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COPOLYMERIZATION OF CHLOROMETHYLSTYRENE AND DIVINYLBENZENE IN THE ABSENCE OR PRESENCE OF POLY(VINYL CHLORIDE)

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ABSTRACT

Studies of the copolymerization of chloromethylstyrene (CMS) and divinylbenzene (DVB) were done in the presence or absence of poly(vinyl chloride) (PVC) in order to prepare anion-exchange membranes of excellent performance by the paste method. The copolymerization rate decreases when PVC is added and increases when the DVB quantity is increased in the presence of PVC. The copolymerization rate of the isomers of CMS and DVB increases in the following order: p -DVB > m -DVB > p -ethylvinylbenzene > p -CMS > m -CMS \approx m -ethylvinylbenzene. This order is not affected by the presence of PVC. The copolymerization of CMS and DVB takes place partially in PVC particles.

INTRODUCTION

Ion-exchange membranes are prepared as follows: the base polymers are first prepared by copolymerization of styrene (St) and divinylbenzene (DVB), vinylpyridine, and DVB, or chloromethylstyrene (CMS) and DVB; and then

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ion-exchange groups are introduced into these base polymers. The authors have already reported on the "paste method," a method for preparation of ion-exchange membranes [1] in which the monomer paste, consisting of the monomer, a free-radical polymerization initiator, and fine poly(vinyl chloride) (PVC) powder, is coated onto poly(vinyl chloride) cloth; the monomers are copolymerized; and then ion-exchange groups are introduced into the base membrane. We have also reported on the copolymerization of St and DVB in the presence of PVC [2]. In this paper the copolymerization of CMS and DVB in the absence or presence of PVC is studied to lead to anion-exchange membranes of improved performance.

EXPERIMENTAL

Materials

Commercial CMS (com-CMS) from Seimi Chemical Co. Ltd was washed successively with a dilute aqueous solution of sodium carbonate and with water, dried with anhydrous sodium sulfate, and then distilled under reduced nitrogen atmosphere prior to use. Com-CMS was a mixture of *m*-CMS (69.9%), *p*-CMS (22.7%), *m*- α -chloromethylstyrene (*m*- α -CMS 3.9%), *p*- α -chloromethylstyrene (*p*- α -CMS 2.6%), and unknown components (0.8%). The purification method of commercial DVB (com-DVB) obtained from Sankyo Chemical Co. Ltd and benzoyl peroxide (BPO) was described in a previous paper [3]. Com-DVB was a mixture of *m*-DVB (40.7%), *p*-DVB (16.7%), *m*-ethylvinylbenzene (*m*-EVB 29.0%), *p*-ethylvinylbenzene (*p*-EVB, 10.9%), *m*-diethylbenzene (1.8%), and *p*-diethylbenzene (0.9%). Fine PVC powder made by emulsion polymerization was obtained from Nippon Geon Co. Ltd.

Copolymerization Procedure

A mixture of freshly distilled monomers (com-CMS, com-DVB), PVC, and BPO was used. The mixture (~1 g) was put into a glass ampule (60 mm in length and 12 mm in diameter) and degassed in three freeze-thaw cycles under nitrogen. Thereafter the ampules were sealed under vacuum. The copolymerization was carried out in an oil bath at constant temperature for 10 to 600 min. The copolymerization was stopped by freezing the ampules in a Dry Ice-methanol mixture after a given reaction time. The chilled ampules were carefully broken, and the content of the ampules was treated overnight with 10 mL of benzene or tetrahydrofuran containing 0.1% of hydroquinone. Tetrahydrofuran

was used in the case of CMS-DVB-BPO-PVC copolymerization system. Then the mixture was poured into 200 mL of methanol, agitated for 1 day, filtered through a 4G glass filter and evacuated at 60°C to constant weight. The monomer conversion was obtained gravimetrically. For copolymerization in the presence of PVC, the conversion was determined by subtracting the amount of PVC added to the monomers from that of the resultant polymer mixture.

Determination of Copolymer Composition

The copolymer composition was determined from the concentrations of the residual monomers. The concentration of residual monomers in the precipitation solvent (methanol) was measured by gas chromatography using a Perkin-Elmer 900 Gas Chromatograph with a column of pluoronic L-84 and a FID, with the volume of the precipitation solution adjusted to 250 mL and *m*-diethylbenzene (*m*-DEB) was used as internal reference. A small amount of the unpolymerized monomers might be adsorbed in the precipitated polymer. However, as this would decrease the quantity of all the monomers in the copolymerization, the conversion of monomers and the copolymer composition were calculated from the GC results. (This will be called volumetric method.) Figure 1 shows that the gravimetric and the volumetric methods

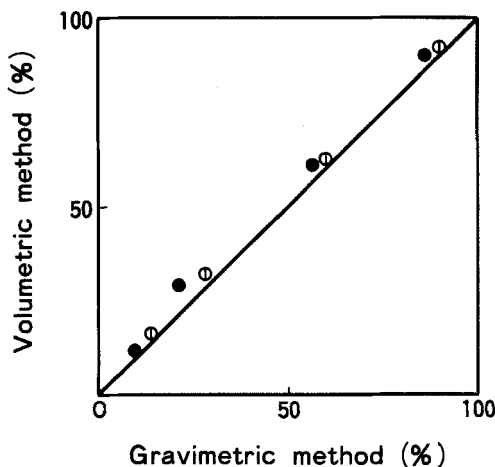


FIG. 1. Relationship between conversions obtained by the gravimetric and the volumetric methods. Com-CMS-com-DVB systems in the presence (●) or absence (○) of PVC at 80°C. Com-DVB/(com-CMS + com-DVB) = 0.07; BPO/(com-CMS + com-DVB) = 0.03; PVC/(com-CMS + com-DVB) = 0.2 by weight.

gave consistently similar values, but that the conversion from the volumetric method was slightly higher than that from the gravimetric method. These differences may be attributable to the formation of some oligomers.

Morphology

The paste composed of com-CMS/com-DVB/BPO/PVC in the ratio 2.63/0.36/0.09/1.0 by weight was coated on the reinforcing fabric of poly(vinyl chloride), wrapped with poly(vinyl alcohol) film, and heated at 80°C for 8 h. Then, specimens were prepared by ultramicrotome and stained by osmium tetroxide as described in a previous paper [4]. The morphological analysis of the CMS-DVB-PVC composite was performed by scanning transmission electron microscopy. Further, the composite was quaternized with trimethylamine, and then the counterion was converted to chromic ion. The distribution of chlorine atoms in the PVC and on the chromic ion attached to the ion-exchange group was observed by analytical electron microscopy (JEOL: Model JEM-200CX, EDS: TN 5500).

RESULTS AND DISCUSSION

Figure 2 shows that the rate of copolymerization increases with temperature and also that the copolymerization rate accelerates in the early stage, then becomes steady, and finally decreases gradually. The autoacceleration takes place in the earlier stage as copolymerization temperature increases, since the increase of viscosity resulting from monomer conversion retards the termination of growing polymer radicals. At higher monomer conversion, the rate of copolymerization gradually decreases due to the decrease in the monomer concentration and the low mobility of the monomers in the highly viscous medium.

Figure 3 shows the Arrhenius plot of initial polymerization rate (R_p) vs the reciprocal of temperature. The activation energy was calculated to be 23.7 kcal/mol from the slope of the straight line in Fig. 3. The activation energies for polymerization of the components are reported to be 15.6 kcal/mol for CMS [5], 20 kcal/mol for St-*m*-DVB [6], 17.4 kcal/mol for St-*m*-DVB-PVC [2], and 21.0 kcal/mol for St-*m*-DVB-Hypalon [3]. Thus the magnitude of activation energy of com-CMS-com-DVB was approximately the same as that observed in the polymerization of St-*m*-DVB system.

Figure 4 shows the effect of BPO concentration on the time-conversion curve. The relationship between initial polymerization rate and BPO concentration is shown in Fig. 5. The exponent for, i.e., the order with respect to,

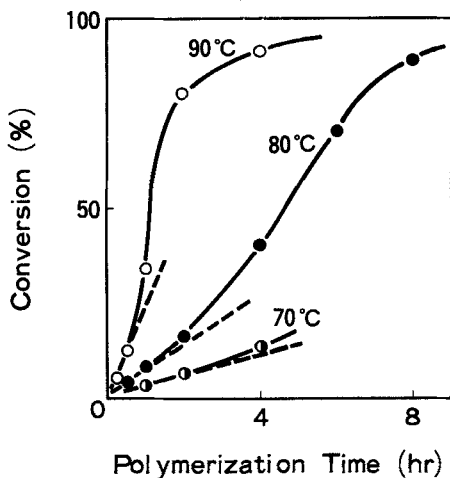


FIG. 2. Effect of copolymerization temperature on time-conversion curves. Com-DVB/(com-CMS + com-DVB) = 0.056; BPO/(com-CMS + com-DVB) = 0.01 by weight: (○) 90°C, (●) 80°C, (◐) 70°C.

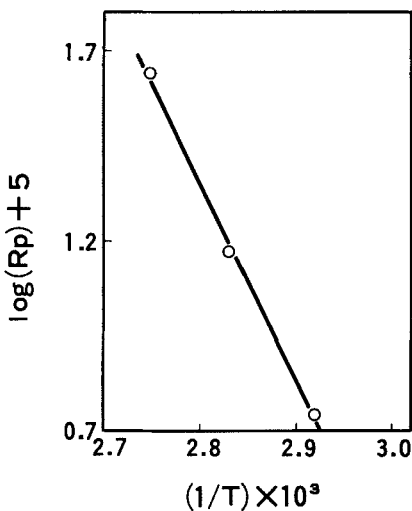


FIG. 3. Arrhenius plot.

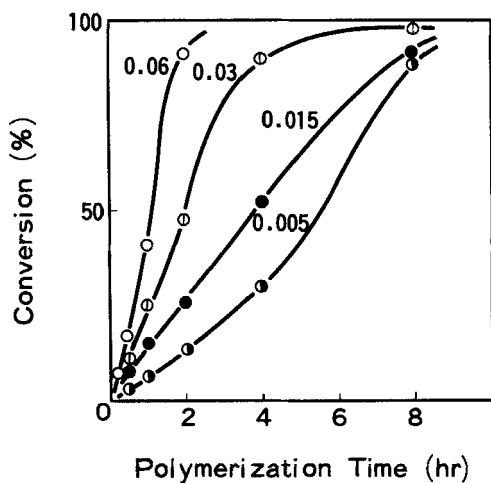


FIG. 4. Effect of BPO quantity on time-conversion curves at 80°C. Com-DVB/(com-CMS + com-DVB) = 0.056; BPO/(com-CMS + com-DVB): (●) 0.005, (●) 0.015, (○) 0.03, (○) 0.05, (○) 0.06 by weight.

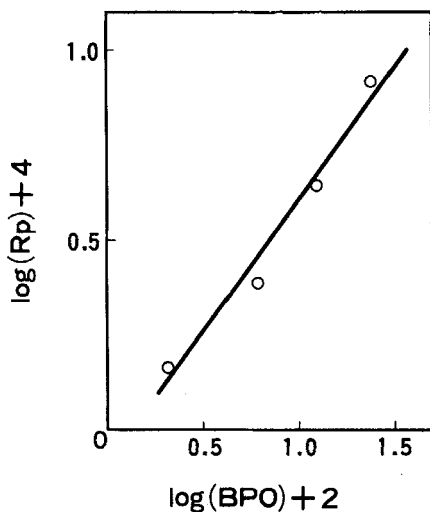


FIG. 5. Plot of $\log(R_p)$ vs $\log[BPO]$ at 80°C. R_p in $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$; $[BPO]$ in mol/L .

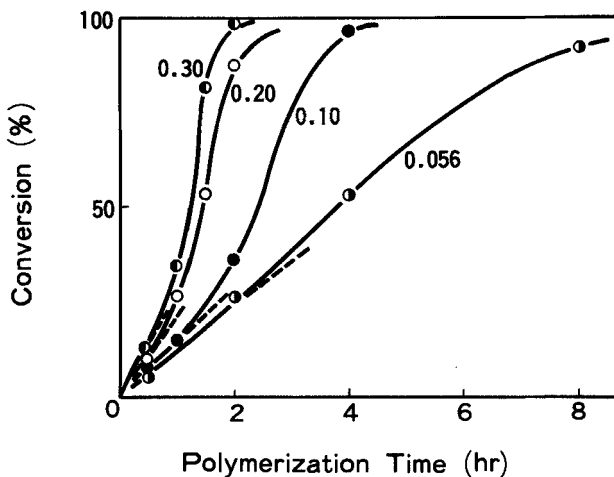


FIG. 6. Effect of com-DVB quantity on time-conversion curves at 80°C. BPO/(com-CMS + com-DVB) = 0.015; com-DVB/(com-CMS + com-DVB): (●) 0.056, (●) 0.1, (○) 0.20, (●) 0.30 by weight.

BPO concentration was 0.69. The exponents for BPO concentrations were reported to be 0.5 in the CMS-BPO system [5], 0.67 in the *St-m*-DVB-PVC system [2], and 0.61 in the *St-m*-DVB-Hypalon system [3]. These results show that, in crosslinking polymerization, monomolecular and bimolecular terminations occur simultaneously because diffusion of the polymer radical is retarded as the viscosity of the copolymerization system increases.

Figure 6 shows the effect of com-DVB concentration on the time-conversion curve. As the com-DVB concentration increases, the initial copolymerization rate increases and the autoacceleration starts earlier. This can be explained as follows: The copolymer is crosslinked at an early stage because of the high concentration of divinyl monomer, and therefore biradical termination is hindered in such a viscous medium. These phenomena have also been observed in the methyl methacrylate-ethylene glycol dimethacrylate system [7].

Figure 7 shows the effect of the addition of PVC on the time-conversion curve. The rate of copolymerization is slower in the presence of PVC than in its absence. In this copolymerization system, PVC is present as a plastisol. Therefore, the copolymerization takes place both inside and outside the PVC particles because monomers and BPO are partly impregnated into them. The copolymerization behavior on the outside of the PVC particles would be the

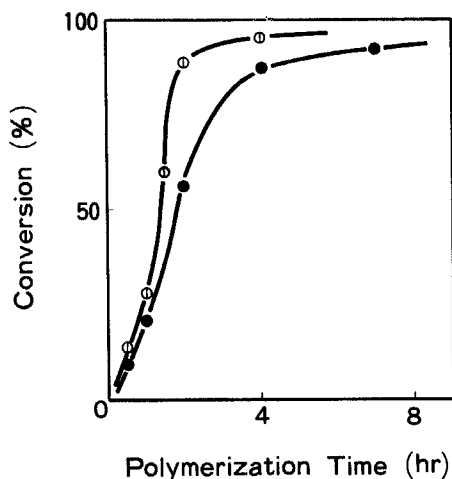


FIG. 7. Time-conversion curves of com-CMS-com-DVB systems in the presence (●) or absence (○) of PVC at 80°C. Com-DVB/(com-CMS + com-DVB) = 0.07; BPO/(com-CMS + com-DVB) = 0.03; PVC/(com-CMS + com-DVB) = 0.2 by weight.

same as that in the absence of PVC, while in the interior of the PVC particles, the rate of copolymerization is depressed by slower diffusion of the monomers due to the matrix of poly(vinyl chloride) chains. Moreover, the conversion is lower in the presence of PVC. In order to clarify copolymerization of monomers in PVC particles, the morphology of the CMS-DVB-PVC composites was examined by STEM, and the results are discussed in the following.

Figure 8 shows the relationship between the conversion of the various isomers measured by gas chromatography and that of the total conversion by the gravimetric method for the copolymerization of the com-CMS-com-DVB system. Similarly, the copolymerization behavior of the com-CMS-com-DVB-PVC system is shown in Fig. 9. The following results were obtained from analysis of the copolymerization behavior:

- (1) The rate of copolymerization of *m*- and *p*-DVB is faster than that of other monovinylbenzene derivatives
- (2) The rate for *p*-isomers is faster than that for *m*-isomers
- (3) The rate for monomers decreases in the order $p\text{-DVB} > m\text{-DVB} > p\text{-EVB} > p\text{-CMS} > m\text{-CMS} \approx m\text{-EVB}$

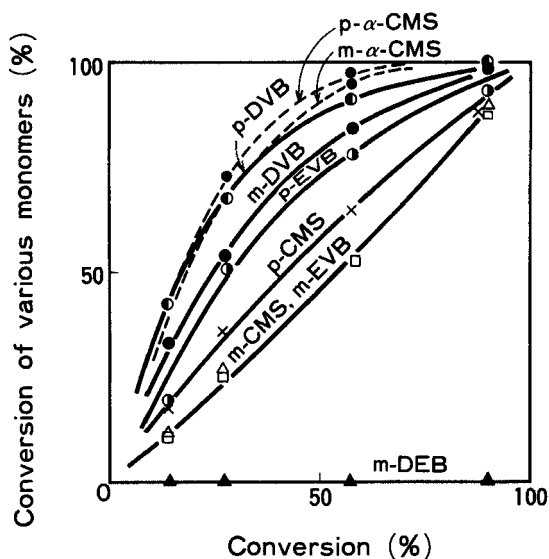


FIG. 8. Conversion of various monomers vs total monomer conversion in the absence of PVC at 80°C. Com-CMS/(com-CMS + com-DVB) = 0.07; BPO/(com-CMS + com-DVB) = 0.03 by weight. (○) *p*-DVB, (●) *m*-DVB, (◐) *p*-EVB, (X) *p*-CMS, (◑) *m*-CMS, (△) *m*-EVB, (▲) *m*-DEB, (---●---) *m*,*p*- α -CMS.

- (4) The reactivity of those monomers is not affected by the presence of PVC
- (5) *m*- α -CMS and *p*- α -CMS show almost the same behavior in the copolymerization system, and the rate of disappearance of α -CMS in this system is similar to that of *p*-DVB

It is understandable that the rate of copolymerization of DVB is faster than that of monovinylbenzene derivatives because DVB has two active vinyl groups attached to the benzene ring. The rate of copolymerization of *p*-DVB is faster than that of *m*-DVB. As shown in Table 1, the reactivity ratios for St (M_1) and *m*-DVB (M_2) were $r_1 = 0.605$, $r_2 = 0.88$ [11] and those for St (M_1) and *p*-DVB (M_2) were $r_1 = 0.77$, $r_2 = 2.08$ [11]. Our results agree with the tendency predicted from these values. Moreover, the relative reactivities of those monomers are not affected by the presence of PVC.

On the other hand, com-CMS contains *m*- α -CMS and *p*- α -CMS. No work has been reported on the polymerization of α -CMS. Only a little work has been re-

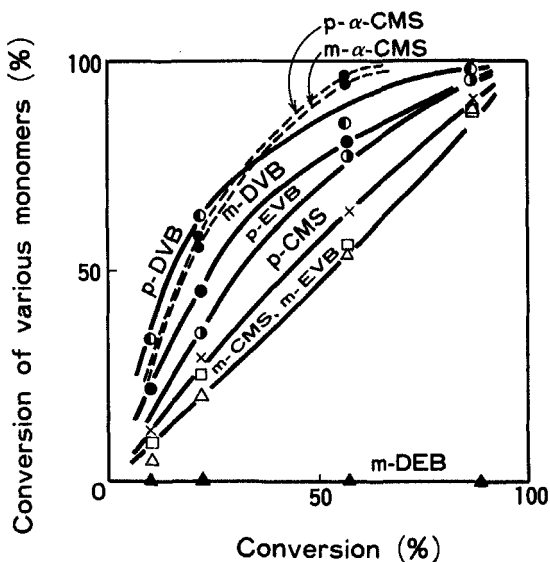


FIG. 9. Conversion of various monomers vs total monomer conversion in the presence of PVC at 80°C. Com-CMS/(com-CMS + com-DVB) = 0.07; BPO/(com-CMS + com-DVB) = 0.03; PVC/(com-CMS + com-DVB) = 0.2 by weight. (○) *p*-DVB, (●) *m*-DVB, (⊙) *p*-EVB, (X) *p*-CMS, (□) *m*-CMS, (△) *m*-EVB, (▲) *m*-DEB, (- - ● - -) *m*, *p*-α-CMS.

TABLE 1. Reactivity Ratios

M_1	M_2	r_1	r_2	Ref.
CMS (<i>o/p</i>) = 2/1	DVB (<i>p/m</i>) = 4/1	0.27	0.86	8
<i>p</i> -CMS	St	1.37	0.72	9
CMS	St	1.41	0.71	10
St	<i>m</i> -DVB	0.605	0.88	11
		0.54	0.58	12
St	<i>p</i> -DVB	0.77	2.08	11

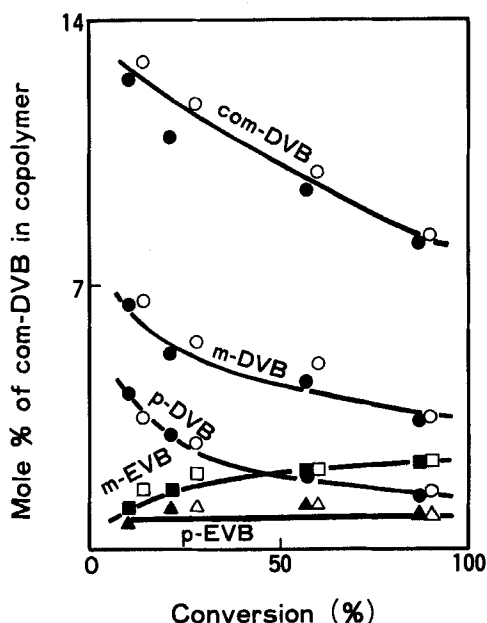


FIG. 10. Relationship between conversion and quantity of com-DVB incorporated in the copolymer in the presence (●, ■, ▲) or absence (○, □, △) of PVC at 80°C.

ported on the polymerization of α -chlorostyrene, namely, that it is hardly polymerized by heat, ultraviolet light, or BPO [13].

On the other hand, the reactivity ratios for St (M_1) and α -methylstyrene (M_2) were $r_1 = 1.3$, $r_2 = 0.3$ [14] and those for St (M_1) and ethyl- α -chloroacrylate (M_2) were $r_1 = 0.08$, $r_2 = 0.30$ [15]. It is said that α -methylstyrene is less reactive than styrene and this may be due to steric hindrance or to the presence of three allylic hydrogens. Ethyl- α -chloroacrylate seems to be reactive. It is difficult to predict the copolymerization behavior of α -CMS from these results since it is thought to be incorporated into the polymer matrix by chain transfer or copolymerization in crosslinking polymerization. The copolymerization behavior of α -CMS is under investigation.

Figure 10 shows the copolymer composition of *m*-, *p*-DVB and *m*-, *p*-EVB at various conversions. The value for com-DVB in Fig. 10 is the sum of *m*-, *p*-DVB and *m*-, *p*-EVB. It is apparent from Fig. 10 that the incorporation of *m*-, *p*-DVB takes place rapidly in the early stage and gradually decreases with

lack of *m*-, *p*-DVB monomer concentration in the polymerization system. For example, the conversion of *p*-DVB is 85% and that of *m*-DVB is about 75% when the total conversion is 50% (Fig. 9). Therefore, in the initial stage, DVB units are incorporated close to each other, and as the copolymerization progresses, DVB is more sparsely distributed in the growing polymer chain.

On the other hand, the reactivity of the two vinyl groups attached to benzene is not the same. Recently, some investigators focused their interest on the reactivity of the pendent double bond and reported that cyclization predominates in crosslinking copolymerization from the analysis of the composition and NMR behavior of low-conversion soluble copolymer of St and 5-60 wt% of ethylene dimethacrylate [16]. Moreover, it is confirmed that the delay in gelation is due to the lower reactivity of the pendent vinyl groups and not to the formation of many intramolecular cyclizations in the copolymerization of St and DVB [17]. Since it is difficult to analyze the crosslinked polymer, the degree of cyclization and crosslinking cannot be determined.

MORPHOLOGY

Specimens were prepared from the composite consisting of com-CMS-com-DVB-PVC powder-PVC fabric, and a STEM micrograph is shown in Fig. 11(A). The dark elliptical particles 0.4-0.8 μm in diameter are the PVC phase. The copolymer of com-CMS and com-DVB is observed as the white areas. This phase separation is attributable to the insolubility of PVC in the solution of com-CMS and com-DVB. Such phenomena were also observed in the copolymerization of the St-DVB-PVC system [4]. Moreover, the interior of the PVC particles is composed of a mixture of the dark-colored network part and white spots, as seen at the high magnification (Fig. 11B). Here, the dark-colored part indicates continuous PVC gel phase and the white spots are copolymer of com-CMS and com-DVB. Since com-CMS, com-DVB, and BPO migrate into PVC particles, copolymerization also takes place in PVC particles. Needless to say, the monomers which cannot migrate into PVC particles copolymerize outside the PVC particles.

Further, in order to confirm the copolymerization of com-CMS and com-DVB in PVC particles, the distribution of chlorine atoms in PVC and chromic ion attached to the fixed ion-exchange group in the composite was observed by analytical electron microscopy. Figure 12(A) shows the x-ray chart of the quaternized copolymer of com-CMS and com-DVB, which represents the

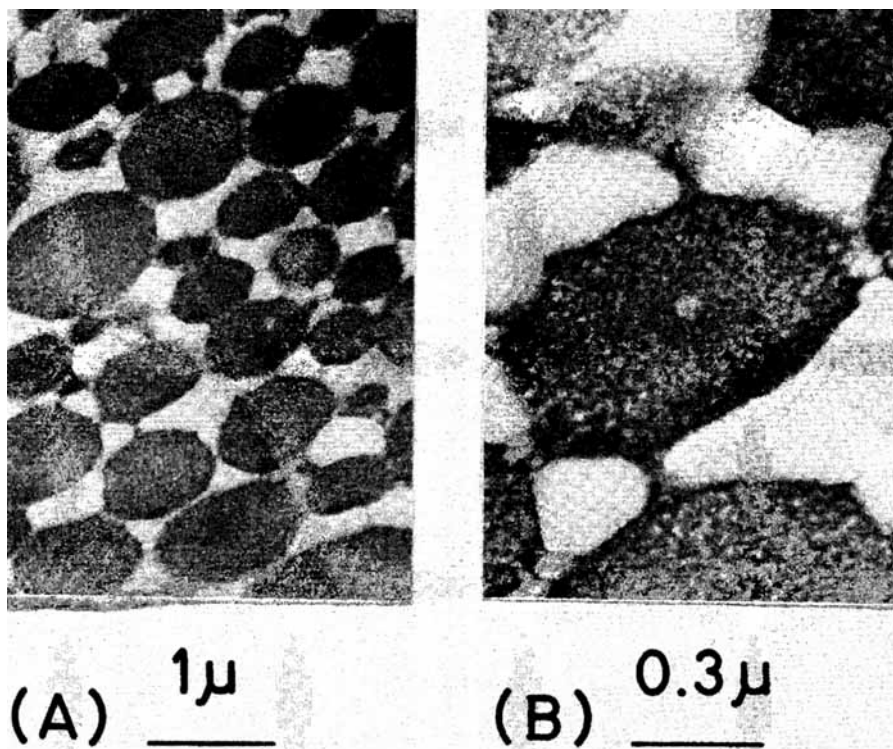


FIG. 11. Cross-section of the composite at two magnifications. Com-DVB/(com-CMS + com-DVB) = 0.07; BPO/(com-CMS + com-DVB) = 0.03; PVC/(com-CMS + com-DVB) = 0.33 by weight. Copolymerization temperature, 80°C; time, 8 h.

white part in Fig. 11(A) (the observed area was about 0.1 μm in diameter). More Cr was found than Cl. The small amount of Cl was observed because it is difficult to convert chloride ion to chromic ion completely by ion exchange. A large amount of Cl and a small amount of Cr were observed in Fig. 12(B) which refers to the PVC part of the composite (the dark-colored elliptical particles in Fig. 11(A)). These observations prove that copolymerization of com-CMS and com-DVB takes place partially in PVC particles. The observations suggest that the morphology of the PVC particles has the characteristics of interpenetrating polymer networks. The copolymer of com-CMS and com-DVB connects at the surface of the PVC particles, which then form a continu-

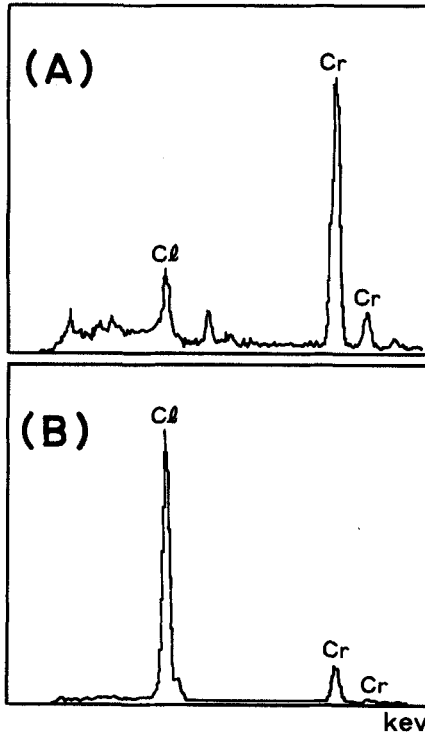


FIG. 12. Results of analytical electron microscopy. (A) Quaternized copolymer of com-CMS-com-DVB part in Fig. 11(A). (B) PVC part in Fig. 11(A).

ous phase. Therefore, the mechanical properties of the membrane are excellent when the membrane is swelled by aqueous electrolyte solution. Consequently, high-performance anion-exchange membranes are obtained by the copolymerization of the com-CMS-com-DVB-PVC system by the paste method.

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