

Relationships between the Synthesis Conditions and the Characteristics of Anion Exchangers

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Synopsis

Several macroporous styrene-divinylbenzene copolymers were prepared using different diluents. The copolymers were chloromethylated with monochlor methyl ether and aminated with *N,N*-dimethyl-2-hydroxyethylamine in order to perform strongly basic anion exchanger, type II. It was established that the network morphology of anion exchanger determines its ion-exchange rate. It was, also established, by means of transmission electron microscopy, that chloromethylation reaction led to the morphological changes in the macromolecular network of the copolymers.

INTRODUCTION

The styrene-divinylbenzene copolymers are the most used macromolecular network in performing ion exchangers.¹

The macroporous copolymers are used more and more in synthesis ion exchangers with high mechanical and chemical stability.^{2,3}

It is known that the morphology of the macromolecular network of an ion exchanger plays a fundamental role in the ion-exchange process. The ion-exchange kinetics and the ion selectivity can be manipulated through modification of this network.⁴ The morphology of the macromolecular network depends on the nature and amount of the diluent used in the copolymerization process as well as the quantity of DVB. The morphological changes appear in the network structure of copolymers during its chemical transformations.^{5,6}

This paper deals with the relationships between the kind of macroporous St-DVB copolymers and the ion-exchange rate of strongly basic anion exchangers, type II, obtained on respective copolymers. Also, the authors present the morphological changes in the macroporous network of copolymers during chloromethylation reaction.

EXPERIMENTAL

Materials

The macroporous St-DVB copolymers were carried out by the radical suspension copolymerization of comonomers. DVB technical grade (52.05% DVB, 31.82% ethyl-styrene, 16.13% nonpolymerizable compounds) was used throughout the experiments.

The experimental conditions used for the copolymerization and the compo-

TABLE I
 Parameters of the Copolymerization Process^a

Sample	DVB (%)	Diluent		Removal of diluent
		Type	Amount	
C ₁	10	Polystyrene ($\bar{M}_w = 97,000$)	25 ^b	Extraction with dichloromethane
C ₂	10	PS + toluene	25 + 60 ^b	Extraction with dichloromethane
C ₃	10	PS + gasoline (bp 110–130°)	25 + 60 ^b	Extraction with dichloromethane
C ₄	10	PS + <i>n</i> -heptane	25 + 60 ^b	Extraction with dichloromethane
C ₅	15	<i>n</i> -Heptane	0.45 ^c	Extraction with methanol
C ₆	15	Gasoline (bp 110–130°C)	0.45 ^c	Extraction with methanol
C ₇	10	2-Ethylhexyl alcohol	0.60 ^c	Extraction with methanol
C ₈	15	Gasoline (bp 110–130°C)	0.45 ^c	Steam distillation

^a All copolymerization processes were carried out at 80°C for 16 h. After the extraction of diluents, the copolymers were dried for 24 h at 60°C under vacuum.

^b g/100 g monomers.

^c Volume fraction.

sition of the copolymers are given in Table I. The concentrations of DVB and of diluents have been limited because of technical reasons.

The chloromethylated products were obtained by reaction of the copolymers with chloromethyl methyl ether in the presence of anhydrous ZnCl₂ (copolymer:CMME:ZnCl₂ molar ratio 1:6:0.5) at 50°C for 6 h.

The anion exchangers were obtained by the reactions of the chloromethylated copolymers with a 20% aqueous solutions of *N,N*-dimethyl-2-hydroxyethylamine (1:2, —CH₂Cl:amine molar ratio) at 50°C for 8 h.

All reagents were distilled in vacuum before use.

Methods

The ion-exchange rate was measured as follows: dried anion-exchanger (1 g) was introduced in a thermostated flask at 25°C fitted with a stirrer. Then, an adequate quantity of 0.8*N* Na₂SO₄ aqueous solution corresponding to a ratio of 1:10 meq Cl:SO₄²⁻ was added. The suspension was stirred at 500 rpm. At certain periods of time the aliquots of solution were taken. The chlorine ion content of the aliquots was determined by potentiometric titration with 0.02*N* AgNO₃ aqueous solution. From the determined values the quantity of chlorine exchanged at time *t* was computed and *F(t)* was estimated by means of the equation

$$F(t) = \frac{\text{amount chlorine exchanged at time } t \text{ (meq Cl}^-/\text{g resin)}}{\text{total capacity resin (meq Cl}^-/\text{g resin)}}$$

The results calculated for *F(t)* were plotted vs. time. The ion-exchange rates were measured on the vacuum-dried anion-exchanger beads (40°C) 0.4–0.8 mm in diameter.

For the transmission electron microscopy, the observations were made on the individual beads embedded in a mixture of "Durcupan" resins, which was polymerized at 50°C, for 48 h. Ultrathin cuttings (a few μm thick) were cut on an ultramicrotome LKB-4800 A. The samples obtained above were used to replicate using the two stage technique. Polystyrene and carbon were used as

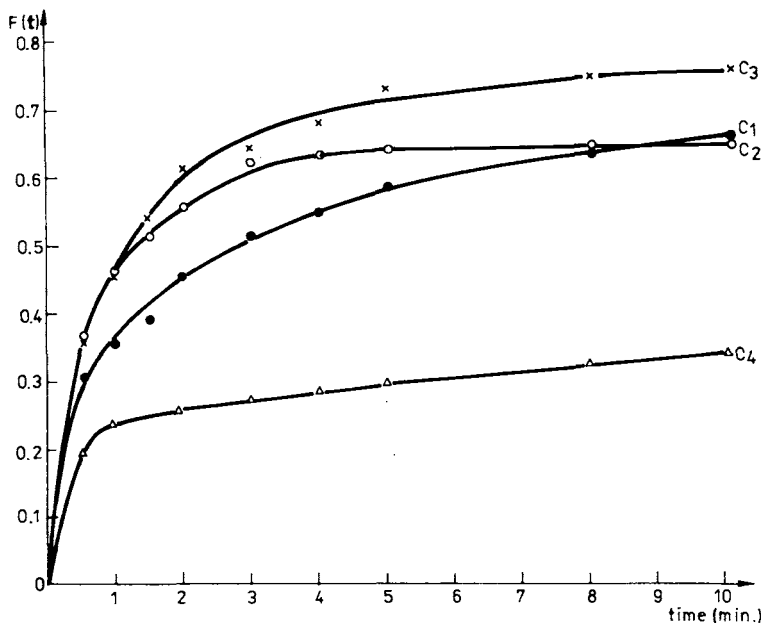


Fig. 1. The ion-exchange rates of the anion exchangers C_1 – C_4 .

materials to prepare replicas, which were metallized with Pd (45°). The replicas were examined in the transmission electron microscope (BS 513 A, Tesla Type).

RESULTS AND DISCUSSION

The network morphology of an ion exchanger depends on the morphology of the St–DVB network and on the morphological changes induced in copolymer during the chemical transformations.

The authors would like to obtain information on these aspects by means of the electron transmission microscopy technique.

It must be pointed out that the technique used by the authors in the microscopy study (the examination of the dried state samples) does not allow a perfect picture on the network morphology of the anion-exchanger samples to be obtained. A better picture of the macromolecular texture of anion exchanger could be obtained on swollen-state samples.

The literature⁷ quotes studies concerning the morphology investigations of the swollen-state cation-exchanger samples.

The ion-exchange rates given a good representation on the difference between the network morphology of the anion-exchanger samples.

The ion-exchange rates of the resins C_1 – C_4 , the anion exchangers on the St–DVB basis performed in the presence of polystyrene or its mixtures, are plotted in Figure 1. One observes from Figure 1 that the anion exchanger C_4 has the slowest exchange rate, though this anion exchanger is performed using a copolymer with the highest porosity.

The differences between the values of exchange rates (Fig. 1) are a consequence of the anion-exchanger morphological structure.

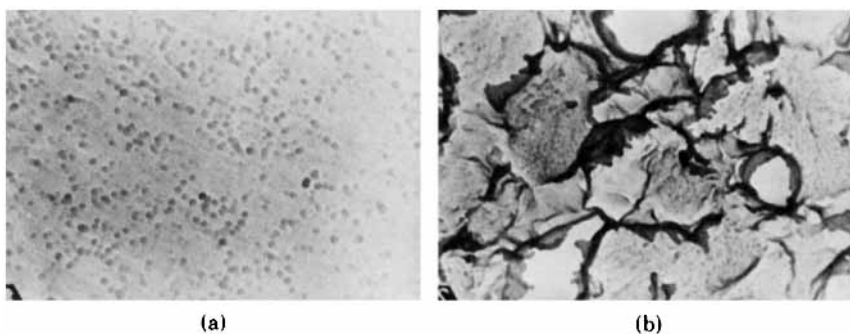


Fig. 2. Electron microscope images of (a) copolymer C_1 ($\times 18,000$) and (b) chloromethylated copolymer C_1 ($\times 18,000$).

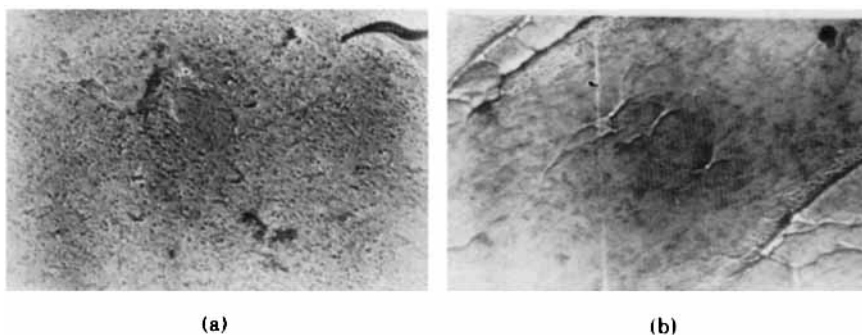


Fig. 3. Electron microscope images of (a) copolymer C_4 ($\times 18,000$) and (b) chloromethylated copolymer C_4 ($\times 18,000$).

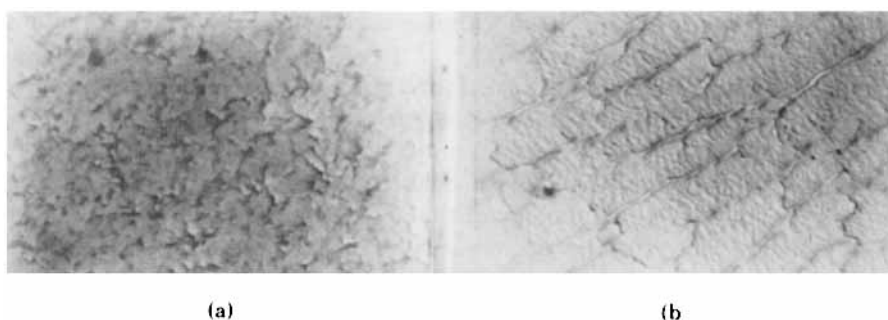


Fig. 4. Electron microscope images of (a) copolymer C_5 ($\times 18,000$) and (b) chloromethylated copolymer C_5 ($\times 18,000$).

The chloromethylation reaction leads to the morphological changes in the copolymers C_1 – C_4 . A fusion phenomenon of the microspheres takes place during this reaction; when these fusion phenomena are strong, the “compact” polymer area will be obtained.

The strongest morphological changes were observed for the copolymers C_1 and C_4 (Figs. 2 and 3). The appearance of the “compact” polymer area could

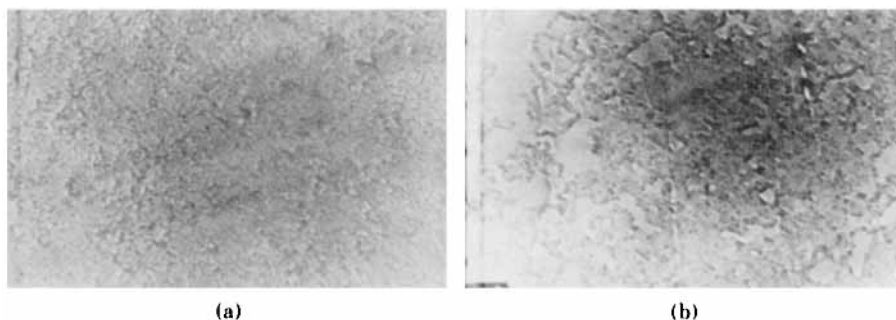


Fig. 5. Electron microscope images of (a) copolymer C_6 ($\times 18,000$) and (b) chloromethylated copolymer C_6 ($\times 18,000$).

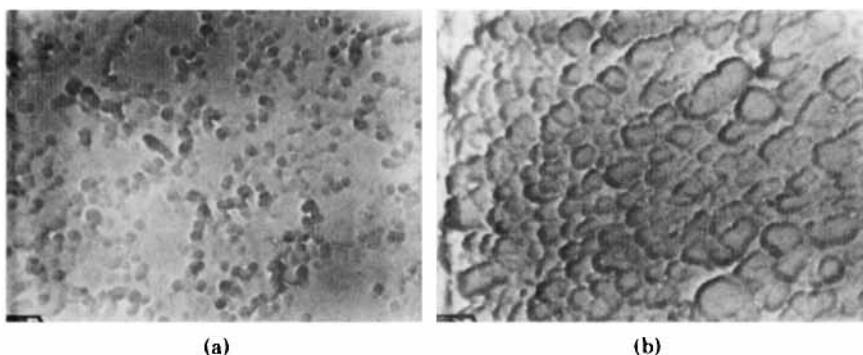


Fig. 6. Electron microscope images of (a) copolymer C_7 ($\times 18,000$) and (b) chloromethylated copolymer C_7 ($\times 18,000$).

very likely explain the slowing down of the ion-exchange rate, as was noticed in the case of the anion-exchanger samples (C_1, C_4).

The macromolecular network of the copolymers C_5 – C_7 undergoes morphological transformations during the chloromethylation reactions in the same manner as the previous copolymers.

Figures 4–6 show the morphological changes of the copolymers C_5 – C_7 . The macromolecular network of the copolymer C_5 has a compact structure [Fig. 4(a)], but, during the chloromethylation reaction, a destruction of these agglomerations could take place, resulting in the appearance of the individualized microspheres [Fig. 4(b)]. For the rest of the copolymers an agglomeration of the microspheres during the chloromethylation can be observed.

It is interesting to compare the surface areas of the copolymers and of the chloromethylated samples (Table II). Broadly speaking, during the chloromethylation reaction the surface area decreases (except in samples C_7 and C_8 where the surface area increases appreciably). This may suggest that the diminution of the surface area takes place because of the fusion of the microspheres when the interstices between them disappear. The structure of the copolymers which have a flexible network collapses during the removal of diluent (C_3) or on drying (C_7). The collapsed macromolecular network reexpands during the chloromethylation, and the surface area increases.

TABLE II
Surface Area Values of the Copolymers and Its Chloromethylated Samples

Sample	Surface area (m ² /g) ^a	
	Copolymer	Chloromethylated product
C ₁	6.20	4.87
C ₂	11.81	10.89
C ₃	12.90	10.45
C ₄	16.32	10.91
C ₅	60.88	30.82
C ₆	32.21	28.42
C ₇	3.06	24.81
C ₈	0.71	25.63

^a Surface area was measured using the nitrogen-adsorption method (BET).

In conclusion, one can assert that the morphological change of the macromolecular network on the St-DVB basis occurs during the chloromethylation reaction. These morphological modifications depend on the copolymer morphology, which is a function of the diluent-polymer factor and the amount of the diluent and DVB used in the copolymerization process.

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