

Synthesis of the New Cation Exchange Resins Having Poly (Styrene-Caprolactone) Units

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The crosslinked polystyrene-polycaprolactone , PS-PCL-, block copolymers were prepared by the copolymerization of styrene and poly(caprolacton dimethylmethacrylate) (PCL-DM). The molecular weights of polycaprolactone, PCL, PCL-DM were 1250 and 2000. The swelling in H₂O or CHCl₃ of the sulfonated and unsulfonated block copolymers were determined under comparable conditions and investigated. The capacities of the obtained ion exchange resins were 1.31 and 1.10 meq/g.

Introduction

Macrointermediates such as macroinitiators, macromonomers and macrocrosslinkers are important in polymer modification leading to block and graft copolymers¹⁻³.

The process of ion exchange occurs between an exchanger and a solution⁴. Swelling ratios of ion exchangers decreased as the degree of crosslinking increased⁵. At equilibrium with an infinite amount of ion exchange 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 crosslinking⁶.

Most of the ion exchange resins were prepared from styrene and divinylbenzene crosslinked copolymers in bead form. We previously synthesized ion exchangers starting from the styrene-PEG-DM-400, -600, -1000, -1500, -3000, -10,000 and -35,000 and MIM-400, and 1500⁷. This study concerns the preparation of a new ion exchange resin that has differential properties using the styrene and biodegradable PCL-DM-1250 and -2000. The vinylization reaction of PCL with methacryloyl chloride is shown below:

mixture was refluxed for 1 h at 40 °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 (S=O)₂ symmetric and asymmetric stretching vibrations at 1300 and 1100 cm⁻¹, respectively and (S-O-C) peak at 603 cm⁻¹ (see Figure 3).

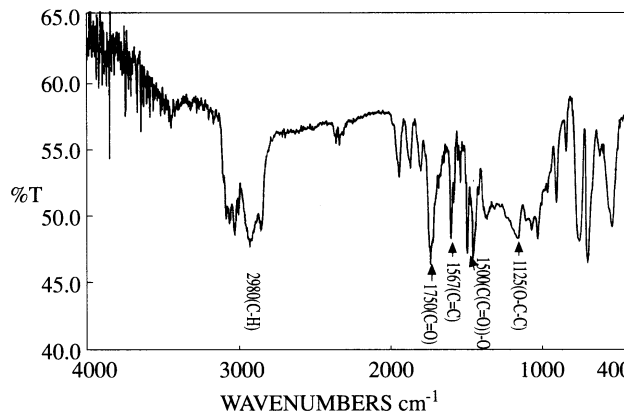
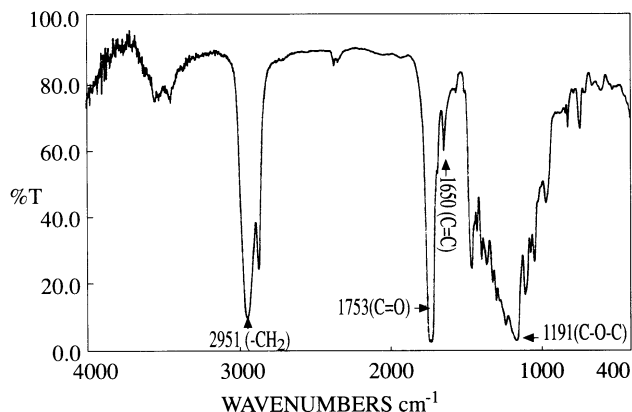


Figure 1. FTIR spectrum of PCL1250

Figure 2. FTIR Spectrum of Poly(styrene-b-PCL-1250) Block Copolymer

Determination of Swelling Ratios of Crosslinked Block Copolymers, Poly(Styrene-b-PCL) and Sulfonated Block Copolymers, R-PS-PCL:

The swelling ratios of the crosslinked block copolymer and sulfonated block copolymers were determined by storing 0.2 g of the samples in 50 mL of CHCl₃ or H₂O for 24 h at 20 °C. The swelling ratio, q_v , was calculated using the following equation⁹:

$$q_v = \frac{V_{\text{dry polymer}} + V_{\text{solvent}}}{V_{\text{dry polymer}}} = \frac{V_{\text{swollen polymer}}}{V_{\text{dry polymer}}}$$

where $V_{\text{dry polymer}}$, is the volume of dry polymer and V_{solvent} is the volume of the solvent. The swelling ratios of the crosslinked block copolymers and sulfonated block copolymers are presented in Table 1.

Table 1. Preparation of the Sulfonated Ion-Exchanger Resins

Run	Types of Ion Exchange Resin	Macrointermediate			Polym. time(h)	Conversion of Styrene (wt %)	Swelling ratio of Crosslinked Block Copolymer, q_v ,		Sulfonated Ion Exchanger			capacity (meq/g)	
		PCL (g)	DM+AIBN (g)	Styrene (g)			in water	in CHCl ₃	S content (wt%)	Swelling ratio, q_v ,		found	calc.
1	R-PCL DM-1250	1.250	+0.05+	9.50	10	98	1.40	13.63	1.90	1.70	14.8	1.31	0.60
2	R-PCL DM-2000	1.960	+0.05+	9.60	10	99	1.30	10.60	2.32	3.25	18.23	1.10	0.73

Determination of Ion-Exchange Capacities of Ion Exchangers:

For this purpose, a certain amount of ion exchanger resins were kept in 100 mL of 1×10^{-2} M UO₂²⁺ or 1×10^{-2} M La³⁺ solutions for 24 h. Using these solutions, their absorbances were measured spectrophotometrically. Then, the absorbance measurements of these solutions were taken and the ion-exchange capacities of ion-exchanger resins were calculated using the absorbance values with the calibration curves obtained with standard solutions. The ion exchange capacities of ion-exchangers were also determined volumetrically and by conductimetric EDTA titration. The capacity of the ion-exchange resins were obtained volumetrically as follows: 200 mL of a 5 wt % NaCl solution containing 0.8 g of NaOH and 0.5 g of the prepared resin were kept overnight. Then, 25 mL of the solution from the mixture was taken with a pipette and titrated with 0.1 M HCl. The capacity of the ion-exchanger was calculated using the acid consumption. All the polymerization conditions and the results are shown in Table 1.

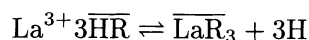
Table 2. Selectivity Coefficient of La^{3+} on Cation-Exchange Resins

Run No	Type of Resin	$K_{\text{H}^+}^{\text{La}^{3+}}$
1	Dowex-50w	18.2 ¹¹
2	Dowex-50w-4	14.1 ¹¹
3	Dowex-50	6.16 ^{12,13}
4	R-PS-PCL-1250	0.25(This study)
5	R-PS-PCL-2000	0.01(This study)

Theoretical Approach

Investigation of Ion-Exchange Equilibrium of Ion-Exchange Resins:

Since ion-exchange 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 law, the equilibrium constant $K_{\text{H}^+}^{\text{La}^{3+}}$ for the ion exchange reaction is

$$K_{\text{H}^+}^{\text{La}^{3+}} = \frac{[\overline{\text{LaR}_3}][\text{H}^+]}{[\text{La}^{3+}][\overline{\text{HR}}]}$$

where the square brackets indicate concentrations of the species within¹⁰.

The rare earth metal used was lanthanum. Aqueous solutions of the rare earth metal were prepared by dissolving pure $\text{LaCl}_3 \cdot \text{H}_2\text{O}$ in deionized water. The results were taken out batchwise and most of the results were resins at 25°C. A mixture of ion-exchange resins and the rare earth solution was shaken for 24 h in a flask with a stopper. The initial $\text{LaCl}_3 \cdot \text{H}_2\text{O}$ concentration was from 1.0×10^{-2} to 5×10^{-2} mol/L. 0.2 g of ion exchange resins, 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 spectrophotometrically. 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-exchange resins, R-PS-PCL-1250 and R-PS-PCL-2000, in Table 1 are shown in Figure 3.

Results and Discussion

We attempted to prepare cation exchange resins with PCL units, by the polymerization of styrene with PCL-DM s and then by the sulfonation process of these cross linked polymers. Analyses of the resins were carried out by taking FTIR spectra and elemental sulphur analysis (see Figures 2,3 and Table 1). Table 1 includes the emulsion polymerization conditions and the results. In each run, crosslinked block copolymers were obtained in high yield (98-99 %).

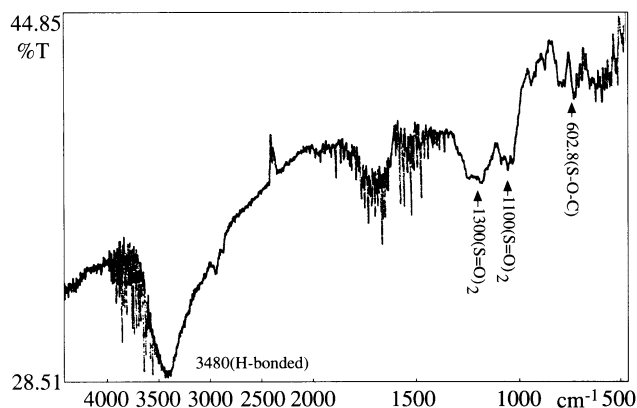


Figure 3. FTIR Spectrum of R-PS-PCL-1250 Ion-Exchange Resin

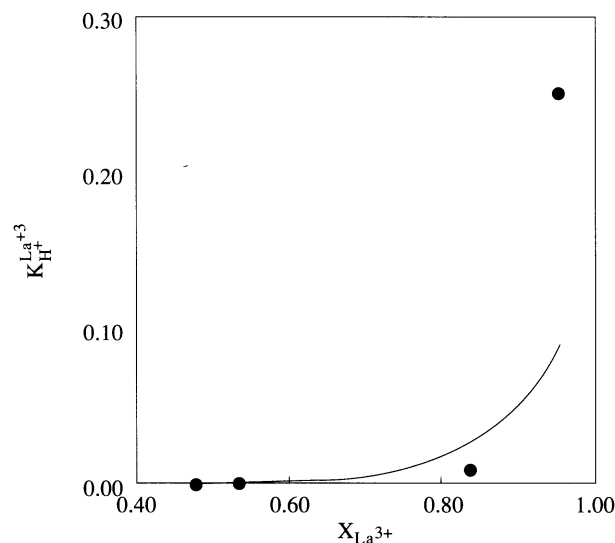


Figure 4. Selectivity values of La^{+3} hydrogen exchange on exchanger resins as a function of the mole fraction in the resin phase.

(Δ) (HR, C=1.31 meq/g) R-PS-PCL-2000+ $\text{La}^{+3} \rightleftharpoons$ (R-PS-PCL-1250)₃La + 3H⁺.

To investigate the effects of macro cross-linkers of different molecular weights on crosslinking degree and ion exchange capacity, different macrocrosslinkers of molecular weights were used in the block copolymerization reaction. For this purpose, the molecular weights of the macrocrosslinkers were 1250 and 2000. The crosslinked Poly(Styrene-*b*-PCL) block copolymers were produced from PCL-1250, 2000 with styrene as described above. The swelling ratios of Poly(Styrene-PCL -1250, -2000) in water or CHCl_3 were considerable: 1.4, 13.6; 1.3, and 10.6, respectively. The swelling ratios of R-PS-PCL-1250 and R-PS-PCL-2000 in water and CHCl_3 were 1.7, 14.8, 3.25, and 18.23, respectively. The capacity of ion exchange resin depends on the molecular weight of the macrocrosslinkers, the reaction time and the crosslinkage degree. It is shown that the molecular weight of the macrocrosslinker has not been affected by the crosslinkage degree or the ion exchange capacity. The maximum capacities of the ion exchangers are shown in Table 1. When the polymerization time was 10 h the resulting experimental data showed that ion exchange resins have the same ion exchange capacity as ion exchange resin, R DM-1000, based on PEG DM, i.e., the ion-exchange capacity of the ion exchange resins decreased with increasing polymerization time, crosslinkage degree, and molecular weight of the crosslinker⁷. Because of the polar sulfone groups of resins, the swelling ratio of cation exchanger, in water or CHCl_3 is higher than the swelling ratio of the untreated crosslinked block copolymer. In the last column of Table 1, experimental capacities are higher than calculated capacities. In this case, it was found that the counter ions were changed in the ion exchanger surface. The sulfonation of the inner core of the resin does not affect the ion exchange reaction. It means that the capacities of ion exchangers were filled at 3×10^{-2} M La^{+3} concentration of equilibrium solutions. The mole fraction of La^{+3} ions in the resin phase loaded as 0.5; in comparing the selectivity constant, K of $\text{La}^{+3} + \text{R-PCL-DM-1250}$, with that of $\text{La}^{+3} + \text{R-PCL-DM-2000}$ in equilibrium showed the selectivity constants to be dissimilar. The selectivity coefficient of R-PS-PCL-1250 is tenfold larger than R-PS-PCL-2000 in high mole fraction. As a comparison, the capacity of the R-PS-PCL-1250 resin was greater than that of the R-PS-PCL-2000. In the ion exchange reaction, there is a significant difference of 0.2 meq/g. When the crosslinkage in the ion exchange increases, the ion-exchange capacity and resin porosity decrease. Thus, the capacity of R-PS-PCL

-2000 is lower than that of R-PCL DM-1250. The selectivity coefficients of the ion exchanger resins are shown in Table 2. 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 2. The obtained cation- exchange resins selectivity constants versus La^{3+} ions are changed as 0.25 for R-PS-PCL-1250 and as 1.1×10^{-2} for R-PS-PCL-2000 in the loaded $x\text{La}^{3+}=0.9$ approximately. Figs. 4 and 5 show selectivity values of La^{3+} -hydrogen exchange on exchange resins as a function of the mole fraction in the resin phase. In the Dowex-50W (HR, C=4.85 meq/g), $\text{Co}(\text{NH}_3)_6^{3+} + \text{LaR}_3$, and in the Dowex-50W -4(HR, C=4.12 meq/g), $\text{Cr}(\text{en})_3^{2+} + \text{LaR}_3$ ion exchange reactions, K selectivity constants were found to be 18.2 and 14.1, respectively¹¹. The selectivity of the Dowex-50 ion exchange resin to the La^{3+} ions is 6.16^{12,13}.

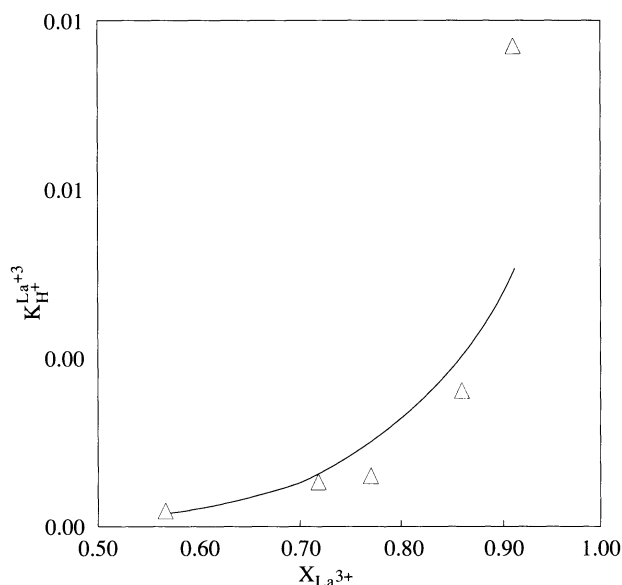


Figure 5. Selectivity values of La^{+3} hydrogen exchange on exchange resins as a function of the mole fraction in the resin phase.

(Δ) (HR, C=1.10 meq/g) $\text{R-PS-PCL-2000} + \text{La}^{+3} \rightleftharpoons (\text{R-PS-PCL-2000})_3 \text{La} + 3\text{H}^+$.

The selectivity of R-PS-PCL-1250 and R-PS-PCL-2000 to the lanthanum ions increases as the ion-exchange capacities increase as shown in Table 1. The differences in selectivity and capacity are due to the different crosslinkage degree and the different molecular weight of the crosslinker. Figures 4 and 5 show that the selectivity increases as the ion load is increased. The relationships of $K_{\text{H}^+}^{\text{La}^{+3}}$ to $X_{\text{La}^{3+}}$ are shown as a curve for all ion exchange equilibria according to the equation $K_{\text{H}^+}^{\text{La}^{+3}}$. Since ion exchange occurs in the inner region of the resins, the selectivity increases as the mole fraction of the lanthanum ions in the resin surface increases. Because of the difference of ion-exchange capacities, the selectivities of resins are different.

Experimental results showed that the selectivity of 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. In addition to this, in higher concentrations, some of the electrolyte become attached to the resin pore. This caused the formation of an ion pair of La^{3+} in the resin with a cross ion¹⁰.

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