanning electron microscopy (SEM). Figure 8(A)–(C) shows the influence of additive salt on the cross-section view of PMMA/PC = 9/1 blend membrane. In Fig. 8(A) a dense structure is observed that results in a low-gas permeability with no salt additive. However, there is a spongelike structure in Fig. 8(B) where the $CuCl_2 \cdot 2H_2O$/DMF (S = 0.045) was added to the PMMA/PC blend membrane. Thus, the gas permeabilities were significantly improved by the salt additive. Compared with Fig. 8(B), Fig. 8(C) shows that the pore size shrunk with increasing the salt additive from S = 0.045 to 0.067. These phenomena may be due to the fact that complex formation in the PMMA/PC blend membrane increases with increasing salt content, resulting in a

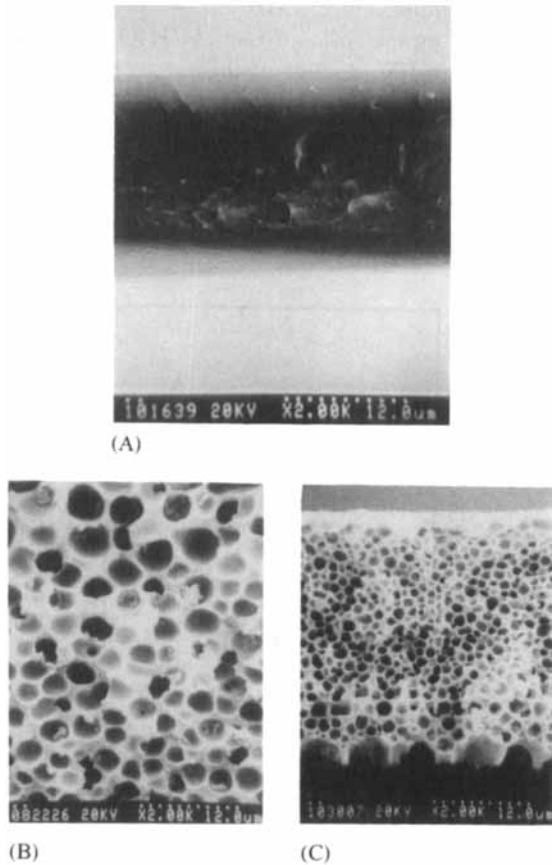

FIG. 8 SEM of PMMA/PC = 9/1 blend/complex membranes (cross section). (A) No additive, (B) $CuCl_2 \cdot H_2O$/DMF (S = 0.045), (C) $CuCl_2 \cdot H_2O$/DMF (S = 0.135).

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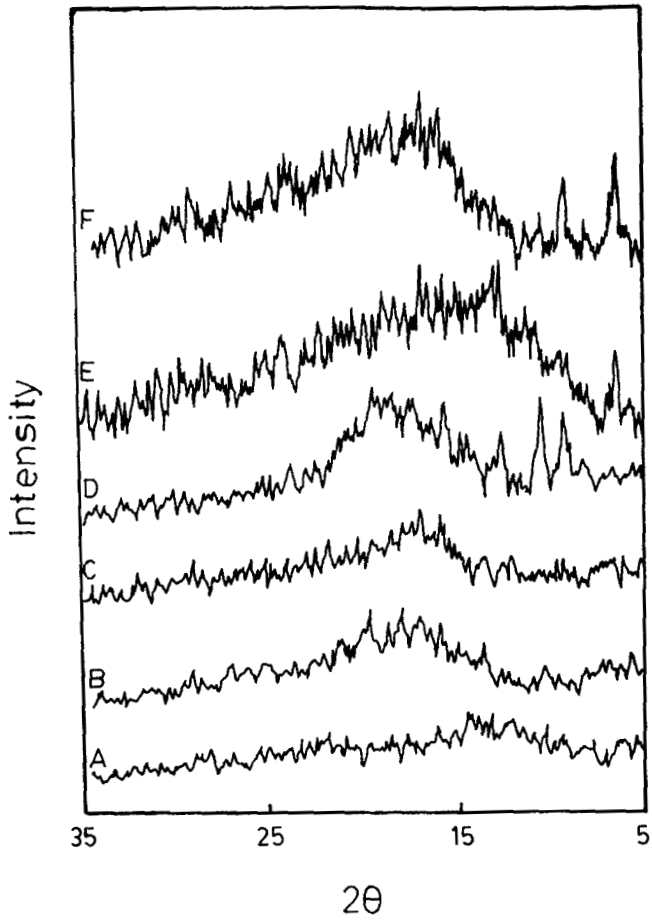

FIG. 9 X-ray diffraction patterns of polymeric membranes (PMMA/PC-rich blend or with complex). (A) PMMA, (B) PC, (C) PMMA/PC = 1/9, (D) PC + $CuCl_2 \cdot H_2O$/DMF (S = 0.045), (E) PMMA + $CuCl_2 \cdot H_2O$/DMF (S = 0.045), (F) PMMA/PC = 1/9 + $CuCl_2 \cdot H_2O$/DMF (S = 0.045).

decrease of the pore size in the membrane. Thus, gas permeabilities decreased and O_2/N_2 selectivity increased. These observations correspond to the results shown in Fig. 7.

The Crystallinity of Salt Additive Complexing PMMA/PC Blend Membrane

Runt et al. (15) proposed that the preparation conditions of a blend polymer (such as blend procedure, blend preparation temperature, solvent

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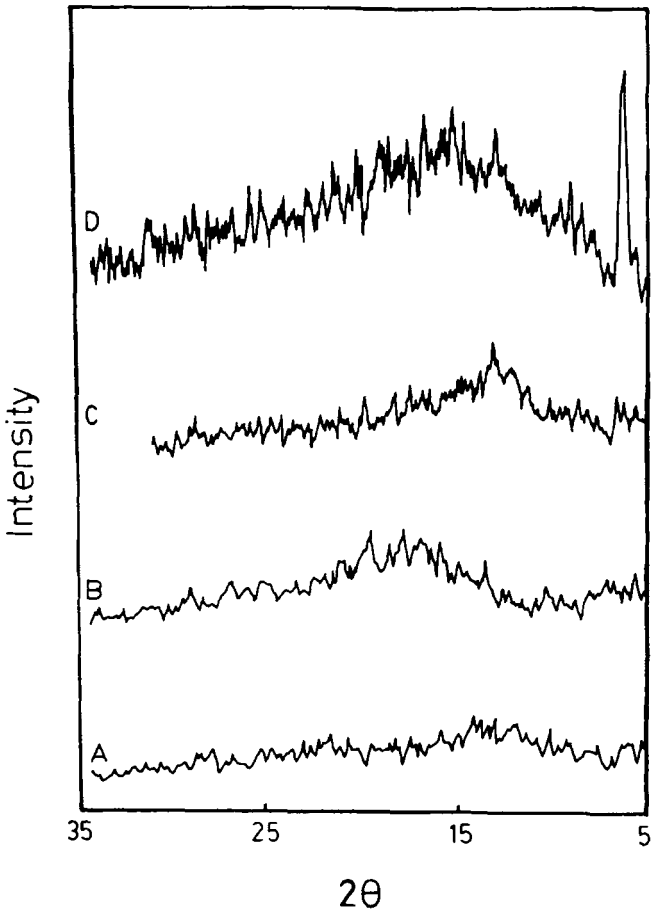

FIG. 10 X-ray diffraction patterns of polymeric membranes (PMMA-rich/PC blend or with complex). (A) PMMA, (B) PC, (C) PMMA/PC = 9/1, (D) PMMA/PC = 9/1 + $CuCl_2 \cdot H_2O$/DMF (S = 0.097).

evaporation rate, blending solvent, film thickness, etc.) would affect the development of crystallinity and the miscibility of a blend membrane. Chiou et al. (1) indicated that a PMMA/PC blend cast from THF solution crystallized but a PMMA/PC = 50 wt% blend cast from CH_2Cl_2 solution did not. It is suggested that phase separation from a CH_2Cl_2 solution is faster than that from a THF solution. In our study the PMMA/PC = 1/9 immiscible blend membrane did not show crystallization (Fig. 9, Curve

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C). Conversely, the PMMA/PC = 9/1 miscible blend membrane shows crystallization resulting from miscibility (Fig. 10, Curve C). The crystallinity of the salt additive complexing PMMA/PC = 1/9 blend membrane is higher than that of the PMMA/PC blend membrane with no salt additive as shown in Fig. 9 (Curves C and F). This may result from improvement in the miscibility between PMMA and PC caused by salt addition. For complexing PMMA/PC = 9/1 blend membranes, adding salt increases the crystallinity of the membrane further, as shown in Fig. 10 (Curve D). Thus, the crystallinity of a PMMA/PC blend membrane is related to the miscibility and the salt additive.

CONCLUSIONS

In this study it was found that the miscibility of PMMA/PC blend polymer in dichloromethane is a function of blend composition. PMMA/PC-rich blend membrane not only has microphase separation but also has a high selectivity for oxygen to nitrogen and good thermal stability resulting from the filled effect of the PMMA dispersion phase. Adding a metal salt to the blend improves the miscibility of a PMMA/PC-rich blend membrane according to DMA and DSC studies. The gas permeabilities of the metal salt added complex PMMA/PC-rich and PMMA-rich/PC blend membranes are higher than those of the corresponding noncomplexing blend membrane, although there is no obvious effect on the composition for the PMMA/PC = 8/2–2/8 blend systems. The crystallinity of a PMMA/PC blend membrane is related to the miscibility and the metal salt additive.

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