Preparation and Characterization of Membranes with Positively Charged Main Chain from Polyethylenimine

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SYNOPSIS

A membrane, which has positively charged groups in the polymer main chain, was prepared from polyethylenimine by crosslinking and successive alkylation. Dibromoalkane was used as a crosslinking agent. The crosslinked membrane was alkylated using methyl iodide under several conditions. Elemental and ICP emission analyses were introduced to measure the rates of alkylation and quaternization. From the membrane potential measurement, the effective charge density was estimated. The highest value was about 1.0 M, which was obtained by a prolonged alkylation time. This value was larger than that of some commercial ion exchange membranes. The effective charge density, which was obtained by the last alkylation procedure, was 10 times larger than that of the former one, though the rate of quaternizing increased by less than a factor of two. This implies that the activity constant in the membrane increased when the charge density is increased. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Synthetic charged membranes have been important, not only in the physical and chemical studies of model systems, but also in industrial applications, such as seawater desalination, ultra-purified water manufacturing, salt production, and waste water disposal.[1,2] Also, the membranes have been studied as models of biomembranes in the fields of biology, medicine, biochemistry, and physiology.[2]

In general, the electric charges are placed on polymer side chains in synthetically charged membranes. On the other hand, we have been interested in polyphosphates and ionenes as samples, which have charged groups directly on the polymer main chains.[3-7] In this study, membranes, which have charged groups on the polymer main chain, were prepared from polyethylenimine (PEI) by crosslinking and alkylation, in order to examine the effects of the charged groups.

We used several dibromoalkanes as crosslinking agents, because a charged membrane should be composed of only $-CH_2-$ and $-N-$ residues, as will be shown. Samples were prepared to alkylate these membranes by CH_3I.

The measurement of membrane potential is one of the methods that was used to characterize the charged membranes. By applying the theory of Teorell,[8] Meyer, and Sievers (TMS),[9] which is composed of the Donnan equilibrium[10] and the Nernst Planck's ion flux equations, to the experimental results, characteristic parameters of charged membranes, such as charge density and ion mobility in the membrane, can be determined. Membrane charge density is one of the relevant parameters used to understand the state of the charge groups in the membrane.[11]

EXPERIMENTS

Preparation of Polyethylenimine (PEI) Membranes

Membranes were prepared by crosslinking PEIs (Nippon Shokubai Kagaku Kogyo Co., Ltd.), whose mol wts were 300, 1200, and 10,000, respectively. As crosslinking agents, 1,4-dibromobutane, 1,6-dibro-

mohexane, 1,8-dibromooctane, 1,9-dibromononane, and 1,10-dibromodecane (Tokyo Kasei Kogyo Co., Ltd.) were used. After mixing with the crosslinking agents and ethanol, the PEIs were cast on teflon petri dishes at 20, 50, 60, and 80°C. The PEIs were wrapped in PVDC film prior to the casting to prevent ethanol evaporation.

Alkylation of Membranes

Alkylation of the membranes was carried out as follows. First, unreacted crosslinking agents in the PEI membranes were removed with a Soxhlet extractor for 8 h, using ethanol as a solvent. Second, after drying at 60°C for 6 h in a vacuum oven, the membranes were alkylated by methyl iodide under three different temperature conditions of 40, 60, and 80°C. Alkylation was done in a flask with solvents using 30 mL CH₃I and 0.5 g membrane in an oil-bath at 40°C, and in an autoclave at 60°C and 80°C. The alkylated samples were soaked in aqueous 2 N KOH solution for 12 h to remove halogen ions, which might be left in the membranes. The samples were then washed with deionized water for 12 h to remove any KOH remaining in the membranes. The samples were finally dried at 60°C for 6 h in a vacuum oven to prepare them for elemental analysis.

Measurement of Rate of Alkylation by Elemental Analysis

The rate of alkylation was determined by comparing the C/N ratios of PEI before and after crosslinking. The C/N ratios were measured by an elemental analyzer (Yanagimoto, High speed CHN corder MT2).

Measurement of Rate of Quaternized Nitrogen Atoms in PEI by ICP Emission Analysis

Samples were soaked in 3 M KI for 24 h to coordinate HI with the quaternary nitrogen atoms. Amounts of coordinated I^- were measured by the ICP emission analyzer (Shimazu ICPS-1000 II).

Measurement of Membrane Potential

A schematic diagram of a potential measurement cell, whose compartments are separated by a membrane, is shown in Figure 1. The membrane area contacting the solution is 3.14 cm². The solution, circulating in the two compartments, contained the same electrolytes in different concentrations. The ratio of high to low concentration was five. Glass electrodes (Toa, HS-205 C) and a voltmeter (Toa, ION-METER) were used under nitrogen atmosphere. The measurement temperature was about 20°C. The electrolyte concentration of the dilute side varied from between 1×10^{-3} to 0.3 M. If the ion concentration in the dilute side exceeded 0.3 M, which corresponded to 1.5 M in the concentrated side, all the PEI membrane was cracked and successively destroyed.

Measurement of Rate of Swelling

The samples were soaked in deionized water for 24 h and their weights were measured. The samples were then dried at 60°C for 6 h in vacuum and their weights were again measured. The rates of swelling, q, were calculated as shown in eq. (1), where the weights of dried and wet samples are shown as DW
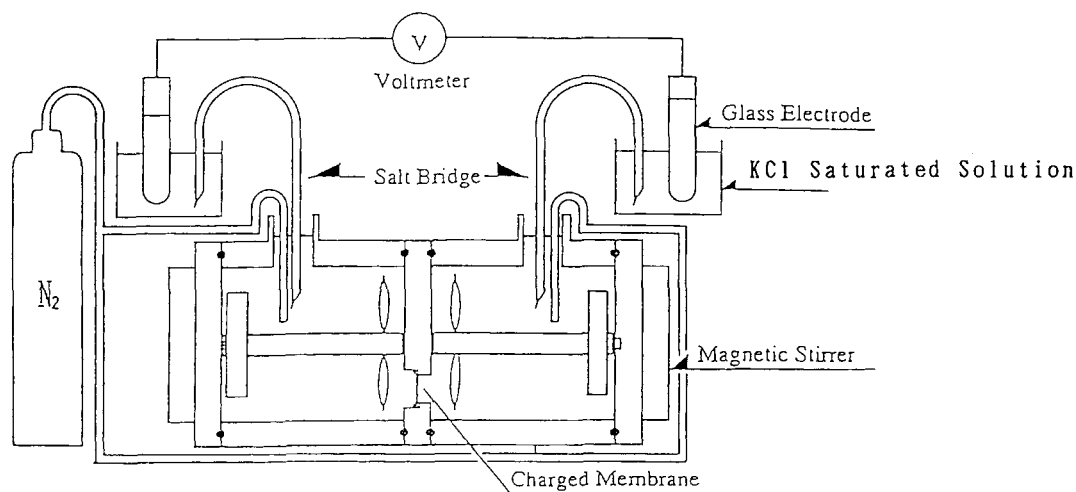

Figure 1   Apparatus for membrane potential measurement.

and WW, respectively. The density of the membrane measured by pycnometer was 1.2 g/cm^3.

$$q = \frac{(WW - DW)/1.0 + DW/1.2}{DW/1.2} \quad (1)$$

RESULTS AND DISCUSSION

Membrane Preparation

Membrane preparation and alkylation could be carried out according to the following different procedures. (1) alkylation is performed after preparing the PEI membranes and (2) alkylation is performed prior to membrane preparation.

The latter reaction produces better alkylation than crosslinking, because the reactivity of CH_3I is higher than that of the crosslinking agents. After different amounts of CH_3I reacted with the nitrogen atoms, the crosslinking reaction was not uniform. Because the rate of crosslinking is one of the important factors for membrane characterization, each sample is expected to have a small difference in the rate of crosslinking for this study. Therefore, it is preferable to crosslink PEI before the alkylation by CH_3I for the preparation of membranes, which should have the same rate of crosslinking. Consequently, the first method was adopted. Three kinds of PEI, whose mol wts were 300, 1200, and 10,000 were used.

A reliable membrane, which physically had sufficient strength in water, was prepared from PEI 1200. PEI 300 required a larger amount of crosslinking agent and a higher reaction temperature for membrane formation than those for PEI 1200. A brittle membrane was prepared from PEI 10,000.

Since PEI has a large number of branches,[12,13] which cause many intramolecular crosslinking reactions, it is difficult to achieve adequate intermolecular crosslinking reactions. When 1,4-dibromobutane and 1,6-dibromohexane were used as crosslinking agents, the membranes could not be prepared, because the agents' chains were too short to form the intermolecular crosslinking.

In our study, membranes must have sufficient physical strength for measurement of the membrane potential in the aqueous salt solution. The optimum condition applied in this study consisted of using PEI 1200 (0.7 g), mixed with 1.9-dibromononane (1.2 g), and ethanol (5.0 mL). The mixture was placed on a teflon petri dish (diameter, 9 cm), was sealed by a PVDC film, and was cast for 44 h at 50°C. The membrane thicknesses were 300 to 400 μm.

Crosslinking agents might react at one end only during the crosslinking reaction. However, the results of elemental analysis of pure PEI 1200 and crosslinked PEI 1200 showed that the amounts of halogen were not increased substantially. Considering this result, the reaction of crosslinking agents only at one end is negle.

Further Alkylation

Membranes were alkylated with CH_3I by the method discussed.

The rates of alkylation, measured by elemental analysis, are shown in Table I with the conditions of sample preparation. The rates are indicated by the number of the methyl groups linked with 100 nitrogen atoms. By comparing S40A44 with S80A44, S40E44 with S80E44, and S40D44 with S80D44, it is clearly shown that the rates of alkylation were increased as reaction times were increased. On the other hand, S40N44 is comparable to S40N88.

The rate of alkylation of S80D44 was the highest of all the samples; the highest reaction temperature

Table I   Rates of Alkylation and Alkylation Condition

Sample	Temperature (°C)	Solvent	Time (h)	Rate of Alkylation by Methyl Iodide
S40N44	40	No Solvent	44	16
S40A44	40	Acetone	44	11
S40E44	40	Ethanol	44	58
S40D44	40	DMF	44	79
S40E22	40	Ethanol	22	46
S40N88	40	No Solvent	88	12
S80A44	80	Acetone	44	27
S80E44	80	Ethanol	44	73
S80D44	80	DMF	44	129

Table II   Rates of Crosslinking, Alkylation, and Quaternizing

Sample	Rate of Crosslinking	Rate of Alkylation	Rate of Quaternizing
Sample 1'-O-OH	47	47	17
Sample 1'-1-OH	47	162	42
Sample 2'-1-OH	47	119	—
Sample 2'-2-OH	47	163	36
Sample 2'-3-OH	47	182	58
Sample 1-O-OH	50	50	—
Sample 1-1/2-OH	50	118	—
Sample 1-1-OH	50	142	—

(80°C) and a solvent (DMF), which enhances alkylation reactivity,[14] caused this high rate. However, the physical reliability of the sample was not good. Consequently, the alkylation conditions that we adopted involved ethanol as the solvent and the reaction temperature of 40°C.

In alkylated membranes, the nitrogen atoms might be coordinated with the HBr or HI produced during the alkylation. This means that the nitrogen atoms have a positive charge, and further alkylation could be difficult. Therefore, to increase the rates of alkylation of the membranes, the removal of halogen by soaking in 2 N KOH and alkylation with CH$_3$I was repeated. Table II shows the rates of alkylation and quaternizing, which were measured by ICP emission analysis. Crosslinked PEI membranes were soaked in 2 N KOH for 12 h and subsequently in H$_2$O for 12 h. These samples are designated as sample 1. Samples, which were not soaked in 2 N KOH, are designated as sample 2. Sample 1 and 2, alkylated for 44 h under the conditions cited above, serve as sample 1-1 and sample 2-1, respectively. These 1-1 and 2-1 samples were soaked in 2 N KOH and subsequently in H$_2$O after drying at 60°C for 6 h in a vacuum oven.

Samples 1-1 and 2-1 were further alkylated by the same process, are indicated as sample 1-2 and sample 2-2, and were alkylated three times to form sample 2-3. Portions of samples 1 and 2 were alkylated for 22 h instead of 44 h and were designated as sample 1-$\frac{1}{2}$ and sample 2-$\frac{1}{2}$. Some samples were used for elemental analysis. These were soaked in 2 N KOH for 24 h and subsequently in H$_2$O for 24 h; — OH was tagged on the end of the sample code.

Finally, all samples, except those for elemental analysis, were dried at 60°C for 6 h in a vacuum oven and were soaked in 1 M KCl for 24 h to make Cl$^-$ the counter ions. These prepared samples were supplied for the membrane potential measurements, and — Cl was tagged on the end of the sample code for identification.

In Table II, superscript ' means that the rate of alkylation of this sample is different from that of the sample without the superscript. Table II shows that the rates of alkylation increased in the order of the repeated number of alkylation reactions. The rates of alkylation of sample 1'-1 are as much as that of sample 2'-2. The rates of quaternizing increased in the order of sample 1', sample 2'-2, and sample 2'-3. Sample 1'-1 and sample 2'-2 have the same rate of alkylation. These results show that alkylation by CH$_3$I is completed easily after the membranes were prepared and washed with KOH aq. The rates of alkylation and quaternizing increased with repeated alkylation. It is concluded that the removal of the HI or HBr from the nitrogen atoms is one of the important factors for obtaining higher rates of quaternizing.

Effective Charge Density

Figure 2 shows the results of membrane potential measurements. The abscissa is the KCl concentration in the lower concentration compartment.

Generally, the TMS theory can be applied to this system, in which a charged membrane separates two aqueous solutions containing different concentrations of an electrolyte. This theory assumes that the membrane potential is the sum of diffusion potentials derived from the differences between cation and anion mobilities, and of the Donnan potential, due to the Donnan equilibrium. The following equation is applied to the system, where two 1-1-type electrolyte solutions are separated by a charged membrane.

$$\Delta\phi = \frac{RT}{F} \ln \frac{C_d(1 + (2\,C_0/QC_x)^2)^{1/2} + 1}{C_0(1 + (2\,C_d/QC_x)^2)^{1/2} + 1}$$

$$- \frac{RT}{F}\,W \ln \frac{(1 + (2\,C_d/QC_x)^2)^{1/2} + W}{(1 + (2\,C_0/QC_x)^2)^{1/2} + W} \quad (2)$$

where

$$Q^2 \equiv \frac{\gamma_+ + \gamma_-}{\kappa_+ + \kappa_-} \quad \text{and}$$

$$W \equiv \frac{\omega_+ - \omega_-}{\omega_+ + \omega_-}$$

The first part of the right side of eq. (2) stands for the Donnan potential and the second part for the diffusion potential. Using eq. (2), the effective charge density, QC_x, and the reduced ion mobility,
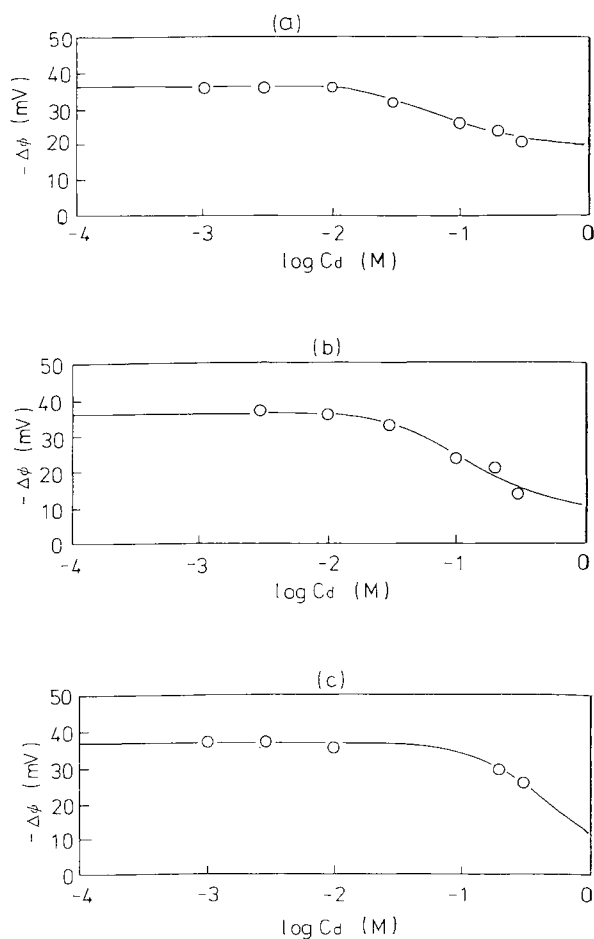

Figure 2 Membrane potential of various samples. (a) sample 1-0-Cl, (b) sample 1-$\frac{1}{2}$-Cl, and (c) sample 1-1-Cl.

Table III Effective Charge Density (QC_x), Reduced Mobility (W), and Concentration Ratio of External Solution (r)

Sample	QC_x	W	r
Sample 1-0-Cl	1.28×10^{-1}	5.27×10^{-1}	4.15
Sample 1-1/2-Cl	2.50×10^{-1}	2.40×10^{-1}	4.20
Sample 1-1-Cl	1.22	5.03×10^{-2}	4.17

W, were calculated from the experimental results, shown in Figure 2 and Table III. Generally, in the calculation of eq. (2), the concentration ratio of the two electrolyte solutions, C_d/C_0, is assumed to be constant. However, the activity constants of the solutions and the distribution constants of the ions are controlled by the electrolyte concentration, and a constant concentration ratio would not be reliable. Therefore, in this study, the concentration ratio is considered to be a variable to fit the experimental results to the TMS' equation.

It is observed clearly in Tables II and III that the higher the rate of alkylation or quaternizing that the samples have, the larger their effective charge densities become. This fact implies that alkylation promotes the charge loading of a membrane. The highest effective charge density obtained is about 1.0 M (sample 1-1-Cl), which is higher than that of commercial ion exchange membranes. The rate of alkylation, and also the effective charge density of sample 1-$\frac{1}{2}$-Cl, are twice as high as those of sample 1-0-Cl. On the other hand, the effective charge density of sample 1-1-Cl is about 5 times higher than that of sample 1-$\frac{1}{2}$-Cl. This fact means that the effective charge density is remarkably enhanced by a prolonged reaction time.

The factors controlling the effective charge density, calculated from the membrane potential, are presumed to be as follows.

Dissociation of Charged Group

The charged groups in these membranes are the nitrogen atoms in PEI. The alkylation of the nitrogen atoms in the samples was primary, secondary, tertiary, or quaternary. The dissociation constant of the quarternary nitrogen atom is nearly one. For other nitrogen atoms, the influence of OH^- dissociation must be considered.

Because the rate of quaternizing of sample 1-0-Cl and sample 1-1-Cl was not measured, the rate of quaternizing of sample 1-0 and sample 1-1 is esti-

mated from Table II. In Table II, it can be assumed that a similar rate of alkylation means a similar rate of quaternizing. Since samples 1-0 and 1'-0 have similar rates of alkylation (50 and 47), the rate of quaternizing of sample 1-0 should be similar to that of sample 1'-0 (17); also, similar rates of alkylation of sample 1-1 and 1'-1 (142 and 162) imply a rate of quaternizing of around 40 for sample 1-1, which is similar to that of sample 1'-1.

The PKa of PEI in aqueous solution has been measured by other workers.[15,16] It is reported that the PKa values, corresponding to the concentrations of the electrolyte, are about 7 to 9. This means that some of the primary, secondary, and tertiary alkylated nitrogen atoms in the membranes used in our experiment might be coordinated with H^+ to be charged.

In addition, the distance between two nitrogen atoms in PEI is about 3.7 A, so a charged group could be hindered by the neighboring effects of a dissociated charged group.[17,18] Therefore, some nitrogen atoms could not be charged. Since the rate of quaternizing of sample 1-1-Cl was about 40%, it is suggested that, in this membrane, dissociation of the quaternary nitrogen atoms is predominant, and dissociation of primary, secondary, and tertiary nitrogen atoms might be considerably suppressed. On the other hand, dissociation of primary, secondary, and tertiary atoms should be considered when the rate of quaternizing is low; for example, in sample 1-0-Cl the rate of quaternizing is about 20%. The rates of increase in charge by protonation of primary, secondary, and tertiary atoms in sample 1-0-Cl might be greater than those in sample 1-1-Cl.

In conclusion, it can be said that the increase in the charge density of sample 1-1-Cl, relative to that of sample 1-0-Cl, would be less than two times. Therefore, an increase of 10 times in the effective charge density observed in Table III could not be explained by an increase only in the real charge density, C_x.

Influence of Swelling

The swelling ratios were 2.07 for sample 1-0-Cl and 2.40 for sample 1-1-Cl, and no significant difference was observed. This fact suggests that the repulsive forces between charged groups are nearly equivalent, or that the rate of crosslinking of PEI membranes are sufficiently high in both samples. Therefore, the influence of swelling on the effective charge density could be negligible.

Activity and Distribution Constant

Comparing the change in effective charge density, QC_x, with the change in charge density, C_x, implies that when the charge density is increased, the Q value is also increased. In eq. (2), Q is a function of the activity constant γ_+, γ_- of ions in the membrane and distribution constant κ_+, κ_- of ion in the membrane, where the κ value is that for a membrane having no charged group. If the influence of charged groups can be neglected, then it can be said that the difference in membrane structures has no influence on the κ value in this study. Therefore, the variation in the Q value, due to the variation in the κ_+, κ_- value, is negligible, and only the variation in γ_+, γ_- should be considered. In general, the variation in γ_+, γ_- is expressed by the additivity rule, as follows[19]:

$$\gamma_- = \gamma_-^0(C_+)\frac{C_+ + \alpha X}{C_+ + X}$$
$$\gamma_+ = \gamma_+^0(C_+) \tag{3}$$

where

$$0 < \alpha < 1$$

According to eq. (3), the Q value is less than one.[19] Also, the equation implies the larger the charge density of a membrane becomes, the smaller the γ_- value becomes. However, our results imply that the activity constant in the membrane increased when the charge density is increased.

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