# Characterization and Polymerization of Metal Complexes of Poly(ethylene glycol) Diacrylates and the Synthesis of Polymeric Pseudocrown Ethers

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Polymeric pseudocrown ether networks were formed in situ by the photopolymerization of poly(ethylene glycol) diacrylate (PEGDA)/transition metal complexes. The metal–monomer complex led to a near circular conformation of the monomer in which the two reactive end groups are brought into close proximity; thus, the probability of intramolecular cyclization (i.e., pseudocrown ether formation) is increased. Complexes of cobalt(II), nickel(II), zinc(II), cadmium(II), chromium(III), copper(II), neodymium(III), and lithium were characterized using FTIR and UV–vis spectroscopy. Metal–monomer interactions were characterized and the importance of coordinated water and anions was elucidated. A novel technique of replacing coordinated waters by monomeric ether oxygens was discovered. Pseudocrown ether network formation was confirmed via a study of the polymerization kinetics of cobalt(II): PEGDA systems in which a decrease in autoacceleration was observed with increasing pseudocrown ether formation.

## Introduction

A novel class of compounds known as pseudocrown ethers is being developed as a low cost, low toxicity alternative to classical crown ethers. Classical crown ethers have proven to be effective in ion separations, but these molecules may be 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 because the starting materials are common and inexpensive, and the synthesis is relatively simple, requiring only a few steps. Pseudocrown ethers are nontoxic because these systems are polymeric and therefore nonbioavailable. The binding characteristics of classical and pseudocrown ethers to metal ions are similar because the basic structure of the crown is nearly the same. Classical crown ethers have been incorporated into polymeric hosts to reduce the risk of releasing them to the environment, but these systems are still very expensive and often difficult to synthesize.[1–3]

Pseudocrown ethers are formed via a cyclopolymerization reaction of poly(ethylene glycol) diacrylates (PEGDA) 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. 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, enhancing the probability that the monomer will cyclopolymerize. The resulting polymer is a cross-linked network with pendant pseudocrown ether moieties.[4] This synthesis is depicted in Scheme 1.

Mathur et al. found experimental and molecular simulation results supporting the template ion theory[4,5] of pseudocrown ether synthesis. The $^1H$ NMR spectra of the complexes of chromium(III) chloride and tin(II) chloride to poly(ethylene glycol 300) (PEG300) both had downfield shifts for the peak position for the end-group hydroxyl protons. This shift was attributed to the cations withdrawing electron density from the ether oxygens of the ethylene glycol chain, resulting in an inductive deshielding of the local (hydroxyl) protons. Similar results were found by other researchers with respect to ionic association to poly(ethylene oxide) chains.[6,7] Molecular dynamics simulations confirmed the reduction in end-to-end distances for oligomers of ethylene glycol in the presence of cations,[4] and this phenomenon was confirmed experimentally by fluores-

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† The University of Colorado at Boulder.
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(1) Smid, J. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 364.
(2) Blasius, E.; Janzen, K. P.; Klien, W.; Klotz, H. V.; Nguyen, B.; Nguyentien, T.; Pfieffer, P.; Scholten, G.; Simon, H.; Stockemer, H.; Toussaint, A. *J. Chromatogr.* **1980**, 147.
(3) Blasius, E.; Janzen, K. P. *Pure Appl. Chem.* **1982**, *54*, 2115.
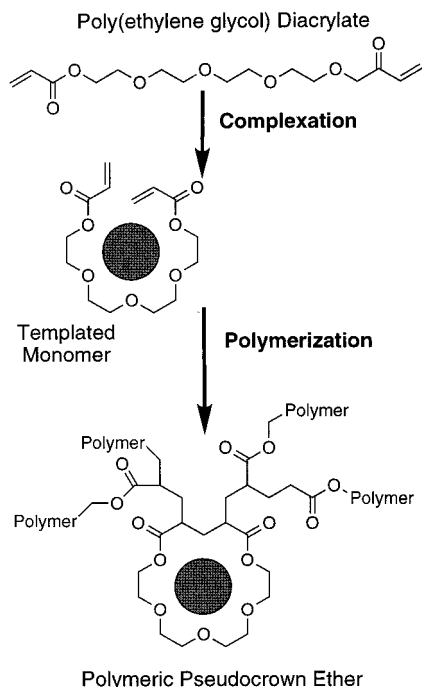
(4) Mathur, A. M.; Scranton, A. B. *Sep. Sci. Technol.* **1995**, *30*, 1071.
(5) Mathur, A. M.; Scranton, A. B. *Sep. Sci. Technol.* **1997**, *32*, 285.
(6) Ono, K.; Honda, H. *Macromolecules* **1992**, *25*, 6368.
(7) Yanagida, S.; Takahashi, K.; Okahara, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1294.

**Scheme 1.  Synthesis of Polymeric Pseudocrown Ethers Using PEGDAs and Templating Ions**



cence spectroscopy of pyrene-end-labled tetra- and pentaethylene glycol.[5] Several other researchers have produced polymers with cyclic structures by cyclopolymerization[8,9] of divinyl monomers to form pseudocrown ethers. Typically, the divinyl monomer also forms random cross-links with the fraction of cyclization being highly dependent on reaction conditions. Warshawsky et al. also describe a technique to produce similar compounds.[10]

In this contribution the complexes of various metal salts to poly(ethylene glycol 200) diacrylate (PEG200DA) have been characterized because the understanding of these complexes is critical for the synthesis of polymeric pseudocrown ethers via Scheme 1. The PEG200DA monomer is a mixture of diacrylated oligomers of ethylene glycol with an average molecular weight of 200 for the ethylene glycol chain. The average number of repeat units is 4.5 and the mixture is mostly tetra- and pentaethylene glycol diacrylate. This mixture can be separated into solutions enriched in each oligomer, but one of the goals of this research was to produce an inexpensive alternative to classical crown ethers; therefore, the PEG200DA solution was used as it is commercially available without any further purification or separation of the different oligomers.

This paper also investigates the kinetics of network formation and the effects that templating has on the degree of cross-linking. The extent of autoacceleration in highly cross-linked systems is a function of the cross-linking density, because autoacceleration arises from the relative diffusion limitations of propagating and terminating radicals.[11–14] For the PEG200DA system

any cyclopolymerization that occurs (i.e., pseudocrown ether formation) will decrease the cross-linking density and, therefore, decrease the magnitude of the rise in polymerization rate due to autoacceleration. Provided the metal salt used as a templating ion does not adversely affect the polymerization kinetics via radical scavenging or chain transfer, a reduction in the extent of autoacceleration can be used as evidence for pseudocrown ether formation.

The goals of this paper are to understand the nature of metal salt/PEG200DA complexes, to use those complexes to synthesize polymeric pseudocrown ethers, and to prove experimentally the formation of these crown structures in the polymer network. Ancillary studies have characterized the polymerization kinetics and investigated the use of pseudocrown ethers in facilitated transport membranes for metal ion separations.[15,16]

## Experimental Section

**Solubility.** To determine the degree to which cations complex with poly(ethylene glycol) diacrylate monomers, solubility experiments were conducted. Metal salts (all salts from Aldrich, Milwaukee, WI) were added, in small quantities, to PEG200DA (Polysciences, Warrington, PA) until further dissolution was not possible. Subsequently, the mixtures were stirred in the presence of excess salt for 3 days to ensure that the solubility limit had been reached. The total amount of salt that resulted in the saturation of the monomers was used to calculate the solubilities, which are reported as the mole fraction of dissolved salt to monomer. Thus, assuming that there are no uncomplexed ions in the solution, a solubility of 1.0 indicates that every monomer is complexed to a metal ion, given the assumptions. Solubility values of greater than 1.0 are possible if noncomplexed ions exist or the complex formed has greater than a 1:1 metal/ligand ratio.

The normal solubility limits were measured at room temperature (298 K). To enhance the strength and abundance of the complex, the solutions that reached equilibrium under ambient conditions were placed with excess salt in a vacuum desiccator. The motivation for doing this drying was to remove waters of hydration from the solvation sphere of the metal ion, to be replaced by ether oxygens from the monomer. This will strengthen the complexes already in existence by increasing the number of attachment points to the monomer as well as increasing the overall fraction of complexed monomers. About 5 g of the monomer complex was placed in a glass culture dish with a known amount of excess salt (typically 25–50% more than the amount added to reach equilibrium under ambient conditions). Molecular sieves (Fisher, Pittsburgh, PA) were treated in an oven at 250 °C for 2 days to remove adsorbed water and organics and then used as the desiccant. Once the predried molecular sieves were placed in the desiccator, the monomer complexes and excess salt were sealed inside and the pressure was reduced by 10–15 Torr (from atmospheric pressure). The complexes took from 3 days to a week to reach the new equilibrium and typically a change in the color of the system was observed with a shift in the peak positions of the UV–vis spectrum.

**UV–Vis Spectroscopy.** The UV–vis spectra were obtained for the metal/monomer complexes formed under ambient

(8)  Butler, G. B. *Cyclopolymerization and Coyclocopolymerization*; Marcel Dekker: New York, 1992.

(9)  Yokota, K.; Matsumura, M.; Yamaguchi, K.; Takada, Y. *Makromol. Chem. Rapid. Commun.* **1983**, *4*, 721.

(10)  Warshawsky, A.; Kalir, R.; Deshe, A.; Berkovitz, H.; Patchormik, A. *J. Am. Chem. Soc.* **1979**, *101*, 4249.

(11)  Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, 84.

(12)  Kloosterboer, J. G.; Lijten, G. F. C. M. In *Cross-linked Polymer Chemistry*; Dickie, R., Labana, S., Bauer, R., Eds.; American Chemical Society: Washington, DC, 1988; Vol. 367.

(13)  Allen, P.; Simon, G.; Williams, D.; Williams, E *Macromolecules* **1989**, *22*, 809.

(14)  Kurdikar, D. L.; Peppas, N. A. *Polymer* **1994**, *35*, 1004.

(15)  Elliott, B. J.; Willis, W. B.; Bowman, C. N. *Marcomolecules* **1999**, *32*, 3201.

(16)  Elliott, B. J.; Willis, W. B.; Bowman, C. N. *J. Membr. Sci.* **1999**, in press.

*Complexes of Poly(ethylene glycol) Diacrylates*

*Chem. Mater., Vol. 12, No. 3, 2000* **635**

conditions and for the dried complexes. Because of the high molar absortivities of the complexes, quartz glass sample holders with a path length of 1.0 or 0.1 mm were used (NSG Precision Cells, Inc., Farmingdale, NY). The quartz sample holders were placed in the chamber of a Hewlett-Packard 8452A diode array spectrophotometer (Hewlett-Packard, Palo Alto, CA), and a background spectrum was taken. The metal/monomer complex sample was added to the quartz holder and the spectrum was taken over a range from 190 to 800 nm.

**FTIR Spectroscopy.** The same samples used for the UV–vis spectroscopy study were analyzed using FTIR spectroscopy. A drop of the monomer complex was placed between KBr salt windows (Aldrich) and analyzed in a Nicolet Magna-IR 750 Series II spectrophotometer (Nicolet, Madison, WI). A dry air purge was used to eliminate all moisture from the analyzer.

**Differential Scanning Calorimetry.** Solutions of monomers were prepared for analysis in a differential scanning calorimeter (Perkin-Elmer, Norwalk, CT) using PEG200DA with varying amounts of the given metal salt as the templating ions and 1 wt % of the photoinitiator 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) (Ciba-Geigy, Hathorne, NY). A mono-chromatic light source of wavelength 365 nm and intensity of 3.5 mW/cm$^2$ was used to polymerize the monomers. Sample masses were maintained between 0.8 and 1.2 mg for accuracy and reproducibility of experiments. The sample thickness was not allowed to exceed 0.1 mm to avoid excess light absorption by the metal salts. The transmittance at 365 nm of the metal/monomer/photoinitiator solution was measured for 0.1 mm thick samples using the UV–vis spectrophotometer. The experimentally measured transmittance was used to determine the actual light intensity in the sample that resulted in initiation of the DMPA. A blank aluminum pan was used as a reference sample, and the monomer sample was purged with nitrogen for 5 min to remove dissolved oxygen following which the sample pans were irradiated with monochromatic ultraviolet light at a wavelength of 365 nm for 15 min. This technique is similar to previous work.[17–19]

## Results and Discussion

**Complexation Studies.** The complexation reaction between the monomer and the metal ion is the keystone of this research. This step in the synthesis controls the abundance and size of the pseudocrown ethers formed upon polymerization; however, the variation in crown size is dictated by the lengths of the original monomer. Given the PEG200DA monomer with mostly penta- and tetra- ethylene glycol diacrylate, the two most likely crown sizes possible are [18]-pseudocrown-5 and [21]-pseudocrown-6. The greater the concentration of the metal/monomer complex, which brings the two reactive monomer end groups into close proximity, the greater the number of pseudocrown ethers that will be formed during polymerization via intramolecular cyclization.

Table 1 summarizes the solubility of selected metal salts in PEG200DA. The solubility is defined as the ratio of moles of metal ion to moles of monomer.

Some observations can be made about the solubility of metal salts in PEG200DA. The ion, generally, has to be able to complex with the ether oxygens of the monomer for solubility to be observed. This fact will be confirmed in the FTIR results section. In most cases waters of hydration are required for the monomer to coordinate the ion. Ions with a low charge per surface

**Table 1. Ionic Radius, Charge per Surface Area, and Solubilities$^a$ in PEG200DA for Various Metal Salts**

| type of metal salt | ionic radius, nm | charge/surf. area (e/nm$^2$) | solubility (mole frac. complexed) |
|---|---|---|---|
| Li(CF$_3$SO$_3$) | 0.060 | 22.1 | 1.029 |
| Cu(CF$_3$SO$_3$)$_2$ | 0.060 | 44.2 | 0.911 |
| NaI·2H$_2$O | 0.095 | 8.82 | 0.796 |
| Li(NO$_3$) | 0.060 | 22.1 | 0.500 |
| Cd(NO$_3$)$_2$·4H$_2$O | 0.097 | 16.9 | 0.449 |
| Zn(CF$_3$SO$_3$)$_2$ | 0.074 | 29.1 | 0.415 |
| Co(NO$_3$)$_2$·6H$_2$O | 0.074 | 29.1 | 0.266 |
| Zn(NO$_3$)$_2$·6H$_2$O | 0.074 | 29.1 | 0.248 |
| Cu(NO$_3$)$_2$·(2.5)H$_2$O | 0.060 | 44.2 | 0.226 |
| Nd(NO$_3$)$_3$·6H$_2$O | 0.105 | 21.5 | 0.185 |
| CrCl$_3$·6H$_2$O | 0.069 | 50.2 | 0.159 |
| AlCl$_3$·6H$_2$O | 0.050 | 95.5 | 0.155 |
| Ni(NO$_3$)$_2$·6H$_2$O | 0.072 | 30.7 | 0.125 |
| Mg(CF$_3$SO$_3$)$_2$ | 0.065 | 37.7 | 0.099 |
| NiCl$_2$·6H$_2$O | 0.072 | 30.7 | 0.041 |
| Na(CF$_3$SO$_3$) | 0.095 | 8.82 | 0.026 |
| Na(NO$_3$) | 0.095 | 8.82 | 0.017 |
| MgCl$_2$·6H$_2$O | 0.065 | 37.7 | 0.014 |
| Cr(NO$_3$)$_3$·9H$_2$O | 0.069 | 50.1 | 0.007 |
| CaCl$_2$·H$_2$O | 0.099 | 16.2 | 0.005 |
| CdCl$_2$·2.5H$_2$O | 0.097 | 16.9 | 0.003 |
| K(NO$_3$) | 0.133 | 4.50 | 0.001 |
| Ba(NO$_3$)$_2$ | 0.143 | 7.78 | 0.000 |
| Rb(NO$_3$) | 0.149 | 3.58 | 0.000 |
| CrCl$_2$ | 0.084 | 22.8 | 0.000 |
| CrCl$_3$ | 0.069 | 50.2 | 0.000 |

$^a$ The solubility is defined as the mole ratio of metal ion to monomer.

area typically do not complex; however, a high charge per surface area does not guarantee a complex will form. While alkali metal ions should form complexes readily with the ether oxygen donor ligands (see following section), only Li(NO$_3$), Li(CF$_3$SO$_3$), and NaI·2H$_2$O behave in this manner here. This complex formation is apparently disfavored with the other alkali ion salts which were studied.

On the basis of the hard/soft acid/base (HSAB) principle for complex formation,[20,21] which states that complexes are preferentially formed between hard acids and hard bases or between soft acids and soft bases, the alkali metal ions should form the most stable and abundant complexes with the ether donor ligands and hence should make excellent templating ions for poly(ethylene glycol) diacrylates. Complexes are preferentially formed between hard acids and hard bases or between soft acids and soft bases. Alkali metals are hard acids and the poly(ethylene glycol) diacrylate monomer, with its oxygen donor atoms, will act as a hard donor and hence alkali and alkaline earth metal ions should be the best electron acceptors to form metal/monomer complexes with this ligand. The transition metal ions are, by comparison, softer acceptors and while they can form complexes with poly(ethylene glycol) diacrylates, on HSAB theory grounds an analogous monomer with secondary amine donor atoms instead of ether oxygens should form much stronger complexes to transition metals. Although the transition metal salts were needed to complex the monomers and initially create the pseudocrowns, once the crown structure was covalently fixed in the polymer and the polymer was swollen with water, the crowns were selective toward alkali metals as expected.[16]

(17) Goodner, M. D.; Lee, H. R.; Bowman, C. N. *Ind. Eng. Chem. Res.* **1997**, *36*, 1247.

(18) Kannurpatti, A.; Lu, S.; Bowman, C. N. *Macromolecules* **1996**, *29*, 7310.

(19) Young, J. S.; Kannurpatti, A. R.; Bowman, C. N. *Macromol. Chem. Phys.* **1998**, *199*, 1043.

(20) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(21) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581.

Attempts were made to induce the nonhydrated alkali metal salts to form complexes by wetting the PEG200DA monomer. Experiments were performed in which water was added either directly to the monomer (less than 1%) or via wet nitrogen gas that was bubbled through the monomer. In both cases there was a phase separation upon the addition of the salt. It appeared that any added water was immiscible with the monomer solution and the desired complex formation was not possible.

Thus far, it has been demonstrated that waters of hydration are initially required for complex formation between transition metal salts and PEG200DA and that excess water dissolved into the monomer is detrimental to complex formation. The presence of water has yet another important bearing upon complex formation. As discussed in the Experimental Section, the metal ion/monomer complexes formed under ambient conditions were placed in a vacuum desiccator, in the presence of excess salt, in an attempt to exchange coordinated water molecules with ether oxygen atoms from the monomer. A very interesting observation was made: partial dehydration of the metal ion produced a higher concentration of the desired metal ion/monomer complexes. Infrared and UV−vis spectroscopy confirmed that the new complexes formed during dehydration contained a reduced amount of coordinated water and the appearance of new or stronger peaks were assigned to the metal ion/ether interactions. All of the salts tested for solubility were used in their maximum hydration state, typically hexahydrated. For example, $Ni(NO_3)_2 \cdot 6H_2O$ was found to form a complex with a finite maximum concentration under ambient conditions. When placed in the vacuum desiccator in the presence of excess salt, the concentration of the nickel(II)/monomer complex increased and the number of waters of hydration was reduced from 6 to 2 per ion on average (peak height at 3350 cm$^{-1}$ was reduced by 66% during the drying process). Similar results were found for $Co(NO_3)_2 \cdot 6H_2O$ and $CrCl_3 \cdot 6H_2O$. The spectroscopy results will be discussed in a later section and the increased solubilities that occur as a result of the partial drying technique are summarized in Table 2.

Both $Ni(NO_3)_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$ formed an increased concentration of complexes when the partial drying technique was used. The solution formed by $CrCl_3 \cdot 6H_2O$ under ambient conditions was opaque and the UV−vis spectrum suggested the system was most likely a colloidal solution. When it was dried in the

**Table 2. Metal Solubilities[a] in PEG200DA for Metal Salts under Ambient Conditions and Using a Vacuum Desiccator for Forced Replacement of Waters of Hydration**

| metal salt | normal solubility (ambient conditions) | enhanced solubility (vacuum dissector) |
|---|---|---|
| $Ni(NO_3)_2 \cdot 6H_2O$ | 0.125 | 0.225 |
| $Co(NO_3)_2 \cdot 6H_2O$ | 0.266 | 0.415 |
| $CrCl_3 \cdot 6H_2O$ | colloidal at 0.159 | homogeneous at 0.159 |
| $Zn(NO_3)_2 \cdot 6H_2O$ | 0.248 | problematic |
| $Cd(NO_3)_2 \cdot 4H_2O$ | 0.449 | problematic |

[a] The solubility is defined as the mole ratio of metal ion to monomer.

desiccator, the solution became transparent and the UV−vis spectrum indicated that there was now present a very clean and distinct type of complex, containing no colloidal chromium salt. The value of 0.159 for the solubility of $CrCl_3 \cdot 6H_2O$ in PEG200DA under ambient conditions is artificially high due to the colloidal chromium salt but the solubility value for the dried sample, also 0.159, is believed to be accurate. This proposal was supported by the infrared spectra of the respective systems, which indicated a much stronger metal/monomer interaction in the dried $Cr^{3+}$ sample.

When $Zn(NO_3)_2 \cdot 6H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ were placed in the vacuum desiccator in the presence of excess salt, they formed polymers spontaneously within 24 h. In fact all of the metal/monomer complexes spontaneously polymerize in time, but the $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $CrCl_3 \cdot 6H_2O$ salts form systems that are stable for several weeks and therefore are practical for the intended purpose. The complexes generally take between 3 and 7 days to reach maximum solubility, so accurate values for $Zn(NO_3)_2 \cdot 6H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ could not be measured due to the rapid onset of polymerization. The values for the solubility of $Zn(NO_3)_2 \cdot 6H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ under ambient conditions were relatively high so these salts still show some promise for the synthesis of pseudocrown ethers, despite the inability to increase the complex concentration via drying without taking precautions to prevent polymerization.

The dependence of solubility upon the size of the metal ion relative to the monomer is difficult to interpret from the data in Table 1 because so many variables affect the solubility. A better way to demonstrate the ion size dependence of solubility is to use the same metal salt with monomers of varying length. To this end, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $CrCl_3 \cdot 6H_2O$ were dissolved in diethylene glycol diacrylate (DEGDA) and PEG200DA. DEGDA, with only two repeat units of ethylene glycol per monomer, is too short to completely enclose the chromium, cobalt, or nickel ion. Thus, any complex formed by DEGDA would be weaker than that of the PEG200DA which has monomers with four and five repeat groups of ethylene glycol and can more completely enclose these ions. Table 3 summarizes the results of these solubility studies. A mixture of DEGDA and triethylene glycol (TEG) was made such that the concentration of acrylate groups of this solution was equivalent to that of pure PEG200DA, to help eliminate the effects of composition differences on the comparison. Clearly, the size of the monomer relative to the ionic diameter is important in binding and the results demonstrate the role of the chelate effect in these

(22) Jorgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon Press: London, 1962.

(23) Nyquist, R. A.; Kagel, R. O. *Handbook of Infrared and Raman Spectra of Inorganic Compounds and Organic Salts*; VCH Publishers: New York, 1992; Vol. 4.

(24) Pretsch, E.; Clerc; Seibl; Simon. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: New York, 1983.

(25) *The NALCO Water Handbook*; McGraw-Hill Book Company: New York, 1979.

(26) Lightfoot, P.; Mehta, M. A.; Bruce, P. G. *Science* **1992**, *262*, 883.

(27) Forster, D. J.; Heuts, J. P. A.; Davis, T.P. *Kinetic Aspects of Cobalt Mediated Free Radical Polymerization*; Polymer Division, Royal Austrailian Chemical Institute: Gold Coast, Australia, 1998; p 671.

(28) Steward, A. G.; Haddleton, D. M.; Muir, A. V. G.; Willis, S. L. *Catalytic Chain Transfer Polymerisation of Functional Methacrlates*; American Chemical Society: Washington, DC, 1998; p 459.

(29) Waterson, J. L.; Haddleton, D. M.; Harrison, R. J.; Richards, S. N. *New Cobalt Catalysis For Use In Acrylic Polymerisations*; American Chemical Society: Washington, DC, 1998; p 457.

**Table 3. Solubility$^a$ of CrCl$_3$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O and Co(NO$_3$)$_2$·6H$_2$O vs Monomer Length**

| metal salt | monomer | solubility (mole fraction) |
|---|---|---|
| CrCl$_3$·6H$_2$O | PEG200DA | 0.16 |
| CrCl$_3$·6H$_2$O | DEGDA | 0.0092 |
| CrCl$_3$·6H$_2$O | DEGDA/TEG | 0.031 |
| Ni(NO$_3$)$_2$·6H$_2$O | PEG200DA | 0.13 |
| Ni(NO$_3$)$_2$·6H$_2$O | DEGDA | 0.0050 |
| Ni(NO$_3$)$_2$·6H$_2$O | DEGDA/TEG | 0.045 |
| Co(NO$_3$)$_2$·6H$_2$O | PEG200DA | 0.27 |
| Co(NO$_3$)$_2$·6H$_2$O | DEGDA | 0.011 |
| Co(NO$_3$)$_2$·6H$_2$O | DEGDA/TEG | 0.056 |

$^a$ The solubility is defined as the mole ratio of metal ion to monomer.
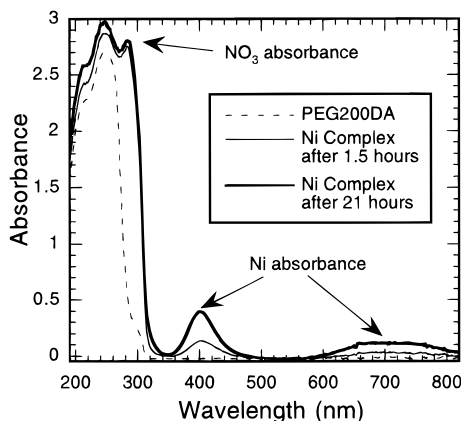


**Figure 1.** UV−vis spectra for the uptake of Ni(NO$_3$)$_2$·6H$_2$O by PEG200DA.



**Figure 2.** UV−vis spectra for Ni(NO$_3$)$_2$·6H$_2$O dissolved in water, Ni(NO$_3$)$_2$·6H$_2$O complexed with PEG200DA, and the dried complex of Ni(NO$_3$)$_2$·6H$_2$O and PEG200DA. The aqueous Ni(NO$_3$)$_2$·6H$_2$O spectrum is plotted on the right axis.

systems. For each metal ion, the ligand with higher number of ether oxygens is significantly more effective in causing complex formation.

**UV−Vis Spectroscopy.** UV−vis spectroscopy was used to monitor complex formation. The transition metals have absorbances in the visible range that arise due to the ligand composition.

**Nickel Complexes.** The spectra of complexes of Ni(NO$_3$)$_2$·6H$_2$O with PEG200DA were compared to the spectrum for pure PEG200DA and are displayed in Figure 1. The increasing uptake of the nickel salt with time is evident. A third spectrum was taken after 164 h; however, it showed only slight differences.

Ni(NO$_3$)$_2$·6H$_2$O complexes with PEG200DA relatively quickly. Most of the complex has formed after 1 day, and it reaches equilibrium under ambient conditions after 3 days of constant stirring. New peaks associated with the uptake of Ni(NO$_3$)$_2$·6H$_2$O appear at 290, 402, and a broad peak from around 600−800 nm. To obtain spectra representative of the addition of Ni(NO$_3$)$_2$·6H$_2$O, the spectrum of pure PEG200DA was subtracted from the spectra of the metal ion/monomer complexes. The subtracted spectra for the standard and dried complex of Ni(NO$_3$)$_2$·6H$_2$O are presented in Figure 2 along with the spectrum of aqueous Ni(NO$_3$)$_2$.

The aqueous Ni(NO$_3$)$_2$·6H$_2$O spectra has peaks at 250, 302, 395, and a broad peak at roughly 720 nm. The peaks at 395 and 720 nm correspond very well with the values published by Jorgensen for the octahedral Ni(H$_2$O)$_6^{2+}$ complex.[22] The peak at 302 nm is assigned to the solvated nitrate ion by analogy with the published spectrum for KNO$_3$ in water.[21] Pretsch lists the peak location for a nitrate or other negatively charged species
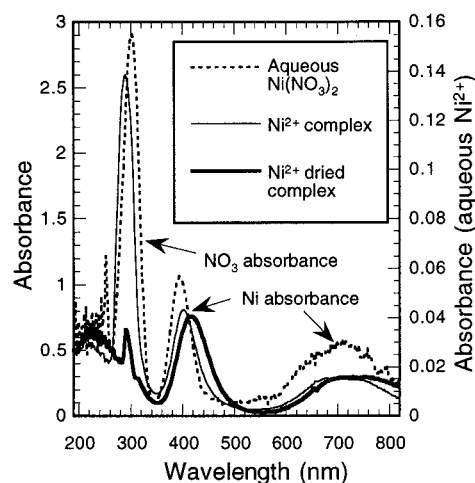
complexed with the acrylate group as ~390−400 nm.[24] In the present work, the nitrate is not believed to complex with the acrylate group in the metal monomer complexes because there are no FTIR spectral data consistent with that phenomenon.

The Ni(NO$_3$)$_2$·6H$_2$O complexed with PEG200DA under ambient conditions has peaks, indicating that there is no change in the coordination geometry of the nickel ion relative to the aqueous solution (402 and 600−800 nm). The shifts in the position of the bands do indicate a small change to the coordination environment of the nickel ion relative to the hexaaquo complex, implying that the nickel ions in this solution are complexed at least in part by ether oxygen atoms of the PEG200DA monomer. Since the nickel ion in aqueous solution is coordinated by the oxygen atoms of water, and in the case of the monomer complex, by the oxygen atoms of the monomer, it is expected that the peak locations of the UV−vis spectra would be similar, yet not exact, if the ligand field splitting provided by the ether oxygen atom is about the same for the oxygen atom in water. This argument is reasonable yet is not conclusive. It is known from the IR studies that coordinated water molecules remain in the metal ion/monomer complex, and thus, the ligand field producing the bands observed at 402 and 700 nm most likely arises from a mixed donor set of atoms, comprising water molecules, ether oxygen atoms, and possibly coordinated anion. The peak associated with the solvated NO$_3^-$ ion is shifted from 302 to 290 nm for the monomer complex. This shift is assigned to the change in the environment of the anion, from solvation in water to solvation by the polyether monomer.

When the Ni(NO$_3$)$_2$·6H$_2$O/PEG200DA complex formed under ambient conditions is placed in a vacuum desiccator to remove coordinated water, some very interesting changes occur in the electronic spectrum. The peak at 402 nm for the normal monomer complex shifts to 416 nm for the dried monomer complex. Also, the peak at 290 nm, assigned to nitrate ion, nearly disappears. The shift in the peak at ~402−416 nm is representative of the fact that the nickel atom further changes the composition of the ligands in the primary coordination sphere. Presumably, more ether oxygen atoms are
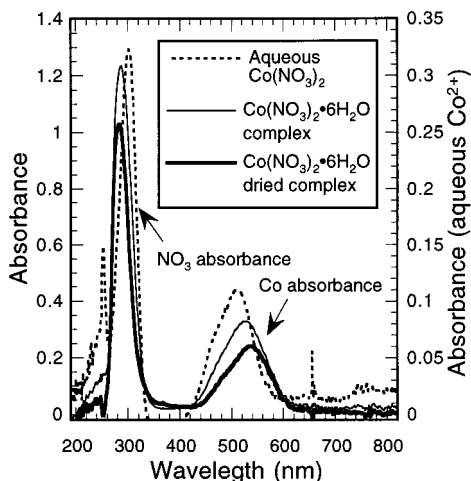
**Figure 3.** UV–vis spectra for $Co(NO_3)_2\cdot6H_2O$ dissolved in water, $Co(NO_3)_2\cdot6H_2O$ complexed with PEG200DA, and the dried complex of $Co(NO_3)_2\cdot6H_2O$ and PEG200DA. The aqueous $Co(NO_3)_2\cdot6H_2O$ spectrum is plotted on the right axis.

bound to the nickel, or else the nitrate ion becomes involved in coordination. The near disappearance of the peak at 290 nm is fascinating. Two hypotheses are that the nitrate ion coordinates to the nickel ion, inducing a shift in the position of the band to higher energy such that intense bands due to PEG200DA mask it, and thus, the absorbance apparently disappears. The other possibility is that the peak position is sensitive to the degree of solvation of the anion by water and the removal of the water causes a shift in the band position, but this is considered less likely as similar shifts have not been seen on drying systems using nitrate salts of other ions.

**Cobalt Complexes.** UV–vis and FTIR absorption spectra of complexes of $Co(NO_3)_2\cdot6H_2O$ were prepared using the same procedure as for the $Ni(NO_3)_2\cdot6H_2O$ spectra. The results for studies of the aqueous solution of $Co(NO_3)_2$, the $Co(NO_3)_2\cdot6H_2O$/PEG200DA complex, and the dried $Co(NO_3)_2\cdot6H_2O$/PEG200DA complex are displayed in Figure 3.

The aqueous $Co(NO_3)_2\cdot6H_2O$ spectrum corresponds well to the published values for an octahedral $Co(H_2O)_6^{2+}$ complex[2] (511 nm, shoulder at ~450–465 nm). The peaks at 253 and 302 nm are attributed to the presence of the solvated $NO_3^-$ anion.

The $Co(NO_3)_2\cdot6H_2O$ complexed with PEG200DA under ambient conditions has a spectrum that indicates no change in coordination geometry relative to the aqueous sample (528 nm, shoulder at ~460–470 nm). The bands for the hexaaquo/metal ion complex are shifted to slightly lower energy for the monomer complex, and it is reasonable to conclude that the shifts arise from oxygen atoms of the monomer complexing with the cobalt ion. The peak associated with the $NO_3^-$ anion is shifted in a consistent manner as $Ni(NO_3)_2\cdot6H_2O$.

When the $Co(NO_3)_2\cdot6H_2O$/PEG200DA complex formed under ambient conditions is placed in a vacuum desiccator to remove coordinated water molecules, similar changes occur in the absorbance spectrum as were found in the $Ni^{2+}$ system. The peak at 528 nm for the normal monomer complex shifts to 535 nm for the dried monomer complex. However, the free $NO^{3-}$ peak does

not change significantly. There is a slight decease in absorbance and a shift from 290 to 284 nm. The lack of a decrease in peak intensity (i.e., shift to lower wavelengths) indicates that the phenomenon observed for the $Ni(NO_3)_2\cdot6H_2O$ complex is not as prevalent for the $Co(NO_3)_2\cdot6H_2O$ complex. The most likely explanation is that the nitrate ion is less capable of binding to the cobalt ion than to the nickel ion, and so a "coordination shift" of the 290 nm band is not observed in this case. If this analysis is the case, then cobalt should make a better templating ion as it would be more likely to bind only to ether oxygens rather than to the anion, especially once some of the coordinated water molecules have been removed via drying. The shift in the $Co^{2+}$ peak (528–535 nm) is representative of the fact that the cobalt atom further changes the composition of the ligands in the primary coordination sphere, with presumably more ether oxygen atoms binding to the cobalt ion, replacing water.

**Chromium Complexes.** Solid $CrCl_3\cdot6H_2O$ contains the green tetraaquo dichloro cation, $Cr(H_2O)_4Cl_2^+$. When this solid salt is dissolved into water, it initially retains this complex structure but the ion slowly hydrolyzes to the hexaaquo form. Since the $d^3$ ion possesses significant ligand field stabilization energy, chromium(III) is the slowest of all the transition metals to exchange its ligands and, as a result, the equilibrium solution is not reached for about 24 h. The initial solution of $CrCl_3\cdot6H_2O$ in water has a spectrum in good agreement with literature values for the $Cr(H_2O)_4Cl_2^+$ ion[22] (266, 440, and 630 nm). The baseline is also elevated which is a characteristic of the light scattering associated with colloidal or aggregated aqueous metal solutions. The equilibrium water solution should contain hexaaquo chromium, $Cr(H_2O)_6^{3+}$ and a precipitate of chromium polymer aggregates. Chromium forms macromolecular structures even at low pH.[25] The absorption spectrum was taken of the supernatant liquid and used as the spectrum of the equilibrium complex in water. Peak locations were in reasonable agreement with the published values for the $Cr(H_2O)_6^{3+}$ complex[22] (294, 394, and 572 nm; vs 265, 407, and 574 nm).

In the $CrCl_3\cdot6H_2O$/PEG200DA complex, the most likely situation is that the chromium ions retain their chloride ligands, and the shifts in peak positions relative to the tetraaquo dichloro chromium ion reflect replacement of coordinated water by ether oxygens (290, 458, and 642 nm). Notably, the peak shifts are to lower energy, in keeping with the results seen for both the $Ni^{2+}$ and $Co^{2+}$ ions. Also, the monomeric complex is opaque, and therefore it is likely that a portion of the chromium salt exists in a colloidal or aggregated state.

When the $CrCl_3\cdot6H_2O$/PEG200DA complex is dried, the peak positions do not change significantly. They are located at 286, 459, and 628 nm. There is, however, a significant change in the optical clarity of the solution as it becomes very transparent, and the baseline problem observed in the other samples no longer exists. The dried complex is therefore a solution of monomers that are chelating independent chromium ions. The positions of the bands in the spectrum of the dried sample imply that chloride ion is retained in the chromium coordination sphere, but the insignificant shifts upon drying do
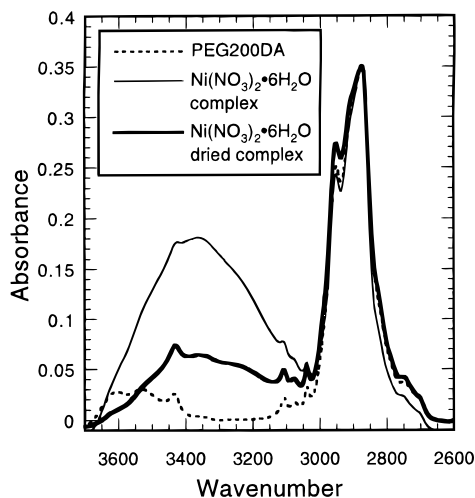
**Figure 4.** FTIR spectra (3600–2600 cm$^{-1}$) for PEG200DA, the Ni(NO$_3$)$_2$·6H$_2$O/PEG200DA complex, and the dried Ni-(NO$_3$)$_2$·6H$_2$O/PEG200DA.

not support further ether oxygens replacing water molecules as ligands during the drying process.

**Other Metal Complexes (Cu$^{2+}$, Cd$^{2+}$, Li$^{1+}$, Zn$^{2+}$, Nd$^{3+}$).** The aqueous Cu(NO$_3$)$_2$ spectrum has a peak that corresponds to the tetragonally distorted Cu(H$_2$O)$_6^{2+}$ complex[22] (793 nm). As in the case of the previous nitrate salts, there are peaks at 254 and 301 nm attributed to the NO$_3^-$ anion.

The ions of some metals such as cadmium, lithium, and zinc do not have metal ion based UV–vis absorbances from the complexes they form with PEG200DA. It is still possible, however, to use UV–vis spectroscopy to obtain experimental evidence for metal ion/monomer complex formation by monitoring a shift in the PEG200DA spectra to higher wavelengths. The spectrum for PEG200DA has a shift from ~270 to ~300 associated with formation of the Zn(NO$_3$)$_2$·6H$_2$O, Cd-(NO$_3$)$_2$·4H$_2$O, and Li(NO$_3$)/PEG200DA complexes.

Aqueous Nd(NO$_3$)$_3$ has a characteristic pattern of weak bands in the visible range that creates a light purple hue. Because of the core character of the f orbitals, f–f transitions of lanthanide ions are generally unaffected by a change in ligands; hence, the visible bands of Nd$^{3+}$ cannot be used to support exchanges of water by ether oxygens in the primary coordination sphere of the ion. However, the characteristic shift in the PEG200DA spectrum for the metal/monomer complex around 270–300 nm is observed for the Nd$^{3+}$ ion, indicating complex formation.

**FTIR Spectroscopy.** FTIR spectroscopy was used to help identify how the metal ions and the monomer interact on the molecular level. This technique is very powerful at looking at specific functional groups such as the C=C, and the C=O double bonds of the acrylate moiety. Unfortunately, the ether bond does not give rise to such a strong and distinct peak as the bonds of the acrylate group. The relative amount of water present in the samples can also be quantified with respect to the drying technique, with the removal of coordinated waters being readily observable.

**Nickel Complexes.** The FTIR spectra for PEG200DA, the Ni(NO$_3$)$_2$·6H$_2$O/PEG200DA complex, and the dried Ni(NO$_3$)$_2$·6H$_2$O/PEG200DA complex are compared in Figure 4. The strong double peak at 2800–3000 cm$^{-1}$
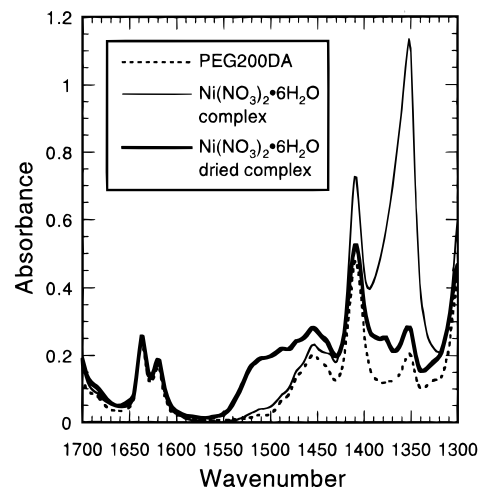


**Figure 5.** FTIR spectra (1700–1300 cm$^{-1}$) for PEG200DA, the Ni(NO$_3$)$_2$·6H$_2$O/PEG200DA complex, and the dried complex of Ni(NO$_3$)$_2$·6H$_2$O/PEG200DA.

is characteristic of the aliphatic C–H bond stretching. Since the number of C–H groups does not vary during the drying process, this peak is useful as an internal standard in the quantification of water loss during drying. The PEG200DA monomer was thoroughly dried so the peaks between 3400 and 3650 cm$^{-1}$ are not related to water but most likely arise from overtone or combination bands. The broad peak between 3000 and 3650 cm$^{-1}$ present in the spectra of the two complexes is due to O–H stretching of coordinated water. A significant fraction of this water was removed during the drying procedure, with the peak height at 3350 cm$^{-1}$ reduced by 66%. Thus, on average, each nickel ion lost four of its original six coordinated water molecules.

The FTIR spectra for the dried metal/monomer complexes contained new absorbance characteristic for each individual metal ion. There typically was a stronger absorbance for the dried complex, indicating that this procedure enhanced the concentration of the desired complex. In the case of Ni(NO$_3$)$_2$·6H$_2$O the spectrum for the standard complex has a very distinct peak at 1352 cm$^{-1}$ (Figure 5) and a very subtle peak at 834 cm$^{-1}$ (not shown) which may be due to uncoordinated nitrate ion (literature value 1390 and 831 cm$^{-1}$). Upon drying of the complex, there was a fairly strong new absorbance in the 1500 cm$^{-1}$ region, which is in the region expected for one of the peaks of coordinated nitrate ion, and the peaks at 1352 and 834 cm$^{-1}$ which are expected for uncoordinated nitrate ion are no longer present. Taken together with the UV–vis spectra, some of the vacant nickel ion coordination sites produced by loss of water are clearly occupied by nitrate anions, but this feature does not rule out coordination of ether oxygens from the monomer as well. Significantly, the peaks assigned to C=C and C=O stretching were not shifted in either of the complexes relative to their position in the spectrum of the monomer. The lack of any shift in peak location indicates that neither of the double bonds in the acrylate functional group was incorporated in the complex. This behavior is advantageous for two reasons. If the metal complexed the reactive C=C double bond, the polymerization kinetics may be altered and the analysis of the polymerization rate data would be difficult. Also, if the metal complexed with the acrylate group and not
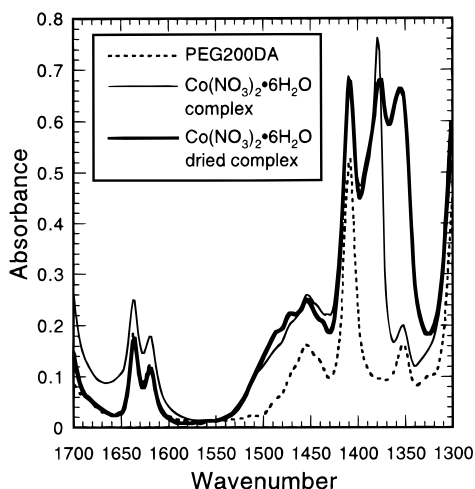
**Figure 6.** FTIR spectra for PEG200DA, the $Co(NO_3)_2 \cdot 6H_2O$/ PEG200DA complex, and the dried complex of $Co(NO_3)_2 \cdot 6H_2O$/ PEG200DA.



**Figure 7.** FTIR spectra for PEG200DA, the $CrCl_3 \cdot 6H_2O$/ PEG200DA complex, and the dried complex of $CrCl_3 \cdot 6H_2O$/ PEG200DA.

the central ethylene glycol chain, the circular conformation that is required for pseudocrown ether formation would not be obtained.

**Cobalt Complexes.** The spectra for complexes from $Co(NO_3)_2 \cdot 6H_2O$ have similar characteristics to the nickel nitrate analogues. At 3400 cm$^{-1}$ the reduction in the peak for water was 70%; thus, on average each cobalt ion lost approximately four of the original six coordinated water molecules. This removal is a good indication that the desired metal/monomer complex was formed, especially since the UV–vis spectra suggested that the nitrate was not incorporated in the solvation sphere upon drying, nor was their any evidence from the IR spectra for a coordinated nitrate peak at ~1500 cm$^{-1}$. Since the electronic spectrum indicates that the cobalt ion retains six coordination upon drying, ether oxygen atoms likely replace the removed water ligands. It would be possible for the PEG200DA monomer to enclose the metal along the square plane and one water of hydration to be situated along each vertical axis. This confirmation would have a high probability of leading to the formation of pseudocrown ethers upon photopolymerization.

The FTIR spectrum for the dried metal/monomer complex for cobalt nitrate hexahydrate also contained new characteristic absorbances. The spectrum of the cobalt complex is more detailed than the nickel complex spectrum, and this feature probably represents the fact that cobalt forms more direct attachments to the monomer. As shown in Figure 6, the standard cobalt complex has a broad overlying absorbance from 1525 to 1400 cm$^{-1}$ with a very distinct peak at 1375 cm$^{-1}$ which may be due to uncoordinated nitrate ion (literature value 1390 cm$^{-1}$). When the complex is dried, the same broad absorbance from 1525 to 1400 cm$^{-1}$ is retained but there is a decrease in the peak at 1375 and a new very distinct peak at 1350 cm$^{-1}$. As in the case of the nickel complex, neither of the double bonds in the acrylate functional group is incorporated in the cobalt complex since there is again no shift in the peaks associated with these bonds. Since water ligands are lost and the acrylate group and the nitrate ion do not coordinate, the cobalt ion is clearly interacting with the monomer and forming the desired complex.
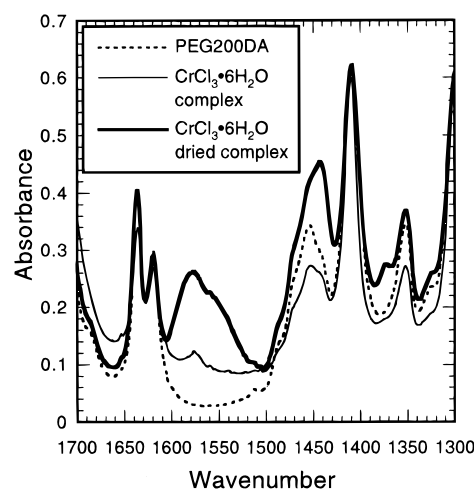
**Chromium Complexes.** Although the most interesting and informative results of templating ions comes from the Ni$^{2+}$ and Co$^{2+}$ studies, the spectrum from Cr$^{3+}$ yields an important fact. The Co$^{2+}$ spectrum has an absorbance in the range of complexed NO$^{3-}$ that was not assigned as such. It was instead assigned as a monomer/metal interaction. Because all other evidence did not support Co$^{2+}$/NO$^{3-}$ complexation this assertion seems reasonable. Another example of a metal ion that produces this monomer/metal interaction in the range of 1550 cm$^{-1}$ is Cr$^{3+}$. In this case, CrCl$_3 \cdot 6H_2O$, which contains no nitrate anion, was used. The absorbance observed is not due to the chloride anion as it would appear in the 200–400 cm$^{-1}$ range.

At 3150 cm$^{-1}$, there is a 59% decrease in the peak height for the water absorbance upon drying, thus on average between three and four of the original six water molecules are removed from each chromium complex. This loss represents one or two water ligands from Cr-$(H_2O)_4Cl_2^{+}$ plus two waters of hydration. As discussed in the UV–vis section, the CrCl$_3 \cdot 6H_2O$ complex formed under ambient conditions was cloudy and opaque but became transparent upon drying. This behavior is interpreted as indicating that the removal of some of the water ligands has been accompanied by the coordination of ether oxygens from the monomer, resulting in formation of stable, discrete complexes with no aggregation of chromium centers. The chromium complex formed under ambient conditions was not very stable when other solvents were added and a chromium-containing precipitate was observed in less than 1 min. The dried CrCl$_3 \cdot 6H_2O$/PEG200DA complex was much more stable in these solvents, and no appreciable precipitation occurred in these samples on the time scale required for work up and subsequent polymerization reactions.

As with the other ions, the peak locations for the C=C and C=O bonds were not shifted, indicating no complexation of these groups to the metal ion. A broad peak at 1580 cm$^{-1}$, with a pronounced shoulder at 1560 cm$^{-1}$, appears on the spectrum of the dried complex, along with a higher intensity for the peak at 1440 cm$^{-1}$ (Figure 7). Although the origin of these peaks is not clear, they are taken as being associated with complex-

ation of the monomer to the chromium ion. There is some indication of the presence of these new peaks in the spectrum for the standard complex. There is an elevated baseline with weak peaks at 1575 and 1440 cm$^{-1}$.

The FTIR data for the nickel, cobalt, and chromium complexes have important similarities. All three exhibit the reduction in the number of coordinated water molecules upon placing the complexes in a vacuum desiccator. The extent of the removal of waters appears to vary from one complex to the next, but all had on average between three or four of the original six waters removed. In the case of the nickel ion, both IR and UV−vis spectroscopy indicated that some of the vacant coordination sites were taken up by coordination of nitrate ion. In all three cases, the metal ions do not incorporate any coordination from the acrylate functional group as neither of the characteristic absorbances shows a shift in peak location. It is believed that the removal of water ligands is accompanied by the binding of ether oxygens from the monomer to all three metal ions and hence the results suggest that all three metals could make suitable templating ions with cobalt showing the most promise. The solubility limit is highest for cobalt, and the removal of coordinated water ligands appears to result in the most incorporation of ether oxygens from the monomer. Hence, it is believed that the most abundant and most ideal conformations would result from the cobalt complex.

**Other Metal Complexes (Zn$^{2+}$, Cd$^{2+}$, Nd$^{3+}$, and Li$^{1+}$).** Zn(NO$_3$)$_2$·6H$_2$O and Cd(NO$_3$)$_2$·4H$_2$O are both salts of Group 12 transition metals and therefore have the same valence shell electronic configuration, and, thus, similar complexation behavior with PEG200DA is anticipated. Both the zinc and cadmium complexes have a new peak at 1377 cm$^{-1}$ assigned to uncomplexed nitrate ion. Because of the problems with spontaneous polymerization, the zinc and the cadmium complexes could not be dried to see if there were shifts in this peak to lower wavenumbers as found in the Co$^{2+}$ system.

The complex of Nd(NO$_3$)$_3$·6H$_2$O has a broad peak ∼1500 cm$^{-1}$. This peak is ascribed to coordination of nitrate to the Nd$^{3+}$ ion. Notably, there is no peak at 1350 cm$^{-1}$ for uncoordinated nitrate. The Nd$^{3+}$ complex does not require drying to induce nitrate coordination since the relatively large ionic radii of the early lanthanide ions leads them to possess coordination numbers in excess of six (commonly nine). Hence, the Nd$^{3+}$ ion can accommodate nitrate coordination without removal of any of the six water ligands. The ligands of the neodymium ion are believed to be a mix of water, nitrate, and ether oxygen atoms.

Although LiNO$_3$ had a very high solubility in the monomer, the UV−vis and FTIR spectra for this system showed the least amount of change upon the addition of the salt to the monomer. The FTIR spectra had no distinct peak due to uncoordinated nitrate ion, suggesting that there is coordination of nitrate to the lithium ion. It is likely that ether oxygen atoms complete the coordination sphere of the lithium ion. There is literature precedence for this behavior in work by Bruce et al.[26] They found that lithium triflate dissolved in poly-(ethylene glycol) possessed a trigonal bipyramidal lithium ion, with two equatorial sites occupied by oxygen atoms

**Table 4. Reduction in the Polymerization Rate as Evidence for Pseudocrown Ether Formation in Co(NO$_3$)$_2$·6H$_2$O/PEG200DA Systems**

| complex type | metal monomer ratio | % convn | normalized rate max, s$^{-1}$ | total % reduction in rate |
|---|---|---|---|---|
| pure PEG200DA | 0:1 | 78 ± 1 | 1.62 ± 0.15 × 10$^{-1}$ | 0.0 |
| normal complex | 0.12:1 | 81 ± 4 | 1.45 ± 0.04 × 10$^{-1}$ | 10.5 |
| dried complex | 0.12:1 | 74 ± 4 | 1.17 ± 0.10 × 10$^{-1}$ | 28.0 |
| dried complex | 0.17:1 | 80 ± 5 | 1.04 ± 0.10 × 10$^{-1}$ | 35.9 |
| normal complex | 0.27:1 | 75 ± 1 | 1.29 ± 0.07 × 10$^{-1}$ | 20.2 |
| dried complex | 0.27:1 | 67 ± 3 | 7.92 ± 1.21 × 10$^{-2}$ | 51.1 |

from two bridging triflates and the remaining three coordination positions being occupied by ether oxygen atoms.

**Differential Scanning Calorimetry.** The peak rate of reaction during autoacceleration is used as a measure of the mobility of the reacting species. Cross-linking decreases the mobility of monomers and oligomers and, therefore, increases autoacceleration. The cross-linking density is decreased by the formation of pseudocrown ethers because the diacrylate self-cyclizes and forms a linear polymer segment with a pendant crown as opposed to forming a cross-link with another propagating chain. Increasing the number of pseudocrown ethers will decrease the cross-linking of the system and, thus, decrease the autoacceleration.

Since the polymerization kinetics are being used as evidence for crown formation, other variables that can effect the rate must be eliminated from the experimental study. The two main potential means by which a metal salt can decrease the polymerization rate are radical scavenging and chain transfer. Cobalt(II) cannot scavenge radicals as the cobalt(I) oxidation state is not energetically favorable under normal conditions. Chain transfer of propagating radicals in methacrylate systems occurs in some low-spin cobalt porphyrin complexes.[27,28] These chain-transfer agents are effective in controlling the molecular weight of methacrylate polymerizations and much less effective on acrylate systems.[27,29] These complexes have very specific structural requirements, including the porphyrin ring and bridging BF$_2$ groups; thus, Co(NO$_3$)$_2$·6H$_2$O is not expected to act similarly as a chain-transfer agent to PEG200DA. Studies of the kinetics of hydroxyethyl methacrylate and poly(ethylene glycol) monoacrylates, both monomers that can only form linear polymers, confirmed that Co(NO$_3$)$_2$·6H$_2$O does not radical scavenge nor cause significant levels of chain transfer in these systems.[15]

The systems chosen to study the decrease in rate from pseudocrown ether formation were the normal and dried complexes of Co(NO$_3$)$_2$·6H$_2$O and PEG200DA with 1% DMPA, the photoinitiator. Because the metal/monomer complexes varied in metal concentrations and coordinated water content, the light absorption at 365 nm varied from sample to sample. No more than a 10% reduction in light intensity was observed for any of the samples, and therefore, can only be responsible for very small changes in the rate.

With the reduction in rate for the decreased light intensity known to be small, the decrease in the rate maxima is nearly entirely a result of pseudocrown ether formation. The results from the kinetics studies are listed in Table 4 for the various complexes of Co(NO$_3$)$_2$·6H$_2$O with PEG200DA. The percent conversion is

calculated from the measured heat released and the known theoretic heat of reaction for PEG200DA of 529 J/g, which is calculated based on the heat of reaction of a lauryl acrylate bond (20.6 kJ/mol).[30] The maximum rate of heat release (in units of W/g monomer) is divided by the heat of reaction to yield the normalized rate maximum (in units of $s^{-1}$), and the total percent reduction in rate is based on this normalized rate maximum. Experiments were performed isothermally at 30 °C so potential differences in heat capacity for metal containing samples are irrelevant.

The two most significant results from this study are that pseudocrown ethers are synthesized in increased number due to templating and the dried cobalt(II) complex produces more crowns than the nondried complex at the same metal ion concentration. Also, increasing the concentration of the templating ion increases the number of pseudocrown ethers formed.

## Conclusions

The ultimate goal of this work is to synthesize inexpensive, nontoxic polymeric pseudocrown ethers, and this synthesis has been accomplished using metal ion/PEG200DA complexes which form the pseudocrown ethers via a templated intramolecular cyclization in situ during photopolymerization. The formation strength of the complex as measured by the relative solubility of the salts in PEG200DA did not strictly follow the expected trends predicted by hard/soft acid/base theory. The alkali metals did not form the highest concentration of complexes as the theory would predict, possibly due to the lack of waters of hydration in these salts. The nickel ion in $Ni(NO_3)_2 \cdot 6H_2O$ binds to the ether oxygens

of PEG200DA and retains some waters of hydration. Upon the removal of some of the waters of hydration, nitrate anion and additional ether oxygens replace the waters and the maximum solubility concentration of the complex is increased from 13% to 23% of total monomer complexed. The cobalt ion in $Co(NO_3)_2 \cdot 6H_2O$ also complexes to the ether oxygens of PEG200DA. Upon drying, the removed water molecules are replaced by ether oxygens. The drying process increased the maximum solubility of the cobalt complex from 27% to 42% of total monomer complexed. The initial complex formed by $CrCl_3 \cdot 6H_2O$ seems to be colloidal or containing aggregated chromium polymers; however, the dried complex is homogeneous and does not contain colloidal or aggregated ions. $Cu(NO_3)_2 \cdot 2.5H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$ and $Li(NO_3)$ also form complexes with the PEG200DA monomer.

From the vacuum-drying process, the $Ni(NO_3)_2 \cdot 6H_2O$/PEG200DA complex and the $Co(NO_3)_2 \cdot 6H_2O$/PEG200DA complex each lost approximately four of the original six water molecules and the $CrCl_3 \cdot 6H_2O$/PEG200DA complex lost between three and four water molecules. All three of these complexes display changes in the coordination sphere of the metal ion upon partial drying consistent with enhanced ether oxygen binding.

The formation of pseudocrown ethers was observed via a reduction in the peak polymerization rate during the autoacceleration phase of network formation. Rate data indicate that cobalt(II):PEG200DA complexes form polymeric pseudocrown ethers and reduce the crosslinking density relative to pure PEG200DA. The dried complexes compared to the normal complexes (at equivalent metal ion concentrations) formed more pseudocrown ethers. The percent decrease in the rate was approximately doubled for the dried complexes.

(30) Moore, J. E. *Chemistry and Properties of Cross-linked Polymers*; Labana, S.S., Ed.; Academic Press:  New York, 1977; p 535.