# Microstructure of Cation Exchange Membranes Prepared by the Paste Method

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## Synopsis

   The microstructure of a cation-exchange membrane (Neosepta CL-25T) prepared by the paste method was investigated by microscopic examination, x-ray microanalysis, scanning electron microscopic observation, and determination of pore size distribution of the porous membrane obtained by selective decomposition of the cation-exchange resin component (R-resin) of the membrane. Both the cloth part and the other part were characterized by uniform distributions of the colloidal R-resin (under 0.1 $\mu$m) in poly(vinyl chloride) (PVC). This structural feature made it possible to understand comprehensively the properties of the cation exchange membranes prepared by the paste method. The mechanism of the formation of such microheterogeneity is explained in terms of the microphase separation of the styrene (St)–divinylbenzene (DVB) copolymer from PVC during polymerization.

## INTRODUCTION

   Most of the ion-exchange membranes for industrial use are reinforced by fiber meshes for improvement of dimensional stability, brittleness, low burst strength, hydrodynamic permeability, and so on.[1,2] Poly(vinyl chloride) (PVC) cloth is usually used as the reinforcing material to prepare ion-exchange membranes by the paste method.[3–7]

   When classifying ion-exchange membranes into homogeneous and heterogeneous membranes according to their uniformity, little attention is paid to the presence of fiber mesh. However, fiber mesh usually occupies a large proportion of the total membrane volume. Its structure therefore should have a great influence on the electrochemical properties of the membranes.

   In this study, attention was focused on the structure of the PVC cloth part in a cation-exchange membrane (Neosepta CL-25T) prepared by the paste method. Its structural features revealed under microscopic examination and x-ray microanalysis were compared with those of the cloth part in a cation-exchange membrane prepared by another method. The Neosepta membrane was then converted to a PVC porous membrane having no ion exchangeability according to the hydrogen peroxide treatment described in our earlier article.[8] The pore structure of the membrane was investigated in detail because it was reasonably supposed to reflect the distribution of the R-resin in the Neosepta membrane.
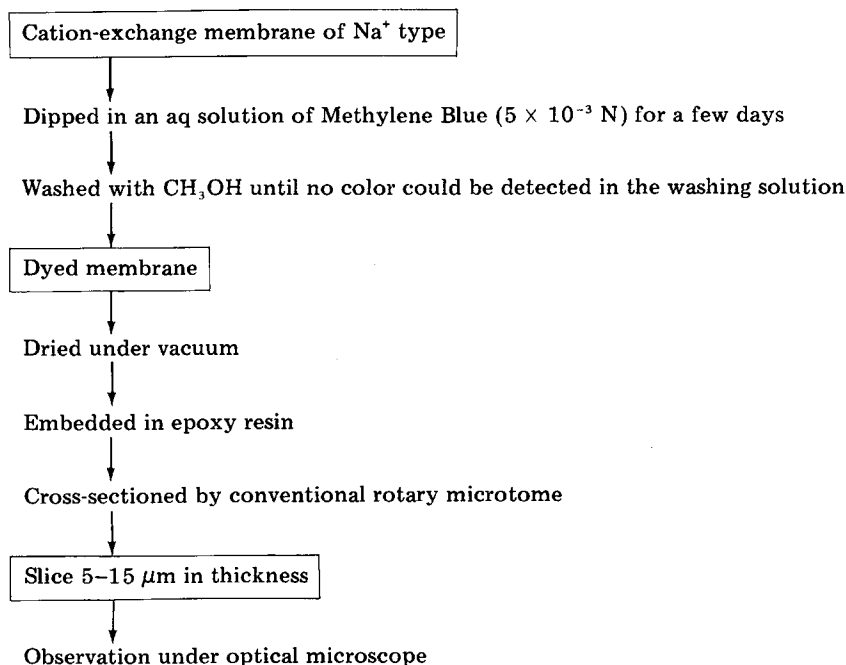
## EXPERIMENTAL

### Cation-Exchange Membranes

The membranes used were Neosepta CL-25T (Tokuyama Soda Co.) prepared by the paste method and Nepton CR-61 AZL183 (Ionics Inc.). The latter is usually classified as a homogeneous membrane. Their characteristics, measured by the usual methods,[9,10] are listed in Table I.

### Microscopic Examination

The presence or absence of ion-exchange groups in the cloth part of the membranes was examined by observing whether the cloth part was stained or not with Methylene Blue, a common cationic dye, in the following manner:

| Cation-exchange membrane of Na$^+$ type |

Dipped in an aq solution of Methylene Blue (5 × 10$^{-3}$ N) for a few days

Washed with CH$_3$OH until no color could be detected in the washing solution

| Dyed membrane |

Dried under vacuum

Embedded in epoxy resin

Cross-sectioned by conventional rotary microtome

| Slice 5–15 $\mu$m in thickness |

Observation under optical microscope

### X-Ray Microanalysis

The distribution of the counterions in Neosepta CL-25T was studied by using an electron probe microanalyzer (JSM-50A from Jeol Ltd.). Both the scanning electron micrograph and the CuK$_\alpha$ x-ray image were taken over the same area on the cross section of Neosepta CL-25T in the Cu$^{2+}$ form. A line scanning CuK$_\alpha$ x-ray profile was also taken from the same sample. The sample was prepared in the following manner. Neosepta CL-25T was saturated with Cu$^{2+}$ ions in an aqueous solution of CuCl$_2$ and thoroughly washed with deionized water and then dried, embedded in an epoxy resin, and cross-sectioned. The cross section was polished with emery paper (No. 1000) and subsequently with $\gamma$-alumina (particle

TABLE I
Characteristics of the Cation-Exchange Membranes Used

| Trade name | Manufacturer | Matrix | Ionic group | Reinforcing material | Thickness, mm | Capacity, mequiv/g dry membrane | Electric resistance,[a] $\Omega \cdot cm^2$ | Burst strength,[b] $kg/cm^2$ |
|---|---|---|---|---|---|---|---|---|
| Neosepta CL-25T | Tokuyama Soda Co. | PVC–polystyrene | —$SO_3^-$ | PVC synthetic fiber[c] | 0.19 | 1.75 | 3.0 | 3–5 |
| Nepton CR-61 AZL 183 | Ionics Inc. | Polystyrene | —$SO_3^-$ | Acrylic synthetic fiber[d] | 0.60 | 1.90 | 6.2 | — |

[a] Measured in 0.5$N$ NaCl solution (25°C) by using an ac bridge at 1 KHz.
[b] Measured by using a Mullen tester (apparatus similar to that described in ASTM Test Method D744).
[c] Teviron cloth available from Teijin Co.
[d] Dynel cloth, a copolymer of acrylonitrile and vinyl chloride, available from Union Carbide Chemicals Co.

size 0.5 $\mu$m). After it had been fixed on a cylindrical copper disk, the surface was stripped to a very slight extent by using an ion etching device (IB-3 from Eiko Engineering Co.) which employed a beam of argon ions. This treatment gave rise to a remarkable distinction between the cloth part and the other part in the scanning electron micrograph of the cross section. Finally, it was coated with a thin layer of carbon by use of a vacuum evaporating apparatus.

## Hydrogen Peroxide Treatment

The Neosepta membrane was converted to the $Fe^{3+}$ form by repeated batch equilibrations with a large excess of $0.1N$ $FeCl_3$ solution. After washing with deionized water, it was treated with 5% hydrogen peroxide solution at room temperature for 100 min, by which the R-resin was selectively dissolved, and thus a PVC porous membrane was obtained.[8]

## Measurement of Pore Size Distribution of the Porous Membrane

Pore size distribution of the PVC porous membrane was investigated with a mercury porosimeter (Model 1520 SM from Carlo Erba Scientific Instruments Div.).

This technique is based upon Washburn's relationship[11] that the pressure $P$ required to force pure mercury into a capillary of radius $r$ is $(-2\gamma \cos \theta)/P$, where $\gamma$ is the surface tension of mercury and $\theta$ is the contact angle of mercury with the material of the capillary. By using the values[12] of $\gamma = 480$ dyn/cm and $\theta = 140°$ for the contact angle of mercury with PVC,[13] the following relation can be obtained:

$$r \text{ (Å)} = 75,000/P \text{ (kg/cm}^2) \tag{1}$$

The experimental procedure consisted in measuring the cumulative volume change of mercury which occurred as the dry membrane sample, initially surrounded by mercury under vacuum, was subjected to increasing pressure (0–1500 kg/cm$^2$). From the measured volume–pressure curve, the pore size distribution curve was obtained by using eq. (1). The sample was prepared in the following manner: the membrane of 12 cm$^2$ was washed thoroughly with deionized water, freeze-dried, and then cut into small pieces ($\sim$0.5 $\times$ 0.5 cm).
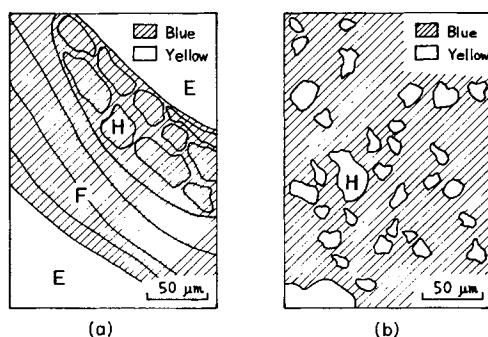


Fig. 1. Sketches of the cross sections of (a) Neosepta CL-25T (at an intersecting point of strands of the cloth) and (b) Nepton CR-61 AZL 183 stained with Methylene Blue, as observed in the microscope: (H) section of a filament; (F) strand consisting of several filaments; (E) epoxy resin.
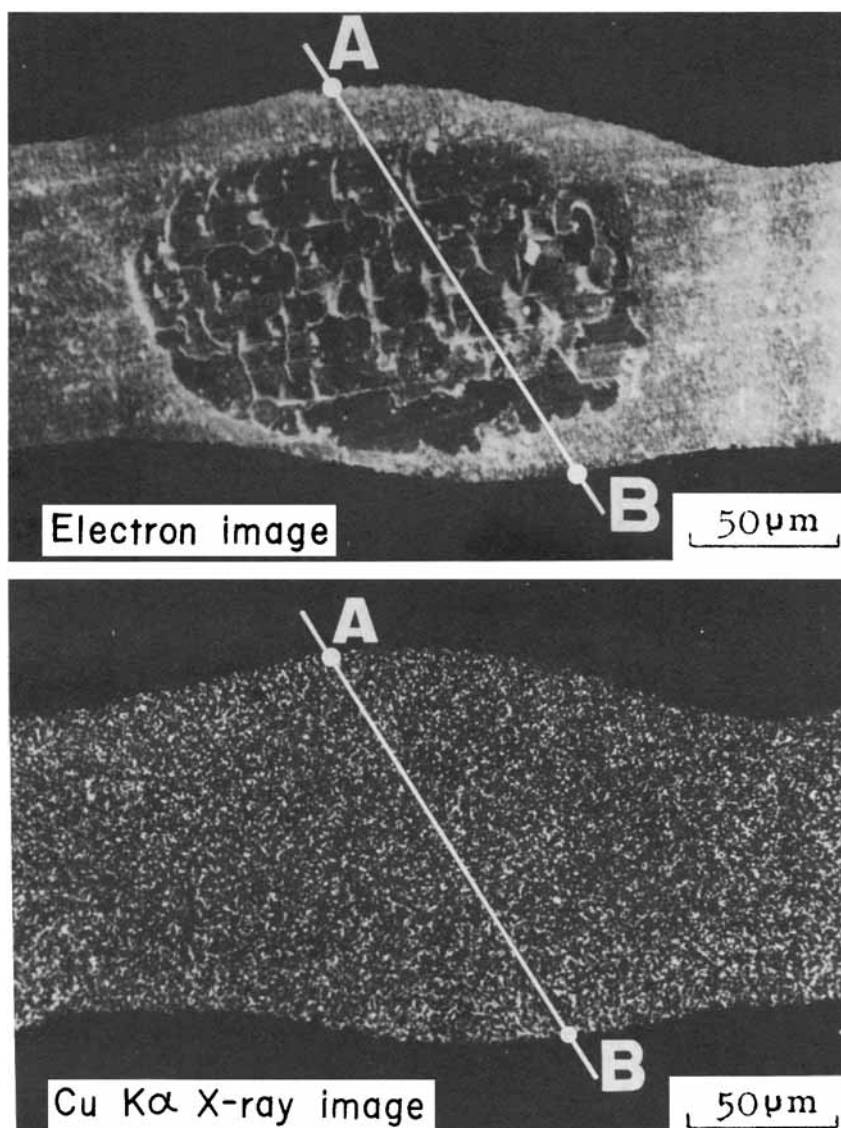
Fig. 2. Electron probe microanalyzer scanning pictures of the cross section of Neosepta CL-25T ($Cu^{2+}$ form) cut perpendicularly to a strand consisting of several filaments.

## Scanning Electron Microscopic Observation of the Porous Membrane

The surface and the cross section of the porous membrane were observed by scanning electron microscopy with the same apparatus described above. The cross section was obtained by breaking the membrane at liquid nitrogen temperature. The sample membranes were freeze-dried, fixed on cylindrical copper disks, and then coated with a thin layer of gold to avoid charging in the microscope.
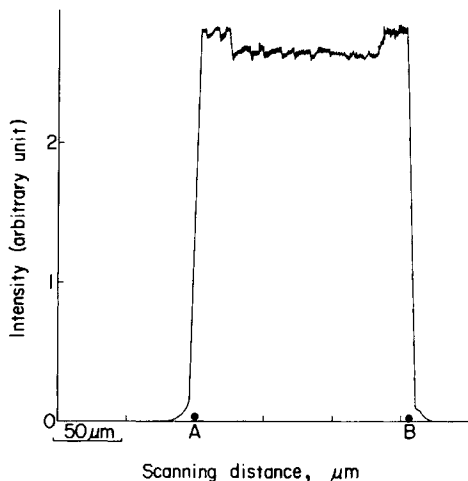
Fig. 3. CuK$_\alpha$ x-ray profile along the A–B line marked in Fig. 2.

## RESULTS AND DISCUSSION

Figure 1 shows the sketches of the cross sections of the cation-exchange membranes stained with Methylene Blue as observed in the microscope. The cloth part of Nepton CR-61 was not dyed. On the other hand, the whole cross section of Neosepta CL-25T has the ion-exchange groups even in the filaments of the cloth. This means that Neosepta CL-25T membrane as a whole has a relatively homogeneous structure.

The above finding is confirmed by Figure 2, which shows both the electron image and the CuK$_\alpha$ x-ray image of the cross section of Neosepta CL-25T (Cu$^{2+}$ form). No localized distribution of the Cu$^{2+}$ ions can be found. Figure 3 shows the relative concentration of Cu$^{2+}$ ions measured along the A–B line marked in Figure 2. It is noteworthy that there is no significant difference in the distri-
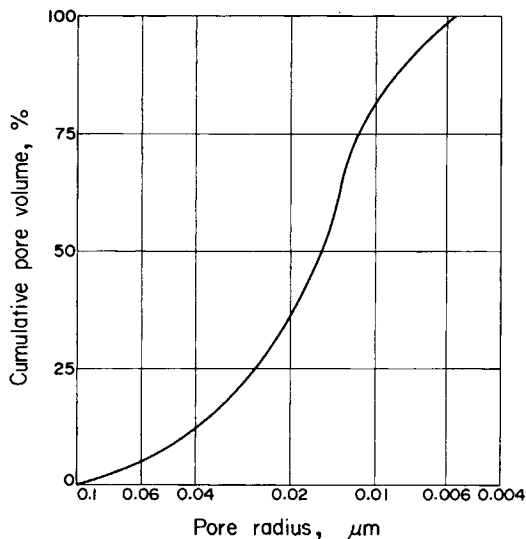


Fig. 4. Mercury porosimetry curve for the porous membrane obtained by hydrogen peroxide treatment of Neosepta CL-25T.
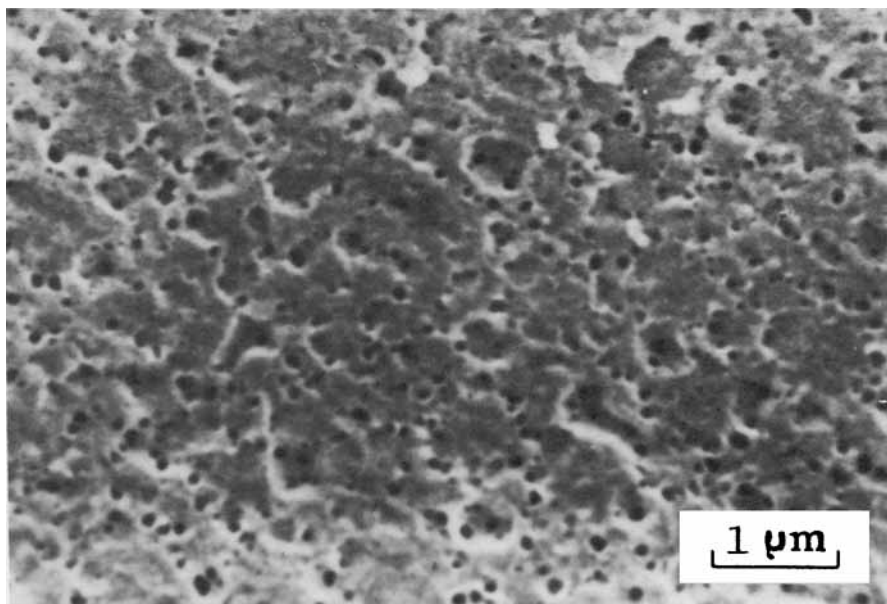
Fig. 5. Scanning electron micrograph of surface of the porous membrane obtained by hydrogen peroxide treatment of Neosepta CL-25T.

bution of the counterions between the cloth part and the other part. It is concluded that sulfonic acid groups are homogeneously distributed in the whole Neosepta membrane within the confidence limits of the method employed (3 $\mu$m).

Neosepta CL-25T is prepared by the following method. A fine powder of PVC is mixed with a monomeric mixture mainly consisting of styrene (St), divinylbenzene (DVB), and benzoyl peroxide (BPO) in order to prepare a paste, and this is coated onto a Teviron (PVC) cloth. The composite thus obtained is heated to polymerize the monomers and to convert the powdery PVC into a filmy gel; the sulfonic acid groups are then introduced into the resin component (St–DVB copolymer) of the resultant base membrane. The above-mentioned structural feature of this membrane indicates that a considerable part of the monomeric mixture in the paste penetrates deep into the filaments of the PVC cloth during the elevation in temperature. It also suggests that the monomeric mixture content of the cloth part becomes nearly equal to that of the other part before the beginning of polymerization.

Nepton CR-61 may probably be prepared by the following method.[14,15] A Dynel (vinyl chloride–acrylonitrile copolymer) cloth is sandwiched between two plates. Then, a solution of St, DVB, and diluents (for example, toluene) is poured into the space. The mixed solution is polymerized to form a film. After that, ionic groups are introduced into the film. However, Nepton CR-61, in marked contrast with Neosepta CL-25T, has no ion exchange groups in the cloth part. This difference seems to be ascribable to the fact that vinyl chloride–acrylonitrile copolymer has less affinity for the monomers than PVC.

The pore structure of the PVC porous membrane obtained by treating Neosepta CL-25T with hydrogen peroxide was investigated in detail. The apparent
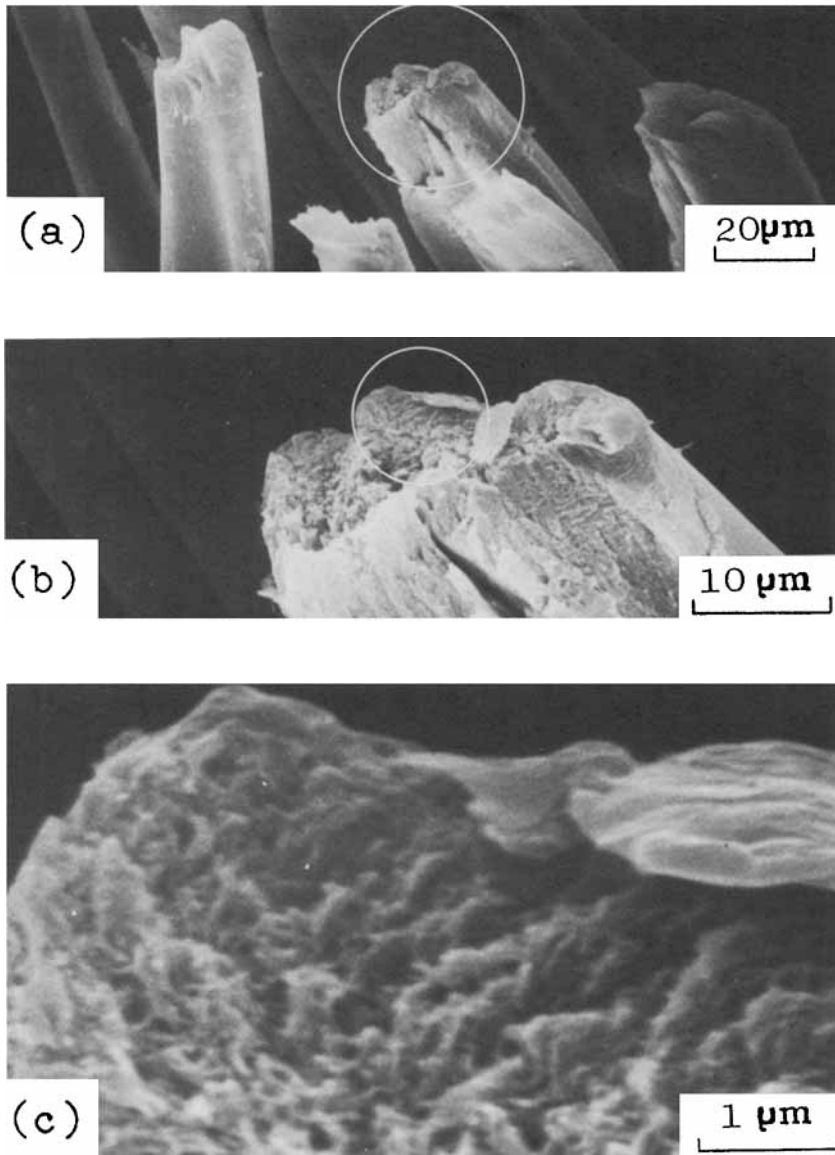
Fig. 6.  Cloth part of the porous membrane obtained from Neosepta CL-25T observed in scanning electron microscope at various magnifications.

pore radius estimated from its hydrodynamic water permeability was 0.014 $\mu$m.[8] The pore radius distribution is shown in Figure 4.   The pore radius ranges from 0.005 to 0.1 $\mu$m, which is compatible with the apparent pore radius.   Evidently the maximum slope of the curve corresponds to the range of maximum pore density.

Figure 5 shows the scanning electron micrograph of the surface of the porous membrane, clearly demonstrating the presence of micropores with a pore size distribution.   Contrary to expectation, it does not exhibit any aggregate of the PVC fine powder used as raw material.   At first glance the pores may seem a little

larger than expected in light of the apparent pore radius. A probable explanation for this is as follows. The apparent pore radius was determined by applying Hagen–Poiseuille's law on the basis of the simple assumption that the pores are cylindrical and perpendicular to the membrane surface, while the water permeability of the real membrane must be dependent largely on the pore size of the narrowest part along the water pathway.

The cross-sectional view of the porous membrane (Fig. 6) also shows the presence of fine pores in the cloth part. This indicates the presence of the R-resin in the cloth part of Neosepta CL-25T, which is in accord with the experimental results obtained by the microscopic observation and x-ray microanalysis of the membrane. The pores are of the same order in size as at the membrane surface. This explains the S-shaped pore size distribution curve having one maximum slope (Fig. 4). It is considered that the cloth part and the other part in Neosepta CL-25T resemble each other in the distribution of the R-resin.

The pattern shown in Figure 5 could result from the swelling of the PVC fine powder in the monomers accompanied by the disappearance of the contours of the particles and then a microphase separation of the St–DVB copolymer from the PVC gel phase during polymerization. The pattern shown in Figure 6 could also result from a similar microphase separation following a nearly uniform distribution of the monomers in both the cloth part and the other part. As PVC is miscible with the monomers but not with the copolymer, such microphase separations do occur. This is inferred from the fact that a fine powdery polymer is formed when St and DVB are polymerized in kerosene, which is miscible with the monomers but immiscible with polystyrene.

The cation-exchange membranes prepared by the paste method have excellent flexibility. Their electric resistance is considerably low in spite of the use of PVC cloth and fine powder. These features, for example, are understandable on the basis of such microstructure, as both the R-resin and PVC form continuous phases, entangling each other in the colloidal orders in the whole membranes. The microphase separation during polymerization should be affected by various factors such as the PVC/monomer ratio, the DVB/monomer ratio, the polymerization temperature, etc. The details must be clarified in the future.

## References

1. M. Block, *Chem. Ind. London,* **50,** 2099 (1967).
2. F. Helfferich, *Ion Exchange,* McGraw–Hill, New York, 1962, p. 61.
3. Y. Mizutani, R. Yamane, H. Ihara, and H. Motomura, *Bull. Chem. Soc. Jpn.,* **36,** 361 (1963).
4. Y. Mizutani, R. Yamane, and H. Motomura, *Bull. Chem. Soc. Japan,* **38,** 689 (1965).
5. Y. Mizutani, W. Teshima, and S. Akiyama, Jpn. Pat. 410,368 (1963).
6. Y. Mizutani, R. Yamane, and H. Motomura, Jpn. Pat. 448,778 (1965).
7. Y. Mizutani, W. Teshima, S. Akiyama, R. Yamane, and H. Ihara, U.S. Pat. 3,451,951 (1969).
8. Y. Mizutani and M. Nishimura, *J. Appl. Polym. Sci.,* **14,** 1847 (1970).
9. For example, T. Yamabe, and M. Senoo, *Ionkōkanjushi-Maku (Ion Exchange Membranes),* Gihōdō, Tokyo, 1964, p. 213; H. Shimizu and Y. Kosaka, *Ionkōkan-Maku (Ion-Exchange Membranes),* Kyōritsu, Tokyo, 1963, p. 117.
10. Y. Onoue, Y. Mizutani, and R. Yamane, *Denki Kagaku,* **27,** 482 (1959).
11. E. W. Washburn, *Proc. Natl. Acad. Sci. U.S.A.,* **7,** 115 (1921).

12. M. C. Wilkinson, *Chem. Rev.*, **72,** 575 (1972).

13. D. L. Engle, *The Internal Pore Structure of Polyvinyl Chloride Resins,* Reprint #212, American Instrument Co., Inc., Silver Spring, MD, 1963.

14. T. Sata, Modification of Properties of Ion-Exchange Membranes, thesis, Kyūshū University, 1974, pp. 3–8.

15　J. T. Clarke, U.S. Pat. 2,731,411 (1956).