

# Synthesis of Some New Cation-Exchanger Resins

SEVİL SAVAŞKAN,<sup>1</sup> NECATİ BEŞİRLİ,<sup>1,\*</sup> and BAKİ HAZER<sup>1,2,†</sup>

<sup>1</sup>Karadeniz Technical University, Department of Chemistry, Trabzon 61080, Turkey; <sup>2</sup>TÜBİTAK Marmara Research Center, Department of Chemistry, P.O. 21 Gebze, Kocaeli, Turkey

## SYNOPSIS

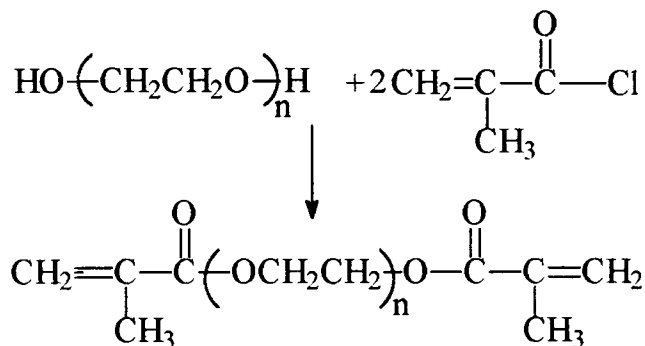
Polystyrene-PEG crosslinked block copolymers were prepared from styrene copolymerization by either poly(ethylene glycol dimethacrylate) (PEG-DM) or macromonomer initiators (MIM).  $M_w$  values of PEG of PEG-DM were 400, 600, 1000, 1500, 3000, 10,000, and 35,000, and of MIM, 400 and 1500. Swelling in H<sub>2</sub>O or CHCl<sub>3</sub> of the sulfonated and unsulfonated block copolymers were determined under comparable conditions and found to vary significantly. The ion-exchange capacity and selectivity coefficients of these ion-exchange resins were investigated. The capacities of the obtained ion exchangers were varied between 0.4 and 2.9 meq/g. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The process of ion exchange occurs between an exchanger and solution.<sup>1</sup> Swelling ratios of ion exchangers were decreased by the force of increasing crosslinkage degree.<sup>2</sup> At equilibrium with an infinite amount of ion-exchanger resins, the free energy of the system would decrease with embedment of water by dilution of the internal solution, liberating the free energy of mixing and decreasing electrostatic

repulsion between neighboring fixed ions. This process is limited by the finite elasticity of the resin, imposed by the crosslinking.<sup>3</sup>

Most of the ion-exchange resins were prepared from styrene and divinylbenzene crosslinked copolymers in bead form. This work refers to the synthesis of ion exchangers starting from the styrene PEG-DM-400, -600, -1000, -1500, -3000, -10,000, and -35,000, and MIM,<sup>4-8</sup> -400, and -1500. The vinylization reaction of PEG with methacryloyl chloride is shown below:



\* Permanent address: Uludağ University, Department of Chemistry, Görükle, Bursa, Turkey.

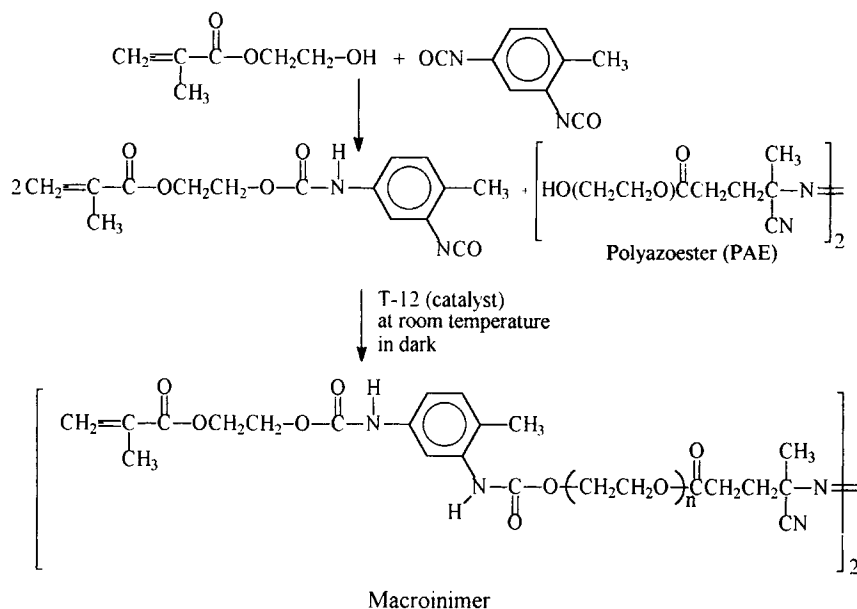
† To whom correspondence should be addressed.

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PEG-DM-400, -600, -1000, -1500, -3000, -10,000, and -35,000 and MIM-400 and -1500 were synthesized from 0.01 mol hydroxyethyl methacrylate (HEMA), 0.01 mol toluenediisocyanate (TDI), and 0.05 mol PAE-400 and -1500. The reaction of macroinimers can be shown as follows:



### Synthesis of PEG-DM-400, -600, -1000, -1500, -3000, -10,000, and -35,000

In a typical procedure for PEG-DM-400, 40 mmol of PEG-400, 2 mg of hydroquinon, 8.5 mL of triethylamine, and 50 mL of  $C_2H_4Cl_2$  were stirred at room

## EXPERIMENTAL

### Materials

Hydroxyethyl methacrylate (HEMA), toluenediisocyanate (TDI), PEG-400, -600, -1000, -1500, -3000, -10,000, and -35,000 (numbers refer to the molecular weights of PEG) and the other reagents were used as purchased. Styrene was washed with 10% aqueous NaOH solution, dried over  $CaCl_2$  and  $CaH_2$ , respectively, and then distilled under reduced pressure just before use.

### Instrumentation

FTIR and NMR spectra of the products were taken on a Perkin-Elmer 1600 FTIR and Bruker AC 200L 200 MHz NMR spectrometer, respectively. The sulfur content of ion-exchanger resins was determined by using the Carlo Erba 1106 Model microanalyzer. Equilibrium concentrations of  $La^{3+}$  were determined by spectrometric (Varian Techtron-635 Model UV-VIS) and potentiometric (YSI-31 Model Conductometer) methods.

temperature in a flask. Methacryloyl chloride, 88 mmol, in 10 mL of  $C_2H_4Cl_2$  solution was gradually added to this solution at room temperature. After 3 h stirring, the product was obtained, filtered, and precipitated from petroleum ether. The viscous liquid was dried under vacuum. PEG-DM-600 was also a viscous liquid and the others obtained by the same procedure above were white solids. Figure 1 shows a typical FTIR spectrum of a PEG-DM and Figure 2 shows a typical NMR spectrum of a PEG-DM. IR ( $cm^{-1}$ ); 1710 (C=O), 1650 (C=C), 1100 (C—O—C). NMR ( $\delta$ , ppm); 2.0 ( $CH_3$ ), 3.5 ( $-CH_2-O-CH_2-$ ), 5.6–6.2 (vinylic protons).

### Synthesis of MIM-400 and MIM-1500

To obtain MIM-400, 10 mmol of TDI, 10 mmol of HEMA, and 50 mL of  $CHCl_3$  were stirred for 1 h under  $N_2$ . Then, 15.5 g of PAE-1500 (5 mmol) in 100 mL of  $CHCl_3$  and 0.02 g of a stannous octoate (T-12) as a catalyst were added to this solution. After 5 h stirring, the solvent was evaporated under reduced pressure. The waxy solid was dissolved in 30

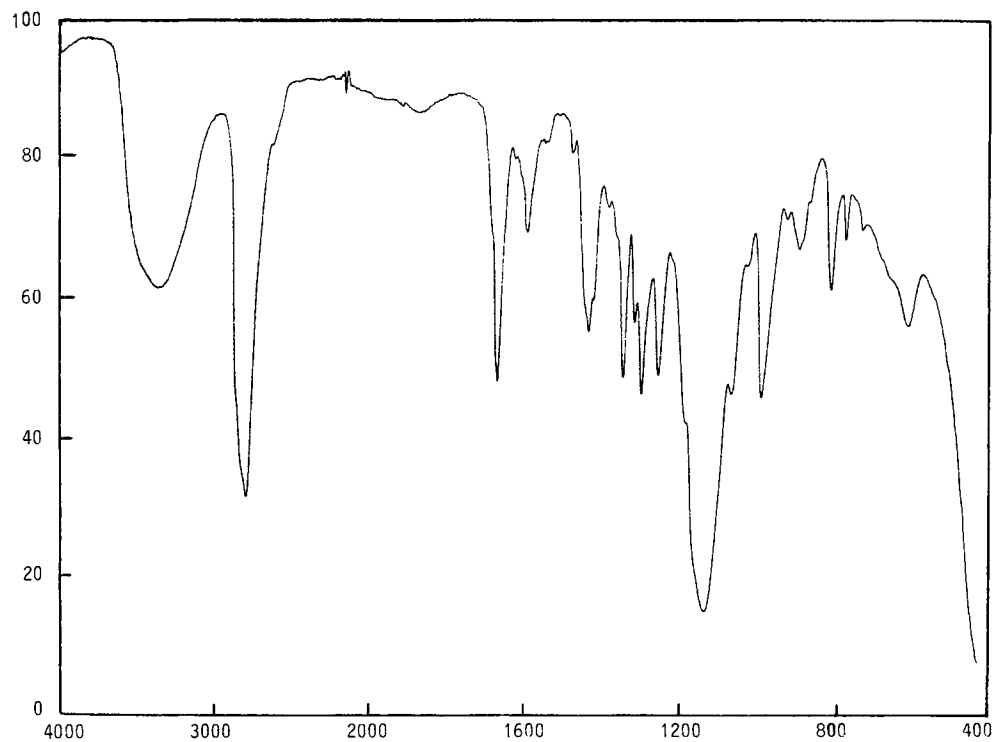


Figure 1 FTIR spectrum of PEG-DM-400.

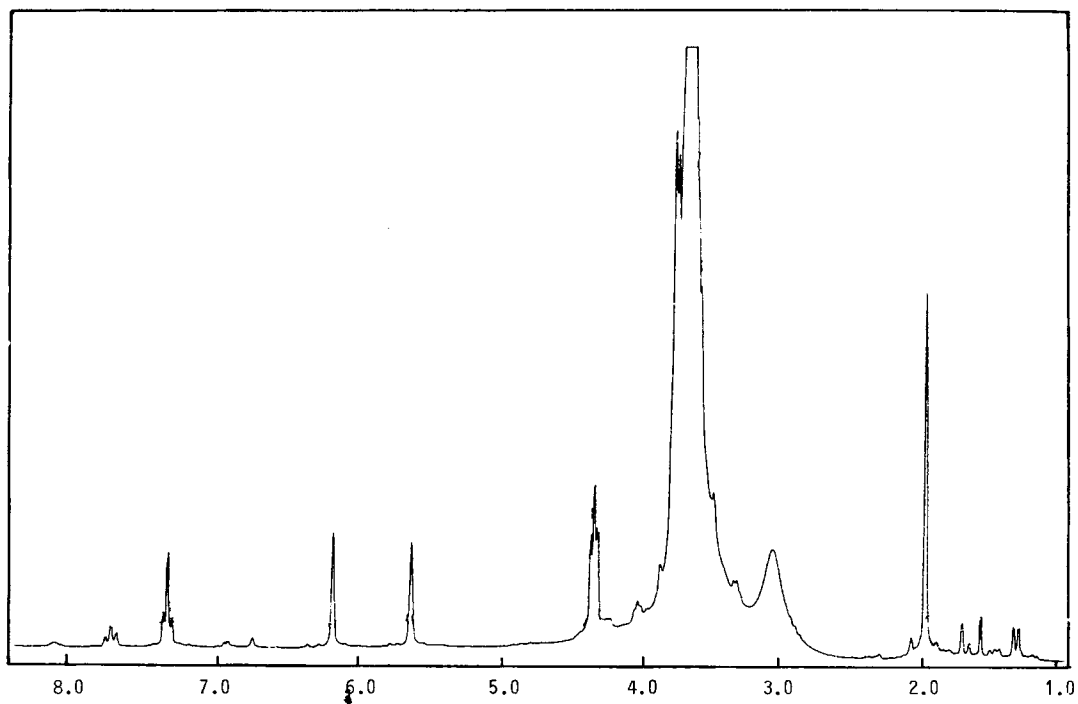


Figure 2 <sup>1</sup>H-NMR spectrum of PEG-DM-400.

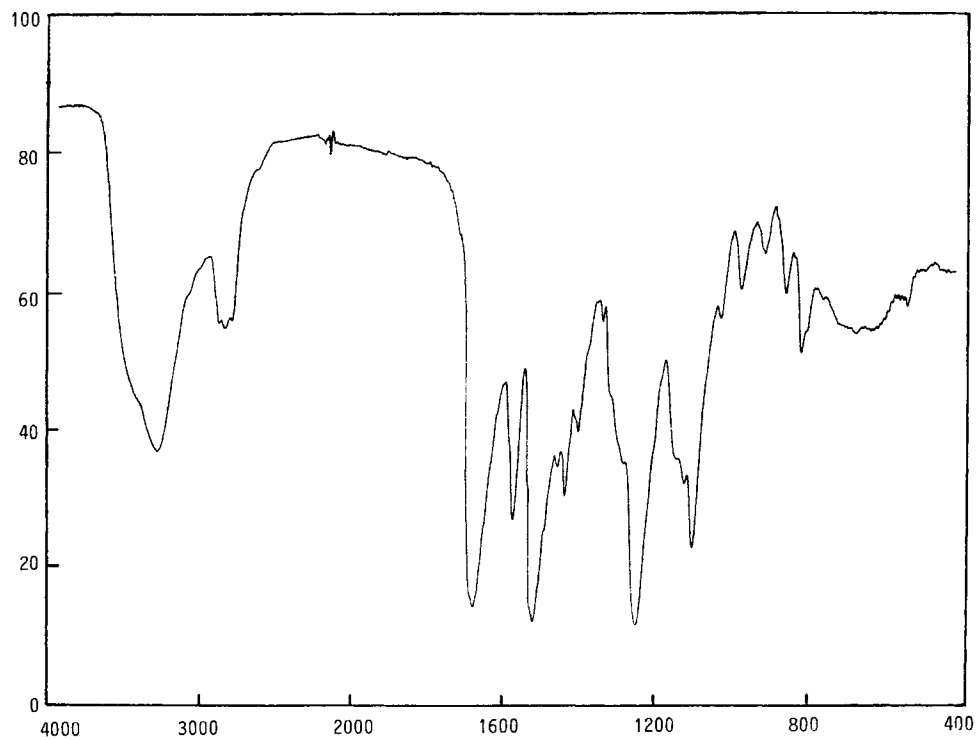


Figure 3 FTIR spectrum of MIM-400.

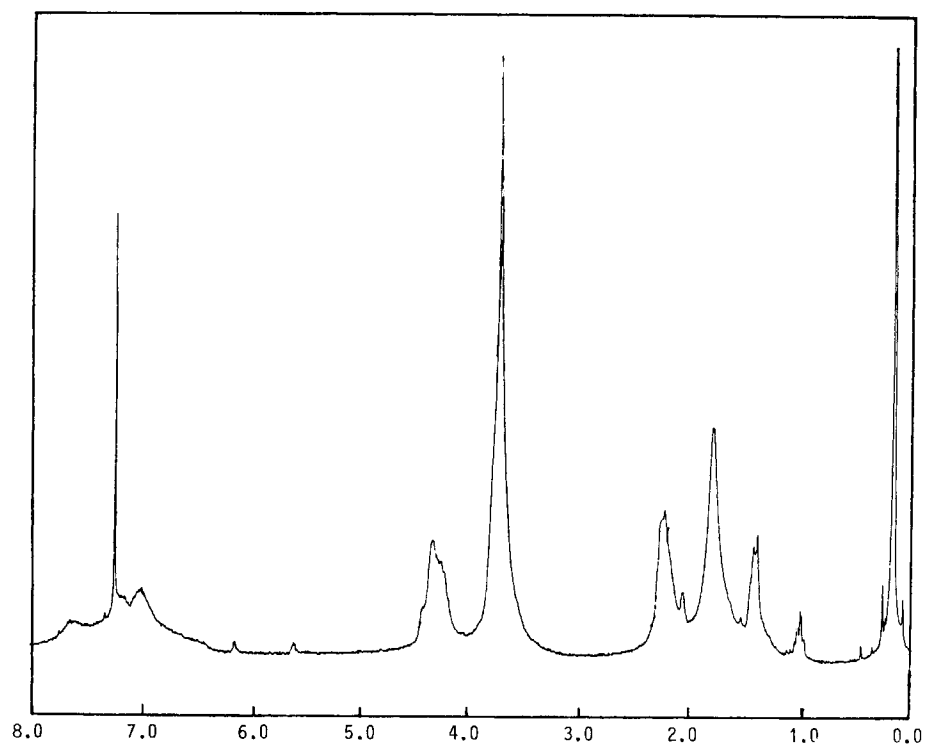


Figure 4 <sup>1</sup>H-NMR spectrum of MIM-400.

mL of  $\text{CHCl}_3$  and precipitated in the mixture of diethyl ether/petroleum ether (1 : 1). The viscous liquid was dried under vacuum. The MIM-1500 obtained by the same procedure was a white solid. IR ( $\text{cm}^{-1}$ ); 3300 ( $-\text{NH}$ ), 1710 ( $\text{C}=\text{O}$ ), 1600 ( $\text{C}=\text{C}$ ) and the characteristic peaks of PAE (see Fig. 3). NMR ( $\delta$ , ppm); 5.6 and 6.2 (vinylic protons) and the characteristic peaks of polyazoester (see Fig. 4).

#### Poly(styrene-*b*-PEG) Crosslinked Block Copolymers with Macrointermediate Polymerization of Styrene with PEG-DMs

In a 250 mL three-necked round-bottom flask with a mechanical stirrer, condenser, and short path glass was put 0.05 g gelatin, 0.768 g  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , 0.05 g AIBN, and 90 mL deionized water at  $80^\circ\text{C}$  under a  $\text{N}_2$  atmosphere for 3 h. Then, 87.4 mmol of styrene and 0.90 mmol of PEG DM-400, -600, -1000, -1500, -3000, -10,000, or -35,000 were added to this solution dropwise. After 3 h stirring, the polymerization content of the flask was poured into cold water and kept in the refrigerator for 24 h. Then, this mixture was filtered and washed with methanol, deionized water, and dried under vacuum. In some experiments, polymerization was carried out at  $65^\circ\text{C}$  for 20 h, followed  $80^\circ\text{C}$  for 2 h in the case of 22 h total polymerization time. IR spectra of the poly(styrene-*b*-PEG) crosslinked block copolymers showed the characteristic peaks of PS and PEG (see Fig. 5).

#### Styrene Polymerization with MIM-400 or MIM-1500

Styrene, 9.089 g, and MIM-400, 0.4338 g, were gradually added to a solution of 0.1 g of gelatin and 0.02

g of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  in 25 mL deionized water under  $\text{N}_2$  atmosphere at  $80^\circ\text{C}$ . After 3 h stirring, the resulting polymer was precipitated into cold water. The precipitated polymer was filtered and washed with methanol and water and dried under vacuum at room temperature. IR spectra of crosslinked PS-PEG block copolymers contained the characteristic peaks of both polystyrene (PS) and PEG segments (see Fig. 6).

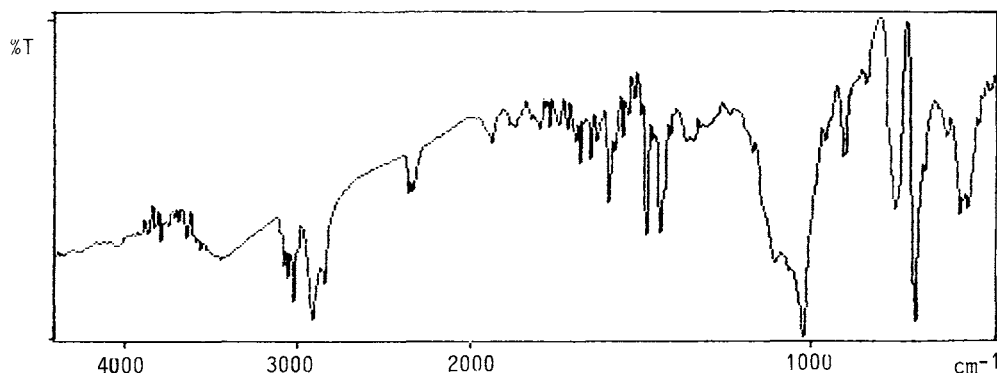
#### Sulfonation of the Crosslinked Block Copolymers Obtained by Using PEG-DMs (R-DM) and MIMs (R-MIM)

$\text{P}_2\text{O}_5$ , 13 g, in 5 mL of concentrated  $\text{H}_2\text{SO}_4$  was added to, by stirring, a suspension of 5 g of crosslinked PS-PEG block copolymer swollen previously in 40 mL cyclohexane.<sup>9</sup> The mixture was refluxed for 1 h at  $40^\circ\text{C}$ . The suspension was poured into cold water. The obtained beads were filtered off, washed with methanol and water, and dried under vacuum. After sulfonation of the crosslinked block copolymers, their IR spectra showed the characteristic  $-\text{S}-\text{O}-\text{C}-$  bands at  $1300$  and  $603$   $\text{cm}^{-1}$  (see Figs. 7 and 8).

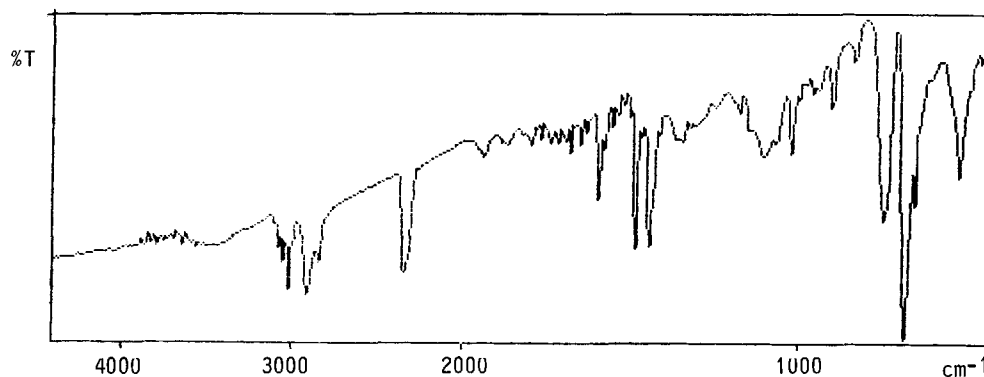
#### Determination of Swelling Ratios of Crosslinked Block Copolymers and Sulfonated Block Copolymers (R-DM and R-MIMs)

The swelling ratios of the polymers in water were determined by rinsing 0.5 g of the polymer in 100 mL of water at room temperature for 24 h. The swelling ratio was calculated by the following equation:

$$\text{Swelling ratio} = \frac{W_{sp} - W_{dp}}{W_{dp}} \times 100$$



**Figure 5** IR spectrum of crosslinked poly(styrene-*b*-PEG) block copolymers obtained by the styrene polymerization with PEG-DM-400.



**Figure 6** IR spectrum of crosslinked poly(styrene-*b*-PEG) block copolymers obtained by the styrene polymerization with MIM-400.

where  $W_{sp}$  = weight of the swollen polymer and  $W_{dp}$  = weight of the dried polymer.

#### Determination of Ion-exchange Capacities of Ion Exchangers

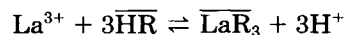
For this purpose, a certain amount of ion-exchanger resins were kept in 50 mL of  $1 \times 10^{-2} M$   $CoCl_2$  and 50 mL of  $1 \times 10^{-1} M$   $Co(NH_3)_6Cl_3$  solutions for 24 h. Using these solutions, their absorbances were measured spectrophotometrically. Then, absorbance measurements of these solutions were taken and the ion-exchange capacities of ion-exchanger resins were calculated using the absorbance values with calibration curves obtained with standard solutions. The properties of ion-exchanger resins obtained are shown in Table I. The capacity of ion-exchanger resins were also obtained volumetrically as follows: 200 mL of a 5 wt % NaCl solution containing 0.8 of NaOH and 0.5 g of the resin prepared were kept overnight. Then, 25 mL of the solution from the

mixture was taken by a pipette and titrated by 0.1M HCl. The capacity of the ion exchanger was calculated using the acid consumption. Table I shows all the polymerization conditions and the results.

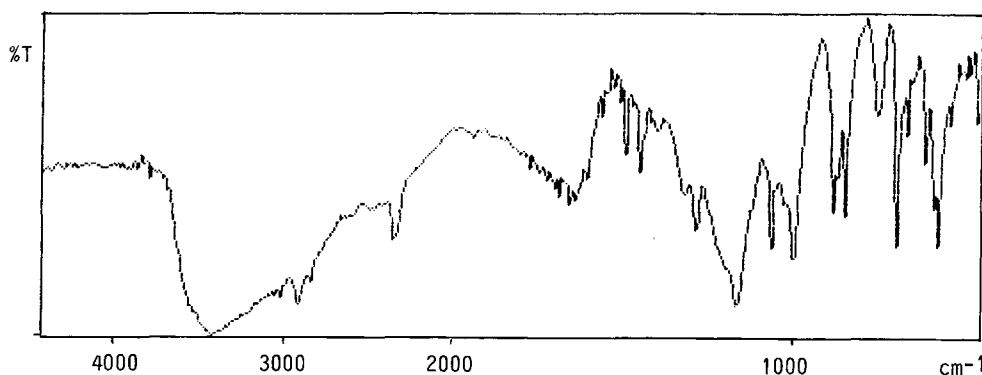
#### THEORETICAL APPROACH

##### Investigation of Ion-exchange Equilibrium of Ion-exchanger Resins

Since ion-exchanger resins act as a cation exchanger, the trivalent rare earth metal (lanthanum) ions  $La^{3+}$  in the liquid phase exchange with  $H^+$  ions in the ion-exchanger phase. The overall ion exchange reaction is



where overscoring indicates that a species is present in the ion-exchanger phase. From the mass action



**Figure 7** IR spectrum of R-DM-400 (sulfonated block copolymer).

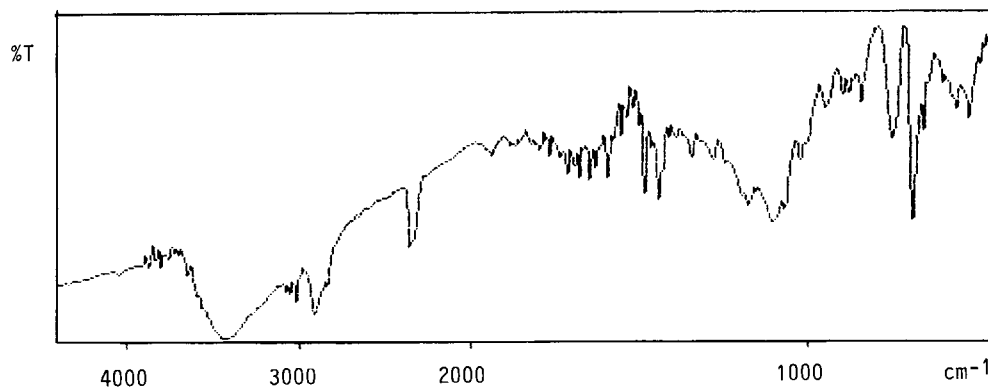


Figure 8 IR spectrum of R-MIM-400 (sulfonated block copolymer).

law, the equilibrium constant  $K_H^{La^{3+}}$  for the ion-exchange reaction is

$$K_H^{La^{3+}} = \frac{[\overline{LaR_3}][H^+]}{[La^{3+}][\overline{HR}]}$$

where the square brackets indicate concentrations of the species within.<sup>10</sup>

The rare earth metal used was lanthanum. Aqueous solutions of the rare earth were prepared by dissolving pure  $LaCl_3 \cdot H_2O$  in deionized water. Experiments were carried out by a batchwise method and most of data were taken at temperature 25°C. A mixture of ion-exchanger resins and the rare earth solution were shaken for 3 h in a flask with a stopper. The  $LaCl_3 \cdot H_2O$  initial concentration was from  $1.0 \times 10^{-2}$  to  $5.0 \times 10^{-2}$  mol/L. Ion-exchanger resins, 0.2 g, were equilibrated with these solutions. After the equilibrium was reached, the mixture was filtered and the filtrate was saved for analysis. The solution samples were analyzed for the rare earth metal by conductimetric EDTA titration. The content of the rare earth metal in the resin phase was determined from the liquid-phase balance. The selectivity curve for the  $La^{3+}$ -hydrogen system on ion-exchanger resins, R-DM-400 (run no. 1), R-DM-600 (run no. 2), R-DM-1500 (run no. 6), R-MIM-400 (run no. 14), R-MIM-1500 (run no. 15), and R-MIM-1500 (run no. 16) in Table I are shown in Figures 9 and 10, respectively.

## RESULTS AND DISCUSSION

We attempted to prepare cation-exchange resins having PEG units by the polymerization of styrene with PEG-DMs or MIMs and then by the sulfonation process of these crosslinked polymers. Char-

acterization of the resins prepared was carried out by taking their NMR and FTIR spectra (see Figs. 1-8). Table I includes the emulsion polymerization conditions and the results. In each run, crosslinked block copolymers were obtained in high yield (86-100%).

To investigate the effects of the time of polymerization on crosslinkage degree and ion-exchange capacity, the block copolymerization reaction was done partly at 3 and 22 h. For this purpose, the polymerization of crosslinked poly(styrene-*b*-PEG) was carried out in a manner as described above. The swelling ratios in water crosslinked polymers were considerable (48-313 wt %). As a comparison, the swelling ratios of the resins with a shorter polymerization time (e.g., 3 h) were greater than those with a longer polymerization time (22 h).<sup>11</sup>

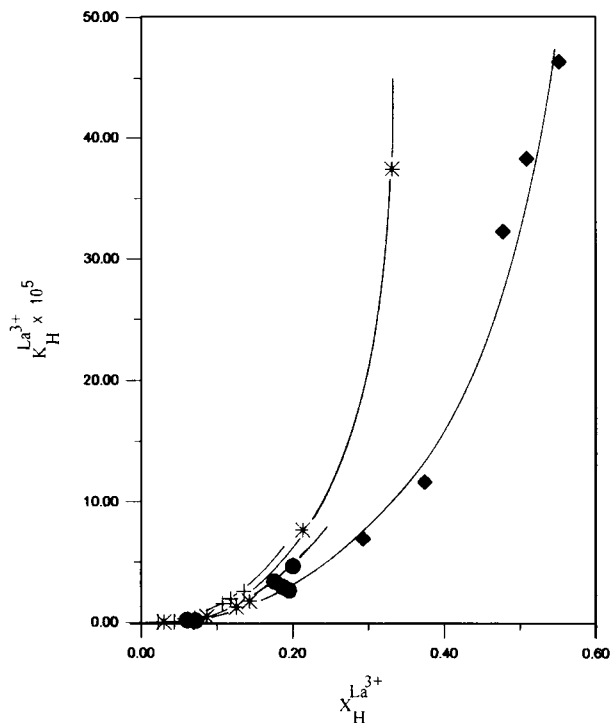
The maximum capacities of ion exchangers are reported in Table I. The capacity of the resulting ion-exchange resin depends on the reaction time, on the molecular weight of macrocrosslinkers, and on the crosslinkage degree. When the time of polymerization was 22 h, the resulting experimental data showed that ion-exchanger resins have lower ion-exchange capacity, i.e., ion-exchange capacity of ion-exchanger resins decreased with increasing of the polymerization time, crosslinkage degree, and molecular weight of the crosslinker. Because of the polar sulfone groups of resins, the swelling ratio of cation exchangers in water is higher than the swelling ratio of the untreated crosslinked block copolymer. In the last column, calculated capacities are higher than are experimental capacities. In this manner, sulfonation of the inner core of the resin does not effect the ion-exchange reaction. The mol fraction of  $La^{3+}$  ions in the resin phase loaded as 0.2; in comparing the selectivity constant  $K$ ,  $La^{3+}$

Table I Preparation of the Sulfonated Ion-exchanger Resins

Run No.	Types of Ion Exchange	Macrointermediate			Polymerization Time (h)	Conversion of Styrene (Wt %)	Swelling of Crosslinked Block Copolymer in Water (Wt %)	Sulfonated Ion Exchanger			
		PEG-DM (g)	+AIBN (g)	+MIM (g)				Styrene (g)	S Content (Wt %)	Swelling in Water Wt (%)	Capacity (meq/g)
								Found	Calcd		
1	R-DM-400	0.5000	+0.20		3	98	231	13.02	311.00	2.8158	3.2971
2	R-DM-600	0.6200	+0.05		3	100	210	7.30	300.00	2.0400	2.2800
3	R-DM-600	0.6200	+0.05		22	99	173	6.32	210.00	0.5560	1.9739
4	R-DM-1000	2.0240	+0.20		3	86	123		143.00		
5	R-DM-1000	2.0240	+0.05		6.5	88	101	7.77	133.46	0.5425	2.4000
6	R-DM-1500	0.6700	+0.50		3	90	159	9.80	280.80	1.8075	2.5000
7	R-DM-1500	1.4238	+0.05		22	88	102	10.89	200.00	0.5761	3.4000
8	R-DM-3000	2.7740	+0.05		3	98	261	5.66	399.23	0.2997	1.7600
9	R-DM-3000	2.770	+0.20		3.5	95	242	5.37	323.20	0.2949	1.6779
10	R-DM-10000	9.0740	+0.05		7	91	76	7.78	105.00	0.5058	2.4290
11	R-DM-10000	9.0740	+0.05		22	96	60	8.80	80.00	0.2606	2.2550
12	R-DM-35000	31.570	+0.05		7	98	313	10.29	467.54	0.9923	1.5000
13	R-DM-35000	31.570	+0.05		22	90	48	10.29	63.04	0.2740	3.2100
14	R-MIM-400			0.4338	3	92	128	8.58	171.00	0.6743	2.6810
15	R-MIM-1500			1.4238	3	89	227	6.09	303.00	1.0130	1.9038
16	R-MIM-1500			4.0000	4	90	217	4.13	290.00	0.6165	1.2900

Resins prepared according to the reactions PEG-DM + AIBN + styrene  $\xrightarrow{+ \text{AIBN}}$  R-DM-400 and -35,000 and MIM-400 and -1500  $\xrightarrow{+ \text{AIBN}}$  R-MIM-400 and -1500 and the properties of synthesized block copolymers and ion-exchanger resins.





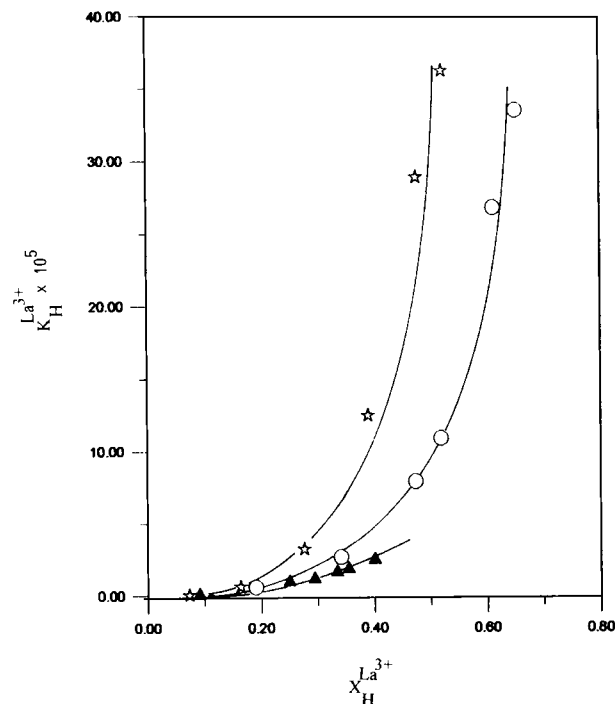
**Figure 9** Selectivity values of  $\text{La}^{3+}$ -hydrogen exchange on exchanger resins as a function of mol fraction in the resin phase: (+) (HR,  $C = 2.1858$  meq/g)  $\text{R-DM-400} + \text{La}^{3+} \rightleftharpoons (\text{R-DM-400})_3\text{La} + 3\text{H}^+$ ; (\*) (HR,  $C = 2.0400$  meq/g)  $\text{R-DM-600} + \text{La}^{3+} \rightleftharpoons (\text{R-DM-600})_3\text{La} + 3\text{H}^+$ ; (●) (HR,  $C = 1.8075$  meq/g)  $\text{R-DM-1500} + \text{La}^{3+} \rightleftharpoons (\text{R-DM-1500})_3\text{La} + 3\text{H}^+$ ; (◆) (HR,  $C = 0.9923$  meq/g)  $\text{R-DM-35,000} + \text{La}^{3+} \rightleftharpoons (\text{R-DM-35,000})_3\text{La} + 3\text{H}^+$ .

+ R-DM-600,  $\text{La}^{3+}$  + R-DM-1500,  $\text{La}^{3+}$  + R-DM-35000 in equilibrium showed the selectivity constant to be similar. The ion-exchanger capacity of R-DM-400 and R-DM-600 are closer each other. Having a selectivity constant as a guide, the result was expected to be similar. Also, the structure of these resins should be same. When the crosslinkage in the ion exchanger increases, the ion-exchange capacity and resin porosity decreases. Table II indicates the selectivity coefficients of some resins. When ion-exchange capacity increases, selectivity is also increased. The investigated ion exchange in the equilibrium reaction for the selectivity constant is shown in Table II. The obtained cation-exchanger resins and selectivity constants of  $\text{La}^{3+}$  are changed from  $0.69 \times 10^{-5}$  to  $6.4 \times 10^{-5}$ . On the Dowex-50W (HR,  $C = 4.85$  meq/g),  $\text{Co}(\text{NH}_3)_6^{3+} + \text{LaR}_3$ , and on the Dowex-50W-4 (HR,  $C = 4.12$  meq/g),  $\text{Cr}(\text{en})_2^{3+} + \text{LaR}_3$  ion-exchange reactions,  $K$  selectivity constants were found to be 18.2 and 14.1, respectively.<sup>12</sup>

The selectivity of the Dowex-50 ion-exchanger resin to the  $\text{La}^{3+}$  ions selectivity is 6.16.<sup>13,14</sup>

The selectivity of R-DM-400 and R-DM-600 vs. the lanthanum ions increases as the crosslinking degree increases as shown in Table II. However, the crosslinkage on the surface of RM-DM-1500 is higher than that in the center, so the selectivities of R-MIM-400 (run no. 14 in Table II) and R-MIM-1500 (run no. 15 in Table II) are increased by increasing the ion-exchange capacity. The reasons for the difference in selectivity and capacity are due to the different polymerization times. This has been attributed to the inhomogeneity of the resin which contains the functional group in different environments.<sup>15-17</sup>

Figures 9 and 10 show that the selectivity increases by increasing the ion loaded. The relationships of  $K_H^{\text{La}^{3+}}$  vs.  $X_H^{\text{La}^{3+}}$  are seen to be a curve for all ion-exchange equilibrium according to the equation  $K_H^{\text{La}^{3+}}$ . Since ion exchange occurs in the inner region of the resins, the selectivity increases as the mol fraction of the lanthanum ions in the resin face



**Figure 10** Selectivity values of  $\text{La}^{3+}$ -hydrogen exchange on exchanger resins as a function mol fraction in the resin phase: ( $\Delta$ ) (HR,  $C = 0.673$  meq/g)  $\text{R-MIM-400} + \text{La}^{3+} \rightleftharpoons (\text{R-MIM-400})_3\text{La} + 3\text{H}^+$ ; ( $\star$ ) (HR,  $C = 1.0130$  meq/g)  $\text{R-MIM-1500} + \text{La}^{3+} \rightleftharpoons (\text{R-MIM-1500})_3\text{La} + 3\text{H}^+$ ; ( $\circ$ ) (HR,  $C = 0.6165$  meq/g)  $\text{R-MIM-1500} + \text{La}^{3+} \rightleftharpoons (\text{R-MIM-1500})_3\text{La} + 3\text{H}^+$ .

**Table II** Selectivity Coefficient at  $x_{\text{H}}^{\text{La}^{3+}} = 0.2$   
Charged on Cation-Exchange Resins

Run No.	Type of Resin	$K_{\text{H}}^{\text{La}^{3+}} \times 10^6$
1	R-DM-400	4.3979
2	R-DM-600	6.4284
6	R-DM-1500	3.6992
12	R-DM-35000	5.2981
14	R-MIM-400	0.6867
15	R-MIM-1500	4.1419
16	R-MIM-1500	0.9375

increases. As a conclusion, the selectivities of all resins prepared are similar. This is the result for all resins having same network.

Experimental results showed that selectivity of  $\text{La}^{3+}$  ions in lower concentration is small but the selectivity increased in higher concentration. Hence, exchanging the ion on the surface of the resin causes the lower concentration. The exchanging ion inside the bead exchanged in higher concentration. Beside this, in higher concentrations, some of the electrolyte was attached in the resin pore. This caused the formation of an ion pair of  $\text{La}^{3+}$  in the resin with a cross ion.<sup>10</sup>

The total solution concentration has a complicated effect on selectivity.<sup>18</sup> At very high solution concentrations, special effects are observed, including selectivity. Special problems are revealed which are not encountered in dilute aqueous solutions, since measurements are usually carried out as distribution measurements of a lanthanum ion between the resin and a bulk electrolyte. Particularly as the resin invasion becomes appreciable, so much so that nonexchange electrolyte concentrations may become higher than the concentration of exchange sites when the external solution becomes very concentrated, water activities decrease and, therewith, the resin swelling, so that the pressure-volume term becomes unimportant. Because of above results, the

selectivities of the other ion-exchanger resins were not examined except in run nos. 1, 2, 12, 14, 15, and 16.

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