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Polymerization Kinetics of Pseudocrown Ether Network Formation for Facilitated Transport Membranes

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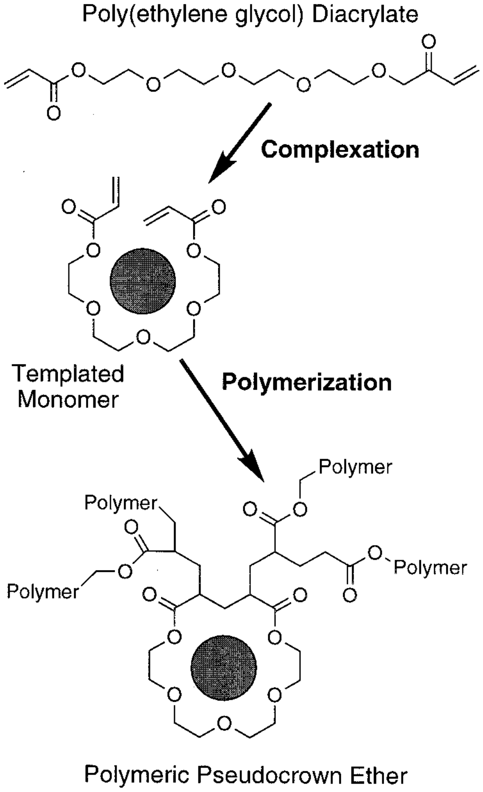
ABSTRACT: Pseudocrown ethers were synthesized from the photopolymerization of metal complexes of poly(ethylene glycol 200) diacrylates (PEG200DA) to yield polymeric networks that can be used in facilitated transport membranes. Metal ions that potentially could be used as molecular templates were screened by first characterizing the polymerization of hydroxyethyl methacrylate (HEMA) in the presence of the metal salts. Thermal polymerizations and photopolymerizations were used to elucidate which metals adversely effect the polymerization reaction via radical scavenging, chain transfer, light absorption, and other side reactions. HEMA polymerizations were used to investigate these effects because only linear polymers can form, and there will be no rate effects from cyclization. Photopolymerizations of templated PEG200DA exhibited a decrease in autoacceleration as an indication of pseudocrown ether formation due to the reduction in the degree of cross-linking with cyclization. Four metal salts, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and $Cd(NO_3)_2{\cdot}4H_2O$, were found to make suitable templating ions. Although $Cu(NO_3)_2{\cdot}(2.5)H_2O$ and $CrCl_3{\cdot}6H_2O$ formed appropriate complexes with PEG200DA, these metals act as radical scavengers and did not permit the desired polymerization. The peak rate was decreased up to 69% for the partially dried Co(II)/PEG200DA complex at a metal concentration of 1.27 M. Facilitated transport membranes exhibited a selectivity of 1.3 for potassium over sodium and 27.5 for potassium over neodymium, and a benchmark comparison was made to an analogous polymer inclusion membrane that contained dibenzo-18-crown-6 as the carrier which had similar selectivities.

Introduction

Pseudocrown ethers are a novel class of compounds that are being developed as a low-cost, low-toxicity alternative to classical crown ethers.[1−6] Classical crown ethers have proven to be effective in ion separations, but the small molecules are bioavailable and can cause adverse effects in living organisms. Furthermore, the synthesis of classical crown ethers involves many steps, and therefore these compounds are often quite expensive. Pseudocrown ethers are inexpensive and nontoxic because the starting materials are common and inexpensive and the synthesis requires only a few simple steps, resulting in a polymeric system that is nonbioavailable. Pseudocrown ethers are being investigated to address the need to remove metal ions from aqueous sources for applications varying from environmental remediation to pollution prevention and metal ion recovery. Facilitated transport membranes have been synthesized using the pseudocrown ethers as fixed site carriers for the selective transport of cations.

Pseudocrown ethers are formed via a cyclopolymerization reaction of poly(ethylene glycol) diacrylates (PEGDA's) that results in a network that contains pendant groups with a similar structure to crown ethers due to the ethylene glycol chain of the monomer (see Scheme 1). To synthesize pseudocrown ethers, PEGDA monomers are templated with metal ions via the metal/ether oxygen complexation, thus bringing the two reactive acrylate end groups into close proximity and enhancing the probability that the monomer will cyclopolymerize. The polymeric pseudocrown ethers are formed in situ during free radical photopolymerizations and can be made into bulk adsorption resins or membranes. The resulting polymer is a cross-linked network with pendant pseudocrown ether moieties.[7]

Scheme 1. Pseudocrown Ether Synthesis from Templated PEGDA



The metal:monomer complexation has been previously studied with numerous spectroscopic techniques.[8] The nature of the metal:monomer complexation, the ligands of the solvation shell, and the roles of anions, coordinated water, and waters of hydration were elucidated in this study.[8] Metal cations that showed the most

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promise for use as templates for the pseudocrown ether synthesis were cobalt(II), nickel(II), zinc(II), and cadmium(II). A novel technique of complex formation via the replacement of coordinated water with ether oxygens of the monomer was described. This process leads to complexes of the desired geometry for templating and pseudocrown formation. The production of polymeric pseudocrown ether networks was confirmed for the cobalt(II):PEG200DA system via a study of the kinetics of photopolymerization and an observed reduction in the rate maximum during autoacceleration.[8]

Radical chain polymerizations exhibit a phenomenon known as autoacceleration, which is a dramatic rise in the reaction rate that occurs as the reaction proceeds. Normally, one would expect the rate of polymerization to gradually decrease with time as the concentrations of the monomer and the initiator decrease. The exact opposite behavior is generally observed in highly cross-linked systems, in which the rate of termination becomes diffusion limited before the rate of propagation; thus, the rate increases with conversion. This behavior is most commonly termed autoacceleration and may also be referred to as the gel effect, the Trommsdorf effect, and the Norrish–Smith effect.[9]

Autoacceleration arises from the fact that the propagation step and the termination step are effected in differing degrees by the viscosity and mobility of the reactive species in the polymerizing system. Propagation involves a small molecule (the monomer) and a large molecule (a polymer chain with a radical end), whereas termination involves two large molecules (two polymer chains with radical ends) that must come together. As the conversion increases, the mobility of both of these species decreases, and logically the termination step becomes diffusion limited prior to the propagation step becoming diffusion limited. Because initiation is continual, and the termination of radicals is suppressed, there is a net increase in the concentration of radicals; therefore, the rate of polymerization increases.

This phenomenon of autoacceleration can be used to indicate pseudocrown ether formation. Specifically, the *decrease* in the autoacceleration in systems of PEG200DA with template ions relative to pure PEG200DA is evidence of pseudocrown formation, which is a result of the diacrylate monomer self-cyclizing (Figure 1). When the PEGDA monomer is incorporated into the polymer network via the reaction of one of its double bonds, the other *pendant* double bond may react with another growing chain, and thus form a cross-link, it may remain unreacted, or it may react with itself to form a pseudocrown ether. The more pseudocrown ethers that are formed, the less cross-linked the system will be for a given double-bond conversion. The less cross-linked the system is, the greater the mobility and, therefore, the more rapidly the termination reaction can occur.

Because we are using a decrease in the rate to indicate pseudocrown ether formation, we must also confirm that the presence of the metal ion in these systems does not otherwise alter the polymerization kinetics. The metal ions used in this study were screened to determine that they did not scavenge radicals via redox reactions, they did not increase the mobility of the reacting medium via chain transfer reaction that might decrease the molecular weight of polymer chains formed, nor did they interfere with the initiation step via light absorption. Polymerizations of hydroxyethyl methacrylate (HEMA) solutions containing dissolved metal salts were investigated because cyclization is not possible with monovinyl monomers. With the potential effects of cyclization eliminated, potential side reactions could be detected, and those metal ions responsible could be removed from the list of template ions to be studied.

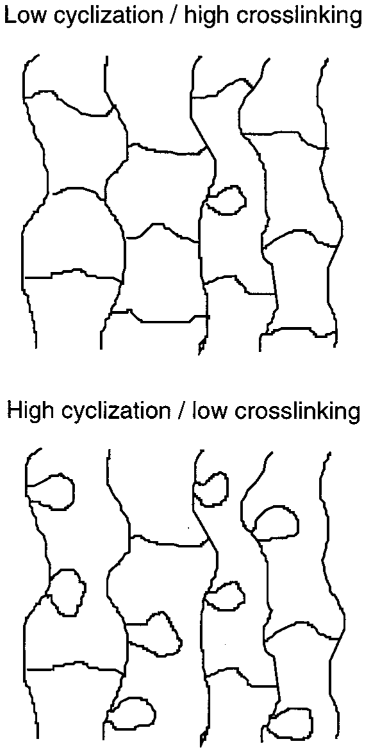

Figure 1. Representation of the network structure for low and high degrees of cyclization (i.e., pseudocrown ether formation).

With the formation of polymer networks containing pseudocrown ether moieties established, membranes containing these networks can be produced that exploit the pseudocrown ethers as fixed site carriers for facilitated transport. To this end, a porous polyethylene membrane support was modified by polymerizing the pseudocrown ethers in situ within the pores and void space of the support. This resulted in a composite membrane in which the polyethylene provided the structural durability and membrane geometry, while the acrylate-based pseudocrown ether network provided the regions of ion transport and the fixed site carriers for selectivity.

A polymer inclusion membrane (PIM) containing dibenzo-18-crown-6 was used as a benchmark comparison of the pseudocrown ether membrane. This PIM was synthesized from the same polyethylene support and the same monomer composition and percent cross-linking agent, but diethylene glycol diacrylate was used instead of PEG200DA to ensure no spontaneous pseudocrown ether was formed. The selectivity was provided by the physically entrapped crown ether which is known to have a selectivity for potassium over sodium.

Experimental Section

Thermal Polymerizations. Monomer samples were prepared by mixing hydroxyethyl methacrylate (HEMA) in which the inhibitor, monomethyl ether of hydroquinone (MEHQ), was removed with a standard packed column, 1 wt % 2,2′-azobis-(isobutyronitrile) (AIBN), and 8 wt % of one of the following metal salts: $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot (2.5)H_2O$, and $CrCl_3 \cdot 6H_2O$. About 10 mg of this solution was micropipetted into an aluminum sample pan for the differential scanning calorimeter (Perkin-Elmer). The monomer sample was loaded into the DSC, and a blank aluminum pan was used as the reference sample. Lids were not used with the sample pans so that the samples could be exposed to the nitrogen atmosphere. The system was purged with nitrogen for 10 min at 25 °C to remove dissolved oxygen and establish a thermal baseline. The sample chamber temperature was then raised to 70 °C and held for 45 min. At the end of the polymerization the samples were reweighed to determine whether any HEMA had volatilized due to the high temperatures. Typically, there was less than a 10% weight loss, and the final weight was used as the initial weight when normalizing the data. It was assumed that all of the evaporation occurred during the 10 min purge and temperature ramp up to 70 °C. Once the reaction began, the evaporation should diminish as the mobility decreases; therefore, the final weight was assumed to be the initial weight immediately prior to polymerization.

Photopolymerizations. Monomer samples were prepared from both HEMA and PEG200DA. Mixtures of HEMA and $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Cd(NO_3)_2 \cdot 4H_2O$ were made using 8 wt % of the metal salt, as in the case of the thermal polymerizations, as well as 1 wt % of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA). Samples of PEG200DA were also made with 1 wt % DMPA, but the metal salt was used at varying concentrations, limited by the maximum solubilities of the complexes formed. Some complexes were used in which water molecules were forced off by vacuum desiccation because these complexes are believed to be more ideal for the templating step of pseudocrown ether formation. The nature of these complexes and solubility limits are presented in a previous work.[8] Sample masses for the photopolymerizations were controlled between 0.8 and 1.2 mg. Because the photopolymerizations were conducted at 30 °C, volatilization was not an issue, so the sample sizes were kept small as this improves the reproducibility of the experiments. The sample pan, and empty reference pan, were purged with nitrogen for 5 min followed by 25 min of irradiation by 3.5 mW/cm^2, 365 nm monochromatic ultraviolet light.

Membrane Synthesis. A porous polyethylene membrane support, provided by the 3M Corporation, was used to produce the composite membranes. This support was produced from high-density polyethylene via the thermally induced phase separation (TIPS) process. The support has a thickness of 71 μm with an average pore size, as measured by the standard bubble point technique,[10] of 0.7 μm and a porosity of between 70 and 80%. The monomer mixture that was added into the pores of the support to form the pseudocrown ether network contained the templated PEG200DA (15 wt %), hydroxyethyl acrylate (HEA) (64 wt %), *N*-vinylpyrrolidinone (NVP) (20 wt %), and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) (1 wt %). This mixture was diluted to a 12.5 wt % solution in chloroform to aid in the application to the membrane support.

As a benchmark comparison, polymer inclusion membranes[11] were synthesized with dibenzo-18-crown-6.[12] The matrix was similar to that used in the pseudocrown ether membranes, and it contained dibenzo-18-crown-6 (2 wt %), diethylene glycol diacrylate (DEGDA) (10 wt %), HEA (67 wt %), NVP (20 wt %), and DMPA (1 wt %). This mixture was also diluted to a 12.5 wt % solution in chloroform. The matrix of the two membranes is identical in composition except that the polymer inclusion membrane contains entrapped crown ethers and has cross-links formed from DEGDA, which is too short to form pseudocrown ethers via cyclopolymerization. The pseudocrown ether membrane has covalently bound crownlike carriers and cross-links that are both formed from the PEG200DA. On the basis of the theoretical number of cyclization reactions, the cross-linking density and the concentration of the carrier species of the two networks are equivalent.

The membranes were polymerized under a nitrogen atmosphere for 30 min using an ultraviolet lamp (Blak Ray) with a light intensity of 10 mW/cm^2. Membrane weights were measured before and after the addition of the polymer, and the weight gain was maintained between 0.08 and 0.10 g added to an area of 12.5 cm^2. The membrane was then soaked twice in methanol for 15 min and then in deionized water overnight. The finished membranes were placed in a U-tube-type membrane tester. Each half of this membrane tester was custom-made by glass blowing an O-ring connection to a large screw-cap test tube. The surface area of the membrane chamber was 12.5 cm^2. The volume of the feed and receiving chambers was about 100 mL. The feed side of the membrane contained 100 mL of an aqueous salt solution containing 100 ppm of Na, K, Ni(II), Zn(II), and Nd(III), all of which had nitrate as the counterion(s). The receiving side contained 100 mL of 0.0015 M HCl and was used to balance the ionic charge on each side of the membrane. Each side was constantly mixed during the diffusion experiments, and 1 mL samples were taken approximately every 12−24 h and analyzed using inductively coupled plasma (ICP) for the metal ion concentrations.

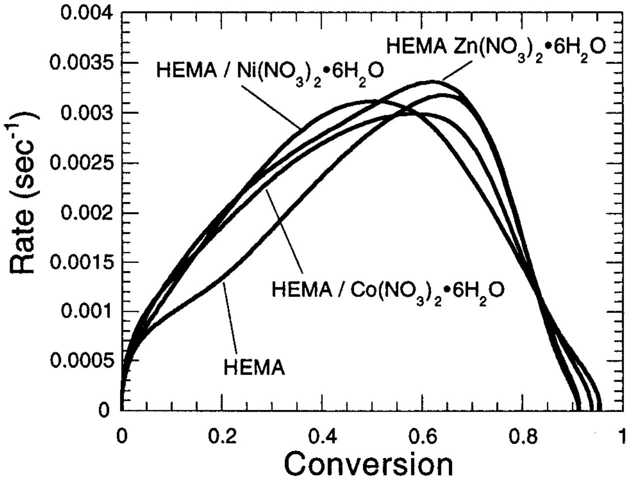

Figure 2. Thermal polymerization rates of HEMA with dissolved metal salts at 70 °C (isothermal).

Results and Discussion

Thermal Polymerizations of HEMA. The following metal salts were dissolved into HEMA at 8 wt %: $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 2.5H_2O$, and $CrCl_3 \cdot 6H_2O$. Thermal polymerizations were performed at 70 °C to determine what the effects of the metals were on the free radical polymerization. Potential reactions include radical scavenging, which would suppress the rate, chain transfer, which might decrease the rate, and other side reactions with either the propagating radical or the reactive double bond. Neglecting any anomalous behavior such as chain transfer and monomeric dimerization, HEMA can only form linear polymer chains. HEMA also has a highly characterized rate profile including autoacceleration.[13] For these reasons it was chosen for this study to investigate undesirable side reactions by the metal salts. A test set of metal salts is needed for the study of templated PEG200DA that does not alter the kinetics by any means other than the cyclization of PEG200DA. This limitation on metal ions to be used is so when a decrease in rate is observed for PEG200DA polymerizations, it can be conclusively assigned to increased cyclization.

The rate of polymerization as a function of conversion for HEMA, HEMA containing $Co(NO_3)_2 \cdot 6H_2O$, HEMA containing $Ni(NO_3)_2 \cdot 6H_2O$, and HEMA containing $Zn(NO_3)_2 \cdot 6H_2O$ is plotted in Figure 2. The rate was divided by the initial monomer concentration. This normaliza-

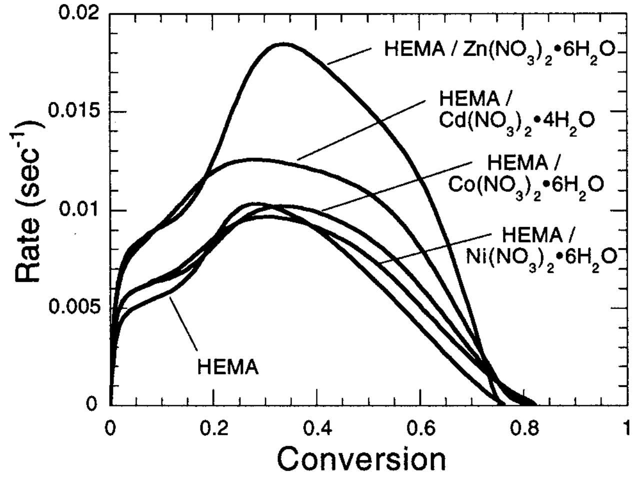

Figure 3. Photopolymerization rate vs conversion for HEMA and HEMA containing various metal salts, all present at 8 wt % (isothermal at 30 °C).

tion makes it possible to compare the kinetics of systems with varying monomer compositions. Neither the general rate profile nor the magnitude or location of the rate maximum is significantly affected with the addition of these metals. Interestingly, the addition of $Cd(NO_3)_2 \cdot 4H_2O$ increased the rate significantly (not shown on plot). Both $Cu(NO_3)_2 \cdot 2.5H_2O$ and $CrCl_3 \cdot 6H_2O$ were found to be severe radical scavengers. The rate profiles would be on the lower baseline of Figure 2 if they were included as they are several orders of magnitude slower. The gel point was not reached in the Cu(II) system while the Cr(III) system produced a polymer with large amounts of unreacted monomer. The Cr(III) ion is not as efficient at quenching the radicals because chromium is the slowest transition metal to exchange its ligands. Given a slower rate of polymerization, it could suppress the rate as effectively as copper. The mechanism of radical quenching involves the reduction of the Cu(II) or Cr(III) to Cu(I) or Cr(II), respectively. These phenomena are macroscopically evident as these reductions involve a color shift.

Given the above results, both $Cu(NO_3)_2 \cdot 2.5H_2O$ and $CrCl_3 \cdot 6H_2O$ were eliminated as potential templating ions for the formation of pseudocrown ethers while $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Cd(NO_3)_2 \cdot 4H_2O$ were all still potential templating ions. For each of these ions, the polymerization reached roughly the same final conversion, and none of these salts decreased the rate maximum significantly. Polymerizations of $Cd(NO_3)_2 \cdot 4H_2O$ and PEG200DA must be analyzed with caution because the maximum rate could be affected by two effects. When the Cd(II) salt was in the presence of HEMA, which can only form linear polymer chains and cyclization is not possible, the rate increased. If the Cd(II) salt templates PEG200DA and increases the amount of cyclization, this should decrease the rate. The competing effects could result in the underestimation of the degree of cyclization.

Photopolymerizations of HEMA. Photopolymerizations of HEMA containing metal salts were performed at 30 °C to determine whether there were any photoinduced adverse effects on the polymerization rate such as photosensitization or light absorption and photoinitiation rate decrease. In the photopolymerization of HEMA with Co(II), Ni(II), Zn(II), and Cd(II) salts, the rate profiles, shown in Figure 3, were either unaffected or the rate was increased. $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ altered the rate profile of HEMA very little, while $Cd(NO_3)_2 \cdot 4H_2O$ increased the rate similar to the thermal polymerization of HEMA, and $Zn(NO_3)_2 \cdot 6H_2O$ significantly increased the rate. In all cases the metal salt did not decrease the rate so they were all investigated in the study of PEG200DA complexes. $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ made the most ideal salts to study due to the only minor effects on the polymerization rate of HEMA. The decreases in rate associated with the Cd(II) and Zn(II) complexes of PEG200DA will potentially result in the underestimation of the rate decreases in PEG200DA systems as there may be competing effects as discussed in the results of thermal polymerizations.

Photopolymerizations of PEG200DA and Metal Complexes. All of the photopolymerizations of metal complexes of PEG200DA resulted in the predicted decrease in polymerization rate due to the increased intramolecular cyclization (i.e., pseudocrown ether formation). The general observations from the study of templated PEG200DA include a decrease in rate that was proportional to both the amount of templating ion incorporated as a complex to the monomer and the relative strength of the complex governed by the electron sharing and number of attachment points to the monomer.

Previous work[8] has demonstrated the unique nature of the Ni(II) and Co(II) complexes. These two metals make excellent template ions to study because they form the desired complexes, they exhibit varying degrees of monomer attachment upon the removal of coordinated water, and they do not adversely affect the polymerization rate as seen in the HEMA studies where potential pseudocrown ether formation is not possible from this linear chain forming monomer. The standard complexes formed with the full six waters of hydration template 12.5% and 26.6% of the monomer for Ni(II) and Co(II), respectively. This percentage corresponds to 0.43 M Ni(II) and 0.89 M Co(II). Upon the removal of four of the coordinated water molecules per metal ion the templating increases to 22.5% and 41.5% (0.62 and 1.27 M) for Ni(II) and Co(II), respectively, again. Both metal complexes increase in concentration with partial drying; however, the average number of monomer attachment points varies between the two. For the case of Ni(II), four waters are removed from the internal solvation shell and are replaced by two nitrate anions and two additional ether oxygens from the monomer on average. For the case of Co(II), four waters are removed from the metal ion and are replaced nearly exclusively by ether oxygens from the monomer. This substitution results in the best conformation of the monomer, four attachment points in the plane and one water on each of the two axis[8] of the trigonal bipyramid. So, in theory, both metal complexes should result in increased pseudocrown ether formation, but the higher concentration, dried complexes should result in more pseudocrowns, and the drying of the Co(II) complex should have the most dramatic increase in pseudocrown ether formation given the complex geometry and strength. Figure 4 displays the possible ligand structures for Ni(II) and Co(II) complexes.

The first example, shown in Figure 5, demonstrates the effect of the concentration of the Co(II) complex. These are standard, nondried, complexes at concentrations of 0.43 and 0.89 M. The decrease in the rate maximum is shown to be a function of the concentration as well as an indicator of enhanced pseudocrown ether

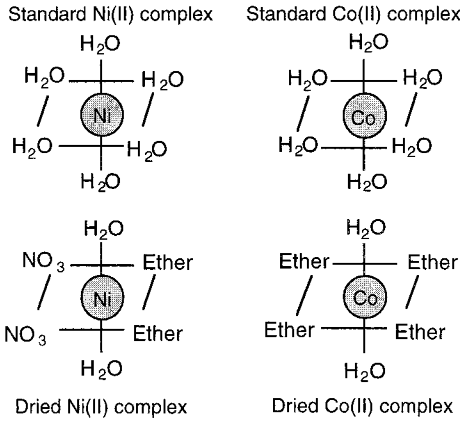

Figure 4. Ligands of the standard and dried Ni(II)/PEG200DA and Co(II)/PEG200DA complexes.

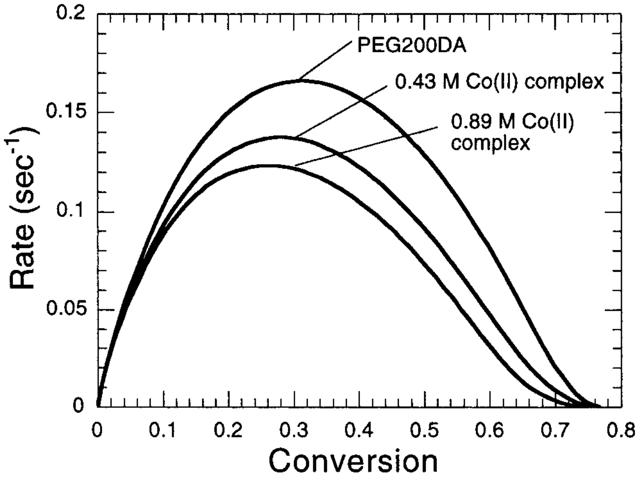

Figure 5. Photopolymerization rate of PEG200DA and PEG200DA templated with the standard Co(II) complexes (isothermal at 30 °C).

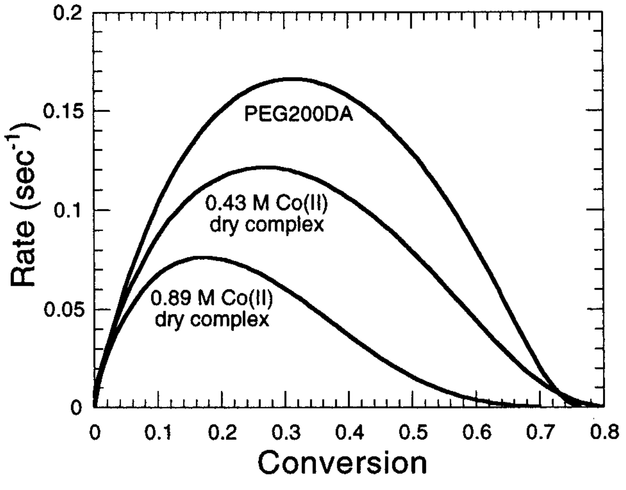

Figure 6. Photopolymerization rate of PEG200DA and PEG200DA templated with the dried Co(II) complexes (isothermal at 30 °C).

formation. Figure 6 shows the same behavior for the corresponding dried complexes of PEG200DA and Co(II), but the effects are much more greatly exaggerated. This effect is due to the fact that the dried complex forms a much more ideal geometry with the two reactive acrylate end groups in close proximity. This behavior is even more pronounced in Figure 7, which compares standard and dried complexes of Co(II) at a concentration of 0.89 M. The rate profiles for PEG200DA and HEMA have different shapes because the onset of autoacceleration for HEMA occurs near 15% conversion while for PEG200DA it occurs at very low conversion.

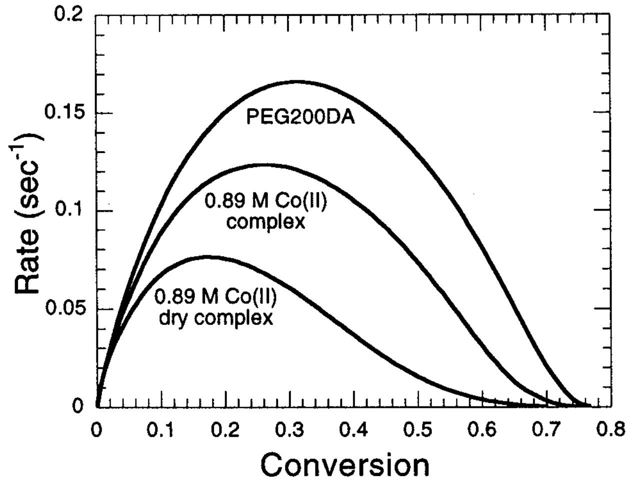

Figure 7. Photopolymerization rate of PEG200DA and templated PEG200DA; comparison of standard and dried Co(II) complexes at a concentration of 0.89 M (isothermal at 30 °C).

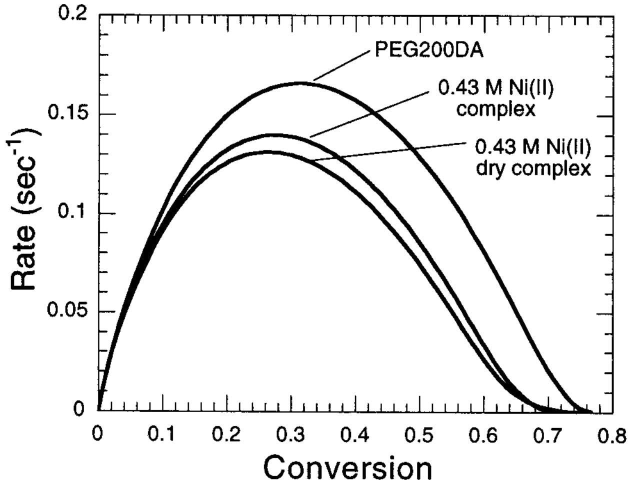

Figure 8. Photopolymerization rate of PEG200DA and templated PEG200DA; comparison of standard and dried Ni(II) complexes (isothermal at 30 °C).

Since it is known that the drying in the Ni(II) complex only results in two additional monomeric attachment points as compared to four for the case of cobalt, it should be seen that the effect that drying the Ni(II) complex has on the rate should be lesser than the corresponding effect in the Co(II) case. This behavior is exactly what is observed. In Figure 8, the rate profiles for the standard and dried Ni(II) complexes are compared, and there is a minimal added decrease from the drying of the complex which is consistent with the fact that drying increases the number of monomeric attachment points less than that of Co(II).

To establish further that the observed polymerization rate decreases are caused by the decrease in cross-linking caused by the formation of primary cycles, a comparison was made to a copolymerization involving PEG200DA and poly(ethylene glycol 200) monoacrylate (PEG200MA). The dried complex of Co(II) at a concentration of 0.89 M in theory will template 27 mol % of the PEG200DA monomers. Those monomers that are templated to form pseudocrown ethers cannot form

Table 1. Summary of the Effects of Various Metal Complexes on the Photopolymerization of PEG200DA

complex type	concentration of metal ion (M)	max rate (s^{-1})	conversion at max rate (%)	time to reach 60% conversion (s)	% reduction in rate max
pure PEG200DA	0.00	0.162	30	6.8	0
Co(II) complex	0.43	0.145	31	8.4	10.5
Co(II) dry complex	0.43	0.117	24	15	28.0
Co(II) dry complex	0.62	0.104	23	20	35.9
Co(II) complex	0.89	0.129	28	9.2	20.2
Co(II) dry complex	0.89	0.079	21	20	51.1
Co(II) dry complex	1.27	0.050	14		69.0
Ni(II) complex	0.43	0.141	26	27	13.0
Ni(II) dry complex	0.43	0.132	27	12	18.3
Ni(II) dry complex	0.62	0.099	19	30	38.9
Cd(II) complex	1.31	0.093	24	12	42.5
Zn(II) complex	0.80	0.082	30	12	49.2

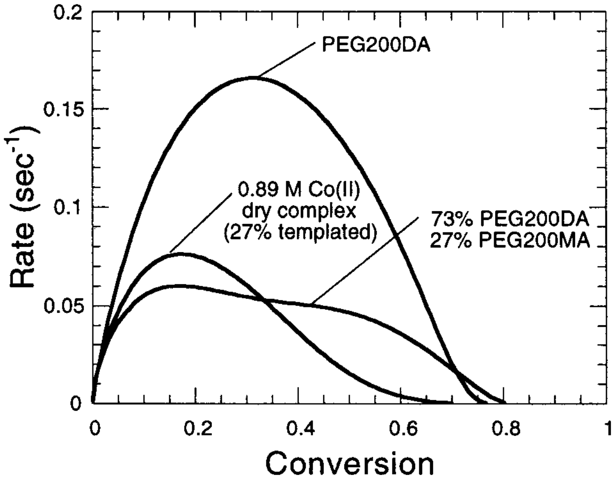

Figure 9. Photopolymerization rate of PEG200DA, PEG200DA templated with the dried Co(II) complex at 0.89 M or 27% theoretic complexation, and a solution of 73 mol % PEG200DA and 27 mol % PEG200MA (isothermal at 30 °C).

cross-links since they form primary cycles. A solution containing 73 mol % PEG200DA and 27 mol % poly(ethylene glycol 200) monoacrylate (PEG200MA) was prepared to imitate the network that theoretically is formed from the cobalt complexed PEG200DA. The decrease observed for the model system of PEG200DA and PEG200MA was very similar to the decrease in rate for the cobalt complex that theoretically had an identical degree of cross-linking. The rate profile for the PEG200DA with 27 mol % PEG200MA is compared to the rate profile for pure PEG200DA and the dried Co(II)/PEG200DA complex in Figure 9. The model system containing the monoacrylate had a slightly lower rate maximum. Additionally, autodeceleration was delayed relative to the PEG200DA. The PEG200DA/PEG200MA rate appears to decrease proportionally with the monomer concentration after 20% conversion. This monoacrylate-containing sample is most likely less cross-linked than the templated PEG200DA; however, the similar rate reduction indicates a similar reduction in cross-linking.

The results of the kinetics studies are summarized in Table 1. Standard complexes of Co(II), Ni(II), Zn(II), and Cd(II) salts as well as dried complexes of Co(II) and Ni(II) salts are presented. The maximum rate, conversion at that rate maximum, time to reach 60% conversion, and the percent reduction in the rate maximum are listed for all except the time to reach 60% conversion for the dried Co(II) complex at 1.27 M since it did not reach that conversion. Aside from the effects due to Co(II) and Ni(II) already discussed, the reduction in rate from Cd(II) and Zn(II) is noteworthy, especially taken in consideration of the rate increases seen for the HEMA polymerizations. All four of these metals should be considered as potential templates for the synthesis of pseudocrown ethers given these results. The understanding of the drying process is clearly important, especially for the Co(II) complex where the number of monomer attachments is greatly increased. As discussed in the previous work, the dried complexes of Cd(II) and Zn(II) were not obtained due to problems with spontaneous polymerization; however, future efforts will investigate these complexes with the assistance of radical inhibitors because the results of the standard complexes show promise.

Facilitated Transport Membranes. As a means of demonstrating the application of these pseudocrown ethers, facilitated transport membranes were synthesized to target the difficult separations of low concentrations of metals in aqueous sources. The pores of a polyethylene membrane support were filled in situ with a polymeric network containing pseudocrown ethers from dried Ni(II)/PEG200DA complexes and compared to an equivalent membrane filled with a network cross-linked with DEGDA (to prevent pseudocrown ether formation) and containing dibenzo-18-crown-6, a well-known chelating agent selective for potassium. In addition, a membrane was produced with nontemplated PEG200DA to demonstrate the significance of templating on pseudocrown ether formation.

The templated pseudocrown ether membrane is a fixed site carrier membrane that should be selective for potassium given the size of the possible rings of 21-pseudocrown-6 and/or 18-pseudocrown-5 from PEG200DA, which is mostly penta- and tetraethylene glycol diacrylate. The dibenzo-18-crown-6 membrane is a polymer inclusion membrane (PIM) in which the carrier species is physically entrapped in the membrane. The mobility of the crown ether in the PIM should be minimal given the 10% cross-linking and should function similar to the covalently bound pseudocrowns. These membranes contained no nonpolar solvent, as is typical in facilitated transport membranes, and were produced from hydrophilic monomers (NVP-*co*-HEA-*co*-PEG200DA). The membranes were contacted directly with the aqueous feed and receiving phases. The hydrogel containing the pseudocrown ethers swelled in the aqueous environment; thus, diffusion is high. The combination of comonomers was selected because it resulted in high hydrophilicity and desirable physical properties (high conversion and mechanical integrity when combined with the polyethylene host).

One potential difference in the two membrane types would be if the crown ether near the surfaces of the PIM

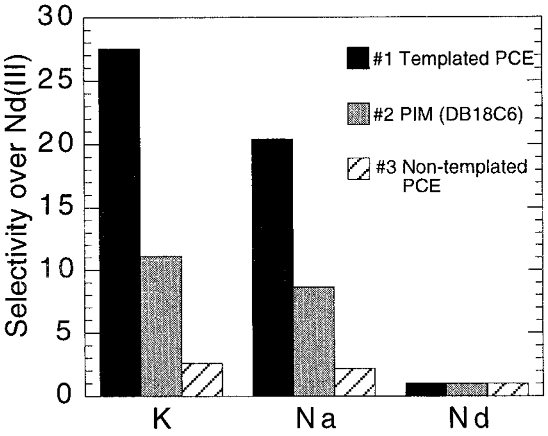

Figure 10. Selectivity of K and Na over Nd(III) for a templated pseudocrown ether membrane (1), a classical crown ether membrane (2), and a nontemplated pseudocrown ether membrane (3).

were to leach out. This behavior would decrease the partitioning coefficient of the metal ions into the membrane as the carrier aids in the metal solubility in the polymer. This leaching is a potential explanation for why the pseudocrown ether membrane outperforms the corresponding membrane containing dibenzo-18-crown-6, as seen in Figure 10. Another potential reason for the higher selectivities observed in the pseudocrown ether membrane is that the degree of cyclization may be higher than expected. This increased cyclization would increase the concentration of the carrier in the pseudocrown ether membrane as well as decrease the cross-linking. The flux of Nd(III) is not be effected by the binding strength of the crowns and pseudocrowns, because neither will bind an appreciable amount of the Nd(III) in the presence of K and Na. The selectivities for K and Na over Nd(III) are presented as preliminary results to demonstrate pseudocrown ether membranes perform similarly to the classical crown PIM's. They are both selective for K over Na and selective for the alkali metals over Nd(III), but the templated pseudocrown ether membrane has higher selectivities for the alkali metals. Future studies will focus on the characterization of pseudocrown ether membranes for the separation of metal ions.

In these membrane transport experiments the feed concentrations were 100 ppm in the metal ions. The flux of neodymium (membranes 1 and 2) was constant within 20%, which is a good indication that the cross-linking densities of the two membranes were similar. The flux of the neodymium should be relatively unaffected by the (pseudo)crown carriers as there will be no appreciable binding so that the neodymium flux is governed by normal diffusion, which will be a strong function of the cross-linking. The nontemplated membrane showed very poor ion separation and the significance of templating PEG200DA to achieve pseudocrown ethers. The selectivities of K over Na were 1.28 and 1.35 for the classical crown PIM and templated pseudocrown ether membrane, respectively. These numbers are in good agreement with the results of Thunhorst et al. in which facilitated transport membranes with covalently bound crown ethers were studied.[14] The membranes examined in this paper and in Thunhorst et al. [14] did not contain any nonpolar solvent to limit Fickian diffusion.

Conclusions

Polymeric pseudocrown ethers were synthesized from the photopolymerization of templated PEG200DA to yield networks that can be used in facilitated transport membranes. Template ions were selected by first characterizing the polymerization of HEMA in the presence of the metal salts. Thermal polymerizations and photopolymerizations were used to elucidate which metals adversely effected the reaction without the effects of cyclization confounding the analysis. Photopolymerizations of templated PEG200DA were studied for a decrease in autoacceleration as indication of pseudocrown ether formation, and facilitated transport membranes demonstrated the utility of these polymer networks in metal ion separations.

Three metal salts, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, and $Zn(NO_3)_2{\cdot}6H_2O$, did not alter the polymerization kinetics significantly during thermal polymerizations of HEMA. $Cd(NO_3)_2{\cdot}4H_2O$ increased the rate while $Cu(NO_3)_2{\cdot}2.5H_2O$ and $CrCl_3{\cdot}6H_2O$ were severe radical scavengers that suppressed the rate. The Cu(II) and Cr(III) salts were found unsuitable for this synthesis, while Co(II), Ni(II), Zn(II), and Cd(II) salts were potentially suitable.

Thermal polymerizations of HEMA with metal salts confirmed that $Co(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ did not have any photoinduced reactions or alter the polymerization kinetics with the use of the photoinitiator DMPA; however, $Zn(NO_3)_2{\cdot}6H_2O$ and $Cd(NO_3)_2{\cdot}4H_2O$ increased the polymerization rate. The Cd(II) salt increased the rate in a similar manner as the thermal polymerization, but the Zn(II) salt increased the photopolymerization rate while the thermal polymerization was not effected by its presence. All four salts were chosen for use in the PEG200DA study since none of them decreased the rate; however, the Zn(II) and Cd(II) results must be analyzed with the understanding that the rate enhancement observed in HEMA polymerizations will confound the analysis.

Photopolymerizations of complexes of PEG200DA and $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and $Cd(NO_3)_2{\cdot}4H_2O$ were found to produce pseudocrown ethers with an observed decrease in the polymerization rate maximum during autoacceleration. Increasing the concentration of the templating complex increased the rate reduction. The use of partially dried complexes, which increases the complex strength, resulted in a decrease in the rate maximum for Co(II) and Ni(II) complexes. This decrease was much larger for the dried Co(II) complex than the dried Ni(II), which is consistent with the relative strength of the complexes formed.

Facilitated transport membranes were synthesized by forming the polymeric pseudocrown ethers in situ in the pores of a porous membrane support. These membranes exhibited a selectivity of 1.3 for potassium over sodium and 27.5 for potassium over neodymium. A benchmark comparison was made to an analogous polymer inclusion membrane that contained dibenzo-18-crown-6 as the carrier and a similar selectivity of potassium over sodium was observed, but there was a decreased selectivity over neodymium for the benchmark membrane relative to the pseudocrown ether membrane.

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