Development of Polyion Complex Membranes for the Separation of Water–Alcohol Mixtures. I. Synthesis and Physical Properties of the Polycations Based on 1,3-Di(4-pyridyl)propane

JONGGEON JEGAL,* JEONG-HOON KIM, YOU-IN PARK, and KEW-HO LEE

Membrane and Separation Lab., Advanced Polymer Division, Korea Research Institute of Chemical Technology, P.O. Box 9, Daedeog Danji, Taejon, 305-606, South Korea

SYNOPSIS

To prepare good polymeric materials for the preparation of the polyion complex membranes useful for water–alcohol separation, polycations were synthesized by the quaternization polymerization of 1,3-di(4-pyridyl)propane with dibromoalkanes or with 1,8-bis(p-toluenesulfonyl)octane. The polycations were characterized by FTIR spectroscopy, viscometery, DSC, and X-ray diffractometry. The polycations were in molecular weight ranges good enough to be used as membrane materials. The polycations were very hygroscopic and easily soluble in highly polar solvents such as water and these properties might be good for the membrane materials. The thermal properties and X-ray diffraction patterns of these polycations suggested that the polycations were semicrystalline and difficult to form crystals by melt crystallization. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation has become important as a method to separate liquid mixtures, especially azeotropic and close boiling-point mixtures. Especially, water/alcohol separations by pervaporation have been carried out often because of the practical interest of industries. There are two types of membranes for separation of water–alcohol by pervaporation: water-selective membranes and alcohol-selective membranes.

To separate out water, selectively, from alcohol solutions with an aim of alcohol purification, a membrane has to be water-selective and have excellent affinity to water. Among the hydrophilic polymers used for the preparation of water-selective membranes, polyacrylic acid and poly(vinyl alcohol) are used widely.[1–5] Many different types of ionomers also have been used with this purpose.[6–10] In recent years, polyion complexes started to be used.[7] Among these hydrophilic polymer systems, polyion complexes are the most hydrophilic with good stability due to ion complexes, which other polymer systems do not have. The polyion complexes are made by the ionic cross-linking between a polyanion that contains anionic sites on the polymer chains and a polycation that contains cationic sites on the polymer chains. The polyion complex structure, consisting of polyacrylic acid (PAA) and a polycation, showed excellent permeation rate and selectivity.[7] It was known that among the polycations ionenes, which have quaternary ammonium groups on the polymer backbone, were effective in giving membranes of higher permselectivities.[7] However, the effects of the ion contents and counterion species of polycations or polyanions on the membrane properties such as selectivity and permeability have been rarely studied so far. On this basis, we tried to synthesize new polymeric materials for polyion complex membrane preparations. The objectives of this research were to study the effects of ion contents and ion species on the membrane properties on the water–alcohol separation by pervaporation.

In this study, syntheses and characterizations of the ionene-type polycations for the preparation of

---

the membranes suitable for our objectives were studied. Polycations were synthesized by quaternization polymerization. The ion contents of the polycations were controlled by using different alkyl dihalides with a different number of methylene units. Polycations with different counterions, bromide and p-toluenesulfonate, were obtained from the polymerization of 1,3-di(4-pyridyl)propane with dibromoalkanes or with di-(p-toluenesulfonyl)octane. Characterization of the polycations was done by various methods to determine if these materials are good for the preparation of polyion complex membranes.

EXPERIMENTAL

Materials

p-Toluenesulfonyl chloride, 1,8-dihydroxyoctane, 1,3-di(4-pyridyl)propane, 1,2-dibromoethane, 1,2-dihydroxyethane, and 1,8-dibromooctane were purchased from the Tokyo Kasei Co. 1,3-Di(4-pyridyl)propane was purified by recrystallization in cyclohexane solution, and 1,2-dibromoethane and 1,8-dibromooctane were purified by recrystallization in ethanol solution. p-Toluenesulfonyl chloride, 1,8-dihydroxyoctane, and 1,2-dihydroxyethane were used without purification. Pyridine and acetonitrile were purchased from Tokyo Kasei Co. and used as the catalyst and solvent, without purification.

Syntheses

1,8-Bis(p-toluenesulfonyl)octane

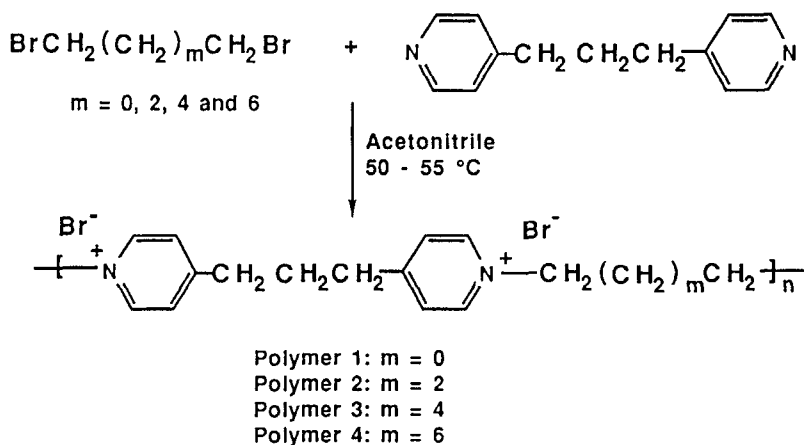1,8-Dihydroxyoctane (10 g, 0.068 mol) was dissolved in 32 mL of pyridine and the resulting solution was

cooled down to around 5°C in an ice bath. p-Toluenesulfonyl chloride (27 g, 0.143 mol) was added in portions over a 20–30 min period. The mixture solution was then stirred for 3 h at a temperature below 20°C, after which it was diluted with 100 mL of hydrochloric acid in 1 L of ice water. The precipitated ester was collected on a chilled funnel and dried. This product was purified by recrystallization in ethanol solution and white needle-shaped crystals were obtained. IR (KBr cm^{-1}): 3066.7 (aromatic C—H stretch), 2933.3, 2844.4 (aliphatic C—H stretch), 1350 [asymmetric S(=O)$_2$ stretch], and 1172.2 [symmetric S(=O)$_2$ stretch].

Polymerization

Polycations were prepared by the quaternization polymerization of 1,3-di(4-pyridyl)propane with dibromoalkanes or with a di-p-toluenesulfonyl octane in the acetonitrile as shown in Schemes 1 and 2.

Preparation of Poly{1,3-bis[4-ethylpyridinium]propane bromide} (Polymer 1)

1,2-Dibromoethane, 6.95 g (0.037 mol), and 1.3-di(4-pyridyl)propane, 7.28 (0.037 mol), were dissolved in 200 mL of acetonitrile and the resulting solution was heated to 55°C and stirred at this temperature for 5 days. The product was precipitated out after 1 day polymerization, and the precipitated product was collected and filtered after a 5 day polymerization and then dried under vacuum at room temperature for 24 h. The product was highly hygroscopic and very soluble in water and methanol. IR (film, cm^{-1}): 3425 (amine salt), 3024 (pyridinium ring C—H stretch), 2947, 2885 (aliphatic C—H stretch), and 1639 (C=C stretch).

BrCH$_2$(CH$_2$)$_m$CH$_2$Br   +

m = 0, 2, 4 and 6

Acetonitrile
50 - 55 °C

Polymer 1: m = 0
Polymer 2: m = 2
Polymer 3: m = 4
Polymer 4: m = 6

Scheme 1   Polymerization of the polycations by the quaternization reaction of 1,3-di(4-pyridyl)propane with dibromoalkanes with different numbers of methylene units.
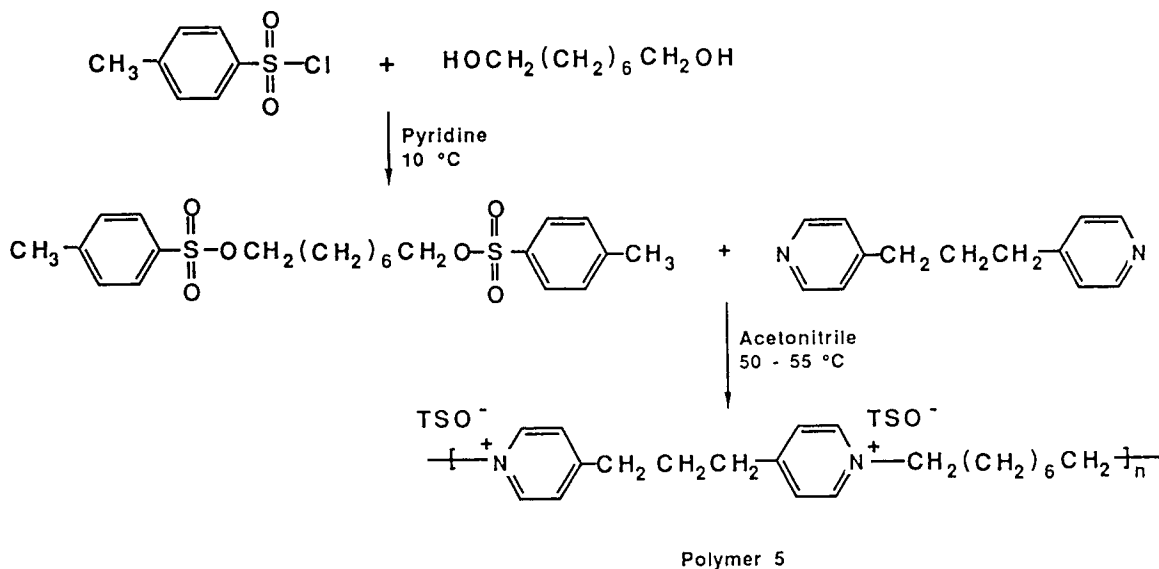
Scheme 2   Synthesis of 1,8-bis(p-toluenesulfonyl)octane and polymer with p-toluene-sulfonate as a counterion.

Preparation of Poly{1,3-bis[4-butylpyridinium] propane bromide} (Polymer 2)

1,4-Dibromobutane, 8.0 g (0.037 mol), and 1.3-di(4-pyridyl)propane, 7.28 g (0.037 mol), were dissolved in 200 mL of acetonitrile and polymerized by the same method as the polymerization of a poly{1,3-bis[4-ethylpyridinium]propane bromide}. IR (film, cm^{-1}): 3425 (amine salt), 3024 (pyridinium ring C—H stretch), 2947, 2885 (aliphatic C—H stretch), and 1639 (C=C stretch).

Preparation of Poly{1,3-bis[4-hexylpyridinium]propane bromide} (Polymer 3)

1,6-Dibromohexane, 9.03 g (0.037 mol), and 1.3-di(4-pyridyl)propane, 7.28 (0.037 mol), were dissolved in 200 mL of acetonitrile and polymerized by the same method as that for the polymerization of a poly{1,3-bis[4-ethylpyridinium]propane bromide}. IR (film, cm^{-1}): 3425 (amine salt), 3024 (pyridinium ring C—H stretch), 2947, 2885 (aliphatic C—H stretch), and 1639 (C=C stretch).

Preparation of Poly{1,3-bis[4-octylpyridinium]propane bromide} (Polymer 4)

1,8-Dibromooctane, 10 g (0.037 mol), and 1.3-di(4-pyridyl)propane, 7.28 g (0.037 mol), were dissolved in 200 mL of acetonitrile and polymerized by the same method as that for the polymerization of a poly{1,3-bis[4-ethylpyridinium]propane bromide}. IR (film, cm^{-1}): 3425 (amine salt), 3024 (pyridi-

nium ring C—H stretch), 2947, 2885 (aliphatic C—H stretch), and 1639 (C=C stretch).

Preparation of Poly{1,3-bis[4-octylpyridinium]propane p-toluenesulfonate} (Polymer 5)

1,8-Bis(p-toluenesulfonyl)octane, 2 g (0.0044 mol), and 1.3-di(4-pyridyl)propane, 0.87 g (0.0044 mol), were dissolved in 100 mL of acetonitrile and the resulting solution was heated to 55°C and stirred at this temperature for 5 days. The solvent of the solution was rotary-evaporated and product was dried under vacuum at room temperature for 24 h. The product was highly hygroscopic and very soluble in water, methanol, and ethanol. IR (film, cm^{-1}): 3433 (amine salt), 3051 (pyridinium ring C—H stretch), 2931, 2858 (aliphatic C—H stretch) 1639 (C=C stretch), 1358 [asymmetric S(=O)$_2$ stretch], and 1188 [symmetric S(=O)$_2$ stretch].

Characterizations

Thermal properties of the polycations were studied with a differential scanning calorimeter (DSC) (DuPont, Model 910 differential scanning calorimeter). Heating and cooling were at a rate of 10°C/min. All reported transition temperatures correspond to the peak maximum of the trace obtained from the intersection points of the tangents drawn to the peak.

Chemical structures of the polycations and monomers were characterized by an infrared spectrophotometer (Bio-Rad, Digilab Division, Model FTS-80, FTIR). The crystallinity and intermolecular distances of the polycations were studied with an X-ray diffractometer (Model D/MAX IIIB Rigaku) using nickel-filtered CuKα radiation with wavelength as 1.54 Å. Inherent viscosities of the polymers were obtained from the polycations solutions (1 g/dL) in methanol by using an Ubbelohde viscometer at 25°C.

RESULTS AND DISCUSSION

Syntheses

Polycations, polymers 1–5, were prepared by the quaternization polymerization of 1.3-di(4-pyridyl)propane with dibromoalkanes with different numbers of methylene units such as dibromoethane, dibromobutane, dibromohexane, and dibromooctane, or with di-p-toluenesulfonyloctane as shown in Schemes 1 and 2. On polymerization, the amine group in the pyridine ring of 1.3-di(4-pyridyl)propane reacted with the carbon atom attached directly to the bromine of 1,2-dibromoethane, e.g., and cationic parts were formed on the polymer backbone, which resulted in the formation of the polycation with bromide counterions. The produced ionic parts on the polymer backbone played an important role on the molecular weight growth on the polymerization. Since the ionic parts were very polar groups, the propagating polymers were becoming

polar due to the accumulating ionic parts on the backbone of the polymers with increasing degree of polymerization. Eventually, the polymers with a certain amount of the ionic parts were too polar to be dissolved in the solvent for polymerization and precipitated. The precipitated polymers could not propagate for the further polymerization and the degree of polymerization could not be increased any more. This kind of phenomenon is more prominent in the case of the polymerization of 1.3-di(4-pyridyl)propane with dibromoalkanes having a small number of methylene units such as 1,2-dibromoethane.

Infrared Studies

The infrared (IR) spectra of the polycations are shown in Figures 1 and 2. They present IR spectra of the poly{1,3-bis[4-octylpyridinium]propane bromide} and the poly{1,3-bis[4-octylpyridinium]propane p-toluenesulfonate}, respectively. Both these spectra show a very strong peak at 3452 cm^{-1}, which is a very typical ionic peak. This peak indicates that these polymers are ion-containing polymers: polycations. The IR spectra of the other polycations, polymers 1–3, containing bromides as counterions and a different number of methylene units, also showed the same pattern as that of a poly{1,3-bis[4-octylpyridinium]propane bromide} but different sizes of aliphatic C—H stretching peaks at 2930 and 2855 cm^{-1}. The polymers with a higher number of methylene units showed bigger sizes of those peaks.
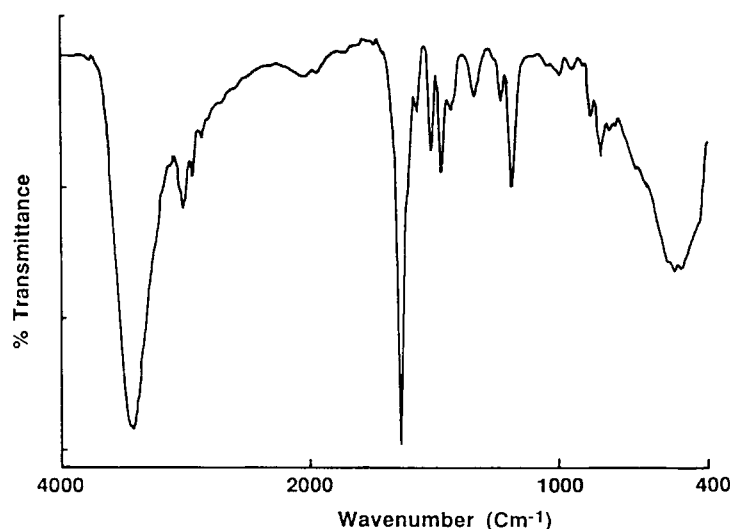

Figure 1   IR spectrum of poly{1,3-bis[4-octylpyridinium]propane bromide}.
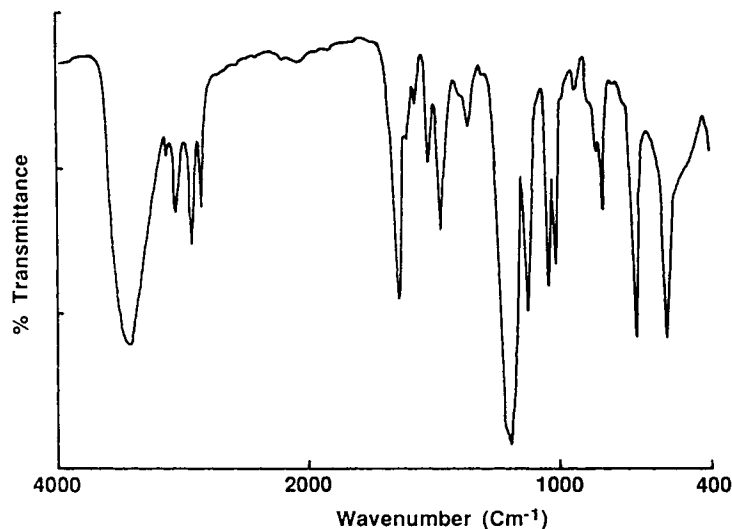
Figure 2   IR spectrum of poly{1,3-bis[4-octylpyridinium]propane p-toluenesulfonate}.

Viscosity Studies

The inherent viscosities of the polycations are shown in Table I. The inherent viscosities of the polycations were increased with decreasing ion contents of the polymers in the order from polymer 1 to polymer 4, as shown in Table I. This result can be explained by the solubilities of the propagating polymers in the polymerization solvent: acetonitrile. As explained in the synthesis part, since the propagating polymers are forming ionic sites on the polymer backbone on the polymerization, the propagating polymers become more polar and, eventually, the polymers that are too polar to be dissolved in the solvent precipitate out and no further polymerization can occur. Therefore, the solubility of the propagating polymers is one of the major factors affecting on the molecular weight of the polymers.

Polymer 1, polymerized from the reaction of 1,2-dibromoethane and 1,-di(4-pyridyl)propane, has the highest ratio of ionic parts to nonionic parts per a repeat unit of the polymer among the synthesized

polycations in this study. This highest ratio of ionic parts to nonionic parts makes the polymer too polar to be dissolved in the solvent in the early stage of the polymerization with a low degree of polymerization, which resulted in low molecular weight and low inherent viscosity. With an increasing number of methylene units of dibromoalkanes from 4 to 8, used for the polymerization, the produced polycations were more soluble in the solvent and higher molecular weight and higher inherent viscosity were obtained. From the inherent viscosities of the polycations, it was found that all the polycations except polymer 1 had molecular weights high enough to be used for membrane preparations.

Solubility Studies

Table II presents the solubilities of the polycations in several solvents having different polarities. All the polycations were hygroscopic, taking moisture in the air, and becoming sticky, easily, due to the

Table I   Inherent Viscosities of the Polycations

Polymers	η_{inh}
Polymer 1	0.10
Polymer 2	0.80
Polymer 3	1.20
Polymer 4	1.25
Polymer 5	1.50

 [a] All viscosities were obtained from the 1 g/dL methanol solution at 25°C.

Table II   Solubilities of the Polycations in Various Solvents

	Water	Methanol	Ethanol	Isopropanol
Polymer 1	VS	S	IS	IS
Polymer 2	VS	S	SS	IS
Polymer 3	VS	S	S	IS
Polymer 4	VS	S	S	IS
Polymer 5	VS	S	S	IS

[a] VS: very soluble; S: soluble; SS: slightly soluble; IS: insoluble.

Table III   Thermal Properties of the Polycations

Polymers	First Heating			First Cooling			Second Heating		
	T_g	T_1	T_2	T_g	T_1	T_2	T_g	T_1	T_2
Polymer 1			153.1						
Polymer 2	51.4	108.6	204.0	67.1	—	—	75.7	—	—
Polymer 3	45.7	106.0	200.0	61.4	—	—	71.4	—	—
Polymer 4	25.0	111.4	191.4	58.6	—	—	70.0	—	—
Polymer 5	1.7	81.2	200.0	—	—	—	-3.3	—	—

ᵃ Heating and cooling rate: 10°C/min.

high polarity that resulted from the formed ionic parts on the polymer backbone. All the polycations showed good solubilities in highly polar solvents but bad solubilities in relatively less polar solvents. All the polycations were soluble in highly polar solvents such as water and methanol. In ethanol, all the polycations except polymers 1 and 2 were soluble. Polymer 1 was insoluble and polymer 2 swelled but not dissolved in ethanol. This is due to the high ion contents. The solubility behaviors of the polycations and the very hydrophilic properties suggest that these polycations will be good candidates as membrane materials for dehydration by the pervaporation process.

Thermal Analysis

The thermal properties of the polycations are shown in Table III and Figures 3 and 4. All the polycations showed glass transition points and two transition

temperature points each on the first heating scan of the differential scanning calorimeter (DSC). The first transition points, T_1, of all the polycations are dehydration steps and the second transition points, T_2, are the crystal melting points.

As shown in Table III, the glass transition temperatures (T_g) of the polymers decreased with increase in the length of the flexible methylene groups in the polymer backbone. This phenomenon is very general in polymer systems and due to the increasing flexibility of the polymer backbone with increase in methylene units. The glass transition temperature also depended on the counterion species of the polycations. The T_g of polymer 4, which has bromides as counterions, is higher than that of polymer 5, which has p-toluenesulfonates as counterions. This result is due to the different sizes of the counterions: p-toluenesulfonate and bromide. Because the size of p-toluenesulfonate is much greater than that of the bromide, the free volume of polymer 5 with p-toluenesulfonate is larger than that of polymer 4,
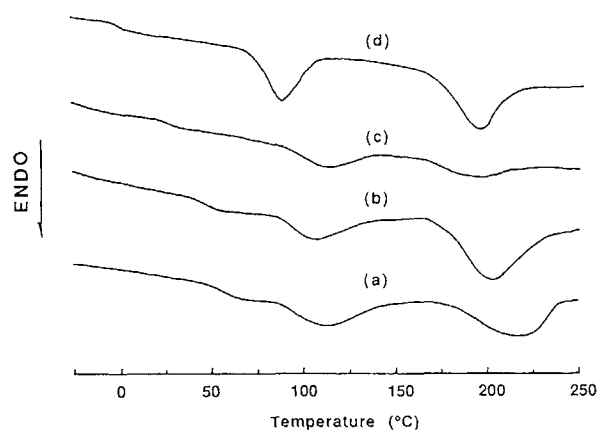

Figure 3   DSC curves for the polycations, obtained from the first heating with a heating rate 10°C/min: (a) polymer **2**; (b) polymer **3**; (c) polymer **4**; (d) polymer **5**.
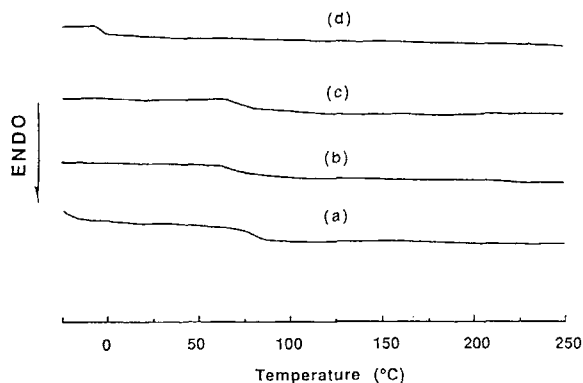
Figure 4   DSC curves for the polycations, obtained from the second heating with a heating rate 10°C/min: (a) polymer **2**; (b) polymer **3**; (c) polymer **4**; (d) polymer **5**.

and this higher free volume of the polymer resulted in the decrease in T_g.

The first transition temperatures of the polycations on the DSC curves, shown in Figure 3, are supposed to be the dehydration steps. These first transition temperatures of the polymers with bromides ranged from around 80 to 130°C and are not changed from polymer to polymer. However, that of the polymer 5, with p-toluenesulfonate, is much lower and ranged from around 50 to 100°C. These results may be due to the different polarizabilities of the counterions. Because the size of the bromide is smaller, more polar, and less polarizable than is the p-toluenesulfonate, water bound to bromides more tightly. The water bound more tightly to the ions, bromides, in the polymers may show dehydration peaks at a higher temperature range on the DSC scan.

From the first cooling and second heating scans of DSC, no transition temperatures but T_g points were observed. This is very typical phenomenon in the case of the polymers containing ions in the polymer backbone. The melt crystallization of these polymers is very slow because of the very strong interactions between the ions and the crystallization of these polymers cannot occur on the cooling scan in DSC with a cooling rate 10°C/min, so that the first cooling and the second heating scan of the polymers do not show any transition temperature point. The T_g points observed on the second heating scan of these polymers have the same tendency as

shown on the first heating scan but have a higher value. From the Table III, it is found that T_g points obtained from the second heating scan are almost 25–35°C higher.

X-ray Diffraction Studies

The X-ray diffraction (XRD) patterns of the polycations are shown in Figures 5 and 6. From these X-ray diffraction patterns, showing sharp crystal peaks at around 21°–23° and overall broad peaks, it is found that all polycations are semicrystalline polymers. The XRD patterns of the polycations, having a same counterion species, do not vary from polymer to polymer. However, the crystal lattice distance (d) of the polycations depended on the counterion species. Figure 6 presents XRD patterns of polymers 4 and 5. From this, it is found that the crystal lattice distance (d) of polymer 5 is longer than that of polymer 4 and this result may be due to the different sizes of the counterions. Because p-toluenesulfonate is bigger than bromide, polymer 5 with p-toluenesulfonate shows a longer lattice distance than that of polymer 4 with bromide.

CONCLUSIONS

Polycations for the preparation of polyion complex membranes useful for the separation of water out of alcohol solutions by the pervaporation process can
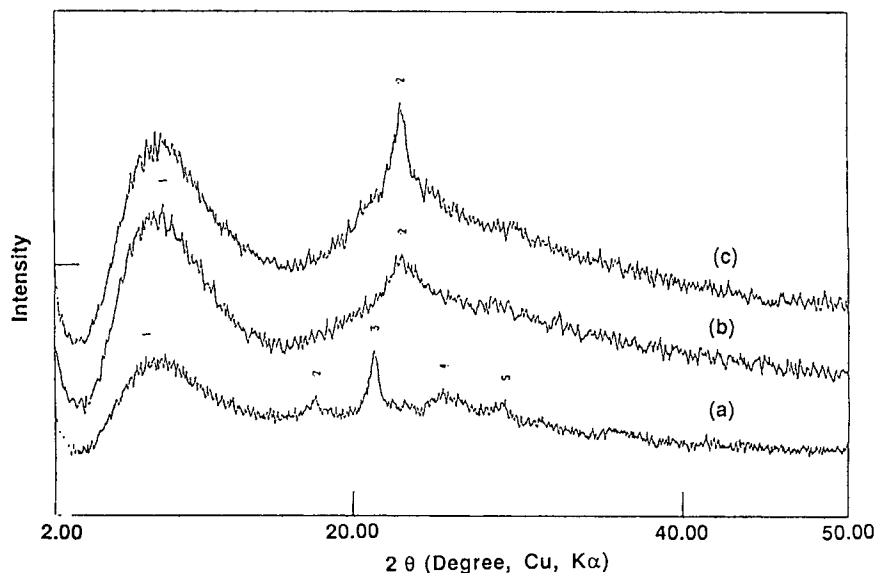
Figure 5   X-ray diffraction patterns of the polycations: (a) polymer **1**; (b) polymer **2**; (c) polymer **3**.
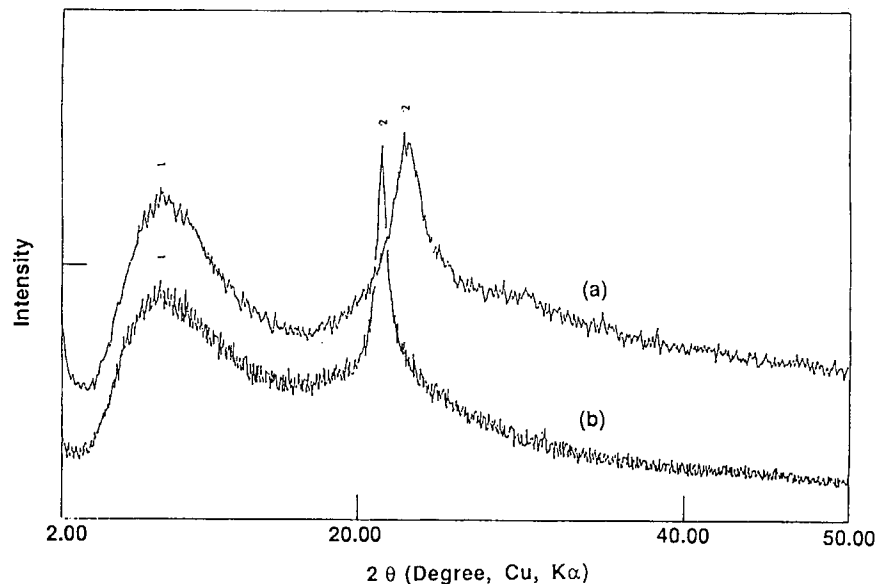
Figure 6 X-ray diffraction patterns of the polycations: (a) polymer 4; (b) polymer 5.

be obtained by the quaternization polymerization of 1,3-di(4-pyridyl)propane with alkyl dihalides. The molecular weights of the polycations were high enough to be used as membrane materials and depended on the solubilities of the propagating polymers in the polymerization solvent. Polycations with better solubilities have higher molecular weights. All the polycations were very hygroscopic and soluble in the highly polar solvents such as water. The solubilities of the polycations depended on the ion contents and different counterion species such as bromide and p-toluenesulfonate. The polycations with high ionic contents showed better solubilities in the polar solvents and lower solubilities in the less polar solvents. These solubility properties suggest that these polycations may be good materials of the membrane for the separation of water out of the alcohol solution. All the polycations with relatively high molecular weights except polymer 1 showed glass transition temperatures, crystal melting temperatures, and dehydration temperatures on the first scanning of DSC. X-ray diffraction of all the polycations suggested that these polymers were semicrystalline polymers and d spacing of the crystals of the polycations depended on the counterions.

REFERENCES

1. T. Hirotsu, K. Ichimura, K. Mizoguchi, and E. Nakamura, *J. Appl. Polym. Sci.*, **36**, 1717 (1988).
2. X. P. Zhao and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **41**, 2133 (1990).
3. W. Y. Chiang and C. M. Hu, *J. Appl. Polym. Sci.*, **43**, 2005 (1991).
4. R. Y. M. Huang and N. R. Jarvis, *J. Appl. Polym. Sci.*, **14**, 2341 (1970).
5. J. Hauser, G. A. Reinhardt, F. Stumm, and A. Heintz, *J. Membr. Sci.*, **47**, 261 (1989).
6. M. Tsuyumoto, H. Karakane, Y. Maeda, and H. Tsugaya, *Desalination*, **80**, 139 (1991).
7. H. Karakane, M. Tsuyumoto, Y. Maeda, and Z. Honda, *J. Appl. Polym. Sci.*, **42**, 3229 (1991).
8. J. Nieuwenhuis, Y. Y. Tan, and G. O. R. Alberda van Ekenstein, *Angew. Makromol. Chem.*, **147**, 83 (1987).
9. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *Polym. J.*, **18**, 447 (1986).
10. M. Yoshikawa, S. Ochiai, M. Tanigaki, and W. Eguchi, *Makromol. Chem. Rapid Commun.*, **9**, 559 (1988).