APPLICATIONS OF CROWN ETHERS IN INDUSTRIAL ANIONIC POLYMERIZATIONS

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APPLICATIONS OF CROWN ETHERS IN INDUSTRIAL ANIONIC POLYMERIZATIONS

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SUMMARY

The effects of the addition of catalytic quantities of macrocyclic polyethers (crown ethers) to anionic-initiated polymerization systems were investigated. Dramatic modifications in the polymerization characteristics of the n-BuLi-styrene-benzene system occurred upon the addition of 15-crown-5. Complete conversion to polymer was obtained in systems containing the complexing agent in less than 10 seconds (least possible measurable time under the employed experimental procedure). The molecular weight of polystyrene produced from the modified system increased to an optimum value as the molar ratio of crown ether to n-BuLi approached 0.5:1. Further addition of the crown ether (molar ratio greater than 0.5:1) caused a decrease in the molecular weight to the same low values obtained in systems containing no complexing agent. The addition of 12-crown-4 to the system produced effects of a lesser magnitude in both the overall rate of polymerization and the molecular weight of the polymer, but the benefits over systems containing no crown were substantial.

The results of the research indicate that in-mold polymerization of styrene with the crown/n-BuLi catalyst system may be feasible. The extremely rapid rate of polymerization and the ability to "tailor" the molecular weight
by varying the crown concentration offer potential in-mold polymerization capabilities that have not been previously defined in the literature.

Moderate increases in the molecular weight of polyisoprene were obtained by the addition of either 15-crown-5 or 12-crown-4 to the n-BuLi-isoprene-heptane polymerization system. Through use of 12-crown-4, the reaction time to reach 100% conversion to polymer was reduced by 67%, while the addition of 15-crown-5 to the system allowed the time of reaction to be reduced by 83% in comparison to systems containing no crown ether.

Attempts to modify polymerization systems employing n-BuNa as an initiator through use of crown ethers proved unsuccessful. Likewise, attempts to modify the bulk anionic polymerization of caprolactam by addition of crown ethers also proved unsuccessful due to instability of the crowns under the polymerization conditions.
CHAPTER I

INTRODUCTION

Crown Ethers

Crown ethers are generally defined as macrocyclic polyethers consisting of repeating \((-\text{O-CH}_2\text{-CH}_2\text{-})_n\) units. The term "crown" refers to the similarity of the molecular models of the compounds to a regal crown and to the ability of these compounds to "crown" cations by complexation.\(^1\)

The field of crown ether chemistry was pioneered by Charles J. Pedersen of the duPont Company, who reported syntheses of many of these compounds and considerable cation complexation data in 1967.\(^2\) Although Pedersen was not the first to synthesize macrocyclic polyethers, he was the first to recognize that the compounds represented neutral synthetic molecules capable of forming stable complexes with metal ions.\(^3\) In his early papers, Pedersen reported that crown ethers complex alkali, alkali earth, transition metal, and ammonium cations. He postulated that the cation in the complex is held in the center of the cyclic molecule of the crown ether by the electrostatic attraction between the positive charge of the cation and the negative dipolar charge on the oxygen atoms symmetrically arranged in the polyether ring.\(^2-3\) This postulation suggested that a relationship should exist between the size of the hole in the center of
a crown ether molecule and the cation diameter. Data reported by Pedersen and Frensdorff⁴ show that the binding constants for metal ions are generally largest when the cation diameter is nearly equal to the hole size in the cyclic molecule. Therefore certain cations may be selectively complexed by specific crown ethers.

Pedersen also devised a simplified system for naming crown ethers, whose nomenclature under IUPAC rules is cumbersome.⁵ The informal names in order consist of: (1) the side-ring substituents, (2) the total number of atoms in the polyether ring, (3) the word "crown," and (4) the number of oxygen atoms in the main ring. Using this system of nomenclature, 1,4,7,10,13,16-hexaoxacyclooctadecane is termed 18-crown-6 (I); 1,4,7,10,13-pentaoxacyclopentadecane is termed 15-crown-5 (II); and 1,4,7,10-tetraoxacyclododecane referred to as 12-crown-4 (III). Although many other crown ethers have been synthesized and classified,⁶ the application of the three named crown ethers in anionic polymerizations is reported in this thesis.
Anionic Polymerization

Several commercially-important monomers, including dienes, olefins, and cyclic ring compounds, are polymerized by anionic initiation. In general, any alkene monomer possessing electron-withdrawing groups such as nitrile, carboxyl, phenyl, and vinyl is capable of participating in anionic-initiated polymerizations. Such monomers contain atoms with a partial positive charge due to the electrophilic nature of the substituent groups. Addition of an anion from an initiator to the monomer can take place at the atom carrying the partial positive charge. The resulting species, with its negative charge obtained from the initiator anion, may then attack another monomer molecule. The entire polymerization process for alkene monomers may be summarized as follows:

Initiation: \[ Y^- + CH_2=CH \rightarrow \delta^+ Y-CH_2-CH \]

Propagation: \[ Y-CH_2-CH + CH_2=CH \rightarrow \delta^+ Y-CH_2-CH-CH_2-CH \]

Termination: \[ Y-\overline{CH_2-CH}^{-n}CH_2-CH + H^+ \rightarrow \delta^+ Y-\overline{CH_2-CH}^{-n}CH_2-CH \]

\[ Y-\overline{CH_2-CH}^{-n}CH_2-CH + M^+ \rightarrow \delta^+ Y-\overline{CH_2-CH}^{-n}CH=CH + MH \]
Metal alkyls are often used as initiators in anionic polymerizations, although monomers with strongly electron-withdrawing substituents can be polymerized with weaker nucleophilic catalysts such as hydroxide or cyanide ions. Much stronger nucleophiles, such as the metal alkyls, are required to polymerize monomers with relatively weak electron-withdrawing substituents. The most useful of the metal alkyl catalysts is n-butyllithium. n-Butylsodium is a stronger base than n-butyllithium, but the sodium compound is much less stable than its lithium counterpart, attacks many common aromatic solvents, and is insoluble in nonpolar alkane solvents. A major drawback to the use of metal alkyl initiators is their high reactivity towards oxygen, carbon dioxide, and water. Therefore, extreme caution must be taken to exclude these impurities from the reaction vessel whenever a metal alkyl serves as initiator.

Impurities may also react with propagating anionic chains to form peroxy and carboxy anions. The resulting anions are not reactive enough to further propagate polymerization and the kinetic chain is terminated. Water and other substances with acidic hydrogens can terminate anionic
chains ends by transfer of a proton.9

The rates of propagation and initiation in anionic polymerizations may vary widely, depending on the nature of the monomer, gegen ion, and the solvent.10 Although the ionic species in the reaction mixture could exist more easily in solvents of high polarity, such solvents cannot be used for several reasons.9 Highly polar hydroxylic solvents such as water and alcohols will react with and destroy most ionic catalysts by proton transfer. Ketones and other polar solvents are capable of preventing initiation of polymerization by forming highly stable complexes with the anionic catalysts. For these reasons, anionic polymerizations are usually carried out in solvents of low polarity. In such a system, distinctly separate ions do not exist as they do in solvents of higher polarity. The ions are instead present in the form of tightly bound ion-pairs.9 Therefore, a propagating anionic chain end has a positive gegen ion in close proximity throughout the polymerization process. The reactivity of the anion increases as the attraction between the ion pair decreases.9

Almost all anionic polymerizations proceed rapidly, but the polymerization of caprolactam, a 7-member heterocycle, to form Nylon 6 is especially rapid. The bulk anionic polymerization is characterized by a brief induction period after which the conversion of caprolactam proceeds with increasing velocity to a maximum value.11-13 The initiating
species for the polymerization is usually formed by the reaction of caprolactam and sodium metal, M (Eq. 1.1):

$$\text{(CH}_2\text{)}_5\text{NH} + M \rightarrow \text{(CH}_2\text{)}_5\text{N}^+ + \frac{1}{2} \text{H}_2$$

(1.1)

The resulting lactam anion reacts with a monomer in the second step of the initiation process by a ring-opening transimidation (Eq. 1.2):

$$\text{(CH}_2\text{)}_5\text{N}^+ + \text{HN-(CH}_2\text{)}_5 \rightarrow \text{(CH}_2\text{)}_5\text{N-CO(CH}_2\text{)}_5\text{N}^+$$

(1.2)

The slow step is responsible for the induction period observed in the polymerization. The primary amine anion produced in this rate-determining step is highly reactive and undergoes a rapid proton-abstraction reaction with the monomer to form an imide dimer and to regenerate the lactam anion (Eq. 1.3):

$$\text{(CH}_2\text{)}_5\text{N-CO(CH}_2\text{)}_5\text{N}^+ + \text{(CH}_2\text{)}_5\text{NH} + \text{(CH}_2\text{)}_5\text{N-CO(CH}_2\text{)}_5\text{NH}_2 + \text{(CH}_2\text{)}_5\text{N}^+$$

(1.3)

Propagation occurs when the lactam anion reacts with a growing imide species (Eq. 1.4) followed by a fast proton-exchange
with the monomer (Eq. 1.5): 9

\[
\begin{align*}
\text{(CH}_2\text{)}_5\text{-N-CO(CH}_2\text{)}_5\text{NH} & \quad + \quad \text{(CH}_2\text{)}_5\text{-N}^-\text{M}^+ \\
\text{(CH}_2\text{)}_5\text{-N-CO(CH}_2\text{)}_5\text{-N-CO(CH}_2\text{)}_5\text{-NH} & \quad + \quad \text{(CH}_2\text{)}_5\text{-NH}
\end{align*}
\]

(1.4)

\[
\begin{align*}
\text{(CH}_2\text{)}_5\text{-N-CO(CH}_2\text{)}_5\text{-N-CO(CH}_2\text{)}_5\text{-NH} & \quad + \quad \text{(CH}_2\text{)}_5\text{-N}^-\text{M}^+ \\
\text{(CH}_2\text{)}_5\text{-N-[CO(CH}_2\text{)}_5\text{NH}_2] & \quad + \quad \text{(CH}_2\text{)}_5\text{-N}^-\text{M}^+
\end{align*}
\]

(1.5)

The anionic polymerization of caprolactam is unique in two respects. First, the monomer itself does not add to a propagating chain. Instead a monomer anion, referred to as an "activated monomer," is the propagating species. Secondly, the growing polymer chain is a neutral species and does not carry a negative charge at its end.

Anionic techniques can be used for styrene homopolymerization, but commercial applications have been rather limited. Several workers have studied the anionic polymerization of styrene and have obtained polymers of relatively low molecular weight. 15, 16 However, an advantage to the
anionic techniques is the narrow molecular weight distributions obtained in the polymerizations. Anionic-initiated polymerizations may also be employed to produce block copolymers of styrene and butadiene. At room temperature, these thermoplastic SBR rubbers act as though they were covalently crosslinked, exhibiting high resilience and low creep. At higher temperatures, however, the anionic-initiated block copolymers readily melt and exhibit flow characteristics, making the processing of the SBR rubbers less troublesome than that of crosslinked polymers.

Consideration has been given to styrene as a candidate for in-mold polymerization. Industry presently polymerizes polystyrene in one step of the manufacturing process and melts and molds the material in a separate second step. Production time and energy could be saved if the molded polymeric product was produced directly from styrene in one step. A basic requirement of in-mold polymerizations is that the reaction time for the process must be short in order to render the procedure economically attractive. Kircher et al. using radically-initiated polymerizations, have investigated the feasibility of producing polystyrene in an in-mold process. The researchers discovered two major problems inherent with their radically-initiated systems. First, low conversions to polymer resulted in a relatively high residual content of monomer in the finished product. Secondly, the slow reaction rate obtained from the radical polymerization dictated a cycle
time for the process of 15 minutes. Although the anionic polymerization of styrene is characterized by both high conversions to polymer and more rapid rates than free radical processes, its applicability to an in-mold polymerization has not gained commercial status.

Statement of the Problem

The polymer industry has always been concerned with the rate of polymerization of commercial monomers. Besides the obvious benefit of increased productivity, extremely rapid rates would also make feasible such practices as in-mold polymerization. Although caprolactam polymerizes to Nylon 6 at a relatively fast rate, the reaction time required for quantitative conversion (5-10 minutes) must be decreased before in-mold polymerization is economically feasible. Other monomers, with their slow rates of polymerization and corresponding long reaction times, present even greater problems in adaptation to in-mold processing.

A major concern in anionic polymerizations is the nature of the ion pairs in the system. The ability of an anion to initiate polymerization increases as the attraction between that anion and its positive gegenion decreases. In order for the rates of polymerization to increase in a system, the number of "loose" (solvent-separated) ion pairs must also increase. One method of decreasing the attraction between the ion pairs and thus increasing the reactivity of the initiating anion is by complexation of the cation. Although
the effects of several cationic complexing agents on anionic polymerizations have been studied, little reported research has been directed toward the utilization of unsubstituted crown ethers in the production of commercially-important polymers. This research is concerned with the effects of the addition of catalytic quantities of the unsubstituted crown ethers 12-crown-4, 15-crown-5, and 18-crown-6 to conventional industrial anionic polymerizations. These effects are projected to increase reaction rates, increase productivity, offer a wider choice of metal catalysts and solvents, and promote energy savings. Attempts will be made to define optimum systems which most clearly demonstrate the beneficial effects of the crown ethers. Comparisons will be made between systems containing the macrocyclic polyethers and "blank" systems without the complexing agents, and conclusions will be drawn concerning the applicability of crown ethers in industrial anionic polymerizations.

Review of the Literature

The rate of an anionic polymerization is highly dependent on the nature of the ion pairs present in solution. A tight ion pair is much less reactive than a loose ion pair. The population of loose anion-cation pairs may be increased slightly by judicious selection of reaction temperature, solvent, and cation. Cationic complexing agents have the ability to increase the population of loose ion pairs to a much larger extent than has previously been attained with
careful temperature, solvent, and cation selection.

Polyglycol dimethyl ethers (glymes) are relatively weak cationic complexing agents. Swarc et al. have shown that the reactivity of sodium polystyryl in tetrahydrofuran is enhanced by the addition of small amounts of glymes. The beneficial effects gained by the use of glymes in anionic polymerizations are limited and have not been exploited industrially. In addition to being weak complexing agents, the use of glymes in anionic polymerizations is also limited by the fact that the ether linkages are readily cleaved by metal alkyls, such as n-butyllithium and n-butylsodium. Macrocyclic polyethers, however, are apparently not cleaved as readily as are linear ethers in the presence of strong bases and are therefore more attractive candidates for applications in industrial anionic polymerizations.

Cryptates are macrobicyclic polyaza-polyoxa compounds that are capable of serving as ligands for complexing various metal cations. The three-dimensional cryptate surrounds the complexed cation, rather than merely encircling the ion as does a crown ether. Thus a cation which has been complexed by a cryptate is less accessible to anion and solvent than a cation complexed by a crown ether. Lehn and his coworkers have designed numerous cryptates and developed multi-step reaction sequences to synthesize the compounds. The high cost of synthesizing cryptates limits the utilization of these compounds on an industrial scale (commercially priced
at greater than $100 per gram$^{39}$, although they have been shown in the laboratory to greatly increase the rates of polymerization of several monomers initiated by anionic catalysts.$^{40-43}$

In a series of papers published in 1974, Boileau et al. discussed various aspects of the use of cryptates in anionic polymerizations.$^{40-43}$ The catalysts used in the study are represented by the following general formula:$^{40}$

![Chemical structure](attachment:chemical_structure.png)

where $m=n=p=2$ noted as [222] compound

$m=m=2; p=1$ noted as [221] compound

$m=2; n=p=1$ noted as [211] compound

In all of the polymerizations, the molar ratio of the above cryptates to initiator was equal to or greater than unity.$^{40}$

Boileau first investigated the effects of cryptates on polymerizations initiated by alkali metals.$^{40}$ He discovered the addition of cryptates produced several desirable results. When styrene was polymerized in benzene or tetrahydrofuran by metallic lithium in the presence of [211], the rate of polymerization was increased considerably over that experienced when [211] was not present. In addition, the presence of [211] totally suppressed the induction period
characteristic of the system when [211] was absent. Methyl methacrylate in tetrahydrofuran was polymerized by lithium naphthalene and [211], sodium naphthalene and [221], and potassium naphthalene and [222] with quantitative yields of polymer being obtained after one minute of polymerization for all systems. The polymerization of isoprene in benzene by n-butyllithium and [222] led to the formation of polar structures at an increased polymerization rate. An increased reactivity was noted when tetrahydrofuran was substituted for benzene. The increased reactivity was contributed to the existence of the complexed ion-pairs in equilibrium with the free ions. Ethylene oxide was polymerized in tetrahydrofuran by carbazylpotassium and [222] with a yield of 100% being obtained after 24 hours of polymerization at 20°C. In order to obtain a yield of 100% in the absence of [222], the polymerization must be carried out for 4 to 5 days at 40°C.40

After demonstrating the advantages gained by the addition of cryptates to already existing polymerization systems, Boileau and his coworkers extended their work to the development of new initiators which through the use of cryptates are soluble in low-dielectric constant solvents.41 Solutions of alkali metals and their organic complexes in solvents in which they are ordinarily either insoluble or only slightly soluble were investigated. The new species initiated the polymerization of butadiene, isoprene, styrene, methyl methacrylate, and 2-vinyl pyridine.41 For example, an alcoholate
will not ordinarily initiate the polymerization of styrene in benzene, but by adding [222] the polymerization took place instantaneously. Upon attempting polymerization of propylene sulfide by potassium thiocyanate in tetrahydrofuran, Boileau obtained no polymer after 72 hours at room temperature. Upon the addition of [222] to the system, 100% conversion of propylene sulfide to polymer was obtained after 72 hours at room temperature. The results show that the use of cryptates allows the initiation of the anionic polymerization of some monomers which do not polymerize under the same conditions without the complexing agents.

Kaempf et al. prepared initiators for radical anion-initiated polymerizations by placing tetrahydrofuran containing [222] in contact with an alkali metal mirror. The ratio of complexing agent to dissolved metal in the initiator was controlled by varying the time, \( t_c \), in which the THF solution was allowed to remain in contact with the metal mirror. When these initiators were used to polymerize styrene, polymers were obtained with number-average molecular weights much higher than expected. The molecular weights were lowered to a more reasonable value by increasing \( t_c \), but very broad molecular weight distributions were obtained.

Cryptates have also proven useful in the anionic polymerization of lactones. Deffieux and Boileau have shown that [222] increases the yields obtained by initiation with KOH, KCNS, CH₃OOK, KCl, or NaCl in polymerizations of
β-propiolactone and ε-caprolactone in toluene after 100 hours at room temperature. Using KOH as initiator and [222] as the ligand, the two workers obtained a yield of 61% for β-propiolactone in benzene after 2 days. In systems not containing [222], a yield of 48% after 20 days in toluene at 25°C has been attained by using a KOH concentration 30 times greater and a monomer concentration 2 times greater than that used by Deffieux and Boileau. When the KOH and β-propiolactone concentrations were increased respectively to 2500 and 9 times that used by Deffieux and Boileau, a yield of 62% was reached after 14 days at 10-15°C in systems using toluene as the solvent but containing no cryptate. The use of cryptates thus markedly increased the overall rate of polymerization for β-propiolactone. The increased rate has been ascribed to both an increase in the rate of initiation and an increase in the rate of propagation, but Deffieux and Boileau were unable to conduct a quantitative analysis in their systems due to the heterogeneous nature of the polymerizations.

Although crown ethers are not as powerful complexing agents as cryptates, they are many times more powerful than glymes in their cation binding ability. Facile syntheses of substituted crown ethers appeared several years before those for their unsubstituted analogs. For this reason, reported studies concerning possible applications of crown ethers in anionic polymerizations have dealt mainly
with the substituted derivatives of the complexing agents. Unsubstituted crown ethers have been shown, however, to be better complexing agents than those which are substituted. The unsubstituted structures are not only less bulky but also less rigid, allowing the ligand to wrap more easily around the cation. Unsubstituted crown ethers are now relatively easy to synthesize from commercially-available reagents and as a result may be purchased at relatively low cost compared to cryptates ($1-$2 per gram). Thus from an economic standpoint crown ethers have greater potential for utilization in industrial-scale polymerizations than cryptates.

Halasa and Cheng first reported the polymerization of conjugated dienes using a catalyst comprised of a sodium or potassium hydrocarbon in conjunction with a substituted crown ether. The workers utilized two substituted analogs of 18-crown-6, tricyclohexyl-18-crown-6 and bicyclohexyl-18-crown-6, which are not as effective complexing agents as the unsubstituted crown ether analog. Halasa and Cheng devised systems in which a sodium or potassium hydrocarbon was used in a proportion of 1-10 millimoles per 100 grams of monomer and a crown ether in a ratio of 0.01-1.0 millimoles per millimole of sodium or potassium hydrocarbon. Polymers having 65-85% 1,2-configuration were isolated. A higher degree of conversion and a broader molecular weight distribution were obtained in systems utilizing crown ethers than in those containing no crown. The crown ether-sodium
alkyl catalyst gave polymers with inherent viscosities between 2 and 10, whereas a lithium alkyl alone generally gave polymers with inherent viscosities no higher than 1. Halasa also demonstrated that temperatures as high as 150°C could be used in systems with bi- or tricyclohexyl-18-crown-6 in the presence of a metal alkyl, but cleavage of linear ethers occurred at temperatures higher than 60°C.

In further work, Halasa and Cheng discussed the benefits received from the utilization of substituted crown ethers in the homopolymerization of butadiene and the copolymerization of butadiene and styrene. Previous attempts to polymerize butadiene with organosodium in aliphatic hydrocarbon solvent have produced low molecular weight polymer and low conversion. When the polymerization was modified by the addition of bi- or tricyclohexyl-18-crown-6, polybutadiene was obtained in high conversion and high molecular weight. The conversion increased from 41% to 94.5% as the ratio of n-butylsodium to bicyclohexyl-18-crown-6 decreased from 25.0 to 5.3. The effect of crown ethers on conversion was explained in terms of stabilization of the growing allylic anion by chelation with the crown ether. Such chelation may stabilize the growing end of the polymer chain and prevent termination by disproportionation.

The alkyllithium-catalyzed copolymerization of butadiene and styrene in nonpolar solvents presents several problems. Butadiene has a slower polymerization rate than
styrene in homopolymerization, but a faster rate than styrene in copolymerization. As a result, in batch copolymerization the initial portion of the copolymer chain is mainly butadiene. As the butadiene is exhausted from the system, a block of polystyrene is formed at the end of the copolymer chain. When alkylsodium is substituted for alkyllithium, a copolymer of more randomized structure is obtained, but its low molecular weight prevents its use as a high-quality elastomer. Halasa and Cheng copolymerized butadiene and styrene using n-butylsodium modified by crown ethers. The workers obtained copolymers of high molecular weight, high conversion, and no block polystyrene. Surprisingly, the n-butylsodium to tricyclohexyl-18-crown-6 ratio showed no effect on the molecular weight of the copolymer over the ratio range of 11.3 to 113.0.

Alev et al. described the use of dicyclohexyl-18-crown-6 to prepare stable alkali metal solutions in low dielectric constant solvents. Unlike the n-butyllithium solutions used by Halasa, which are slightly soluble in nonpolar solvents in the absence of crown ethers, the metals themselves are totally insoluble. Polymerizations initiated by the metals in the absence of complexing agents are heterogeneous with the polymer forming on the surface of the metal. With the aid of dicyclohexyl-18-crown-6, stable solutions of sodium, potassium, rubidium, and cesium were prepared by Alev, which initiated the polymerization of
butadiene, isoprene, and methyl methacrylate. Conversions of 70% to 100% were obtained with the use of the substituted crown ether. The attained solutions avoided the inconvenience of heterogeneous reactions. The rate of polymerization increased considerably when dicyclohexyl-18-crown-6 was used in the polymerizations. 67

The influence of dibenzo-18-crown-6 on the kinetics of the anionic polymerization of β-propiolactone has been studied by Slomkowski and Penczek. 71 When lactones are polymerized anionically, low rates of polymerization are obtained at moderate temperatures. 72-74 As the reaction temperature is raised, side reactions such as termination and transfer increase considerably, resulting in lower yields. 74, 75 Slomkowski and Penczek used sodium acetate to initiate the polymerization of β-propiolactone, discovering that a 100-fold increase in the rate of polymerization could be obtained if the sodium counterion was complexed by dibenzo-18-crown-6. In order to obtain the optimum increase in rate, the workers employed molar ratios of crown ether to sodium acetate equal to or greater than 3. The substantial increase in the rate of polymerization allowed Slomkowski and Penczek to lower the temperature of reaction to 35°C, which decreased the rate of termination and transfer reactions. In the absence of the crown ether, no polymerization occurred at 35°C. 71

Yamada et al. 76 used unsubstituted 18-crown-6 to modify the polymerization characteristics of acrylic acid.
Theoretically, acrylic acid can polymerize to either poly (acrylic acid), which consists of carbon-carbon linkages as the main chain, or to a polyester as shown in Figure 1.

[Chemical structure of acrylic acid and polyester]

Figure 1. Two Possible Pathways for Polymerization of Acrylic Acid.

Although many attempts had been made over a period of years to convert acrylic acid to a polyester, all were unsuccessful until recently when the monomer was polymerized to form ester linkages in the backbone. Saegusa and his co-workers used triphenyl phosphine as a catalyst to form the ester. When sodium acetate was used as a catalyst, polymers of extremely low molecular weight were obtained in yields of only 22% after heating for 50 hours at 110°C. Yamada used 18-crown-6 in conjunction with potassium acetate, forming "naked" acetate, to prepare a high molecular weight polyester from acrylic acid. The addition of 18-crown-6 increased the yield to 99% and increased the molecular weight by a factor of 3. Yamada also found that sodium acetate appeared to be as active as potassium acetate when used as a catalyst. However, when sodium acetate was used in conjunction with
18-crown-6, the effect of the crown ether was not as clearly demonstrated as when potassium was the cation.\textsuperscript{76}

Suzuki \textit{et al.}\textsuperscript{79} have demonstrated a unique application of dicyclohexyl-18-crown-6 in the synthesis of a triblock copolymer of poly(methyl methacrylate) and poly(ethylene oxide) (PEO). The workers employed an initiator comprised of a disodium salt of poly(ethylene oxide) and the crown ether. In order for the resulting polymer to exhibit characteristics of a block copolymer, only a very high molecular weight salt of PEO could be utilized. Other workers had successfully utilized a disodium salt of low molecular weight PEO to initiate polymerization of methyl methacrylate in tetrahydrofuran,\textsuperscript{44} but no initiation could be obtained when high molecular weight PEO salts were used.\textsuperscript{80} When Suzuki used dicyclohexyl-18-crown-6 to increase the nucleophilicity of the high molecular weight PEO anion, the polymerization proceeded and PEO-\textsubscript{b}-PMMA was obtained in good yields (85-100\%). Suzuki has ascertained that the PEO-\textsubscript{b}-PMMA prepared in the presence of the crown ether has a higher syndiotactic triad content compared to that prepared in conventional methods, but has projected no hypothesis to explain the phenomena.\textsuperscript{79}

Orvik\textsuperscript{81} has studied the effects of 12-crown-4 and 18-crown-6 on the rates of oligomerization of ethylene oxide in butanol. Both 12-crown-4 and 18-crown-6 increased the rates of oligomerization when sodium hydroxide served as the catalyst, but no such increase could be attained when the
reaction was catalyzed by lithium hydroxide. Orvik concluded that the increase in rates was directly proportional to the strengths of complexation of the cation by the crown. The complexation apparently affected the rates by increasing both the proportion of free alkoxide ion and the reactivity of the ion pair. Orvik also discovered that the addition of the cyclic polyethers to the sodium hydroxide-catalyzed reaction caused a decrease in the amounts of higher adducts formed in the oligomerization, but no changes in product distribution occurred when 12-crown-4 was added to a reaction catalyzed by lithium hydroxide. 81

Dmowski and his coworkers have investigated the effects of 18-crown-6 on the anionic oligomerization of tetrafluoroethylene and hexafluoropropene. 82 Cesium fluoride was used to catalyze the reactions. When the crown ether was used in conjunction with the cesium fluoride in the oligomerization of hexafluoropropene, the rate of conversion of monomer to dimer and trimer increased markedly. Using tetrahydrofuran as solvent and cesium fluoride modified by 18-crown-6 as catalyst, the workers obtained the trimer of hexafluoropropene in yields higher than any previously reported. The increase in yields of oligomers was accompanied by a reduction in the formation of products resulting from the reaction of the monomer with the solvent. In contrast, the addition of the crown ether to systems used in the oligomerization of tetrafluoroethylene produced no marked effect on the rate of reaction, yield, or distribution of the various oligomers. 82
CHAPTER II

EXPERIMENTAL

Instrumentation

Proton nuclear magnetic resonance (NMR) spectra were obtained with a Varian Model T60-A or EM-360A spectrometer utilizing external trimethylsilane (TMS, 12% CH₃Cl solution) as a standard. A JEOL PFT-100 Fourier Transform Spectrometer was used to secure proton-decoupled ¹³C-NMR spectra by signal averaging (TMS internal standard). Infrared spectra (IR) were obtained with a Beckman Model IRIO Spectrophotometer. The 1601 cm⁻¹ absorption of polystyrene was used as a reference peak in all of the IR spectra. Cannon-Fenske Viscometer (ASTM size 50 and 100) were used in all viscosity measurements. The temperature of the viscometers was controlled to within ±5°C through use of a constant-temperature water bath.

Special Apparatus

The high reactivity of metal alkyls toward oxygen and water requires that the chemicals be handled under an inert atmosphere in anhydrous conditions. A Labconco Glove Box Model 50000 was utilized for this purpose. The box was modified to provide inlets and outlets for nitrogen (Linde, extra dry grade). Several containers of dessicant (CaCl₂ and anhydrous P₂O₅) remained open in the box to remove any
residual water. Before using the box, nitrogen was allowed to flow through the system for several minutes, after which the rate of flow was reduced considerably and the outlet closed. The slight positive pressure which resulted inside the box prevented the seepage of oxygen into the system from the surrounding atmosphere.

All polymerizations were carried out in heavy-walled pressure tubes (Ace Glass Co., outside diameter, 1"; length, 8"). In caprolactam polymerizations carried out at high temperatures and pressures, the tubes were sealed with crown caps. In polymerizations at room temperature (styrene, isoprene), the tubes were sealed through use of standard 16×25 mm rubber septums secured by strands of copper wire.

After the tubes had been charged and sealed in the glove box under nitrogen, the vessels were placed on a shaker manufactured by the Burrel Corporation. The shaking reduced the time of polymerization for isoprene.

**Chemicals**

All chemicals used in the syntheses of the various crown ethers were employed as obtained from the manufacturer. Isoprene (Aldrich, Gold Label 99+%), styrene (Eastman, 98%) and caprolactam (Aldrich, practical grade) were purified and dried using standard procedures. Solvents for the polymerizations were also dried and distilled before use. n-Butyllithium (Aldrich) was purchased as a 1.6 M solution in hexane. Sodium-tert-butyl alcoholate, which was used in
the preparation of n-butylsodium was purchased from Mine
Safety Appliances (MSA) Research Corporation.

All viscosity measurements were made either in benzene
(Fisher, Certified A.C.S.) or toluene (Fisher, Certified
A.C.S.) without further purification. 84-86

Safety Considerations

Several of the compounds used in this study present
various hazards which should be considered before their use
in the laboratory. Appropriate safety procedures should be
observed in handling these compounds in order to avoid per­
sonal injury. A few comments concerning each of these
hazardous chemicals and safety procedures are warranted.

Crown Ethers

All cyclic polyethers are potentially toxic to some
degree and should be handled with special care. Pedersen2-5
has reported that the approximate lethal dose for ingestion
by rats of dicyclohexyl-18-crown-6 (closely related in prop­
terties to 18-crown-6) is 300 mg/kg. No cumulative oral
toxicity resulted from a dose level of 60 mg/kg/day. When
the crown was placed on the eye in the form of a 10% propy­
lene glycol solution, some generalized corneal injury,
iridic injury, and conjunctivitis resulted. The crown may
also be absorbed rapidly through the skin, with doses of
130 mg/kg causing death of test animals. Because of these
properties, the chemical has been classified as an extreme
irritant.
Biological tests show that 12-crown-4 has detrimental effects on the human body. Leong and his coworkers have demonstrated on mice that inhalation exposure (0.5 to 1.0 ppm, 7 hr/day, 5 days/week) for 3 weeks resulted in marked atrophy of the testicles, prostrate gland, and seminal vesicles. The testicular atrophy remained for 4 months, while the other organs returned to normal appearance and size in 2-3 weeks. Rats which had been exposed to 12-crown-4 showed reversible degeneration of conditioned behavioral performance, reductions in food and water intake, growth retardation, and body emors.

**Benzene**

The National Institute for Occupational Safety and Health has released data which demonstrates that prolonged exposure to benzene increases the expected incidence of leukemia. Due to the evidence linking the chemical with leukemia, OSHA has enacted an emergency standard which reduces the present allowed level of 10 ppm of air to 1 ppm. The new standard also prohibits any worker from being exposed to benzene in concentrations in excess of 5 ppm average over a 15-minute period. Benzene should be used only with adequate ventilation and should be handled with care utilizing rubber gloves and protective goggles.

**Metal Alkyls**

The metal alkyls used in this study, more specifically \( n \)-butyllithium and \( n \)-butylsodium, are pyrophoric and may
ignite on contact with air. Therefore, the chemicals must be handled under an inert atmosphere with oxygen, water, and carbon dioxide being rigorously excluded. The storage containers for the metal alkyls should be clearly labelled indicating the pyrophoric nature of the chemicals and warning others of the danger associated with exposing the contents to air. Several reviews have recently been published describing techniques of handling air-sensitive materials which are both relatively simple and convenient. These techniques not only insure the safety of those working with the chemicals but also greatly deter the decomposition of the highly unstable compounds.

**Syntheses of Crown Ethers**

The crown ethers used in this study were synthesized using the approach of Cook, Liotta, et al. The approach, which is basically the same for all three ethers, includes the formation of the alkoxide of glycol ethers with a "template" metal base followed by an Sn2 reaction with a dichloride ether. A description of the procedure for synthesizing each of the crown ethers follows.

Recently, improved syntheses of unsubstituted crown ethers have been published. Dale and Daasvatn have utilized a boron trifluoride-etherate system with a template salt to control the cyclopolymerization of ethylene oxide to specific crown ethers. Johns and coworkers have produced 18-crown-6, 15-crown-5 in improved yields by substituting shorter
dichloride ethers in 2-fold excess along with longer glycol ethers into the procedures which follow.

Into a 5-liter, 3-neck round bottom flask, which was fitted with a magnetic stirrer, a condenser, and a ground-glass stopper, were placed 222.5g (1.48 mole) of triethylene glycol (Matheson) and 1 liter of commercial tetrahydrofuran (THF, Fisher, wet). A solution of 218.0 g (3.30 mole pure) of 85% potassium hydroxide pellets (Fisher) in 120 ml of water was added to the flask with stirring. The resulting solution was stirred for 30 min. at ambient temperature during which it turned a dark brown, and considerable heat was evolved. The ground-glass stopper in the flask was replaced by a 500-ml constant-pressure dropping funnel containing 279.6g (1.49 mole) of 3,6-dioxa-1,8-dichloroctane (triethylene glycol dichloride, Eastman) in 200 ml of THF, and the dichloride solution added to the reaction flask in a thin stream with stirring. The contents of the flask were then refluxed for 17 hrs., after which the THF was removed by rotary evaporation (aspirator pressure). The rotary evaporation bath temperature was then raised to ca. 70°C to remove the bulk of the water. To the residue of dark brown solid and liquid was added 1 liter of methylene chloride. The mixture was stirred, and the salts removed by filtration (aspirator suction) and washed with copious solvent. The methylene chloride solution was dried for 18 hrs using anhydrous MgSO₄.
The salt was filtered and washed with solvent, after which the CH₂Cl₂ was removed by rotary evaporation (aspirator pressure). The resulting solution was distilled under vacuum utilizing a Claisen distilling head with built-in cold finger, thermometer well, and Vigreux column. A cold trap cooled by a dry ice-acetone bath prevented low boiling liquids from being pulled into the vacuum pump. A low-boiling fraction was removed by slowly raising the temperature from 25°C to 124°C (0.25 mm). Before continuing the distillation, the cold trap should be inspected to insure that it is not plugged. Several workers have reported dangers associated with a clogged cold trap. If the trap is blocked, the system should not be opened to the atmosphere until the head and distilling flask have cooled. The possibility of a powerful explosion caused by the autoignition of p-dioxane exists if the system is opened before sufficient cooling.

As the distillation continued, 2 fractions were collected over a wide boiling-point range. The first fraction (125-140°C, 0.2 mm) consisted of relatively pure crown which crystallized on sitting. The second fraction, a dark-colored, solid-liquid slush consisting of relatively pure product, was collected from 140°C to 155°C (0.2 mm). A total of 159.7g (41%) of crude 18-crown-6 was obtained.

The 2 fractions were placed in separate erlenmeyer flasks with a Teflon-coated stirring bar and enough acetonitrile to cover the solid. Each fraction formed a crown-
acetonitrile complex. The flasks were then slowly heated in a hood with stirring until the reflux temperature was reached. Additional acetonitrile was added to the flasks until all of the solid dissolved. As the solution was cooled to room temperature with vigorous stirring, the white, crystalline crown-acetonitrile complex precipitated. Each erlenmeyer was capped with a rubber stopper, placed in an ice-acetone bath, and stirring continued to precipitate as much crown as possible. The fractions were then filtered using aspirator pressure, and the complex quickly sealed in a container. The liquid from the 2 filtrations was combined in a 1-liter round bottom flask, and the acetonitrile removed by rotary evaporation. The residue was purified by the complex recrystallization procedure described above using much smaller quantities of acetonitrile. The combined purified complex was placed in a 500-ml round bottom flask fitted with a Teflon-coated stirring bar and vacuum take-off. The flask was connected to a vacuum pump with a hose leading through a pump cold trap cooled by a dry ice-acetone bath. Low heat (40-50°C) and pressure (0.1 mm) were then applied to the stirred flask to remove the volatile acetonitrile. After 10-12 hours, a viscous oil remained which solidified on sitting to hygroscopic crystals of 18-crown-6. A total of 94.4 g (24% yield) of pure 18-crown-6 was collected from the synthesis. The product was characterized by: melting point (36.5°-38°C), NMR (sharp singlet at 3.45 ppm, CCl₄, external
and infrared spectroscopy (absorptions at 2875, 1450, 1120 cm\(^{-1}\)).

\textit{15-Crown-5}\(^6\)

A 3-liter, 3-neck round bottom flask was equipped with a magnetic stirrer and reflux condenser. Into the flask were added 500 ml of 1,4-dioxane and 79.5g (0.75 mole) of diethylene glycol (Aldrich). While the contents of the flask were stirred, a solution of 60g (1.50 mole) of NaOH (98\% pellets) in H\(_2\)O was added. The addition of the NaOH solution resulted in the immediate formation of a heavy, white precipitate and a slight warming of the flask. The mixture was allowed to stir at ambient temperature for ca. 20 minutes. Through use of a constant-pressure dropping funnel, a solution of 140g (0.75 mole) of 1,8-dichloro-3,6-dioxaoctane (Eastman) in 100 ml of dioxane was added to the flask. After refluxing the mixture for 24 hours, the solution was cooled, filtered, and the bulk of the solvent was removed by rotary evaporation (aspirator pressure). The residue was again filtered and the filtrate was dissolved in 500 ml of methylene chloride. The resulting solution was dried over anhydrous MgSO\(_4\), filtered, and the methylene chloride removed by rotary evaporation (aspirator pressure). Vacuum distillation of the residue gave 23.4g (14.2\%) of 15-crown-5 (boiling point, 100°-135°C at 0.2 mm Hg). The compound was characterized by: infrared spectroscopy (CCl\(_4\), 0.1 mm NaCl cell, absorptions at 2875, 1445, 1350, 1280, 1250, 1185, 975, 925 cm\(^{-1}\)), \(^1\)H-NMR (CCl\(_4\), 15-...
external TMS standard, sharp singlet at 3.58 ppm), and 13C-NMR (CDCl₃, internal TMS, proton decoupled, single peak at 70.621 ppm).

12-Crown-4

A 250 ml, 3-neck, round bottom flask was equipped with an internal thermometer, reflux condenser, and magnetic stirring bar. Into the flask were added 70 ml of dimethyl sulfoxide (DMSO) and 9.25 g (0.23 mole) of NaOH (98% pellets). The mixture was stirred for 5 minutes, after which 24.58 g (0.23 mole) of anhydrous lithium perchlorate (City Chem. Corp.) was added in a single portion. The solution which resulted was stirred for 10 minutes during which it attained a milky appearance and warmed to ca. 60°C. After the addition of a solution of 6.21 g (0.10 mole) of ethylene glycol (Fisher) in 15 ml of DMSO, the contents of the flask were stirred at ambient temperature for 15 minutes. Using a constant-pressure dropping funnel, a solution of 18.73 g (0.10 mole) of 1,8-dichloro-3,6-dioxaoctane (Eastman) in 15 ml of DMSO was then added in a thin stream. The system was heated at 110°C for 22 hours with stirring, after which the solution was cooled and filtered. The filtrate was added to 500 ml of distilled water. Four-200 ml aliquots of chloroform were used to extract the water solution. The combined extracts were dried over anhydrous magnesium sulfate, the salt filtered, and the chloroform removed by rotary evaporation (aspirator pressure). Vacuum distillation of the residue gave 2.33 g
(13.2%) of hygroscopic 12-crown-4 (boiling point 67-70°C at 0.5 mm Hg or 118-119°C at 15 mm Hg). The compound was characterized by: infrared spectroscopy (neat, NaCl plates, absorptions at 2925, 1465, 1365, 1280, 1250, 1130, 1100, 1095, 920 cm⁻¹), 'H-NMR (CDCl₃, external TMS, sharp singlet at 3.65 ppm), and ¹³C-NMR (CDCl₃, internal TMS, proton decoupled, single peak at 70.621 ppm).

**Drying of the Crown Ethers**

The crown ethers used in this study all exhibit very strong hygroscopic properties. Since the water present in the crowns is highly detrimental to the metal alkyl catalysts used in anionic polymerizations, various procedures for the removal of the water must be performed. A major portion of the water may be removed by allowing the crowns to stir over molecular sieve absorbent (Linde 4A Molecular Sieves) for 10-12 hours. The crown are then heated to ca. 50°C under high vacuum for several hours, sealed under vacuum, and stored in a dessicator under nitrogen or vacuum until ready for use in a dry box.

**Purification and Drying of Other Materials**

**Solvents**

The solvents were purified and dried using conventional methods.¹⁵,¹⁶ Both benzene and heptane were distilled from sodium metal to receiving flasks which had been dried in an oven at 120°C for 10-12 hours. The condenser used in the
distillations had also been dried under similar conditions. A container filled with dessicant was connected to the distillation apparatus so that any air entering the system passed through the dessicant and was dried. The solvents were stored in sealed containers until ready for use in a dry box.

**Monomers**

Caprolactam (Aldrich) was purified by recrystallizing twice from cyclohexane. Before using, it was placed in a vacuum dessicator at low pressure (0.25 mm Hg) for 48 hours.

Styrene (Eastman), as it is purchased from the manufacturer, is inhibited by 10-15 ppm 4-tert-butylpyrocatechol. The inhibitor was removed by shaking twice with 10% NaOH solution and thrice with distilled water. Anhydrous MgSO₄ was then used to dry the monomer. Finally, the styrene was distilled from sodium metal under vacuum (b.p. 33-35°C at 8 mm Hg) using an apparatus which had been dried in an oven at 120°C for 10-12 hours. Since styrene is capable of thermal polymerization, the distillation should be carried out under relatively low pressures.

Isoprene (Aldrich) may be freed from inhibitors in the same manner as styrene. The decontaminated isoprene was distilled from sodium, but no vacuum was necessary (b.p. 34°C at 760 mm). The monomers were placed in sealed containers in a dessicator and stored in a refrigerator until needed.
Quantitative Analysis of n-Butyllithium Solution

n-Butyllithium (Aldrich) was purchased in the form of a 1.6 M solution in hexane. The low stability of the compound forced the periodic determination of the actual concentration of n-butyllithium in the solution. On the average, this determination was made every two weeks. Although several procedures concerning the analysis of alkyllithium compounds have been published, the most commonly used method is that of Gilman and Cartledge. A description of the procedure follows:

A 3 ml aliquot of n-butyllithium solution was withdrawn by pipette using a suction bulb and added to 10 ml of ether. The solution was hydrolyzed with 10 ml of distilled water and titrated with 1.000 N HCl (Fisher, standard) using phenolphthalein as an indicator to give the total alkali present. Under an atmosphere of nitrogen, a second 3 ml aliquot was removed and added to 10 ml of ether containing 1 ml of 1,2-dibromoethane (Fisher). The solution was swirled gently and allowed to stand for 2 minutes, after which it was hydrolyzed with distilled water and titrated immediately with 1.000 N HCL. The difference between the two titrations gave the quantity of n-BuLi present in solution.

Care must be taken in titrating the latter solution so as to not overstep the endpoint. Vigorous shaking near the endpoint is recommended.
**Preparation of n-Butylsodium**

Organolithium compounds containing normal alkyl groups react with sodium-tert-butyl alcoholate to give a good yield of the alkylsodium compound in a high degree of purity. Thus n-butylsodium may be prepared from n-butyllithium in the following manner:

Under a nitrogen atmosphere in a dry box, a suspension of 0.0643 mole (6.173 g) of sodium-tert-butyl alcoholate (MSA Research Corp.) in 10 ml of dry heptane was placed in a 250 ml round bottom flask. The flask was cooled to 0°C through use of a dry ice bath. The flask was fitted with a constant-pressure dropping funnel, and 90 ml (0.0837 mole) of 0.93 M n-butyllithium solution in hexane (Aldrich) was added slowly to the flask under stirring. The addition of the first few ml of n-BuLi solution caused the alkoxide to partially dissolve. As more n-BuLi was added, n-butylsodium began to precipitate in the form of a fine, white powder. The reaction was completed by stirring for 1 hr at 0°C followed by 1 hr. at 30-40°C. The precipitate was then filtered under N₂, washed with dried heptane, dried overnight under vacuum, and stored in a vacuum dessicator in a dark glass container.

**Viscosity Measurements**

Into a 10 ml volumetric flask were weighed 100 mg. of well-dried polymer. Approximately 10 ml of solvent were added to the flask, and the vessel was placed in a constant-
temperature water bath equilibrated to 20° ± 0.5°C. After the solution acquired the temperature of the bath, the volumetric flask was filled to the graduation mark to give a final concentration of 10 g/l. The polymer solution was then filtered through a sintered glass filter into a clean dry test tube to remove any dust particles which might affect the measurements. Into the wide arm of a Cannon-Fenske viscometer were pipetted 5.0 ml of the solution. The viscometer was placed in a constant-temperature water bath until the temperature had equilibrated at 25° ± 0.5°C. A rubber suction bulb was attached to the small arm of the viscometer, and the solution pulled from the wide arm through the capillary to a point 2 cm above the top graduation mark on the small arm. Care was taken to exclude any air bubbles from the capillary of the instrument. The suction bulb was removed from the small arm, and a stopwatch was used to measure the time required for the meniscus to flow freely from the top graduation mark to a second mark which was a measured distance from the top mark. The measurement was repeated until 3 flow times were obtained which agreed within 0.2 sec.

The experiment was repeated using only the solvent in the viscometer. The flow times for the solvent and polymer solution were used to calculate the relative viscosity from the following equation:

\[ \eta_{rel} = \frac{(\text{solution flow time, sec.})}{(\text{solvent flow time, sec})} \]
Using the relative viscosity, the inherent viscosity was then calculated from the following relationship:

\[ \eta_{inh} = \ln \eta_{rel/C} \]

Where \( C \) was the concentration of the polymer in grams per 100 ml of solvent \((g/dl)\). Three solutions of different polymer concentrations \((C \leq 1.0 \text{ g/deciliter})\) were made, and the inherent viscosity of each was measured. A plot of \( \eta_{inh} \) vs. \( C \) was extrapolated to zero concentration with the intercept defined as the intrinsic viscosity \([\eta]\). Mark and Houwink\(^{102}\) have determined the relationship between the intrinsic viscosity and the molecular weight of the polymer as:

\[ [\eta] = K M^a \]

where \( K \) and \( a \) are constants specific for a particular polymer-solvent system and \( M \) is the polymeric molecular weight. The constants used in this study were as follows:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>@ 25°C</th>
<th>K</th>
<th>a</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>Benzene</td>
<td>(9.5 \times 10^{-5})</td>
<td>0.74</td>
<td></td>
<td>103, 104</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>Toluene</td>
<td>(5.02 \times 10^{-4})</td>
<td>0.67</td>
<td></td>
<td>105, 106</td>
</tr>
</tbody>
</table>

**Polymerization of Styrene Utilizing n-Butyllithium as Catalyst**

**Typical Styrene Polymerization\(^{15,16}\)**

In a dry box under a nitrogen atmosphere, a polymerization tube was charged with 9.0 ml of benzene, 5.0 ml (4.53 g, 43.3 mmoles) of styrene, and a previously-weighed sample of
crown ether (0.005-0.075 mmoles). The crown ether was transferred from a sealed vial to the tube by using three separate 2 ml aliquots of benzene as rinses. The rinses brought the total volume of benzene in the tube to 15 ml. Polymerizations which served as controls were carried out with no crown in the system. The tube was placed in a sand bath heated to relatively low temperatures (30°-40°C), and nitrogen was bubbled through the system for 5 min. The tube was then sealed with a rubber septum which was secured through use of a strand of copper wire. After the tube and contents had cooled to room temperature, an appropriate quantity of n-BuLi solution (0.70-0.75 mmoles of n-BuLi) was added to the system via a hypodermic syringe. In those systems which contained no crown, a red color rapidly developed and persisted. The color, which is due to the formation of styryl anions, could be quenched by oxygen, water, or methanol. In tubes containing crown ethers, an orange-yellow color developed instead of the expected red. The addition of n-BuLi also resulted in the evolution of considerable heat from tubes containing crown, while heat was given off at a much slower rate from systems containing no crown. After the addition of the catalyst, the tube was placed on a shaker for a specified amount of time to allow the reaction to reach completion. The polystyrene was isolated by precipitation in methanol and was placed under vacuum for 48 hours to dry. Intrinsic viscosities of the polymers were measured in benzene at 25°C.
Effect of Crown Ether Concentration on n-BuLi-Styrene-Benzene System

The polymerization described above serves as a model. To clarify the effect of crown ethers upon the molecular weight of a polymer, a series of experiments were run in which the concentration of a particular crown ether was varied while the other reagents were held at a constant concentration. Several polymerization tubes were thus charged with 15 ml of benzene, 5.0 ml (4.5 g, 43.3 mmols) of styrene, and 0.70 mmols of n-BuLi (concentration of 0.033 M) in the manner described above, but each tube contained a different quantity of 15-crown-5 as follows:

<table>
<thead>
<tr>
<th>Tube</th>
<th>15-Crown-5 (g)</th>
<th>15-Crown-5 (mmoles)</th>
<th>15-Crown-5 Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.0295</td>
<td>0.134</td>
<td>0.0064</td>
</tr>
<tr>
<td>3</td>
<td>0.0613</td>
<td>0.279</td>
<td>0.0133</td>
</tr>
<tr>
<td>4</td>
<td>0.0756</td>
<td>0.343</td>
<td>0.0163</td>
</tr>
<tr>
<td>5</td>
<td>0.0938</td>
<td>0.426</td>
<td>0.0203</td>
</tr>
<tr>
<td>6</td>
<td>0.1164</td>
<td>0.529</td>
<td>0.0252</td>
</tr>
<tr>
<td>7</td>
<td>0.1417</td>
<td>0.644</td>
<td>0.0307</td>
</tr>
<tr>
<td>8</td>
<td>0.1809</td>
<td>0.822</td>
<td>0.0391</td>
</tr>
<tr>
<td>9</td>
<td>0.2267</td>
<td>1.03</td>
<td>0.0490</td>
</tr>
</tbody>
</table>

Each polymerization was allowed to continue on a shaker for 24 hours at room temperature before the polymers were precipitated in methanol.

An additional series of polymerization tubes were charged with varying amounts of 12-crown-4 while the concentrations of styrene and n-BuLi were held constant at the previous levels. The tubes contained the following
concentrations of 12-crown-4:

<table>
<thead>
<tr>
<th>Tube</th>
<th>12-Crown-4 (g)</th>
<th>12-Crown-4 (mmoles)</th>
<th>12-Crown-4 Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>.0136</td>
<td>.077</td>
<td>.0037</td>
</tr>
<tr>
<td>3</td>
<td>.0389</td>
<td>.221</td>
<td>.0105</td>
</tr>
<tr>
<td>4</td>
<td>.0654</td>
<td>.372</td>
<td>.0177</td>
</tr>
<tr>
<td>5</td>
<td>.0931</td>
<td>.529</td>
<td>.0252</td>
</tr>
<tr>
<td>6</td>
<td>.1360</td>
<td>.773</td>
<td>.0368</td>
</tr>
</tbody>
</table>

The reaction in each tube was allowed to continue on a shaker for 24 hours at room temperature to ensure complete conversion to polymer.

**Effect of n-BuLi Concentration on Polymerization of Styrene**

O'Driscoll and Tobolsky\(^{16}\) have reported that the intrinsic viscosity of polystyrene varies approximately inversely with n-BuLi concentration in the reaction mixture. In order to confirm the report, a series of polymerizations were conducted in which the styrene concentration was held constant while the n-BuLi concentration was varied. Tubes were thus charged with 15 ml of benzene and 5.0 ml (4.5 g, 43.3 mmoles) of styrene in the manner described above, but a different quantity of n-BuLi was added to each tube as follows:

<table>
<thead>
<tr>
<th>Tube</th>
<th>n-BuLi Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.70</td>
</tr>
<tr>
<td>2</td>
<td>.98</td>
</tr>
<tr>
<td>3</td>
<td>1.96</td>
</tr>
<tr>
<td>4</td>
<td>2.94</td>
</tr>
</tbody>
</table>

The polymerizations were allowed to continue with agitation
for 24 hours at room temperature before precipitation in methanol.

A second series of polymerizations were conducted in which the concentration of \( \text{n-BuLi} \) was varied, but a constant quantity of 15-crown-5 was added to each tube. Each tube contained 15 ml of benzene, 5.0 ml (4.5 g, 43.3 mmoles) of styrene, 0.042 g (0.19 mmoles) of 15-crown-5, and a quantity of \( \text{n-BuLi} \) as follows:

<table>
<thead>
<tr>
<th>Tube</th>
<th>( \text{n-BuLi Concentration (mmoles)} )</th>
<th>( \text{n-BuLi Concentration (M)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.70</td>
<td>.033</td>
</tr>
<tr>
<td>2</td>
<td>.98</td>
<td>.045</td>
</tr>
<tr>
<td>3</td>
<td>1.96</td>
<td>.082</td>
</tr>
<tr>
<td>4</td>
<td>2.94</td>
<td>.113</td>
</tr>
</tbody>
</table>

The polymerizations were conducted for 24 hours at room temperature before termination via precipitation in methanol.

**Effect of Crown Ethers on Rate of Styrene Polymerization**

To define the effects of crown ethers on the overall rate of polymerization of styrene, a study was made to determine the conversion of monomer to polymer as a function of time. A series of 7 tubes, serving as blanks, were charged with 15 ml of benzene and 5.0 ml (4.5 g, 43.3 mmoles) of styrene. Each tube was sealed with a rubber septum and 0.98 mmoles of \( \text{n-BuLi} \) was added as a 1.6 M heptane solution via a hypodermic syringe. The addition of the \( \text{n-BuLi} \) marked time zero. After 5 minutes had passed, the contents of a
single tube were precipitated in excess methanol. Likewise, the contents of the remaining 6 tubes were precipitated at the end of 10, 15, 30, 45, 90, and 180 minutes. The resulting polymers were washed, dried under vacuum for 48 hours, and weighed. The per cent conversion of each of the reactions was then calculated.

A second series of blanks were prepared by adding 2.5 ml (2.26 g, 21.6 mmoles) of styrene to each of 4 polymerization tubes containing 15 ml of benzene. After sealing the tubes, 0.49 mmoles of n-BuLi were added to each of the 4 tubes. The reaction in 1 tube was terminated at the end of 5 minutes. The reactions in the remaining 3 tubes were ended after 10, 30, and 60 minutes. The conversion to polymer was calculated in each case.

A third series of polymerization tubes were charged with 15 ml of benzene, 5.0 ml (4.5 g, 43.3 mmoles) of styrene, and 0.031-0.034 g (0.19-0.20 mmoles) of 12-crown-4. Each of the 5 tubes in the series was sealed with a septum, and 0.74 mmoles of n-BuLi was added to each via a syringe. At the end of 10 seconds, the reaction in one tube was terminated by injecting methanol into the system. The polymerizations in the remaining 4 tubes were ended after 20, 45, 90, and 130 seconds. The polymers were washed and dried, and the per cent conversion calculated for each case.

Preliminary studies using 15-crown-5 in the n-BuLi-styrene-benzene system indicated that 100% conversion to
polymer was attained rapidly. Four tubes were charged with 15 ml of benzene. Styrene and 15-crown-5 were added to the tubes in the following quantities:

<table>
<thead>
<tr>
<th>Tube</th>
<th>Styrene (g)</th>
<th>15-Crown-5 (g)</th>
<th>15-Crown-5 (mmoles)</th>
<th>15-Crown-5 Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.53</td>
<td>0.0163</td>
<td>0.074</td>
<td>0.0035</td>
</tr>
<tr>
<td>2</td>
<td>4.53</td>
<td>0.0416</td>
<td>0.189</td>
<td>0.0090</td>
</tr>
<tr>
<td>3</td>
<td>2.26</td>
<td>0.0138</td>
<td>0.063</td>
<td>0.0034</td>
</tr>
<tr>
<td>4</td>
<td>2.26</td>
<td>0.0394</td>
<td>0.179</td>
<td>0.0097</td>
</tr>
</tbody>
</table>

The tubes were sealed, and 0.74 mmoles of n-BuLi were added to each tube. Polymerization was allowed to continue in Tubes 1 and 2 for 10 sec. at which time 10 ml of methanol were injected into each tube. The reactions in Tubes 3 and 4 were continued for 15 and 30 sec., respectively. The polymers were recovered from each of the four tubes, and the percent conversion calculated for each reaction.

**Polymerization of Isoprene Utilizing n-Butyllithium as Catalyst**

**Typical Isoprene Polymerization**

Into a polymerization tube which had been dried at 120°C for 8-10 hours were placed under nitrogen 9.0 ml of dried and distilled heptane, 5.0 ml (3.4 g, 50.0 mmoles) of isoprene, and a previously-weighed sample (0.048-0.127 mmoles) of dry crown ether. The crown ether was transferred from a sealed vial to the tube by using three separate 2 ml aliquots of heptane, making the total volume of heptane in the tube 15 ml. The tube was placed on a heated sand bath until
vigorous boiling had occurred. Nitrogen was bubbled through the tube as it heated. After the system had been purged through use of the heat and nitrogen, the tube was sealed with a rubber septum and a strand of copper wire was used to secure the septum in place. After the tube and contents had cooled to room temperature, an appropriate quantity (1.40-1.50 mmoles) of n-BuLi/hexane solution was added to the system via a hypodermic syringe. A pale yellow color developed within minutes of the addition of the catalyst. The tube was then placed on a shaker, and the contents allowed to react for a specified length of time (usually 48 hours). The reaction was terminated by pouring the contents of the tube into excess methanol. The precipitated polymer was dried under vacuum for 48 hours and stored for characterization at a later time.

Effect of Crown Ethers Concentration on Polymerization of Isoprene

As in the study of the polymerization of styrene, a series of isoprene polymerizations were run in which only the quantity of crown ether was altered. Thus, a series of tubes were charged in the manner described above with 15 ml of heptane, 5.0 ml (3.4 g, 50 mmoles) of isoprene, and 1.49 mmoles of n-BuLi (n-BuLi concentration in reaction mixture = 0.075 M). A different quantity of 15-crown-5 was then added to each tube as follows:
The tubes were placed on a shaker, and the reactions were continued for 48 hours before termination via precipitation in methanol.

A second series of polymerizations were conducted in which 12-crown-4 was substituted for 15-crown-5. The quantities of heptane, isoprene, and n-BuLi added to each tube remained identical with the 15-crown-5/isoprene series, and 12-crown-4 was added to each tube as follows:

<table>
<thead>
<tr>
<th>Tube</th>
<th>12-Crown-4 (g)</th>
<th>12-Crown-4 (mmoles)</th>
<th>12-Crown-4 Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.0133</td>
<td>0.075</td>
<td>0.0036</td>
</tr>
<tr>
<td>3</td>
<td>0.0345</td>
<td>0.196</td>
<td>0.0093</td>
</tr>
<tr>
<td>4</td>
<td>0.0416</td>
<td>0.236</td>
<td>0.0112</td>
</tr>
<tr>
<td>5</td>
<td>0.0898</td>
<td>0.510</td>
<td>0.0243</td>
</tr>
</tbody>
</table>

The reactions were allowed to continue with agitation for 48 hours, after which the polymers were precipitated in methanol.

**Effect of Crown Ethers on Overall Rate of Isoprene Polymerization**

Five polymerization tubes were charged with 15 ml of heptane and 5.0 ml (3.4 g, 50 mmoles) of isoprene in the
manner described in the previous section. Each of the tubes was sealed with a septum, after which 1.49 mmol of n-BuLi were injected into each of the systems. The addition of the n-BuLi marked time zero. At the end of 6 hours, the reaction in a single tube was terminated by precipitating the polymer in excess methanol. The reactions in the remaining 4 tubes were stopped after 22, 30, 46, and 66 hours. The resulting polymers were washed, dried under vacuum for 48 hours, and weighed. The percent conversion for each reaction was calculated.

A second set of 5 tubes were charged with 15 ml of heptane and 5.0 ml (3.4 g, 50 mmol) of isoprene. Before sealing the tubes, 0.02 g (0.114 mmol) of 12-crown-4 was added to each tube. The injection of 1.45 mmol of n-BuLi into each tube marked time zero. After 2 hours, the reaction in 1 tube was terminated by precipitation of the polymer in methanol. The remaining 4 polymerizations were ended after 4, 6, 8, and 23 hours. The polymers were dried and weighed. The conversion to polymer was calculated in each case.

The experiment was repeated with a third set of 5 tubes, and with 15-crown-5 substituted for 12-crown-4. The quantities of heptane, isoprene, and n-BuLi remained the same as in the two series above, and each tube contained 0.025 g (0.114 mmol) of 15-crown-5. The five reactions were terminated after 1.5, 3, 5, 6, and 10 hours, respectively. After washing and drying the polymers, the
per cent conversion was calculated for each reaction.

**Attempted Polymerization of Styrene Utilizing n-Butylsodium as Catalyst**

Due to the insolubility of n-BuNa in many common organic solvents, polymerizations utilizing the organo-sodium compound as an initiator are normally heterogeneous. Crown ethers have the ability to increase the solubility of ionic species in nonpolar, aprotic solvents. Preliminary studies indicated that molar ratios of 12.0-16.0:1.0 (18-crown-6 to n-BuNa) were required to solubilize n-BuNa in heptane. Therefore, to avoid the inconvenience of a heterogeneous polymerization, molar ratios in the indicated range were used in reaction mixtures. Benzene was originally used as a solvent for the system, but the reactivity of n-BuNa towards the aromatic medium dictated that heptane be used in the polymerization attempts. A typical attempt to initiate polymerization of styrene was conducted as follows:

In a dry box under a nitrogen atmosphere, a polymerization tube was charged with 15 ml of heptane, 5.0 ml (4.5g, 43 mmoles) of styrene, and 0.42g (1.59 mmole) of 18-crown-6. Nitrogen was bubbled through the tube for 5-10 minutes to purge the system of oxygen. A pre-weighed sample of n-BuNa (0.008g, 0.10 mmole) was transferred as a solid from a sealed vial to the polymerization tube. The tube was
sealed with a rubber septum and agitated for 48 hours. The initiator dissolved within minutes after its addition to the tube; however a dark brown-black precipitate formed within 7-12 minutes of the dissolution of the \( n-BuNa \). No polymer was obtained from any of the attempted polymerizations.

**Attempted Polymerization of Isoprene Utilizing \( n-BuLi \) as Catalyst**

Various attempts were made to initiate the polymerization of isoprene utilizing \( n-BuNa \) in conjunction with 18-crown-6 as the catalyst. The attempts were hindered by the low solubility of the organosodium compound and its high reactivity toward the polyether. Systems were investigated which contained molar ratios of crown to \( n-BuNa \) in the range of 0.1-20:1. No polymer was obtained from any of the reactions. A typical attempted polymerization was conducted as follows:

In a dry box under a nitrogen atmosphere, a polymerization tube equipped with a magnetic stirring bar was charged with 15 ml of heptane, 5.0 ml (3.4g, 50 mmoles) of isoprene, and a previously-weighed sample of 18-crown-6 (0.01-0.4g, 0.03-1.6 mmole). Nitrogen was bubbled through the tube for 5-10 minutes before it was sealed with a rubber septum. An appropriate quantity of \( n-BuNa \) (0.1-0.8 mmole) was injected with stirring as a dispersion in heptane. Within minutes a dark brown precipitate formed, and no initiation of polymerization occurred. The mixture was stirred for 48 hours
after which it was poured into excess methanol. No polymer was obtained from any of the mixtures.

**Modification of Caprolactam Polymerization by Crown Ethers**

**Typical Caprolactam Polymerization**

The desired quantity of dried and purified caprolactam (usually 25g) was melted under nitrogen in a polymerization tube at temperatures between 80°-100°C (m.p. of caprolactam, 69°C). A sodium dispersion in xylene corresponding to 0.04-0.08% of sodium based on caprolactam was prepared and added to the molten monomer. The resulting mixture of caprolactam and the sodium salt of caprolactam could be maintained for several hours at 80-100°C without loss of activity. Immediately before the polymerization, a pre-weighed quantity of 18-crown-6 was added to the sample and the tube sealed with a crown cap. In attempts to polymerize the mixture, the tube was brought to a higher temperature (150°C-260°C) as quickly as possible by plunging the tube in a molten Wood's metal bath. Attempts were made to polymerize the mixture at several specific temperatures in the given range.

In control samples which contained no crown, the tubes were sealed after the addition of the sodium dispersion and raised to a temperature of 255°-265°C to initiate polymerization. The expected time lapse from the insertion of the tube into the high-temperature bath to the completion of polymerization was 5-10 minutes. The tubes were then cooled
quickly with water, the caps removed, and the contents placed in storage containers until characterization.

**Attempted Polymerization of Caprolactam at Lower Temperatures**

Attempts to polymerize caprolactam systems containing 18-crown-6 at temperatures between 250°C and 260°C resulted in discoloration of the reaction mixture and no polymer. Halasa and Cheng\(^{25}\) have reported 150°C as the maximum temperatures at which substituted crown ethers may be used in solution polymerization reactions. Although the higher temperatures are required to polymerize caprolactam systems containing no crown and to avoid premature solidification, it was postulated that the addition of crown ethers to the reaction would allow the polymerization to proceed at lower temperatures due to higher anion activation. A series of 4 polymerization tubes were charged with 15g (133 mmoles) of caprolactam, 0.019-0.020g (0.82 mmoles-0.87 mmoles) of sodium metal, and 0.30-0.32g (1.14-1.24 mmoles) of 18-crown-6 in the manner described in the preceding section. The tubes were sealed with metal caps and placed in a molten Wood's metal bath at a specific temperature as follows:

<table>
<thead>
<tr>
<th>Tube</th>
<th>Na (g)</th>
<th>18-Crown-6 (mmoles)</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0190</td>
<td>1.18</td>
<td>200</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>0.0195</td>
<td>1.24</td>
<td>180</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>0.0195</td>
<td>1.14</td>
<td>150</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>0.0201</td>
<td>1.21</td>
<td>110</td>
<td>48</td>
</tr>
</tbody>
</table>

At the end of the specified reaction time, the tubes were
cooled and the contents poured into storage containers. Discoloration of the reaction mixture had occurred in every instance. A hot $\text{H}_2\text{O}$ extraction revealed that no polymer was present in any of the samples.
CHAPTER III

RESULTS AND DISCUSSION

Effect of 15-Crown-5 on the n-Butyllithium-
Styrene-Benzene Polymerization System

Effect of 15-Crown-5 on Molecular Weight

The addition of catalytic quantities of 15-crown-5 resulted in dramatic modifications in the polymerization characteristics of the n-butyllithium-styrene-benzene system. When n-butyllithium was introduced into systems containing no 15-crown-5, an orange-red color quickly developed. The orange-red color of the system converted to a yellow tint as the quantity of 15-crown-5 was increased. The colors indicated carbanion formation, 15,16 while the color change with crown concentration reflected an alteration of electron density around the carbanion by virtue of the counterion complexation.

The complexation of the counterion was further evidenced by the results of a molecular weight study consisting of a series of polymerizations in which only the concentration of 15-crown-5 was altered. All polymerizations in the study were conducted under the same conditions with the exception that the crown ether: n-butyllithium molar ratio was gradually raised from 0:1 to 1.25:1. The resulting
polymers were analyzed for percent conversion and inherent viscosity. All systems resulted in 100% conversion to polymer, but a plot of $\eta_{\text{inh}}$ vs. mmoles of 15-crown-5 used in the polymerizations resulted in a bell-shaped curve with a maximum $\eta_{\text{inh}}$ occurring at a 0.5:1 crown ether to n-butyl-lithium ratio (Figure 2). The increased $\eta_{\text{inh}}$ (and hence molecular weight, Figure 3) apparently resulted from the complexation of the lithium cation by the crown ether. The chelation of the lithium cation apparently stabilizes the carbanion at the end of the growing chain, thus precluding termination via disproportionation and favoring propagation.

Two possible explanations exist for the relationship shown in Figures 2 and 3. First, the complexes formed by crown ethers do not always exhibit a 1:1 stoichiometry of macrocycle to cation. Complexes with stoichiometries of 2:1 and 3:2 (crown:cation) have been prepared and isolated. Also, 1:2 (crown:cation) complexes have been synthesized with 2 cations embedded in 1 ring. The plots indicate that the optimum molar ratio of 15-crown-5 to n-BuLi in the utilized polymerization system was 0.5:1. The results thus lend indirect credence to the possibility that a 1:2 complex exists between the crown ether and the cation. Such a theory suggests that as the molar ratio of crown to n-BuLi was gradually raised to 0.5:1, the chelation of the lithium cation resulted in enhanced propagation of the growing chains due to increased stability and more
Figure 2. Effect of 15-Crown-5 on $\eta_{inh}$ of Polystyrene at a set 0.70 Mmoles of $n$-BuLi. Values for $\eta_{inh}$ were obtained from 1% polymer solutions in benzene at 25°C.
Figure 3. Effect of 15-Crown-5 on Molecular Weight of Polystyrene at a Set 0.70 Mmoles of n-BuLi.
localized charge and thus an increase in molecular weight of the polymer. Further addition of 15-crown-5 (molar ratios greater than 0.5:1) resulted in a decrease of the molecular weight from the optimum value to the same low values obtained from systems containing no crown. The possibility exists that the addition of the larger quantities of the complexing agent increased the concentration of cleavage products from the attack on the ether linkages of the crown by n-BuLi. The products from the crown degradation would be expected to react with the growing polymer chains, prematurely terminating the chain growth and thus lowering the molecular weight.

The second possible explanation for the shape of the curves is based on the existence of a 1:1 complex in the polymerization systems. Although the complexing ability of 15-crown-5 has been investigated, no reports of the isolation and evaluation of 15-crown-5/lithium complexes have been published. Anet, Dale, and coworkers have prepared crystalline 1:1 complexes of a smaller crown ether, 12-crown-4, with several lithium salts. The 1:1 complex theory attempts to explain the shape of the curves from a statistical viewpoint and applies only to polymerizations reaching 100% conversion to polymer. One n-BuLi molecule initiates one growing polymer chain. When no crown ether was present in the system, all n-BuLi molecules were equivalent and initiated polymer chains which grew to a specific molecular weight in a typically narrow molecular weight distribution.
small amounts of 15-crown-5 (molar ratios of crown to \( n\text{-BuLi} \) less than 0.5:1) were added to the system, some fraction of the lithium cations were complexed while a larger portion remained uncomplexed. The growing polymer chains with complexed cations at their ends grew to longer lengths than uncomplexed charged ends due to faster kinetics and chelation stabilization, raising the average molecular weight until an optimum was reached. When molar ratios greater than 0.5:1 (crown: \( n\text{-BuLi} \)) were used, the majority of growing chains had complexed cations at their ends. The complexed chains grew faster than those associated with uncomplexed cations, but with the rapid depletion of, and competition for, monomer being the limiting factor in their growth. Since the number of complexed chain ends in these systems was greater than the number in the optimum system (molar ratio of crown to \( n\text{-BuLi} \), 0.5:1), each polymer chain contained fewer monomer molecules due to rapid monomer depletion, and the average molecular weight dropped from its peak value. In those systems employing a molar ratio of crown to \( n\text{-BuLi} \) equal to unity, all initiator molecules were again near equivalence (nearly all complexed) and the chains grew to the molecular weight experienced when none were complexed. In the completely uncomplexed systems, limitation of molecular weight was thus due to chain end instability to disproportionation and susceptibility to termination by impurities. In systems in which all the counterions were complexed, the 1:1
complex theory dictates that the depletion of monomer prevented the complexed chain ends from growing to the long lengths required for high molecular weight.

The molecular weight of polystyrene produced from the \( n\text{-BuLi}\)-styrene-benzene system proved to be dependent also on the concentration of \( n\text{-BuLi} \) used in the polymerizations. In polymerizations which contained no crown, the molecular weight of the polymer varied approximately inversely with the concentration of \( n\text{-BuLi} \). The addition of a constant quantity of 15-crown-5 to the polymerizations containing various concentrations of \( n\text{-BuLi} \) also resulted in a decrease in molecular weight with increasing \( n\text{-BuLi} \) concentration (Figure 4). The curve utilizing the crown ether in a similar experiment had the same shape as the curve without crown, but the molecular weights were all higher at set \( n\text{-BuLi} \) concentrations for the crown system. The largest molecular weight was observed in the system containing the smallest amount of \( n\text{-BuLi} \) (molar ratio crown to \( n\text{-BuLi} \), 1:3.7). As the concentration of \( n\text{-BuLi} \) was increased (molar ratio crown to \( n\text{-BuLi} \), 1:15), the effect of the crown ether decreased, and the 2 curves approached the same molecular weight as the mmoles of \( n\text{-BuLi} \) approached 3.0.

**Effect of 15-Crown-5 on Rate of Polymerization**

The overall rate of polymerization in the \( n\text{-BuLi}\)-styrene-benzene system increased dramatically upon the addition of 15-crown-5. In a reaction containing no crown ether,
Figure 4. Effect of Concentration of \( n \)-BuLi on \( \eta_{\text{inh}} \) of Polystyrene.
15 ml of benzene, 5.0 ml (43 mmoles) of styrene, and 0.74 mmoles of n-BuLi, 100% conversion to polymer was attained after 20 minutes. Upon the addition of 0.189 mmoles (0.0416g) of 15-crown-5 to the system, complete conversion to polymer was realized in less than 10 seconds (least measurable time under the employed experimental procedure). The addition of 0.074 mmoles (0.0163g) of 15-crown-5 resulted in 92.5% conversion to polystyrene after 10 seconds.

The rate of polymerization decreased as the concentration of styrene was lowered. When 2.5 ml (22 mmoles) of styrene were added to 15 ml of benzene and 0.74 mmoles of n-BuLi, 71% conversion to polymer was obtained after 1 hour. When 0.0627 mmoles (0.0138g) of 15-crown-5 were added to the system, polystyrene was obtained in a yield of 50% after only 15 seconds. When the quantity of 15-crown-5 added to the system was raised to 0.179 mmoles (0.0394g), 90% conversion to polymer resulted after 30 seconds.

No attempts were made to determine whether the increase in overall rate was due to an increase in rate of initiation or rate of propagation. Deffieux and Boileau\textsuperscript{47} used cryptates to obtain increased rates in anionic polymerizations. The workers credited the increased overall rate to an increase in both the rate of initiation and rate of propagation, but presented no experimental evidence to verify the theory. Although the rates of initiation and propagation for the n-BuLi-styrene-benzene system were not defined in the current
Figure 5. Overall Rate Study for Styrene Polymerization Systems Containing No Crown Ether.

(Styrene concentration for Curve 1 = 2.0 M;
Styrene for Curve 2 = 1.0 M)
research, the magnitude of the increased rate experienced when 15-crown-5 was used to modify the system suggested that the complexing agent affected both the rate of initiation and rate of propagation.

The decreased times of reaction obtained through the use of 15-crown-5 compare favorably with those reported by Boileau et al. The workers employed an alcoholate modified by cryptates to initiate the polymerization of styrene in benzene. The addition of the relatively expensive cryptate (more than $100 per gram) to the system allowed the polymerization to occur instantaneously. As reported earlier 100% conversion to polymer was obtained from the n-BuLi-styrene-benzene system in 10 seconds through the use of 15-crown-5. The results indicate that 15-crown-5 is capable of competing with cryptates in producing beneficial effects in anionic polymerization systems. From an economic standpoint, 15-crown-5 ($1.59 per gram) has a much greater potential for utilization in industrial-scale polymerizations than the higher-priced cryptates.

The potential of increased production of industrial polystyrene through use of 15-crown-5 in anionic polymerizations exists due to the extremely rapid reaction rates effected by the complexing agent. In addition, the use of 15-crown-5 in conjunction with n-BuLi may allow the in-mold polymerization of polystyrene. The highly increased rate of polymerization and the ability to "tailor" the molecular
weight by simply adjusting the crown concentration offer molding capabilities.\textsuperscript{22}

**Effect of 12-Crown-4 on the n-Butyllithium-Styrene-Benzene Polymerization System**

**Effect of 12-Crown-4 on Molecular Weight**

The addition of 12-crown-4 to the n-BuLi-styrene-benzene system resulted in modifications of the polymerization similar to those experienced when 15-crown-5 was used as a complexing agent. A variation of the color of the reaction mixture from orange-red to yellow in systems containing 12-crown-4 indicated the complexation of the lithium cation. Data from the following molecular weight study, however, indicated that 12-crown-4 apparently does not complex the lithium cation as well as 15-crown-5.

A series of polymerizations were conducted in which only the concentration of 12-crown-4 was varied. Each polymerization was carried to completion, and the resulting polymers analyzed for inherent viscosity. The molecular weight for each polymer was calculated using the derived intrinsic viscosity and the relevant constants for the Mark-Houwink equation from the literature.\textsuperscript{103,104} A plot of molecular weight vs. mmoles of 12-crown-4 used in each polymerization resulted in a bell-shaped curve (Figure 7) similar in shape to that obtained when 15-crown-5 was used in the system (Figures 2 and 6). The maximum average molecular weight, however, for the 12-crown-4 plot was 31,400g, while an average
Figure 6. Effect of 12-Crown-4 on Molecular Weight of Polystyrene at a β et 0.70 Mmoles of n-BuLi.
Figure 7. Comparison of Effects of 15-Crown-5 (Curve 1) and 12-Crown-4 (Curve 2) on Molecular Weight of Polystyrene. (Each reaction contained 0.70 Mmoles of n-BuLi).
molecular weight of 36,500g was reached using 15-crown-5 as a complexing agent. The results serve as direct evidence that 15-crown-5 activates the n BuLi catalyst in anionic polymerizations more efficiently than does 12-crown-4.

The bell-shaped curve with its optimum molecular weight at a molar ratio of 12-crown-4 to n-BuLi of 0.5:1 may be explained by either of the two postulations which were applied earlier to the 15-crown-5 system (see pp. 54-59). The first theory is based on the existence of a 1:2 (crown:cation) complex. The second hypothesis explains the shape of the curve while maintaining the existence of a 1:1 complex between the crown and the lithium cation. The second theory is supported by the work of Anet, Dale, and coworkers who have prepared crystalline 1:1 complexes of 12-crown-4 with several lithium salts.

Effect of 12-Crown-4 on Rate of Polymerization

When 12-crown-4 was introduced into the n-BuLi-styrene-benzene system, the rate of polymerization increased substantially. Each of 5 polymerization tubes were charged with 15 ml of benzene, 5.0 ml (43 mmoles) of styrene, 0.19-0.20 mmoles (0.031-0.034g) of 12-crown-4, and 0.74 mmoles of n-BuLi. At the end of a specified reaction time, the polymerizations were terminated with methanol, and the percent conversion for each reaction calculated. The results are shown graphically in Figure 8. When 12-crown-4 was omitted from the system, 17% conversion to polystyrene was
Figure 8. Overall Rate Study for Polymerization of Styrene Using 12-Crown-4. Each Reaction contained 0.035g of 12-Crown 4 (0.01 M).
obtained after 5 minutes, 55% conversion after 10 minutes, and 94% conversion after 15 minutes.

The addition of 12-crown-4 thus produced dramatic effects on the rate of polymerization in the n-Bu-Li-styrene-benzene system. The effects, however, were not of the same magnitude experienced when 15-crown-5 was used in the polymerizations (reaction times less than 10 sec. in the optimum defined 15-crown-5 systems). Although 12-crown-4 has been projected from theoretical considerations to be a good complexing agent for lithium, recent discoveries indicate that in practice unsubstituted 12-crown-4 is not as effective in complexing lithium as theory indicated. Comparison of the effects of both 12-crown-4 and 15-crown-5 on the n-BuLi-styrene-benzene polymerization system indicate that 15-crown-5 activates the n-BuLi catalyst more efficiently in anionic polymerizations than does 12-crown-4. Orvik has studied the effects of 12-crown-4 on the rate of oligomerization of ethylene oxide in butanol. The 12-membered complexing agent was unable to effect an increase in the rate of an oligomerization catalyzed by lithium hydroxide, while 18-crown-6 did increase the rate of reaction for a sodium hydroxide-catalyzed system. Orvik concluded that the increase in rate was directly proportional to the strength of complexation of the cation by the crown.
Effect of 15-Crown-5 on n-Butyllithium-Isoprene-Heptane Polymerization System

Effect of 15-Crown-5 on Molecular Weight

The addition of extremely small quantities of 15-crown-5 to the n-BuLi-isoprene-heptane polymerization system resulted in an increase in the molecular weight of the resulting polyisoprene. In polymerizations utilizing molar ratios of crown to n-BuLi less than or equal to 0.17:1.0, complete conversion to polymer was obtained, and the molecular weight of the polyisoprene increased as the molar ratio was gradually raised (Figure 9). However, in polymerizations where molar ratios of crown to n-BuLi were greater than 0.17:1.0, the addition of n-BuLi via a hypodermic syringe to the system resulted in the immediate precipitation of a yellowish-brown solid. The precipitation of the solid usually marked the termination of the reaction, although polyisoprene was obtained from a few such systems in extremely low yields (< 10%).

The appearance of the precipitate caused by an increase in the concentration of crown ether aroused interest concerning the solubility of 15-crown-5 in heptane. Although no quantitative data has been published to the author's knowledge concerning the solubility of crown ethers in normal hydrocarbons, the compounds are apparently only slightly soluble in such media. An early synthesis for 18-crown-6 incorporated purification of the compound by recrystallization from n-hexane, indicating the low solubility of crown ethers in the solvent.
Figure 9. Effect of 15-Crown-5 on Molecular Weight of Polyisoprene at a Set 1.49 Mmoles of n-BuLi.
The addition of n-BuLi to a saturated, or nearly saturated solution of 15-crown-5 in heptane may cause the precipitation of a crown-lithium salt complex. Several reports concerning the precipitation of crown complexes from non-polar media have been published. Cook and Liotta have employed non-polar solvents to recrystallize non-metallic crown/nitride complexes, while numerous crown/metal cation complexes have been isolated from various solvent systems. If the precipitate was indeed a crown-lithium salt complex, the anion necessary to conserve electrical neutrality in the precipitated complex had two possibilities of nature. The anion may have been n-butyl or a polystyryl anion corresponding to the growing chain end. If the propagating anion was the species accompanying the complexed lithium out of solution, the polymerization would be terminated. Stoichiometric precipitation of the butyl anion would also terminate the polymerization. In systems containing less than a molar ratio of 0.17:1.0, crown:n-BuLi, the n-BuLi and growing chain ends apparently remain in solution without precipitation due to the limited solubility of the relevant species.

**Effect of 15-crown-5 on Rate of Polymerization**

The addition of 15-crown-5 to the n-BuLi-isoprene-heptane polymerization system increased markedly the rate at which isoprene was converted to polymer. In a polymerization containing 15 ml of heptane, 5.0 ml (50 mmoles) of isoprene,
1.49 mmol of n-BuLi, and no 15-crown-5, 95% conversion to polymer was obtained at room temperature after 66 hours. As Figure 10 indicates, the addition of 0.025 g (0.114 mmol) of 15-crown-5 to the polymerization produced comparable yields in only 10 hours. The complexation of the lithium cation by the crown ether decreases the attraction between the cation and the negative charge located at the end of the growing polymer chain. The resulting increase in the reactivity of the anion of the propagating chain apparently causes the polymerization to occur at a faster rate than is encountered without the crown ether. Boileau et al. obtained similar increased rates of polymerization through use of cryptates for isoprene systems employing either benzene or tetrahydrofuran as a solvent and n-BuLi as an initiator. 40

The addition of 15-crown-5 to the n-BuLi-isoprene-heptane system thus allowed the polymerization to proceed more rapidly at room temperature than systems containing no crown. Application of 15-crown-5 to industrial anionic polymerizations of isoprene may preclude the need for elevated temperatures and result in substantial energy savings. Production time could also be decreased considerably by modifying anionic industrial polymerizations of isoprene homopolymer or isoprene containing copolymers with 15-crown-5.

Effect of 12-Crown-4 on Molecular Weight

As the molar ratio of 12-crown-4 to n-BuLi in the n-BuLi-isoprene-heptane system was raised from 0:1 to 0.32:1,
Figure 10. Comparison of Overall Rates of Polymerization between Isoprene Systems Containing 0.114 Mmoles of 15-Crown-5 (Curve 1) and those Containing no Crown Ether (Curve 2).
the molecular weight of the resulting polyisoprene increased slightly (Figure 11). When molar ratios greater than 0.32:1 were used, the addition of n-BuLi resulting in the formation of a yellowish-brown precipitate similar in appearance to that observed earlier in certain isoprene polymerizations employing molar ratios of 15-crown to n-BuLi greater than 0.17:1. The precipitate apparently resulted from the low solubility of the crown ether or the resulting complexes in the nonpolar solvent.

Figure 12 compares the ability of 12-crown-4 to increase the molecular weight of polyisoprene to that of 15-crown-5. The plot reveals that 15-crown-5 is more effective in producing larger molecular weights in the n-BuLi-isoprene-heptane polymerization system than is 12-crown-4.

**Effect of 12-Crown-4 on Rate of Polymerization**

The complexation of the lithium cation by 12-crown-4 in the n-BuLi-isoprene-heptane polymerization system allowed the reaction to proceed at a rate much faster than that observed in systems containing no crown. The addition of 0.20g (0.114 mmoles) of 12-crown-4 to a reaction mixture containing 15 ml of heptane, 5.0 ml (50 mmoles) of isoprene, and 1.49 mmoles of n-BuLi gave the results shown in Figure 13. Figure 13 compares the results of the crown system to those obtained from similar systems containing no 12-crown-4. The addition of 12-crown-4 to the polymerization mixture thus increased the rate at which isoprene was converted to polymer. Figures 14
Figure 11. Effect of 12-Crown-4 on Molecular Weight of Polyisoprene at a Set 1.49 Mmoles of n-BuLi.
Figure 12. Comparison of Effects of 15-Crown-5 (Curve 1) and 12-Crown-4 (Curve 2) on Molecular Weight of Polyisoprene Using a Set 1.49 Mmoles of n-BuLi.
Figure 13. Plot of % Conversion vs. Time for Isoprene Polymerization System Containing 0.114 Mmoles of 12-Crown-4 (Curve 1) and No Crown (Curve 2).
Figure 14. A Comparison between the Plots of % Conversion to Polymer vs. Time for Isoprene Polymerization Systems Containing 0.114 Mmoles of 15-Crown-5 (Curve 1) and 0.114 Mmoles of 12-Crown-4 (Curve 2).
and 15, however, indicate that 12-crown-4 was not as effective in increasing the rate of polymerization as was 15-crown-5 under similar conditions. The results indicate that 15-crown-5 more effectively activates n-BuLi in anionic polymerizations than does 12-crown-4.

**Attempted Polymerization of Styrene**

**Utilizing n-BuNa as Catalyst**

Attempts to polymerize styrene utilizing n-BuNa as a catalyst proved unsuccessful due to difficulty in finding a suitable solvent for the system. While the C-Li bond in n-BuLi is believed to be partially ionic and partially covalent, the C-Na bond in n-BuNa is considered to be almost totally ionic. The ionic character of n-BuNa greatly limits its solubility in solvents of low polarity. In addition, n-BuNa is extremely reactive towards all common solvents (especially aromatic solvents) except paraffin-type organics such as neptane.

Attempts to initiate polymerization of styrene in benzene using n-BuNa failed due to the reactivity of the initiator towards benzene. A phenyl ion results from the reaction between n-BuNa and the solvent.

\[
n-C_4H_9Na^+ + C_6H_6 \rightarrow n-C_4H_{10} + C_6H_5Na^+ \]

The phenyl ion is a less "hard" nucleophile than the butyl anion and was apparently unable to initiate the polymerization of styrene.
Figure 15. Plots of % Conversion to Polymer vs. Time for Isoprene Polymerization Systems Containing 0.114 Mmoles of 15-Crown-5 (Curve 1), 0.114 Mmoles of 12-Crown-4 (Curve 2), and No Crown (Curve 3).
Although \textit{n-BuNa} is unreactive towards \textit{n}-heptane, attempts to polymerize styrene in the alkane solvent also proved unsuccessful. The initiator is insoluble in \textit{n}-heptane, but through the use of \textit{18}-crown-\textit{6} quantities of \textit{n-BuNa} sufficient to initiate polymerization could be solubilized in the hydrocarbon. Polystyrene, however, is insoluble in heptane, and the premature precipitation of the growing chains prevented attainment of high molecular weight polymer.

\textit{Attempted Polymerization of Isoprene Using \textit{n-BuNa} and Crown Ethers}

While the C-Li bond in \textit{n-BuLi} is considered to be partially ionic and partially covalent, the C-Na bond in \textit{n-BuNa} is considered to be totally ionic.\textsuperscript{108,128} Due to the ionicity of the C-Na bond, the organosodium compound is intensely reactive and will combine with nearly all substances except nitrogen, the noble gases, and the paraffin hydrocarbons.\textsuperscript{129}

The addition of \textit{n-BuNa} to isoprene polymerization systems containing \textit{18}-crown-\textit{6} resulted in the formation of a dark brown precipitate. No initiation of the polymerization reaction occurred in any of the systems investigated. NMR studies indicated that the precipitate may have resulted from the cleavage of the crown ether by \textit{n-BuNa}. Three tubes were charged with 15 ml of heptane and 0.14g (0.53 mmoles) of \textit{18}-crown-\textit{6}. \textit{n-BuNa} was present as a solid dispersion in heptane so that the molar ratios of crown to added \textit{n-BuNa} in the 3 tubes were 2:1, 1:1, and 0.5:1, respectively. The
resulting precipitate was filtered under nitrogen and the filtrate evaluated by NMR. Spectra for the systems employing molar ratios of 2:1 and 1:1 indicated that a significant quantity of 18-crown-6 remained in solution after the addition of \textit{n}-BuNa. The spectrum for the system containing \textit{n}-BuNa in molar excess to the crown (molar ratio of 0.5:1), however, indicated that only minute quantities of the crown ether remained in solution after the addition of \textit{n}-BuNa. Apparently, the highly nucleophilic nature of the \textit{n}-BuNa cleaved the 18-crown-6 to form products incapable of initiating polymerization,\textsuperscript{27} or the crown was precipitated quantitatively as a complex.

Although the application of unsubstituted 18-crown-6 to anionic polymerizations containing \textit{n}-BuNa proved unsuccessful, Halasa and Cheng\textsuperscript{25,63} have successfully polymerized butadiene and copolymerized butadiene and styrene with beneficial results in the presence of \textit{n}-BuNa modified by bi- or tricyclohexyl-18-crown-6. From an electronic viewpoint, the substituted analogs of 18-crown-6 possess greater stability than the unsubstituted macrocycles due to the presence of the substituent groups. In addition, the 6-membered side rings deter the cleavage of the ether linkages by providing steric hindrance towards attacking butyl anions. No details of the homopolymerization of either isoprene or styrene utilizing crown ethers have been published by Halasa and Cheng.\textsuperscript{25,63}
Effect of 18-Crown-6 on Caprolactam

Polymerization

Attempts to modify the bulk polymerization of caprolactam by the addition of catalytic quantities of 18-crown-6 were unsuccessful. The anionic bulk polymerization of caprolactam requires temperatures in the range of 250°-260° to prevent premature solidification of low molecular weight polymer. When systems containing 18-crown-6 and anion initiators were heated to the desired temperatures, a brown color developed in the reaction mixture. The discoloration apparently resulted from the degradation of the crown ether, as identical systems without crown ether did not develop color. Halasa and Cheng have reported 150°C as the maximum temperature at which substituted crown ethers (bi- or tricyclohexyl-18-crown-6) may be used in solution polymerization reactions. Differential thermal analysis studies on 18-crown-6 have shown that the compound begins to thermally degrade in air at ca. 120°C, shows substantial weight loss at 180°C, and is fully decomposed at 200°C. Since an anion is the propagating species in the polymerization mechanism, any reagent or degradation product which is capable of reacting with the anion would act to terminate the polymerization.

Attempts to lower the temperature of polymerization by the addition of 18-crown-6 also proved unsuccessful. Discoloration of the reaction mixture was obtained even when temperatures as low as 110°C were utilized. Apparently, the
ether linkages of the unsubstituted crown complexing agent were susceptible to attack by the ionic initiator even at 110°C.

No attempts were made to lower the reaction temperature through use of a cocatalyst in conjunction with the crown ether. In the mechanism for the anionic-catalyzed polymerization of caprolactam, the reaction between the lactam anion and the monomer (Equation 3.1) requires a higher energy of activation than any other reaction in the mechanism.\textsuperscript{9,11}

\[
\text{O} \quad \text{O} \quad \text{slow} \quad \text{O} \\
\text{C} + \text{C} \rightarrow \text{C} \\
(\text{CH}_2)_5\text{N}^+ \quad \text{HN-(CH}_2)_5 \quad (\text{CH}_2)_5\text{N-CO(CH}_2)_5\text{N}^+ \\
(3.1)
\]

The addition of certain cocatalysts, especially acyl lactams, essentially eliminates Equation 3.1 from the reaction mechanism, and allows the polymerization to proceed at substantially lower temperatures (100° to 180°C).\textsuperscript{11} As expected, the induction period inherent in Equation 3.1 is reduced markedly by the addition of acyl lactams. With the addition of the cocatalyst to the system, Equation 3.1 is replaced by Equation 3.2:\textsuperscript{11}

\[
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{C} + \text{C} \rightarrow \text{C} \quad \text{C-R} \\
(\text{CH}_2)_5\text{N}^+ \quad (\text{CH}_2)_5\text{NCR} \quad (\text{CH}_2)_5\text{N-CO(CH}_2)_5\text{N}^+ \\
(3.2)
\]

The addition of 18-crown-6 to systems containing acyl lactams
may allow a further reduction in the reaction temperature than has been demonstrated in the literature. By using acyl lactams to lower the energy of activation in conjunction with crown ethers to increase the nucleophilicity of the propagating anion, considerable energy savings could possibly be realized in the bulk anionic polymerization of caprolactam.
CHAPTER IV

CONCLUSIONS

The addition of catalytic quantities of crown ethers to the $n$-BuLi-styrene-benzene system caused dramatic modifications in the characteristics of the polymerization. Comparative studies indicate that 15-crown-5 is more effective in producing beneficial effects on the system than is 12-crown-4. The molecular weight of polystyrene produced from the modified system increased to an optimum value as the molar ratio of crown ether to $n$-BuLi approached 0.5:1. Further addition of the crown ether (molar ratio greater than 0.5:1) caused a decrease in the molecular weight to the same low values obtained in systems containing no complexing agent.

The overall rate for the polymerization of styrene increased markedly with the addition of crown ethers to the reaction system. Systems employing 15-crown-5 as a complexing agent reached 100% conversion to polymer in less than 10 seconds (least measurable time by the reaction methods employed), while similar systems utilizing 12-crown-4 required 130 seconds for complete conversion.

The results of the research indicate that in-mold polymerization of styrene with the crown/n-BuLi catalyst system may be feasible. The extremely rapid rate of polymerization and the ability to "tailor" the molecular weight
by varying the crown concentration offer potential in-mold polymerization capabilities that have not been previously defined in the literature.\textsuperscript{22,25,63}

The characteristics of the n-BuLi/isoprene/heptane polymerization system were also modified by the addition of crown ethers. Through use of 12-crown-4, the reaction time for the system was reduced by 67\%, while the addition of 15-crown-5 to the system allowed the time of reaction to be reduced by 83\% in comparison to systems containing no crown ether. Although large increases in the molecular weight were apparently prohibited by the solubility limitations of the crown ethers in heptane, moderate increases were effected by 15-crown-5 and somewhat smaller increases were realized through use of 12-crown-4. Application of crown ethers to industrial anionic polymerizations would provide a means of increasing productivity without increasing energy usage.

The results indicate that 15-crown-5 may be a more effective complexing agent for the lithium cation than is 12-crown-4. The 12-membered crown ether has been considered from theoretical considerations to be better than the 15-membered ring for the complexation of the lithium cation.\textsuperscript{56} However, in this research, the larger crown produced the greater effects in molecular weight and rate of polymerization in all systems employing n-BuLi. The results thus indicate that, in practice, 15-crown-5 is a better activating agent for n-BuLi in anionic polymerizations than is 12-crown-4.
The addition of crown ethers to systems containing \( n\text{-BuNa} \) produced no detectable beneficial effects on the polymerizations. NMR studies indicated that the initiator apparently either attacked the ether linkages of the complexing agent under mild conditions or caused the quantitative precipitation of the crown in the form of a complex. The insolubility of \( n\text{-BuNa} \) in alkane solvents and its apparent high reactivity towards the macrocyclic ether linkages renders the organosodium compound a less attractive candidate for potential industrial polymerizations employing crown ethers than \( n\text{-BuLi} \).

Attempts to modify the bulk polymerization of caprolactam through use of crown ethers also proved unsuccessful. The complexing agents were apparently unstable at the high temperature required for the polymerization. The instability of the crown ethers at the high temperatures was evidenced by a discoloration of the reaction mixture. In addition, no polymer was obtained from systems employing the complexing agent, while Nylon 6 was obtained in good yields from similar systems containing no crown ether. Attempts to lower the temperature of polymerization were hindered by the high energy of activation required for the initiation of the reaction and by premature growing chain solidification.
CHAPTER V
RECOMMENDATIONS

The n-BuLi-styrene-benzene system modified by 15-crown-5 shows great potential for adaptation to in-mold polymerizations. Attempts should be made to substitute a filler in place of the benzene solvent as a heat dissipater and to determine the feasibility of in-mold processing for the bulk monomer. Crystallinity effects, cracking tendency, and shrinkage characteristics should be defined.

A major concern in the molding process of polymers is the molecular weight distribution of the polymeric material. Before any attempts are made to adapt the 15-crown-5/n-BuLi/styrene system to in-mold processing, the molecular weight distribution of polymers prepared from the system should be determined. Such a study may also provide insights into the mechanism by which the crown ether affects the molecular weight of the polymer.

The properties of polyisoprene vary greatly in typical anionic polymerizations as the amounts of cis 1,4-, trans 1,4-, 1,2-, and 3-4- additions change. The relative amounts of isomers in isoprene polymerizations utilizing crown ethers should be compared to that of systems which contain no crown. Complete thermal and physical properties of polymers prepared from systems containing crown ether should also be compared
to those of polymers prepared in the absence of crown.

The applicability of crown ether to the anionic polymerization of other monomers should be investigated. In particular, the polymerization of butadiene in the presence of crown ethers should be studied. The copolymerization of various dienes with styrene is a logical extension of the research.

Aza crowns are macroheterocyclic complexing agents which contain nitrogen atoms arranged symmetrically around their ring structure.\textsuperscript{130-133} A relatively simple and general synthesis may be employed to prepare 9- to 21-membered aza crowns containing 3 to 7 heteroatoms in yields of 40-90\%.\textsuperscript{134} The methylated aza analog of 18-crown-6 has been shown to complex the lithium cation.\textsuperscript{135} The complexing ability of aza crowns in anionic polymerizations should be compared to that of crown ethers. Aza crowns should be substituted for the oxa crown ethers in the procedures of this work and direct comparisons made between the 2 complexing agents. Conclusions concerning the optimum complexing agent for each system could then be drawn.
APPENDIX 1. EFFECT OF 15-CROWN-5 ON MOLECULAR WEIGHT OF POLYSTYRENE

Each reaction contained 15 ml. of benzene, 5.0 ml (43.3 mmole) of styrene, 0.70 mmole of n-BuLi, and a quantity of 15-crown-5 as follows:

<table>
<thead>
<tr>
<th>Tube</th>
<th>15-Crown-5 (g)</th>
<th>15-Crown-5 (mmoles)</th>
<th>15-Crown-5 Concentration ( )</th>
<th>[η] of Polystyrene</th>
<th>Molecular Weight of Polystyrene</th>
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<td>0</td>
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<td>2</td>
<td>.0295</td>
<td>.134</td>
<td>.0064</td>
<td>.176</td>
<td>24,000</td>
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<td>.0613</td>
<td>.279</td>
<td>.0133</td>
<td>.195</td>
<td>29,900</td>
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<tr>
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<td>.0756</td>
<td>.343</td>
<td>.0163</td>
<td>.226</td>
<td>36,500</td>
</tr>
<tr>
<td>5</td>
<td>.0938</td>
<td>.426</td>
<td>.0203</td>
<td>.214</td>
<td>33,900</td>
</tr>
<tr>
<td>6</td>
<td>.1160</td>
<td>.529</td>
<td>.0252</td>
<td>.196</td>
<td>30,100</td>
</tr>
<tr>
<td>7</td>
<td>.1417</td>
<td>.644</td>
<td>.0307</td>
<td>.164</td>
<td>23,700</td>
</tr>
<tr>
<td>8</td>
<td>.1809</td>
<td>.822</td>
<td>.0391</td>
<td>.153</td>
<td>21,600</td>
</tr>
<tr>
<td>9</td>
<td>.2267</td>
<td>1.03</td>
<td>.0490</td>
<td>.142</td>
<td>19,500</td>
</tr>
</tbody>
</table>

The data is plotted in Figure 3.
APPENDIX 2. EFFECT OF 12-CROWN-4 ON MOLECULAR WEIGHT OF POLYSTYRENE

Each reaction contained 15 ml. of benzene, 5.0 ml (43.3 mmoles) of styrene, 0.70 mmoles of n-BuLi, and a quantity of 12-crown 4 as follows:

<table>
<thead>
<tr>
<th>Tube</th>
<th>12-Crown-4 (g)</th>
<th>12-Crown-4 (mmoles)</th>
<th>12-Crown-4 Concentration (M)</th>
<th>[η] of Polystyrene</th>
<th>Molecular Weight of Polystyrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.139</td>
<td>18,900</td>
</tr>
<tr>
<td>2</td>
<td>.0136</td>
<td>.077</td>
<td>.0037</td>
<td>.141</td>
<td>19,300</td>
</tr>
<tr>
<td>3</td>
<td>.0389</td>
<td>.221</td>
<td>.0105</td>
<td>.171</td>
<td>25,100</td>
</tr>
<tr>
<td>4</td>
<td>.0654</td>
<td>.372</td>
<td>.0177</td>
<td>.202</td>
<td>31,400</td>
</tr>
<tr>
<td>5</td>
<td>.0931</td>
<td>.529</td>
<td>.0252</td>
<td>.157</td>
<td>22,300</td>
</tr>
<tr>
<td>6</td>
<td>.1360</td>
<td>.773</td>
<td>.0368</td>
<td>.140</td>
<td>19,100</td>
</tr>
</tbody>
</table>

The data is plotted in Figure 6.
APPENDIX 3. EFFECT OF CONCENTRATION OF n-BuLi ON MOLECULAR WEIGHT OF POLYSTYRENE

Each reaction contained 15 ml of benzene, 5.0 ml (43.3 mmoles) of styrene, and a quantity of n-BuLi as follows:

<table>
<thead>
<tr>
<th>Tube</th>
<th>n-BuLi (mmoles)</th>
<th>n-BuLi Concentration (M)</th>
<th>η̅_{inh} of Polystyrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.70</td>
<td>0.033</td>
<td>0.101</td>
</tr>
<tr>
<td>2</td>
<td>0.98</td>
<td>0.045</td>
<td>0.094</td>
</tr>
<tr>
<td>3</td>
<td>1.96</td>
<td>0.082</td>
<td>0.070</td>
</tr>
<tr>
<td>4</td>
<td>2.94</td>
<td>0.113</td>
<td>0.064</td>
</tr>
</tbody>
</table>

Each reaction was modified by the addition of 0.42g (0.19 mmoles) of 15-crown-5. The results were:

<table>
<thead>
<tr>
<th>Tube</th>
<th>n-BuLi (mmoles)</th>
<th>n-BuLi Concentration (M)</th>
<th>η̅_{inh} of Polystyrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.70</td>
<td>0.033</td>
<td>0.150</td>
</tr>
<tr>
<td>2</td>
<td>0.98</td>
<td>0.045</td>
<td>0.125</td>
</tr>
<tr>
<td>3</td>
<td>1.96</td>
<td>0.082</td>
<td>0.086</td>
</tr>
<tr>
<td>4</td>
<td>2.94</td>
<td>0.113</td>
<td>0.072</td>
</tr>
</tbody>
</table>

η̅_{inh} of 1% solutions in benzene at 25°C.

The data is plotted in Figure 4.
APPENDIX 4. EFFECT OF 15-CROWN-5 ON MOLECULAR WEIGHT OF POLYISOPRENE

Each reaction contained 15 ml of heptane, 5.0 ml (50 mmole) of isoprene, 1.49 mmole of n-BuLi, and a quantity of 15-crown-5 as follows:

<table>
<thead>
<tr>
<th>Tube</th>
<th>15-Crown-5 (g)</th>
<th>15-Crown-5 mmole</th>
<th>Concentration (M)</th>
<th>[\eta] of Polyisoprene</th>
<th>Molecular Weight of Polyisoprene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.164</td>
<td>5,650</td>
</tr>
<tr>
<td>2</td>
<td>.0107</td>
<td>.048</td>
<td>.0023</td>
<td>.176</td>
<td>6,280</td>
</tr>
<tr>
<td>3</td>
<td>.0185</td>
<td>.084</td>
<td>.0040</td>
<td>.185</td>
<td>6,800</td>
</tr>
<tr>
<td>4</td>
<td>.0280</td>
<td>.127</td>
<td>.0060</td>
<td>.202</td>
<td>7,720</td>
</tr>
<tr>
<td>5</td>
<td>.0602</td>
<td>.274</td>
<td>.0130</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The data is plotted in Figure 9.
APPENDIX 5. EFFECT OF 12-CROWN-4 ON MOLECULAR WEIGHT OF POLYISOPRENE

Each reaction contained 15 ml of heptane, 5.0 ml (50 mmole) of isoprene, 1.49 mmole of n-BuLi, and a quantity of 12-crown-4 as follows:

<table>
<thead>
<tr>
<th>Tube</th>
<th>12-Crown-4 (g)</th>
<th>12-Crown-4 (mmoles)</th>
<th>12-Crown-4 Concentration (M)</th>
<th>([\eta]) of Polyisoprene</th>
<th>Molecular Weight of Polyisoprene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.162</td>
<td>5,600</td>
</tr>
<tr>
<td>2</td>
<td>.0133</td>
<td>.075</td>
<td>.0036</td>
<td>.167</td>
<td>5,810</td>
</tr>
<tr>
<td>3</td>
<td>.0345</td>
<td>.196</td>
<td>.0093</td>
<td>.173</td>
<td>6,120</td>
</tr>
<tr>
<td>4</td>
<td>.0416</td>
<td>.236</td>
<td>.0112</td>
<td>.178</td>
<td>6,390</td>
</tr>
<tr>
<td>5</td>
<td>.0898</td>
<td>.510</td>
<td>.0243</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The data is plotted in Figure 11.
LITERATURE CITED


50. J. Smid, Ibid., 11, 112 (1972).


84. Reference 8, p. 64.

85. Reference 23, p. 46.


96. Reference 8, p. 113.


105. Reference 8, p. 69.


121. H. O. House, School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia, 1977, Private Communication.


