Facilitated Transport of Ethyl Docosahexaenoate Through Solution-Cast Perfluorosulfonated Ionomer Membranes

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ABSTRACT: The facilitated transport of ethyl docosahexaenoate (DHA-Et) through the thin solution-cast perfluorosulfonated ionomer membranes has been studied. The carrier of DHA-Et was silver ion and was immobilized in the support ionomer membrane by electrostatic forces. In this system, the feed phase, membrane phase, and receiving phase had the same solvent. This system was already proved to be highly stable in our previous work. When ethanol/water (85/15) was used as the solvent, the DHA-Et permeance in the cast membrane was about four times higher than that in the commercial Nafion® 117 membrane, due to the smaller membrane thickness. In the case of acetone solvent, a high selectivity of DHA-Et to ethyl oleate of 42 and a high facilitation factor of 153 were obtained. These membrane performances were superior to those of the Nafion® 117 membrane. The effects of membrane preparation conditions, such as annealing temperature and kinds of polar solvents added to the ionomer solution before annealing, on the membrane performance was investigated in detail. Furthermore, small-angle X-ray scattering (SAXS) measurement was carried out to study the membrane structure. The experimental result suggests higher crystallinity in the cast membrane annealed at higher temperature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 961–968, 1999

Key words: facilitated transport; polyunsaturated fatty acid; cast membrane; docosahexaenoic acid; silver ion

INTRODUCTION

Separation of polyunsaturated fatty acids (PUFAs), such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), has attracted attention because EPA and DHA are contained in fish oils with many other fatty acids and must be purified for use as food additives or medical supplies. Several methods of vacuum distillation,[1] liquid chromatography,[2] supercritical fluid extraction,[3] and extraction with silver ion[4] have been attempted to separate the desired components from fish oils.

Recently, separation by the facilitated transport membrane containing silver ion as a carrier has been reported.[5-8] This method has an advantage in that effective separation can be achieved based on the difference in the number of the carbon–carbon double bonds that can complex with silver ion and also in that the amount of expensive silver ion needed can be reduced compared to

the extraction method using silver ion as the extractant. Nishi et al. first reported the separation of ethyl eicosapentaenoate (EPA-Et) and ethyl docosahexaenoate (DHA-Et) from other PUFAs by the facilitated transport membrane.[5,6] This facilitated transport membrane was prepared by incorporating an aqueous silver salt solution in pores of microporous support membrane. Although EPA-Et and DHA-Et were successfully separated by this membrane, the problem from a commercial standpoint is degradation of the membrane performance. The membrane performance was reported to decrease within only 10 h. This degradation is probably due to the leakage of the aqueous carrier solution into the organic feed and receiving phases.

Teramoto et al. carried out experiments on the separation of EPA-Et and DHA-Et in ethyl ester of bonito oil (bonito oil-Et) by using a circulating liquid membrane containing silver ion as a carrier.[8] In this type of facilitated transport membrane, an aqueous silver salt solution was circulated between a stirred vessel containing an organic solution of bonito oil-Et and another stirred vessel containing a receiving organic solvent. In this circulating liquid membrane, high stability is expected because of the abundant carrier solution. Actually, Teramoto et al. reported high stability of the circulating liquid membrane in the separation of benzene from cyclohexane.[9] The necessary complexity of both the equipment and the operation are disadvantages of this type of membrane.

In our series of studies on the separation of DHA-Et by the facilitated transport membrane, we proposed a new type of facilitated transport system where the same solvents were used for the feed phase, membrane phase, and receiving phase.[10] The membrane phase had the same solvent as the feed and receiving phases, so that leakage of the membrane solution into other phases does not occur. In addition, an ion-exchange membrane (Nafion® 117) was used as the support, and silver ion was immobilized in the ion-exchange membrane by the electrostatic force. Due to these two factors, this type of facilitated transport membrane remained stable for more than 200 days. Furthermore, the effects of solvents on membrane performance were investigated in this system.[11] First, the swelling behavior of Nafion® membrane was investigated in various solvents. The solvent contents in the membrane were well correlated with the donor number (DN) of the solvents and were maximized at DN ~ 25–30 kcal/mol. The DN of Guttman is defined as ΔH_{DSbCl_5} with D + $SbCl_5$ = $DSbCl_5$ in 1,2-dichloro-

Figure 1 Chemical structures of DHA-Et and OLA-Et.

ethane, where D is the solvent. Stability constants of the silver ion–DHA-Et complex in various solvents were evaluated from the extraction experiments. The stability constants increased with increasing DN of the solvents. From the balance of the two effects on membrane swelling and stability constants, the solvent with DN ~ 19 kcal/mol, (i.e., aqueous methanol or ethanol solvent), showed the highest permeance of DHA-Et.

Membrane thickness is directly related to solute permeance by these facilitated transport membranes. The thinner the membrane, the higher the permeance. However, use of the commercial Nafion® membrane restricts the change of membrane thickness. For the purpose of obtaining the higher permeance, thinner solution-cast perfluorosulfonic acid ionomer membranes have been prepared and used in the separation of styrene from ethybenzene[12] and CO_2 from CH_4.[13]

In this work, cast membranes of about 40-μm thickness were prepared, and the separation of DHA-Et was attempted in the facilitated transport system by using the same solvent for the feed phase, membrane phase, and receiving phase. The relations between membrane preparation conditions and membrane performance were investigated. Furthermore, the structure of the cast membrane was studied through small-angle X-ray scattering (SAXS) measurement.

EXPERIMENTAL

Materials

DHA-Et (purity 95%) was supplied by Harima Chemicals, Inc. (Kakogawa, Japan). The ethyl oleate (OLA-Et; purity 95%) was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). Methyl palmitate (PAL-Me; purity 99.9%) used as the standard substance in the gas chromatograph analysis was purchased from Wako Pure Chemical Co., Ltd. (Osaka, Japan). Figure 1 displays the

chemical structures of the DHA-Et and OLA-Et. Solvents used were ethanol/water (85/15), acetone, and acetone/water (98/2), (95/5), and (90/10).

Preparation of Cast Membrane

Perfluosulfonic acid ionomer is commercially available as a 5 wt % solution of Nafion® 117 (1100 g equivalent molecular weight) in mixed lower aliphatic alcohols and water. The cast membrane was prepared by procedure similar to that discussed in a previous report.[14] Polar solvents, such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), 2-ethoxyethanol (2EE), and ethylene glycol (EG), were added to the ionomer solution. These solvents were purchased from Nacalai Tesque Inc. (Kyoto, Japan). The weight of the additional solvent was usually adjusted to be twice the dried polymer weight. Then about 5.5 cm^3 of solution was poured into a 9-cm diameter laboratory dish and was allowed to slowly evaporate at room temperature for 20 h. The membrane was annealed in an oven for 3 h. The annealing temperature was varied (120–230°C), and the effect on the membrane performance was investigated. The membrane obtained had H$^+$ as the counterion to the sulfonate side groups. These membranes were converted to the Na salt form, and to the Ag salt form by the same method as reported previously.[10] Silver nitrate was used in making the Ag-form membrane. These membranes were soaked and swollen in the membrane phase solvent before the transport experiment was initiated.

The thickness of the dried membrane was measured by a micrometer (Mitsutoyo, Japan, MDC-25M). It was difficult to determine the accurate thickness of the membrane swollen by the solvent by the micrometer. Therefore, the thickness of the swollen membrane, L_s, was estimated according to the following equation from the thickness of the dried membrane, L_d, and the solvent content (vol %) in the membrane SC:

$$L_s = L_d(100/(100 - SC))^{1/3} \qquad (1)$$

Flux Measurement

The permeation cell and procedure for the transport experiment were the same as reported previously.[10] The feed phase contained DHA-Et, OLA-Et, and the standard substance (PAL-Me) for the gas chromatography, whereas the receiving phase contained only PAL-Me. The same solvent was used for the feed phase, membrane phase, and receiving phase. The DHA-Et and

OLA-Et concentrations in the feed phase were 1.07×10^{-3} mol/dm^3 and 2.13×10^{-3} mol/dm^3, respectively.

Samples were withdrawn from the receiving phase, and the concentrations of DHA-Et and OLA-Et were measured by a gas chromatograph (Shimadzu Co., Kyoto, Japan, GC-14A) with a capillary column (packing: DBWAX-M30-025, J&W Scientific Co., Japan). The permeation cell was immersed in water at 30 ± 0.5°C.

SAXS Measurement

The X-ray beam was generated by a 6 kW rotating-anode X-ray generator (RU-200B, Rigaku Denki Co., Ltd. Tokyo, Japan). CuKα radiation (λ = 0.154 nm) passed through a nickel filter was used for the X-ray beam. An imaging plate (HR-V, Fuji Film Co., Ltd., Japan) was used as the X-ray detector. The measurement time was 24 h. Membrane samples swollen by water were sealed between glass slides to prevent moisture loss during the scan.

RESULTS AND DISCUSSION

Transport Properties in Cast Membrane

In our previous work, we studied the effect of various kinds of solvents on the facilitated transport of DHA-Et when the commercial Nafion® 117 membrane was used as the support.[11] As described earlier, from the balance of two effects on the membrane swelling and the stability constants of complex between silver ion and DHA-Et, the solvent with DN ~ 19 kcal/mol (i.e., aqueous methanol or ethanol solvent), showed the highest permeance of DHA-Et with a selectivity of DHA-Et to OLA-Et of more than 10. Therefore, ethanol/water (85/15) was first selected as the solvent in this work. The permeances and permeabilities of DHA-Et and OLA-Et for both Ag- and Na-form membranes are summarized in Table I. The permeance, R (m/s), is defined as the flux [mol/(m^{2}s)] divided by the solute concentration (mol/m^3) in the feed phase; the permeability, P (m^2/s), was obtained by multiplying the permeance by the membrane thickness (m). The selectivity of DHA-Et to OLA-Et in the Ag-form membrane, the facilitation factor of DHA-Et, the solvent content in the membrane, and the thickness of the swollen membranes are listed in Table II. The selectivity S is defined as the ratio of DHA-Et permeance to OLA-Et permeance, and the facilitation factor F is the ratio of the DHA-Et permeance in the

Table I Permeance (*R*) and Permeability (*P*) of DHA-Et and OLA-Et in the Case of Ethanol/Water (85/15) Solvent

Membrane Type	Counter Ion Type	R(DHA-Et) (m/s)	R(OLA-Et) (m/s)	P(DHA-Et) (m²/s)	P(OLA-Et) (m²/s)
Cast membrane	Na	0.40×10^{-7}	1.08×10^{-7}	0.15×10^{-11}	0.40×10^{-11}
Cast membrane	Ag	30.8×10^{-7}	12.7×10^{-7}	12.8×10^{-11}	5.28×10^{-11}
Nafion® 117	Na	0.025×10^{-7}	0.050×10^{-7}	0.051×10^{-11}	0.10×10^{-11}
Nafion® 117	Ag	7.95×10^{-7}	0.65×10^{-7}	18.4×10^{-11}	1.50×10^{-11}

Additional solvent, DMSO; annealing temperature 200°C.

Ag form membrane to that in the Na form membrane. Thus, *S* and *F* are given by the following equations:

$$S = R(\text{DHA-Et})/R(\text{OLA-Et}) \qquad (2)$$

and

$$F = R(\text{DHA-Et/Ag membrane})/$$
$$R(\text{DHA-Et/Na membrane}) \quad (3)$$

The data for the commercial Nafion® 117 support membrane are also included in Tables I and II. For both the cast membrane and Nafion® membrane, the permeances and permeabilities in the Ag-form membrane were fairly higher than those in the Na-form membrane, due to the effective facilitated transport by silver ion. Furthermore, in both Ag-form membranes, DHA-Et with six double bonds that can complex with silver ion showed higher permeances than OLA-Et with one double bond. The thickness of the cast membrane was about 40 μm, which leads to the higher permeances. For example, the DHA-Et permeance of the Ag-form cast membrane was about four times higher than that of the Ag-form Nafion® membrane. However, the selectivity (2.43) and the facilitation factor (77) of the cast membrane were somewhat lower than those of the Nafion® 117

membrane. This is because the cast membrane was more swollen by the Nafion® membrane, as shown in Table II. Therefore, the concentration of carrier (silver ion) in the membrane became lower, and the efficiency of the facilitated transport of DHA-Et decreased.[12]

Thus ethanol/water (85/15) was not a suitable solvent for the cast membrane to obtain high permeance as well as high selectivity, because the membrane was highly swollen. In our previous work using commercial Nafion® membrane,[11] the use of acetone as the solvent decreased the solvent content ($\sim$ 27 vol %) and increased the selectivity ($\sim$ 17), although the DHA-Et permeance of the Ag form membrane (1.13×10^{-7} m/s) was about one-seventh of that in the case of ethanol/water (85/15). Because the permeance can be increased in the thin cast membrane, acetone is expected to be a better solvent for the cast membrane. The membrane performance, solvent content, and membrane thickness used for acetone as the solvent are listed in Tables III and IV. The fairly high selectivity of 42 was obtained, as was expected. Because the solvent contents of the Na- and Ag-form membranes for the cast membrane were higher than those for the Nafion® membrane, as shown in Table IV, the permeabilities were generally higher for the cast membrane. The cast membrane also showed higher selectivity

Table II Selectivity (*S*), Facilitation Factor (*F*), Solvent Content, and Membrane Thickness in the Case of Ethanol/Water (85/15) Solvent

Membrane Type	S	F	Solvent Content (vol %) (Na Membrane)	Solvent Content (vol %) (Ag Membrane)	Thickness (μm) (Na Membrane)	Thickness (μm) (Ag Membrane)
Cast membrane	2.43	77.0	50	59	36.6	41.6
Nafion® 117	12.2	318	37	56	204	231

Additional solvent, DMSO; annealing temperature 200°C.

Table III   Permeance (R) and Permeability (P) of DHA-Et and OLA-Et in the Case of Acetone Solvent

Membrane Type	Counter Ion Type	R(DHA-Et) (m/s)	R(OLA-Et) (m/s)	P(DHA-Et) (m^2/s)	P(OLA-Et) (m^2/s)
Cast membrane	Na	0.083×10^{-7}	0.23×10^{-7}	0.029×10^{-11}	0.081×10^{-11}
Cast membrane	Ag	12.7×10^{-7}	0.30×10^{-7}	4.30×10^{-11}	0.10×10^{-11}
Nafion® 117	Na	0.0079×10^{-7}	0.026×10^{-7}	0.015×10^{-11}	0.051×10^{-11}
Nafion® 117	Ag	1.13×10^{-7}	0.067×10^{-7}	2.19×10^{-11}	0.13×10^{-11}

Additional solvent, DMSO; annealing temperature 200°C.

and facilitation factor than the Nafion® membrane. Thus the cast membrane was confirmed to be superior to the commercial Nafion® 117 membrane in this transport system.

Figure 2 shows the effect of the annealing temperature in the membrane preparation on the membrane performances in the Ag-form membrane, and the solvent content. With an annealing temperature of 150–230°C, membrane performance (e.g., permeability and selectivity) hardly changed. At an annealing temperature of 120°C, the solvent content was clearly high, thus the solute diffusivity increased, leading to higher permeability. However, the increased solvent content resulted in a decreased silver ion concentration in the membrane. This makes the selectivity lower. Gebel et al. investigated structures of solution-cast perfluorosulfonated ionomer films by wide-angle x-ray scattering (WAXS) and SAXS measurements.[14] They reported that as the annealing temperature increased from 80 to 250°C, the size of the lamellar crystallites in the membrane increased, their internal order probably improved, and a long-range order developed. Also, in our membrane, the lower annealing temperature is expected to bring about the lower crystalline order in the membrane. This is probably the reason that the higher solvent content and the higher permeability were obtained with the annealing temperature of 120°C. Results of our SAXS measurements are described below.

The membrane performance in the Ag-form membrane when various kinds of polar solvents were added to the ionomer solution before annealing is listed in Table V. This membrane performance depended on the kinds of the polar solvents used. The highest selectivity and facilitation factor were obtained with DMSO. The membrane prepared with the addition of DMF showed the highest DHA-Et permeability, with the lowest selectivity of 9.3. The additional solvent probably acts as a plasticizer, and the presence of such solvent enhances the crystalline order development.[14] Thus the membrane structure and the resultant membrane performance are directly related to the kinds of polar solvent used.

Figure 3 depicts the effects of the ratio of the additional solvent weight to the dried polymer weight in the membrane preparation solution. DMSO was used as the additional polar solvent. As can be seen in this figure, selectivity and permeability were hardly influenced by the amount of the polar solvent in this experimental range.

Figure 4 shows the effects of the water content in acetone/water used as the solvent. As the water content increased, the solvent content in the membrane increased, and the membrane became highly swollen. This led to the higher permeability. For example, when only 2 vol % of water was added to acetone, the DHA-Et permeability became more than two times higher than that in acetone alone. Because the higher solvent content brings about the

Table IV   Selectivity (S), Facilitation Factor (F), Solvent Content, and Membrane Thickness in the Case of Acetone Solvent

Membrane Type	S	F	Solvent Content (vol %)		Thickness (μm)	
			Na Membrane	Ag Membrane	Na Membrane	Ag Membrane
Cast membrane	42.2	153	45	28	35.3	34.0
Nafion® 117	16.9	143	27	26	195	194

Additional solvent, DMSO; annealing temperature 200°C.

Figure 2 Effect of annealing temperature on permeability, selectivity and solvent content. Ag-form membrane; additional solvent, DMSO.

Figure 3 Effect of ratio of additional solvent weight to dried polymer weight on membrane performance. Ag-form membrane; annealing temperature 200°C; additional solvent, DMSO.

lower silver ion concentration in the membrane, selectivity decreased with increasing water content in acetone. In our previous work, it was confirmed that the solvent content in the Nafion® membrane showed the maximum at the DN of the solvent of 25–30 kcal/mol.[11] The DNs of acetone and water are

Table V Membrane Performance in the Ag-Form Membrane with Addition of Various Kinds of Polar Solvents to Ionomer Solution

Polar Solvent	P(DHA-Et) (m^2/s)	P(OLA-Et) (m^2/s)	S	F
DMSO	4.30×10^{-11}	0.10×10^{-11}	42.2	153
DMF	4.90×10^{-11}	0.53×10^{-11}	9.3	63.7
2EE	2.50×10^{-11}	0.080×10^{-11}	30.9	27.9
EG	2.30×10^{-11}	0.055×10^{-11}	42.0	28.4

Acetone was used as solvent; annealing temperature 200°C.

Figure 4 Effect of water content in acetone/water on permeability, selectivity, and solvent content. Ag-form membrane; annealing temperature 200°C; additional solvent, DMSO.

17 and 18 kcal/mol.[15,16] Therefore, the addition of water in acetone increases the DN of the solvent. This may be the reason why the solvent content increased with the increase of the volume fraction of water in acetone.

SAXS Result

It was reported that SAXS profile from Nafion® membrane exhibited two maxima at 2θ to ~ 0.6

and 2.6° (2θ being the scattering angle).[17] The SAXS maximum at the smaller scattering angle is associated with crystallinity and was attributed to a long identity period in lamellar crystals. With increasing X-ray crystallinity, the peak intensity increases, and the peak position shifts toward a smaller scattering angle.[17] The maximum at the larger angle is associated with the existence of ionic clusters formed in the membrane. Figure 5 shows the SAXS curves for various membranes. These curves show no second peak at 2θ of 2–3°. Gebel et al. reported that in the SAXS data of the perfluorosulfonated ionomer films, the second maximum is very weak.[14] The existence of no second maximum in Figure 5 may be due to the low power of the X-ray generator and the short measurement time in our experimental condition. The cast membrane prepared at the annealing temperature of 200°C (cast membrane 1) showed the clear peak at 2θ of about 0.7°. The arrow in Figure 5 shows the peak position. On the other hand, the cast membrane 2, annealed at 120°C, had no peak. Therefore, crystallinity is low and the crystalline order does not develop well in the cast membrane 2. This experimental result of the lower crystalline order in the membrane annealed at the lower temperature is accordance with the result of Gebel et al.[14] Thus it was confirmed that the higher solvent content and the higher permeabilities in the cast membrane annealed at 120°C

Figure 5 Small angle X-ray scattering pattern for various membranes. Cast membrane 1: annealing temperature = 200°C; cast membrane 2: annealing temperature = 120°C.

shown in Figure 2 is attributable to the lower crystallinity in this membrane.

Although the clear peak was not observed in the commercial Nafion® 117 membrane, there was a bulging shoulder at the scattering angle of about 0.4°. This is considered to be attributable to the lamellar crystallites. Compared with the results for the cast membrane 1, the peak position in the Nafion® membrane shifted to the lower scattering angle. Therefore, the crystallinity was higher and the lamellar crystallites became thicker in the Nafion® membrane.[17] This may be the reason why higher solvent contents were obtained in the cast membrane annealed at 200°C than in the Nafion® membrane, as shown in Tables II and IV. However, further investigation is needed to clarify the difference in the crystallinity between cast membrane 1 and the Nafion® membrane.

CONCLUSIONS

The selective transport of DHA-Et by the thin solution-cast perfluorosulfonated ionomer membranes was studied. When ethanol/water (85/15) was used as the solvent, the DHA-Et permeance in the cast membrane was about four times higher than that in the commercial Nafion® 117 membrane, due to the thinner membrane thickness. However, the selectivity was lower in the cast membrane, because of the highly swollen structure.

To obtain higher selectivity as well as higher permeance, acetone was used as the solvent. In this case, the solvent content was lower than in the cast of ethanol/water (85/15), which leaded to the high selectivity of 42 and the high facilitation factor of 153. These values were superior to those of the Nafion® membrane with acetone as the solvent.

The effect of the annealing temperature in membrane preparation on membrane performance were investigated. With an annealing temperature as low as 120°C, the solvent content increased and thus a higher permeance with lower selectivity was obtained. Membrane performance was influenced by the kinds of polar solvents added to the ionomer solution, but were hardly influenced by the ratio of the additional solvent weight to the dried polymer weight. The addition of water to acetone used as the solvent was quite useful to increase the permeance. When only 2 vol % of water was added to the acetone, the DHA-Et permeability became more than two times higher than that seen with acetone alone.

SAXS measurement was done to study the membrane structures. In the cast membrane annealed at 200°C, the maximum scattering angle of 0.7° was observed, which is attributable to the lamellar crystallites. On the other hand, there was no distinguished peak in the cast membrane annealed at 120°C, indicating that the crystallinity was low and the crystalline order did not develop well in this cast membrane. This is why the higher solvent content and higher permeability were obtained in the cast membrane annealed at low temperature.

REFERENCES

1. Ackman, R. G.; Ke, P. J.; Jangaard, P. M. J Am Oil Chem Soc 1973, 50, 1.
2. Aveldano, M. I.; van Rollins, M.; Horrocks, L. A. J Lipid Res 1983, 24, 83.
3. Nilsson, W. B.; Gauglite, E. J.; Hudson, K. K.; Stout, V. F.; Spinnelli, J. J Am Oil Chem Soc 1988, 65, 109.
4. Teramoto, M.; Matsuyama, H.; Ohnishi, N.; Uwagawa, S.; Nakai, K. Ind Eng Chem Res 1994, 33, 341.
5. Nishi, Y.; Isozaki, M.; Matsuba, Y. in Proceedings of the 56th Annual Meeting of the Society of Chemical Engineers of Japan, Tokyo, 1991, 65.
6. Nishi, Y.; Nishigaki, H.; Matsuba, Y. in Proceedings of the 24th Autumn Meetings of the Society of Chemical Engineers of Japan, Nagoya, 1991, Vol. 2, 252.
7. Teramoto, M.; Matsuyama, H.; Nakai, K.; Uesaka, T.; Ohnishi, N. J Membr Sci 1994, 91, 209.
8. Teramoto, M.; Matsuyama, H.; Nakai, K. Sep Sci Technol 1996, 31, 1953.
9. Teramoto, M.; Matsuyama, H.; Yonehara, T. J Membr Sci 1990, 50, 269.
10. Kitamura, Y.; Matsuyama, H.; Nakabuchi, A.; Matsui, N.; Doi, Y.; Matsuba, Y. Sep Sci Technol 1999, 34, 277.
11. Matsuyama, H.; Kitamura, Y.; Doi, Y.; Matsuba, Y. J Membr Sci, to appear.
12. Koval, C. A.; Spontarelli, T.; Thoen, P.; Noble, R. D. Ind Eng Chem Res 1992, 31, 1116.
13. Pellegrino, J.; Wang, D.; Rabago, R.; Noble, R.; Koval, C. J Membr Sci 1993, 84, 161.
14. Gebel, G.; Aldebert, P.; Pineri, M. Macromolecules 1987, 20, 1425.
15. Gebel, G.; Aldebert, P.; Pineri, M. Polymer 1993, 34, 333.
16. Okazaki, S.; Sakamoto, I. Solvent and Ion, Sanei Syuppann: Kyoto, Japan, 1989.
17. Fujimura, M.; Hashimoto, T.; Kawai, H. Macromolecules 1981, 14, 1309.