Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Mathur, A. M. and Scranton, A. B.(1999) 'Synthesis and Ion-Binding Properties of Polymeric Pseudocrown Ethers. III. Ion-Binding Studies', Separation Science and Technology, 34: 5, 855 — 861
To link to this Article: DOI: 10.1080/01496399908951150
URL: http://dx.doi.org/10.1080/01496399908951150

SEPARATION SCIENCE AND TECHNOLOGY, **34**(5), pp. 855–861, 1999

Synthesis and Ion-Binding Properties of Polymeric Pseudocrown Ethers. III. Ion-Binding Studies

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ABSTRACT

An ion-induced templatization strategy was used to prepare crosslinked polymeric pseudocrown ethers (PCEs) in situ during a one-step free-radical polymerization. These studies bring to a conclusion the fundamental studies on the templatization process reported in the first two papers of this series. For the PCEs, with nickel as the templating ion and hydroxyethyl methacrylate as the monovinyl comonomer, the ion-binding studies revealed a significant enhancement in the ion-binding capacity associated with the inclusion of the template ion during synthesis. For example, a PCE synthesized with a monomer-to-solvent ratio of 20/80 exhibited an ion-binding capacity that was 7.5 times higher than a control polymer produced under identical conditions except for the absence of the template cations. A PCE synthesized with a monomer-to-solvent ratio of 20/80 exhibited a capacity of 0.3 mg/g polymer for Ni^{2+} cations. Finally, it was observed that the column could be fully regenerated by elution with a small volume of a 1 M HCl solution at 60°C, resulting in the recovery of the bound ions as a concentrated solution.

INTRODUCTION

In two previous papers of this series (1, 2) we reported the fundamental basis of a method for preparing polymeric pseudocrown ethers with potential applications in separations, ion chromatography, and waste management. This scheme for preparing polymer-bound macrocyclic ligands in situ during a

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one-step polymerization is based upon the tendency of oligomeric ethylene glycol diacrylates to assume circular conformations in the presence of template cations, thereby bringing the unsaturated diacrylate end-groups into proximity. If a free-radical polymerization is initiated with a comonomer such as hydroxyethyl methacrylate (HEMA), both double bonds of the templated oligomers may be incorporated into the same kinetic chain, resulting in the formation of pendant loops. The probability of cyclization is increased if the polymerization is carried out in a nonpolar solvent in which the cation itself is insoluble, thus ensuring maximum templatization (and hence primary loop formation). While this previous research has provided evidence of the ion–ligand templatization process, the synthesis and effect of synthesis variables on ion-binding properties of the resulting polymers have not been addressed.

This note brings our previous studies to their logical conclusion by demonstrating that this templatization effect can indeed be used to produce PCEs in situ during a one-step free-radical polymerization. First, the effect of synthesis variables on the resulting PCEs is investigated. Next, the ion-binding properties of PCEs produced in the presence of the template nickel cation are compared to the binding capacity of the control polymers synthesized in the absence of a template cation. Finally, a strategy for complete regeneration of the PCE is presented.

EXPERIMENTAL MATERIALS AND METHODS

Synthesis of Polymeric Pseudocrown Ethers

The PCEs were synthesized based upon an ion-induced templatization scheme previously proposed (1). All chemicals and materials were high purity and were used as received, and all organic solvents and water used were HPLC grade. For the preparation of the PCEs, a saturated solution of nickel in poly(ethylene glycol)-diacrylate (PEGDA200) was employed, while for the poly(HEMA) (control) polymers, pure PEGDA200 (containing no salts) was used. Saturated solutions of the nickel (template cation) in the PEGDA200 were prepared by slowly adding nickelous nitrate to the oligomer under constant stirring at room temperature. The saturated PEGDA200-nickel mixture contained 0.7 g of $Ni(NO_3)_2 \cdot 6H_2O$ in 5 g of PEGDA 200 (0.15 moles of salt per mole of PEGDA200). The free-radical copolymerization of HEMA and PEGDA200 was initiated by UV-light at room temperature (thermal initiation was not employed due to the low boiling point of the synthesis solvent, chloroform). The ratio of monomers to solvent was varied between 20/80 to 50/50 (by weight), and the PEGDA200 oligomer was incorporated at 5 wt% of the total monomers.

A typical synthesis of a crosslinked PCE is described hereafter. In a 4-oz square glass bottle, 0.21 g of PEGDA200 (or the PEGDA200-salt mixture)

was added to 3.84 g of HEMA. Next, 0.042 g of the free-radical photoinitiator (1.0 wt% of all monomers), Irgacure 651 (Ciba-Giegy), was added to the monomer mixture. For a relatively dilute synthesis (20/80 monomer/solvent ratio), 16.0 g of chloroform was added to the reaction mixture. The solution was mixed for approximately 5 minutes in the sealed bottle using a vortex mixer. The photopolymerization was performed by illuminating the sample for 30 minutes with unfiltered light from a 200-W Black-Ray UV lamp (Model B 100AP UVP, Upland, CA).

For the removal of extractables, the crosslinked polymer gel was swollen in 40 mL of methanol, which was replaced daily for 3 days. Next, for removal of methanol from within the gel, the polymer was swollen in a large excess of deionized water, which was replaced daily for 4 days. The polymer was then removed from the bottle and dried in an oven at 80°C for 4–5 days. The crosslinked polymer was then ground in a mortar and pestle to produce polymer particles ranging from several hundred microns to a few millimeters. Finally, the fine polymer particles were swollen in a 0.1 M HCl solution for 2 days to remove the templating cation and other aqueous extractables. The resulting PCE particles were then filtered using Whatman #4 filter paper and stored in deionized water until further use.

Ion-Binding Studies

A jacketed glass column with an internal diameter of 10 mm and a height of 25 cm was used for these experiments. The column temperature was maintained by circulating water from a controlled-temperature water bath through the column's jacket. The water-swollen polymer particles were loaded into the column and were gently compacted by lightly tamping with a rod to ensure uniformity of packing. To condition the column before the ion-binding studies, 50 mL of 1 M HCl was pumped through the column at a rate of 2 mL/min, followed by 50 mL of deionized water (at the same rate). A Perkin-Elmer AA-20 atomic absorption spectrometer was used to determine nickel ion concentrations. The 352.7 nm absorbance line prescribed for nickel was selected to provide maximum sensitivity. A linear calibration curve for the atomic absorption intensity as a function of the nickel ion concentration in the 0–100 ppm range was constructed using standards solutions of nickelous nitrate in HPLC grade water.

The equilibrium ion-uptake studies were performed by pumping 100 mL of a 100 ppm Ni^{2+} solution through the column at a rate of 2 mL/min. The solution exiting the column was collected in successive 5 mL samples, and the nickel ion concentration was determined for each sample and a breakthrough curve was generated for each run. For the PCEs, the nickel ion concentration in the first several 5-mL aliquots was essentially zero, with the ion concentration in the effluent reaching 100 ppm after the column was saturated with

nickel ions. Based upon the difference between the original ion concentration in the input stream and the average concentration in the effluent stream, the maximum amount of Ni^{2+} bound by the column was determined by a material balance. The mass of the bound nickel ions was finally normalized by the mass of the polymer in the column to obtain the value for the ion-binding capacity of the polymer (reported in units of mg of Ni^{2+} bound per gram of polymer).

The most effective method for removing the bound nickel ions from the column was determined based upon literature reports for removing bound cations from polymeric crown ethers (3–7). A series of aqueous HCl solutions with concentrations varying from 0.1 to 1 M were pumped through the ion-saturated column at 2 mL/min at temperatures ranging from 25 to 60°C. The concentration of nickel in the collected eluant was determined by AA spectroscopy.

RESULTS AND DISCUSSION

Polymeric Pseudocrown Ethers Synthesis

The primary objective of the synthesis studies was to identify reaction conditions that produce crosslinked PCEs that swell in water while exhibiting good mechanical properties. Homopolymerizations of (templated) PEGDA200 did not produce useful resins since the resulting polymers exhibited a crosslink density and a ligand density that were too high for efficient use of the pseudocrown ether sites. For this reason it was necessary to copolymerize the templated PEGDA200 with a monofunctional monomer such as HEMA, due to its moderately hydrophilic nature.

A series of experiments was performed to determine appropriate values of the monomer feed composition and the monomer-to-solvent ratio during synthesis. The molar ratio of HEMA to PEGDA200 in the monomer feed had a dramatic impact on the ion-binding properties of the resulting PCEs. It was observed that for a given total monomer-to-solvent ratio, at low PEGDA200 concentrations the ion-binding capacity was negligible despite a fairly high degree of swelling (which also contributed to poor mechanical integrity). Additionally, at high PEGDA200 concentrations the hydrogel once again exhibited negligible ion-binding capacity and a very low degree of swelling. While at low PEGDA200 concentrations the low ion-binding capacity may be attributed to insufficient PCE sites, at high concentrations the low ion-binding capacity may be due to a large fraction of the PEGDA200 contributing toward forming crosslinks rather than pendant PCE loops. To determine an optimum PEGDA200 to HEMA ratio, the amount of PEGDA200 in the monomer feed was varied from 1 to 10 wt% of total monomer weight. It was found that the optimum monomer feed contained PEGDA200 at 5 wt%, and if the

PEGDA200 concentration was either increased or decreased from this value, the ion-binding capacity of the resulting PCE resins was decreased.

The monomer-to-solvent ratio during synthesis was a second reaction variable that played an important role in determining the ion-binding properties of the PCEs. The effect of varying the monomer-to-solvent ratio from 20/80 to 50/50 (w/w) on the ion-binding properties of the resulting polymers is discussed in the following section. Monomer-to-solvent ratios below 20/80 resulted in PCE gels that exhibited poor mechanical integrity and could not be investigated for ion-binding capacity.

Ion-Binding Studies

Figure 1 illustrates experimental results for the ion-binding properties of the PCEs as well as the control resins [crosslinked p(HEMA)] gels prepared under identical monomer concentrations and reaction conditions as the PCE resins (but in the absence of the template cation) at three different monomer-

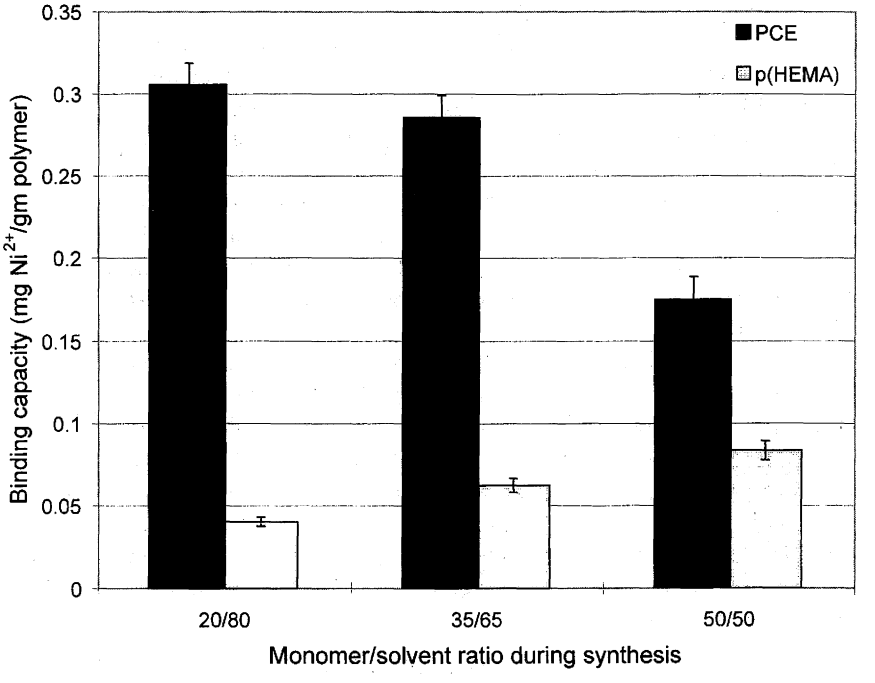

FIG. 1 Experimental ion-binding capacities for the PCEs and control p(HEMA) hydrogels as a function of the monomer-to-solvent ratio during synthesis.

to-solvent ratios. In this figure the average experimental binding capacity for each polymer is indicated by the height of the corresponding bar, while the error bars illustrate the range of experimental values obtained. First, it should be noted that the ion-binding capacities for the PCEs in Fig. 1 are comparable to those reported in the literature for other polymeric pseudocrown ethers. For example, Kahana et al. (3) prepared PCEs in a multistep process involving Freidel–Crafts alkylation of catechol with (choloromethyl)styrene–divinylbenzene (Amberlite XE-305) followed by reaction with polyglycol dihalides. The ion-binding capacities of the resulting polymers range from 0.035 to 0.245 mg/g for Li^+ and from 1.32 to 13.2 mg/g for Cs^+ (3). Second, the figure illustrates that the ion-binding capacity of the PCEs increases as the monomer-to-solvent ratio is decreased.

The most important result shown in Fig. 1 is the enhancement in the ion-binding capacity associated with the inclusion of the template cation during synthesis. For example, the PCE synthesized with a monomer-to-solvent ratio of 20/80 exhibited an ion-binding capacity that was 7.5 times higher than the control gels produced under identical conditions but in the absence of the template ions. The difference is less dramatic for the other two monomer-to-solvent ratios. We believe that this enhancement may be attributed to the ion-induced templatization of the PEGDA200, and the resulting increase in primary cyclization relative to crosslinking. This templatization increases the fraction of the PEGDA200 oligomers that assume a cyclic conformation with a low mean end-to-end distance, thereby bringing the unsaturated acrylate end-groups in proximity. Therefore, templatization enhances the probability that both double bonds of a PEGDA200 unit are incorporated into the same growing chain to yield pseudocrown ether sites. In this manner these ion-binding results suggest that pendant cyclic pseudocrown ethers may indeed be polymerized onto a hydrophilic polymeric support by a one-step free-radical polymerization.

Experiments performed to identify a strategy for regenerating the ion-saturated polymeric pseudocrown ethers suggested the use of a concentrated HCl solution at an elevated temperature for the recovery of the bound nickel ions. When the column was eluted with 1 M HCl at 25°C, 50% of the bound nickel ions were recovered in the first 20 mL of eluant. However, it was found that essentially 100% of the bound nickel ions were recovered at a temperature of 60°C by elution with the same volume of 1 M HCl. In this manner the bound cations may be completely recovered from the PCE with a comparatively small volume of eluant.

CONCLUSIONS

An ion-induced templatization strategy was used to prepare crosslinked PCEs in situ during a one-step free-radical polymerization. A series of studies

was performed to identify optimum reactant concentrations to result in crosslinked PCEs that sufficiently swell in water and demonstrate acceptable mechanical integrity. The ion-binding studies demonstrated an enhancement in the ion-binding capacity associated with the inclusion of the template ion during synthesis. This enhancement was attributed to the ion-induced templatization of the PEGDA200, and the resulting increase in primary cyclization relative to crosslinking during synthesis. In addition, complete regeneration of the saturated PCEs was also achieved. Together, these synthesis, ion-binding, and column regeneration results indicate that this technique could be used to synthesize PCEs with potential applications in separations, ion chromatography, and waste management.

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Received by editor May 9, 1997
First revision received October 24, 1997
Second revision received June 10, 1998