Preparation of *N*-Methoxymethylated Nylon-3 and Application of Its Membrane to Pervaporation of Water/Alcohol Mixture

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Synopsis

Nylon-3 prepared by hydrogen transfer polymerization of acrylic amide was *N*-methoxymethylated by paraformaldehyde/methanol in its formic acid solution. This product was soluble in water, and we were able to obtain a transparent membrane by casting of the solution. Absorbance of the NH group on IR spectrum was decreased by methoxymethylation, and from this depression of absorbance a degree of *N*-methoxymethylation of about 33% was obtained which agreed with the value from elemental analysis. DSC curve of this polymer showed a endothermic peak at 80°C which was assumed to be the T_g and a exothermic peak starting at 180°C which was assumed to be the crosslinking reaction. The degree of crystalinity of this polymer was about 40% which was obtained by deuterium exchange reaction with deuterium oxide. By heating of this polymer membrane up to 190°C, it was changed to an insoluble polymer by the crosslinkage reaction between methoxymethyle and unreacted amide groups. This insoluble polymer membrane was used for the separation of water/alcohol mixture by the pervaporation technique. Through the membrane, water was permeated selectively compared with alcohol and the selective permeation was found to increase by raising the heat treatment temperature.

INTRODUCTION

It is well know that the poly amides like nylon-6 and nylon-6.6 are *N*-methoxymethylated with paraformaldehyde/methanol in their formic acid solutions. The methoxymethylated polyamides are soluble in water/ethanol mixture. However, they become insoluble in these solvents by crosslinking with heat treatment.

Nylon-3 which has amide group in high content in the polymer chain has been prepared from acrylic amide by hydrogen transfer polymerization.[1] This polymer is hydrophylic due to the high content of amide group as described above.[2] Therefore, the methoxymethylated nylon-3 dissolves in water, and, to obtain insoluble hydrophylic membranes, which can be used to separate the mixtures of water/alcohol by pervaporation, it was crosslinked by heat treatment.

In this paper we will examine the preparation and methoxymethylation of nylon-3, and investigate some properties of the polymer and its application for the pervaporation of water/alcohol mixtures.

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EXPERIMENTS

Materials

Nylon-3 was prepared from hydrogen transfer polymerization of acrylic amide according to Masamoto et al.[1] Methoxymethylation of nylon-3 was carried out in its formic acid solution by slowly adding the methanol solution of paraformaldehyde.[3] The reaction was continued for 4 h at 60°C. The product of above reaction was poured into water/acetone (50/50) mixture and neutralized by ammonia water. The solution of product was dialyzed with pure water for 2 days for purification. A membrane of this polymer was prepared by casting its water solution on a polystyrene plate. The membranes thickness used for permeation experiments were 97 μm.

APPARATUS

DSC measurements were carried out by a Shimadzu Thermal Analysis DT-30 apparatus. The degree of deuteration was measured by change of the NH band in IR spectra.[4] Separation characteristics in pervaporation was measured by gas chromatography described in our previous paper.[5] Permeation experiments were carried out at 20°C.

RESULTS AND DISCUSSION

Preparation of Nylon-3

In Figures 1(a) and (b), the IR spectra of obtained nylon-3 and its hydrolysis product are shown, respectively. The IR spectrum of nylon-3 was

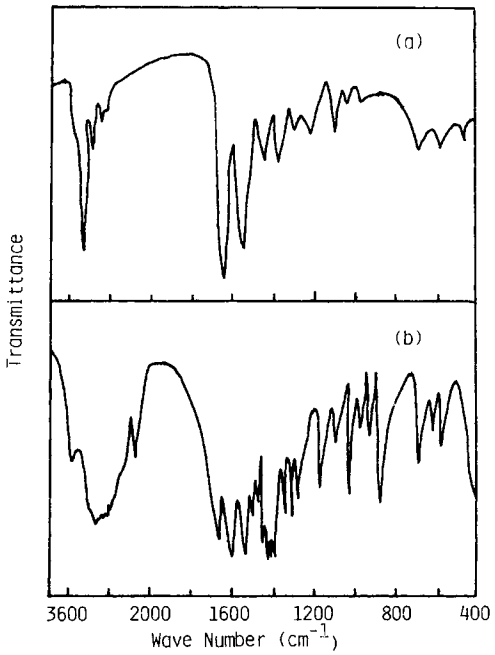


Fig. 1. IR spectra of (a) Nylon-3 and (b) its hydrolysis product.

similar to Masamoto's results,[1] and the ratio of bands of amide II (1535 cm^{-1})/amide I (1640 cm^{-1}), which shows the extent of transfer polymerization compared to a free radical one,[6] was 0.48. This value was close to 0.5 which is the ideal value. The hydrolysis product of the polymer showed not only at a spot similar to the R_f of β-alanine in thin layer chromatography, but the IR spectrum of it also showed similarity to β-alanine as shown in Figure 1(b).

From above these results, it was confirmed that the polymer obtained by this polymerization is nylon-3.

N-Methoxymethylation of Nylon-3

The IR spectrum of *N*-methoxymethylated nylon-3 (*N*-3MM) is shown in Figure 2. Using a decrease of absorbance of the band of amide II (1535 cm^{-1}) by reaction, the degree of *N*-methoxymethylation was estimated to be 33%. Elemental analysis of nylon-3 and *N*-3MM are shown in Table I. Since the polymers are hydrophylic, good agreement between the calculated and observed values for the C/N ratio, in the absence of moisture, was obtained as shown for the result of nylon-3. Using the value of C/N for nylon-3 and *N*-3MM, the degree of *N*-methoxymethylation was obtained as 31%, which is close to the result from the IR spectrum.

SOME PROPERTIES OF *N*-3MM

N-3MM was soluble in water, differing from *N*-methoxymethylated nylon 6.6. From the water solution of *N*-3MM, we could obtain a transparent membrane by casting on a polystyrene plate.

The DSC curve of *N*-3MM is shown in Figure 3. In this curve, an endothermic peak which may be the glass transition was observed, and a broad

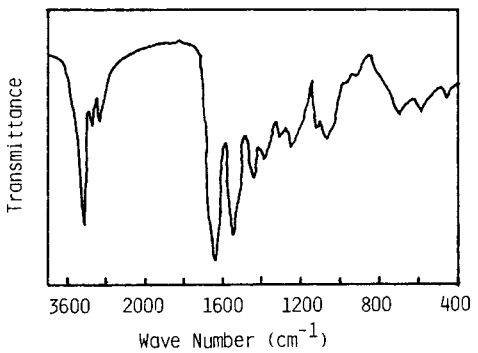


Fig. 2. IR spectrum of *N*-3MM.

TABLE I
Elemental Analyses of Nylon-3 and *N*-3MM

	Calcd (%)				Obs (%)			
	C	H	N	C/N	C	H	N	C/N
Nylon-3	50.69	7.09	19.71	2.57	49.11	7.33	19.35	2.54
N-3MM	52.16	7.88	12.17	4.29	49.93	7.66	16.08	3.11

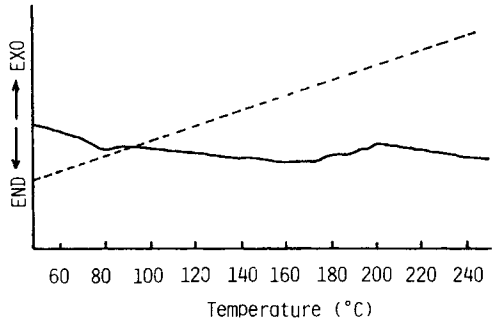
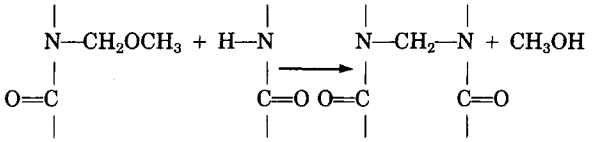


Fig. 3. DSC curve of *N*-3MM.

exothermic peak was observed over the temperature of 180°C. Since the membrane become insoluble in water and other solvents by heat treatment above 180°C, the latter peak may be considered to be the crosslinking reaction as follows[6]:



N-3MM and 190°C-heat-treated *N*-3MM (*N*-3MMHT) membranes were deuterated by hydrogen exchange reaction with deuterium oxide at room temperature.[4] Changes of ν_{NH} (3280 cm^{-1}) and ν_{ND} (2390 cm^{-1}) spectra by deuteration of *N*-3MM and *N*-3MMHT are shown in Figures 4(a) and (b), respectively. By use of the depression of ν_{NH} absorbance with deuteration, the degree of crystalinity was calculated as 40.4 and 37.8% for *N*-3MM and *N*-3MMHT, respectively. It is assumed that because of mobility depression of molecular chains by a formation of crosslinking prior to rearrangement

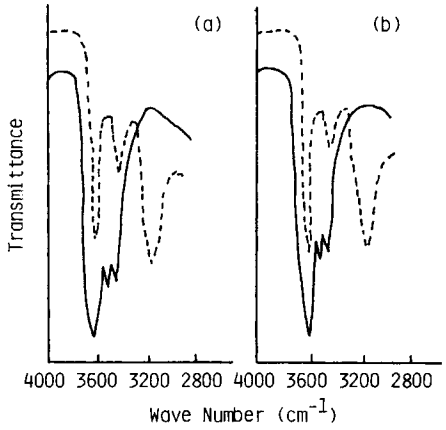


Fig. 4. Changes of IR spectra by deuteration of (a) *N*-3MM and (b) *N*-3MMHT: (—) original; (···) deuterated.

to crystallization the degree of crystalinity of *N*-3MMHT is a little smaller than the original value. A diffraction pattern of X-ray of *N*-3MM showed a similarity to nylon-3. This fact shows that the crystal lattice is formed mainly with nylon-3 molecules.

SWELLING OF *N*-3MMHT WITH WATER

The temperature dependences of swelling of *N*-3MMHT are shown in Figure 5. The degree of swelling of 190°C-treated *N*-3MMHT is larger than that of the one treated at 200°C. Both of the curves showed two-stage behaviors. The lower stages of both curves may be due to the simple sorption of water in the amorphous regions and surfaces of crystallites. And the higher stages may be due to the destruction of crystallites by hot water. It is assumed that the features of curves, especially in higher stages, correspond to the lateral order distributions of these membranes. By use of Flory and Rehner's equation and assuming the χ-parameter (interaction parameter between water and polymer) as 0.6, the molecular weights between crosslinkages were calculated as about 2500 and 300 for 190- and 200°C-treated *N*-3MMHT, respectively. The value for the 200°C-treated *N*-3MMHT was much smaller than the 190°C-treated one. This fact shows that crystallite in the high lateral order region is not destroyed by hot water below 100°C.

PERVAPORATION OF WATER/ALCOHOL BY *N*-3MM MEMBRANE

The degree of swelling of *N*-3MMHT membranes to water, methanol, and ethanol are shown in Table II. The degree of swelling to water is much larger than that of others. A good separation is expected in the systems of

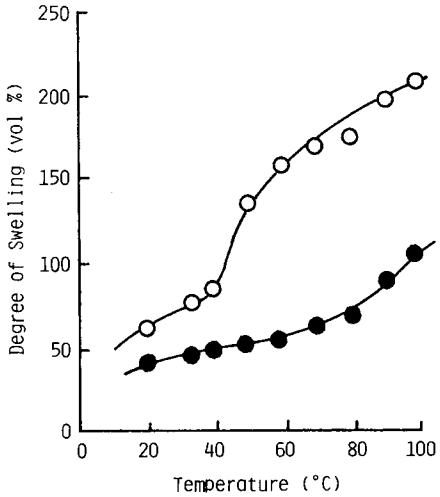


Fig. 5. Temperature dependences of degree of swelling of *N*-3MMHT with water: (○) water/*N*-3MMHT (190°C); (●) water/*N*-3MMHT (200°C).

TABLE II
Degree of Swelling of *N*-3MM Membranes with Water and Alcohol

Membrane[a]	Degree of swelling (vol %)		
	H_2O	CH_3OH	C_2H_5OH
N-3MMHT (190°C)	60.9	22.9	15.4
N-3MMHT (200°C)	49.9	18.3	6.1

[a]( ) = heat-treated temperature; swelling temperature: 20°C.

water/alcohol mixtures by pervaporation. Permeation fluxes of water and methanol from various concentration of feeds are shown in Figure 6. The permeation fluxes vs. feed concentration curves showed typical features of hydrophylic polymer membranes.[7] The permeation fluxes of water decreased monotonically with decreasing of its concentration in mixtures. However, the fluxes of methanol showed maximum at about 20 wt % of methanol in feeds. This result is explained that the diffusivity of methanol increased with the plasticizing effect of water on polymer membrane at a high water concentration region.[8,9] The separation characteristics of these systems are shown in Figure 7. The separation characteristics of the water/methanol system improved without large decrease of permeation flux of water by raising the heat treatment temperature. The permeation fluxes of water and ethanol vs. feed concentration are shown in Figure 8. The permeation fluxes vs. concentration curves of water from water/ethanol mixtures showed a convex one to upward in contrast to the case of water/methanol as shown in Figure 6. The results may be explained in terms of the plasticizing effect

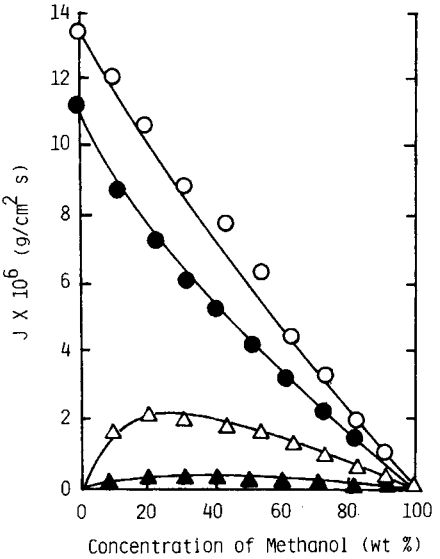


Fig. 6. Methanol concentration vs. permeation fluxes (J) of water and methanol from their mixtures: (○) water/*N*-3MMHT (190°C); (△) methanol/*N*-3MMHT (190°C); (●) water/*N*-3MMHT (200°C); (▲) methanol/*N*-3MMHT (200°C)

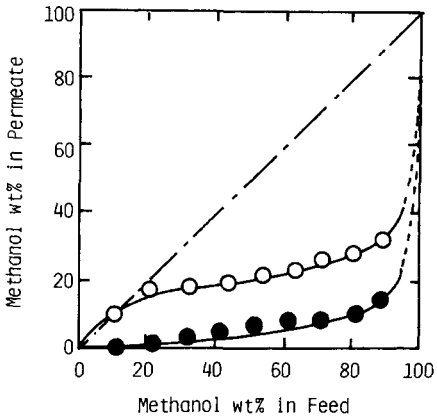


Fig. 7. Separation characteristics of water/methanol mixtures by *N*-3MMHT membranes: (○) water/methanol/*N*-3MMHT (190°C); (●) water/methanol/*N*-3MMHT (200°C).

by water/ethanol mixture is larger than that of water/methanol system. For example, the degrees of swelling of *N*-3MMHT (190°C) by water/methanol and water/ethanol (50/50) were 40 and 50% at 20°C, respectively. It is well known that the degree of swelling of polymer membrane by water/alcohol mixtures increased with increasing by numbers of carbon of alcohol in mixtures.[10] However, the permeation fluxes of ethanol are much lower than methanol. In Figure 9, the separation characteristics of water/ethanol are shown. The separation characteristics of the *N*-3MMHT for water/ethanol are superior to that of water/methanol because of the lower diffusivity of ethanol which has a larger molecular volume than methanol. The product

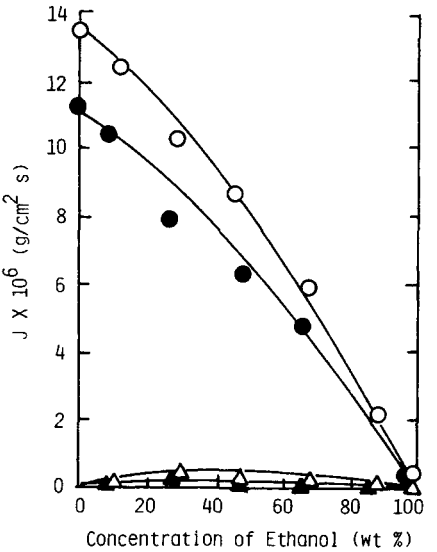


Fig. 8. Ethanol concentration vs. permeation fluxes (J) of water and ethanol from their mixtures: (○) water/*N*-3MMHT (190°C); (△) ethanol/*N*-3MMHT (190°C); (●) water/*N*-3MMHT (200°C); (▲) ethanol/*N*-3MMHT (200°C).

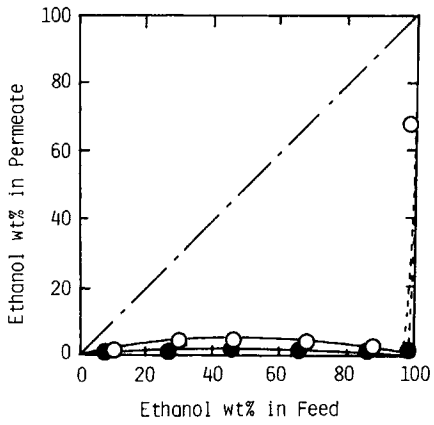


Fig. 9. Separation characteristics of water/ethanol mixtures *N*-3MMHT membranes: (○) water/ethanol/*N*-3MMHT (190°C); (●) water/ethanol/*N*-3MMHT (200°C).

of the separation factor (200) by permeation flux (kg/m^2 h), which is a measure of separation[11] was about 50 for water/ethanol (50/50). This value can be improved by making the membrane thickness.

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