

**SYNTHESIS AND CHARACTERIZATION OF
LIQUID CRYSTALLINE POLYROTAXANES
BASED ON POLY(AZOMETHINE)S**

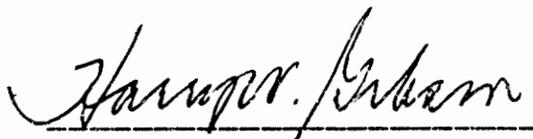
by
Jean Y. Sze

Submitted to the Faculty of
the Virginia Polytechnic Institute and State University in partial
fulfillment of the requirement for the degree of

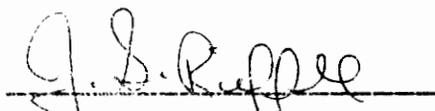
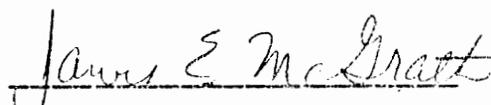
MASTER OF SCIENCE

In
Chemistry

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTALLINE POLYROTAXANES BASED ON POLY(AZOMETHINE)S

BY

Jean Yi-ching Sze

Committee Chairman: Dr. Harry W. Gibson

Department of Chemistry

Polyrotaxanes are new polymers. Macrocyclic molecules, such as crown ethers, are threaded by linear or branched polymer chains. There is no covalent bond between the crown ethers and the polymer backbone. After the crown ethers are threaded onto the polymer backbone, both ends of the polymer can be blocked by large end groups. Polyrotaxanes are the topological isomers of blends of crown ethers and polymers. This architectural modification will produce interesting chemical and physical property changes in the polymer such as T_g and T_m , solubility, tensile strength, flexibility of the polymer.

The study include crown ethers, blocking groups, poly(azomethine)s A and B, poly(azomethine)rotaxanes A and B synthesis, characterization, and property research.

Crown ethers, 21-crown-7, 30-crown-10, 42-crown-14, and 60-crown-20, were synthesized from oligo(ethylene glycol)s and oligo(ethylene glycol) ditosylates with 22-40% yield. The high temperature synthetic method was developed so that the percentage

yield of large crown and the small crowns in the same reaction could be controlled. A new purification method, low temperature recrystallization method was developed. The crown ethers properties included melting points, decomposition temperature, chemical shift on NMR spectra were studied.

A series of blocking groups were synthesized and characterized. Several synthetic routes were studied, and the best route was the Grignard synthesis. The purification method was improved by recrystallization in cyclohexane or carbon tetrachloride. A by-product, bis(p-t-butylphenyl)methanol, was obtained. The new compounds, p-tri(p-t-butylphenyl)methylaniline and p-tri{(p-t-butylphenyl)methylphenol}, were identified by ^1H NMR, FTIR, and elemental analysis.

Poly(azomethine)s A and B are liquid crystalline polymers. They are rigid and strong. They have high T_m 's and do not dissolve in general solvents. To check the reported information, the synthesis and characterization of these polymers were repeated. They precipitated from the reaction solution when their degree of polymerization reached 3-5. They were not thermally stable and were easily hydrolyzed in strong acids and in GPC column.

In order to establish the effectiveness of the blocking groups, a monomeric rotaxane, a di(azomethine)rotaxane, was designed and synthesized. The compound was successfully isolated by multiple reprecipitations and recrystallizations. A 12% yield of this compound was obtained. The largest crown ether that the blocking group could block was 42-crown-14.

ACKNOWLEDGEMENTS

I deeply appreciate Dr. Harry W. Gibson's advice and help. Under his guidance, I successfully synthesized and characterized crown ethers, blocking groups, poly(azomethine)s, di(azomethine)-rotaxanes, and poly(azomethine)rotaxanes; and I can finish my study for my masters degree.

I would like to thank Dr. J. E. McGrath, Dr. J. S. Riffle. I appreciate them for being my committee members and their advice and suggestions. Also I appreciate their group members' valuable discussions and equipment.

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I would like to thank the Department of Chemistry for providing a very good program on polymer chemistry and general help.

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DEDICATION

To my mother and father,

**who brought me up and sent me to continue my education
in The United States**

To Victoria Bond, my big sister,

**who reestablished my confidence and strength,
and helped me in my life.**

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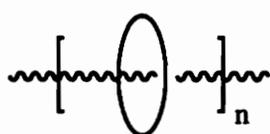
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CHAPTER I

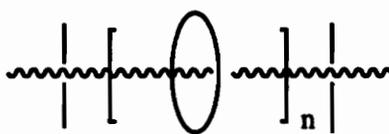
INTRODUCTION AND HISTORY OF POLYROTAXANES, CROWN ETHERS, AND LIQUID CRYSTALLINE POLYMERS

I-A Rotaxanes and Polyrotaxanes

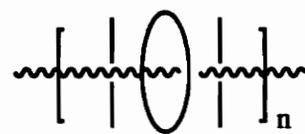
Polyrotaxanes are new polymers which have been developed over the last few years. These new polymers have a special architecture. Macrocyclic molecules, like crown ethers or macrocyclic alkanes, are used as "pearls". Linear or branched polymers are used as "threads". The macrocyclic molecules are threaded by polymer chains. These macrocycles can be threaded on the main chain of the polymers, or they also can be threaded on the side chain of the polymer. There is no covalent bond between macrocycles and polymer chain. After the macrocycles are threaded on the polymer chain, both ends of the polymer chain can be blocked by blocking groups which are big, star-shaped groups which prevent the macrocycles from sliding off of the polymer chain. But if the polymer chain is quite long, and is soft, the blocking groups may not be necessary. Several different polyrotaxanes are shown below. (I-1)



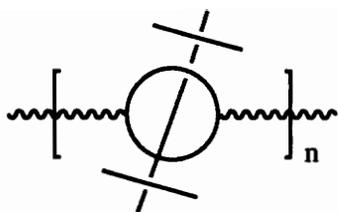
polyrotaxane without
blocking group



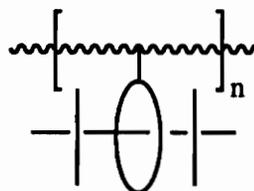
polyrotaxane with
blocking groups



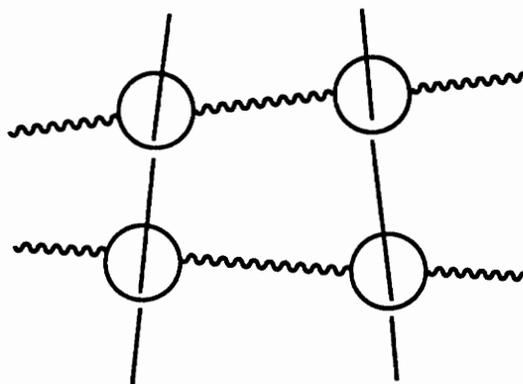
block polyrotaxane



poly(macrocycle)rotaxane



side chain polyrotaxane



physically crosslinked polyrotaxane

I-1 Polyrotaxanes

E. Wasserman is the person who first mentioned this polymer structure theoretically in 1961 [1]. In his publication, he mentioned that a monomer or polymer could have topological isomers. For example, two macrocycles could exist individually and be mixed together, or connected to each other to form the interlocked catenane. (I-2)



2 separated macrocycles

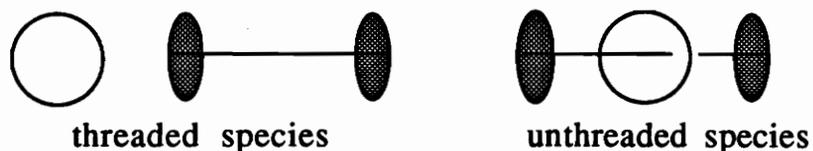


catenane

I-2 Separated macrocycles and a catenane

Wasserman also designed several different rotaxanes with blocking groups and catenanes. He designed a macrocycle which was

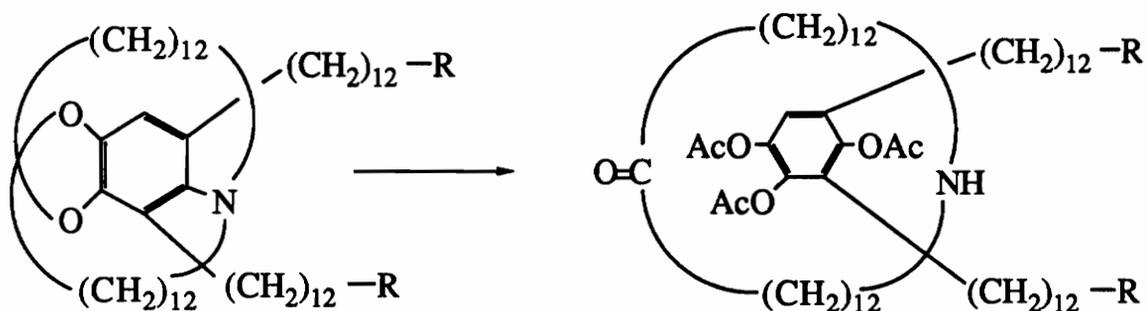
threaded by a linear chain. Both ends of the chain were blocked by blocking groups. (I-3) This compound was topologically different from the mixture of the macrocycle and the linear chain with blocking groups. [1]



I-3 Rotaxane and the blend of a macrocycle and a linear species with end blockers

Wasserman predicted that these topological isomers might be not greatly different in chemical properties, but would have large changes in their physical properties.

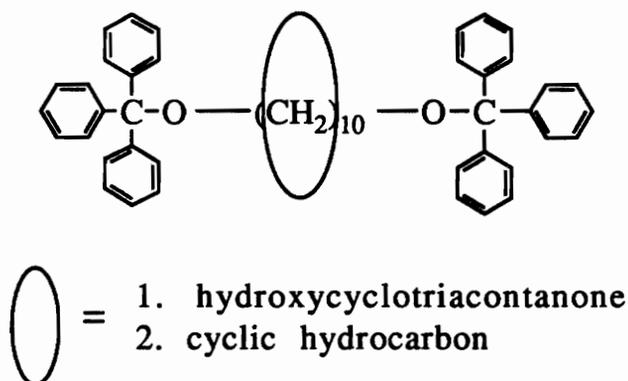
Schill and Zollenkopf synthesized compounds which had macrocycles and linear chains [2]. The macrocycle was bound to the backbone first; then the bonds which connected the macrocycle and the backbone were broken. But the percentage yields of the compounds were very low, only about 0.12%. (Scheme I-A1)



R = Bulky group (e.g. Trityl)

Scheme I-A5 Schill and Zollenkopf made the first rotaxane

Harrison and Harrison made rotaxanes with blocking groups (I-4) [3][4]. Hydroxycyclotriacontanone and cyclic hydrocarbon macrocycles with 25-29 members were threaded by decamethylene diol. Trityl groups were used as the blocking groups. The percentage yield of the rotaxane with hydroxycyclotriacontanone was 6% after 70 cycles using a polymeric anchor for the macrocycle. They prepared the rotaxane using a statistical threading method. They found that the macrocycle should have more than 22 members; if the macrocycle had less than 22 members, it could not be threaded.

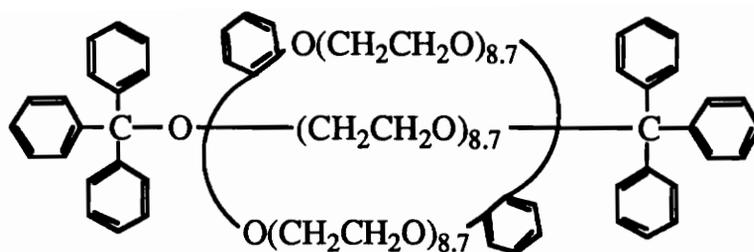


I-4 Alkane based rotaxane with phenylmethyl blocking groups.

Since then, chemists have made various rotaxanes and polyrotaxanes.

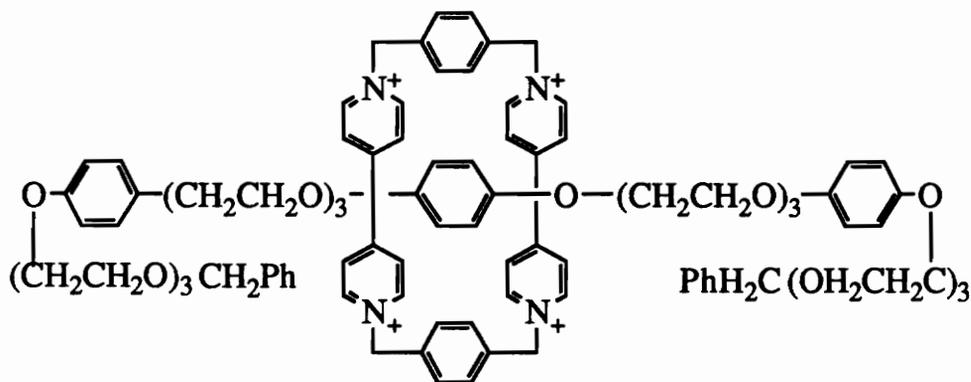
Rotaxanes and polyrotaxanes can be made using different chains and macrocycles. The architecture of rotaxanes and polyrotaxanes may also be different.

Zilkha and his group used ether linked backbones and bisphenylene crown ether macrocycles [5] (I-5). They used dibenzo crown ethers with 30, 44.1, 58.2 members. They reported that the increment of the size of macrocycles and the length of the polyether chain would cause an increment in the amount of threading which increased the percentage yield to 15%.



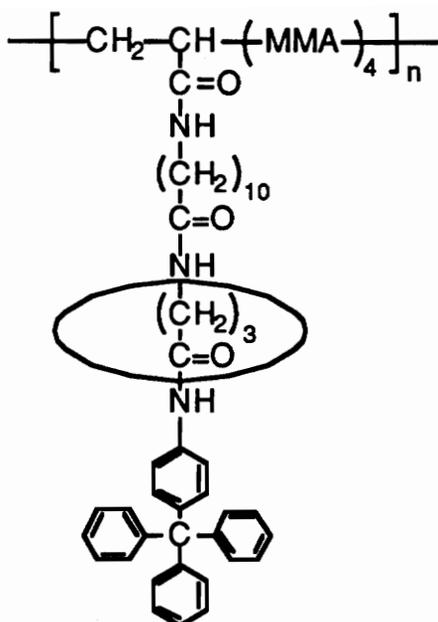
I-5 Ether linked rotaxane

Stoddart and his coworkers used aromatic rings and an ether linked chain as the backbone. The polymer backbone was an electron rich system. The macrocycle was cyclobis(paraquat-p-phenylene)-tetracation, which was a rigid, electron poor macrocycle. The rotaxane was synthesized by host-guest complexation using the self-assembly method. The backbone goes into the macrocyclic cavity to form an electron transfer system. The polyrotaxane was [n]pseudorotaxane (I-6) [6][7].



I-A6 Pseudorotaxane

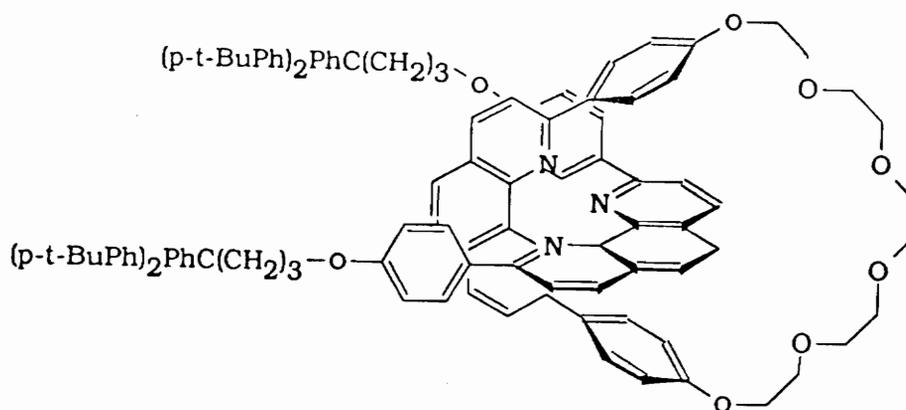
Ritter and Born made a polyrotaxane, on which the macrocycles were not on the main chain of the polymer, but were on the side chain of the polymer [8]. (I-7)



I-A7 2,6-dimethyl- β -cyclodextrin and 11-methacryloyl-aminoundecanoic acid-MMA based side branch rotaxane co-polymer

The macrocycle, 2,6-dimethyl- β -cyclodextrin, was threaded by 4'-triphenylmethyl-11-aminoundecanoic acid; this was a short chain which had an amino functional group at one end, and a blocking group at the other end. They called this a "semi-rotaxane". The "semi-rotaxane" reacted with 11-methacryloyl-aminoundecanoic acid and MMA to make a side branch rotaxane co-polymer.

Recently, Gibson and his group made a phenanthroline rotaxane. The phenanthroline macrocycle was threaded by a claw-shaped phenanthroline bisphenol [12]. Cu^+ was used as the template metal to hold both parts together to form a tetrahedral complex. After the complex was formed, both ends of the claw-shaped phenanthroline were blocked by tris-*t*-butylphenylmethyl blocking groups. Then the Cu^+ was taken off from the compound, leaving the rotaxane (**I-8**). The percentage yield of this rotaxane was 42%.



I-8 A claw-shaped phenanthroline rotaxane

The rotaxane family is increasing in size.

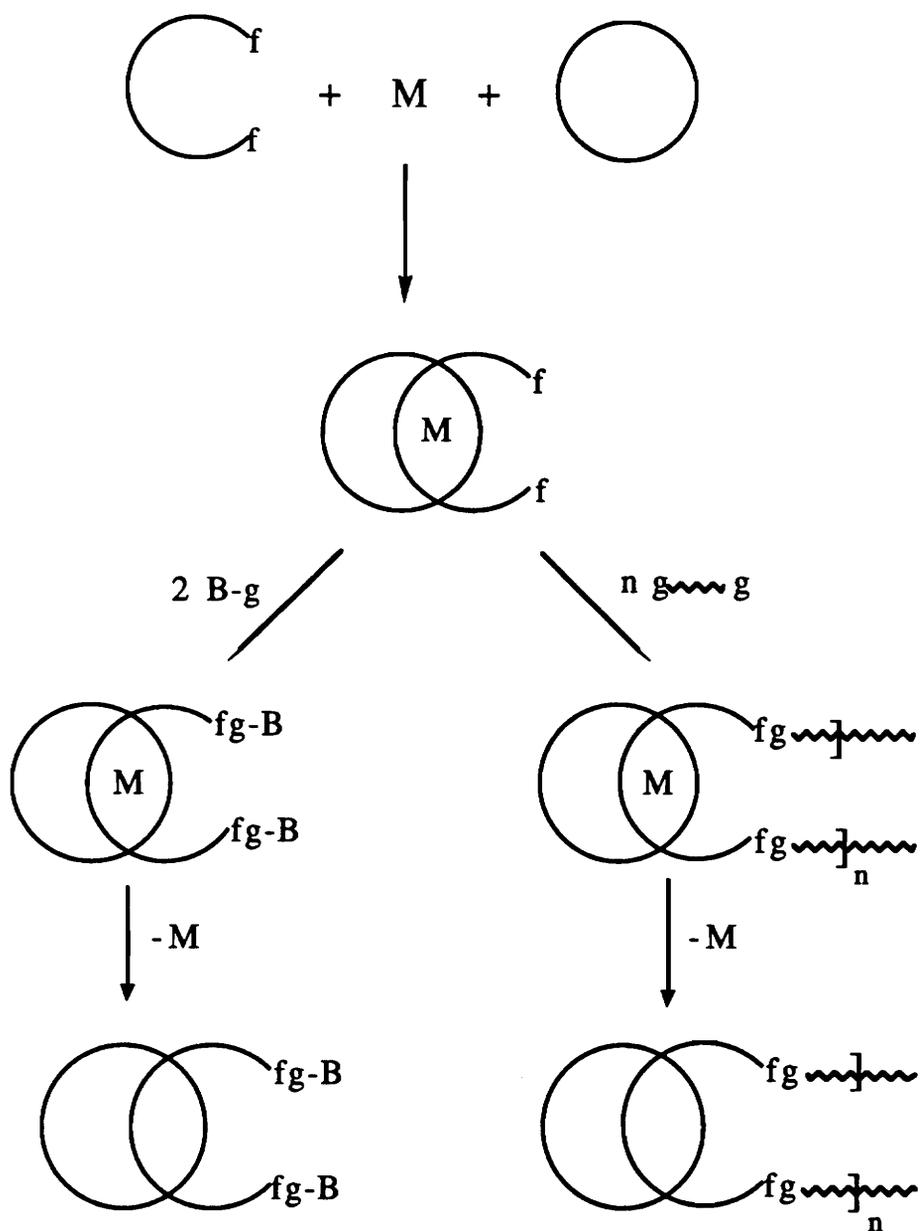
I-B Methods for Synthesizing Rotaxanes and Polyrotaxanes

There are several different methods to synthesize rotaxanes and polyrotaxanes.

1. The Template Methods

Rotaxanes and polyrotaxanes can be made using a template method [9][10][12]. There are two types of template methods that can be used for synthesizing polyrotaxanes.

The macrocycle and backbone are held together using a template metal to form a rotaxane and polyrotaxanes. (Scheme I-B1)

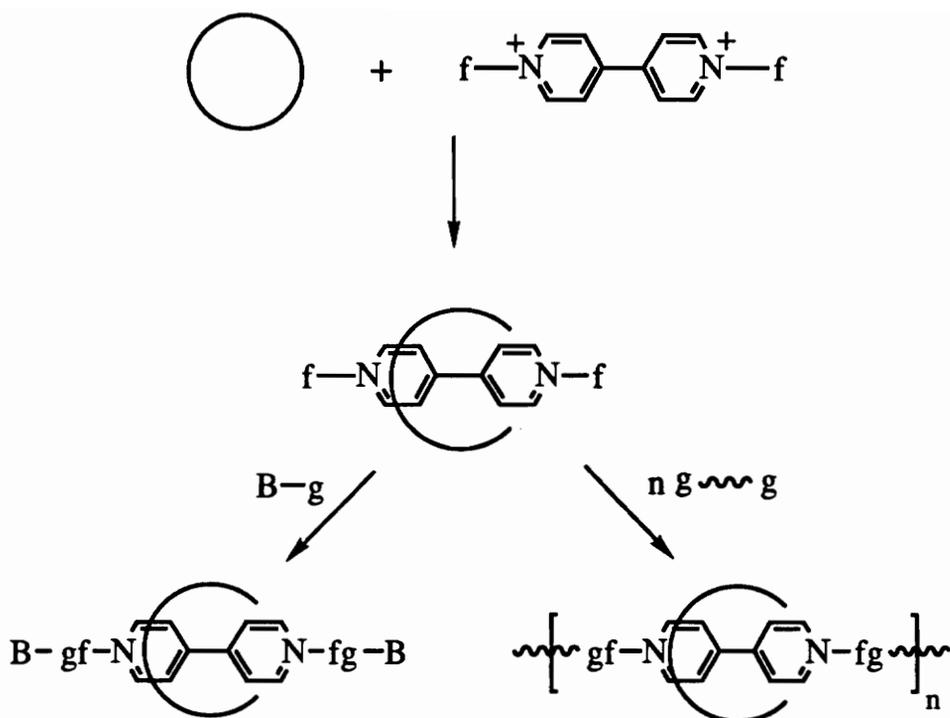


f and g are functional groups. B is a blocking group
 ~ is polymer linkage. is a macrocycle.

Scheme I-B1 Synthesis of rotaxanes and polyrotaxanes using the transition metal template method

For example, the cyclic phenanthroline is threaded by a claw-shaped phenanthroline bisphenol. During the reaction, a transition metal ion (M), for example Cu^{+2} , is used as the template metal to hold these two compounds together to form a complex. The molecular planes of cyclic phenanthroline and claw-shaped phenanthroline bisphenol are perpendicular to each other due to the steric dictates of the coordination sites on Cu^{+2} . Both ends of the claw-shaped phenanthroline bisphenol can be blocked using tris-*t*-butylphenyl-methyl blocking groups, or used to polymerize using other monomers to form block copolyrotaxanes. After the rotaxane has formed, the copper ions are taken out [10][12].

Self-assembled host-guest complexation is another template method to synthesize polyrotaxanes [6][7][13]. Bis(*p*-phenylene)-34-crown-10 is threaded by a bipyridinium unit. BPP34-c-10 is electron rich, and the bipyridinium unit is electron poor. When these components mix together, electron charge transfer will happen, and the π systems will overlap. The bipyridinium unit goes in the cavity of BPP34-c-10. The rotaxane self-assembles. At this stage, if the bipyridinium unit is further polymerized, or both ends of the polymer chain are blocked by blocking groups, a rotaxane or polyrotaxane is synthesized. (Scheme I-B2)



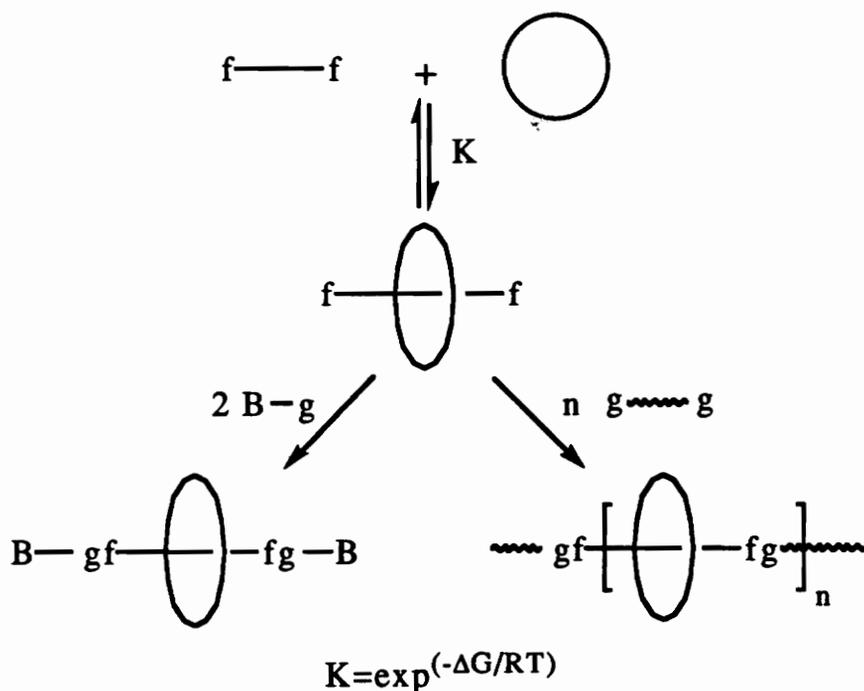
Scheme I-B2 Synthesis of self-assembled host-guest complex rotaxanes and polyrotaxanes

2. The Statistical Threading Method

Rotaxanes and polyrotaxanes also can be synthesized using a statistical threading method [5][11][12]. The polymerization reaction is done in bulk macrocycles or in macrocycle solution. During the reaction, the chains and the macrocycles are mixed together. The system reaches an equilibrium state between the threaded and unthreaded macrocycles and backbones. Therefore, the ratio of the macrocycle and backbone is an important factor. If the pure macrocycle is used as the solvent for polymerization, the threading ratio of the linear species will be the highest. But in some cases, the polymerization will not happen in pure macrocycle, but a macrocycle solution can be prepared. In this case the threading ratio will be lower than in the bulk macrocycle. The threading rate is dependent on the size and the rigidity of macrocycle and the chain.

As Schill and Harrison reported, if the size of the macrocycle is less than 22 members, the macrocycle can not be threaded [2][3]. As Zilkha reported, the chain has to have at least 8 atoms; otherwise the dethreading happens easily. [5] When the rigidity of the macrocycle increases, the threading rate also increases [13].

After the reaction, some macrocycles are threaded on the chain statistically. Both end groups of the chain are connected to large blocking groups, so that the macrocycles will not slide off from the chain. After the reaction is finished, a certain percentage of rotaxane or polyrotaxane can be isolated. This is the most widely used method. (Scheme I-B3)

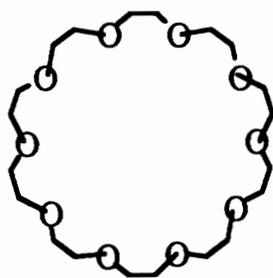


Scheme I-B3 Synthesis of rotaxanes and polyrotaxanes using statistical threading method

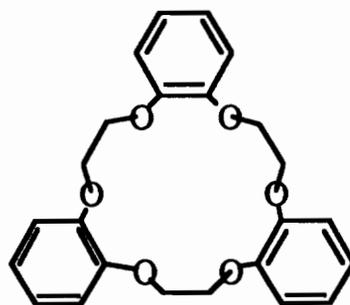
I-C Macroyclic Polyethers (Crown Ethers)

Macrocyclic polyethers (crown ethers) are the compounds in which the ether units and other elements like N, S, O, and/or aromatic rings combine together into large circles. Since the shapes of these large circles look like crowns, people call them "crown ethers".

There are many different kinds of crown ethers. If the macrocycle contains only ether linkages, it is a "crown ether". If the macrocycle also contains N and S, the large cycle can be a "azathiocrown ether". If the macrocycle contains ether linkages and aromatic rings, this kind of macrocycle is an "aromatic crown ether". (I-9)



30-crown-10



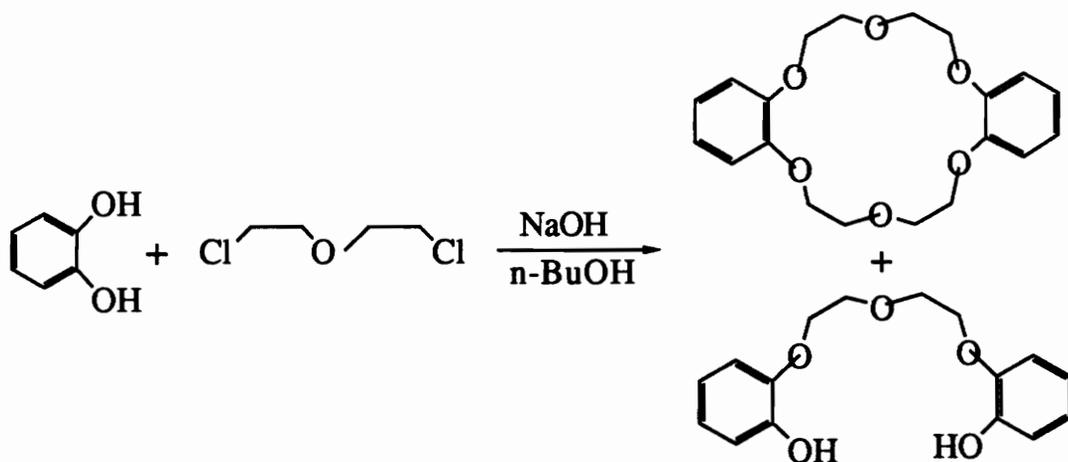
tribenzo-18-crown-6

I-9 Crown ether and aromatic crown ether

Since the crown ethers contain O, N, S elements, they are quite polar. They can be dissolved in polar solvents. The small crowns, for example, 12-crown-4, 18-crown-6, also can dissolve in nonpolar solvents like toluene and benzene. Crown ethers have strong intermolecular forces. They have quite high boiling points. For example, 15-crown-5 boils at 100-135°C under 0.2 mm Hg [13][14][15].

The crown compounds have a history of less than thirty years. Many kinds of crown compounds have been synthesized, they are still being studied by many scientists, and their properties are more and more being known.

The first crown ether compound was synthesized in 1967 by Pederson [14]. He used catechol to react with dichlorodiethyl ether, and he got a mixture of bis(2-o-hydroxyphenoxy ethyl ether) and macrocyclic polyether. (Scheme I-C1)



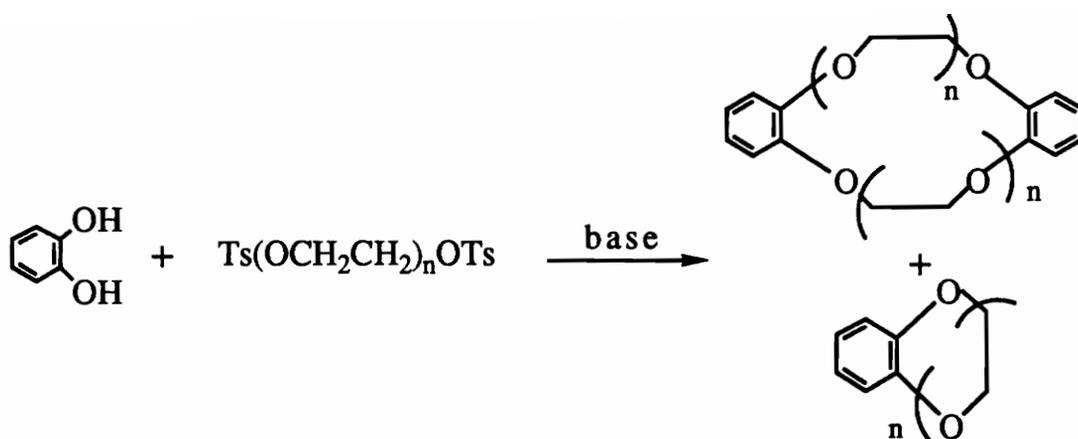
Scheme I-C1 Synthesis of bis(o-phenylene)-18-crown-6 and bis(2-o-hydroxyphenoxy ethyl ether)

Pedersen made 49 crown ethers which included “aliphatic crown ethers”, “aromatic crown ethers”, and “heterocyclic crown ethers”. He found that these crown ethers could form complexes with metals like Li, Na, K, Cs, Ca, Cu, Ag, Ba, and Hg, etc. The metal ion went into the cavity of the crown ether, and interacted with the oxygens. The stability of the complexes depended upon the ionic radius of the cations and the size of the cavity of the crown ethers. If the cation just fits in the cavity of the crown ether, the complex is most stable. Also Pedersen found that these crown ethers dissolved

in most general organic solvents including those with different polarities [15].

Pedersen's wide-ranging research on this new family of compounds created a new area of synthetic chemistry which stimulated the interest of many chemists. Since then, various new crown ethers and their analogues have been synthesized. The structures of the compounds have been analysed, and the properties of the compounds have been investigated. These compounds include not only hydrocarbons linked with oxygen and aromatic rings, but also hydrocarbons linked with sulfur, nitrogen, and phosphorus. Both single cyclic compounds and multi-cyclic compounds have been synthesized.

The aromatic crown ether is one type of crown ether which contains aromatic rings and ether units. The reactants can be catechol and an oligo(ethylene glycol) dichloride or oligo(ethylene glycol) ditosylate. The crown ether can contain one or more aromatic ring. The reaction can be one or more steps. A one step reaction takes place when the catechol and dichloride (or ditosylate) are mixed together and refluxed in the presence of a base, for example, NaOH, and NaH. The aromatic crown ether is synthesized by a statistical method. The product is a mixture of monoaromatic crown ether and diaromatic crown ether [13][16]. (Scheme I-C2) After the reaction, the crown ethers need to be separated. The percentage yield is 11-30%. [13][16]

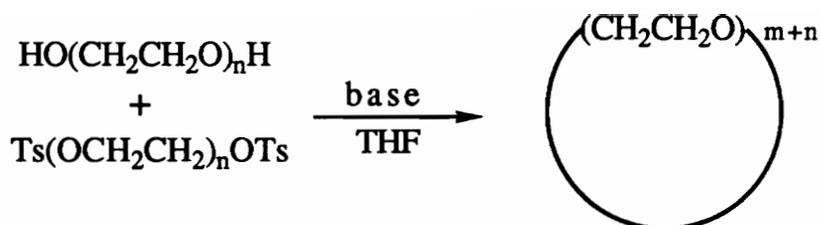


Scheme I-C2 Synthesis of aromatic crown ethers

The two step reaction involves having one of the hydroxyl groups on catechol blocked by a protective group, such as a benzyl group or tetrahydropyranyl group. Oligo(ethylene glycol) dichloride or oligo(ethylene glycol) ditsylate react with the unprotected hydroxyl group on the catechol at both ends. After the hydroxy group has reacted, the other hydroxyl group is deprotected, and reacted with oligo(ethylene glycol) ditsylate. The crown ether is formed. The other reaction conditions are the same as for the one step reaction. The percentage yield is 12-48% [13][16].

The multi-step reaction is similar to that introduced above.

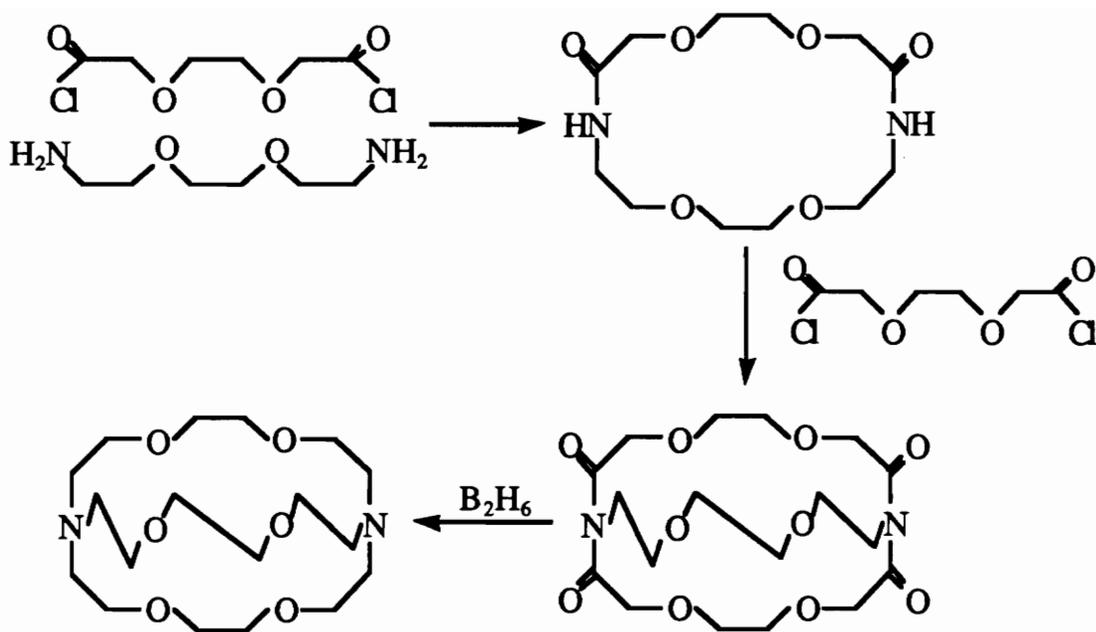
The crown ether is usually synthesized using a one step reaction [17][18]. The reactants are oligo(ethylene glycol) and oligo(ethylene glycol) ditsylate. The reaction is carried on at room temperature in polar solvents. (Scheme I-C3)



Scheme I-C3 Synthesis of a crown ether

After the reaction is finished, the product is a mixture. This mixture contains poly(ethylene glycol)s, small crowns formed from one molecule of oligo(ethylene glycol) reacting with one molecule of oligo(ethylene glycol) ditosylate, large crowns formed from two molecules of oligo(ethylene glycol) reacting with two molecules of oligo(ethylene glycol) ditosylate, and a small amount of catenanes. These products need to be separated. The total percentage yield of small and large crowns is 18-30% [16][17][18].

The multicyclic crown compounds are made by several steps. (Scheme I-C4) The two reactants with reactive groups at both ends of the chains react together to form a monocyclic compound. This monocyclic compound still has two or more (even number) reactive groups. The monocyclic compound can react with other reactants to form multicyclic crown compound(s). Here is an example of a multicyclic crown compound reaction. The percentage yield is about 25% [16].



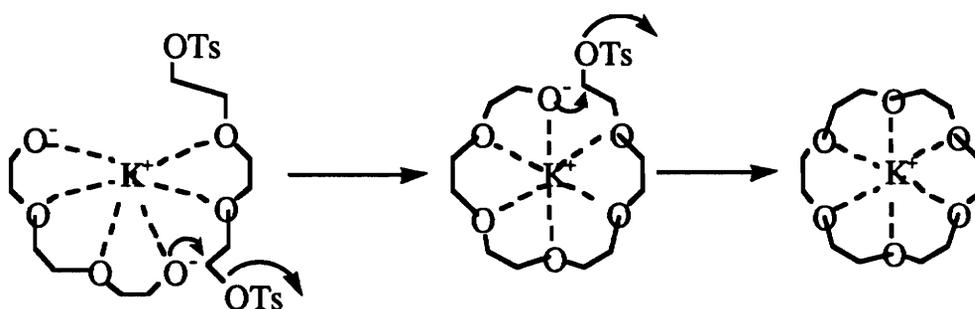
Scheme I-C4 Synthesis of multicyclic crown compound

I-D Synthetic Methods for Crown Ethers

The most common method of synthesis of the macrocyclic compounds is nucleophilic substitution (condensation). This is also called "Williamson ether synthesis" which uses both an oligo(ethylene glycol) and an oligo(ethylene glycol) derivative, such as ditosylate or dichloride, in the presence of a base. The mechanism is that the electrons on the nucleophile such as O, N, S attack the carbon of the other reactant with a leaving group on it. (Scheme I-D1) The reaction is intermolecular, and the reaction takes place at both ends of the reactants [16].

It is very important to include metal ions in the macrocyclic crown reaction. There are O, N, and S atoms in the crown compounds. These atoms have electron lone pairs, and they are electron rich, and they can act as electron donors. The lone pair electrons on O, N, and S atoms are directed toward the inside of the ring. The metal cations

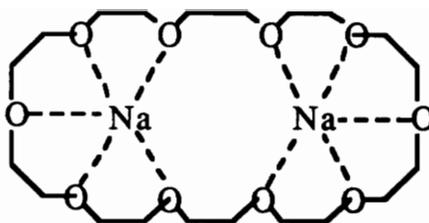
are electron poor, and they can act as electron acceptors. During the reaction, the crown compound and the ion form a complex by ion-dipole interaction. The metal cation is trapped in the crown compound cavity which is similar in size to the cationic diameter. In the complex of crown compound, each electron donor atom is located at an equal distance from the cation. Therefore the metal cation can hold the reactants together, and the reaction can occur at the right place. This is the "template effect". (Scheme I-D1) This kind of complex can still dissolve in organic solvents because crown compounds have hydrophobic groups [16][17][18].



Scheme I-D1 Synthetic mechanism of a crown ether

Selecting the proper size of the metal ion is very significant. If the metal ion is too large or too small for the macrocycle, the macrocycle is not going to be held properly, and the reaction will not go properly. The percentage yield of the product will be very low. For example, Li^+ fits well in the cavity of 12-crown-4 which is quite small; Na^+ fits right in the cavity of 15-crown-5; K^+ fits well in the cavity of 18-crown-6, which is comparatively larger [16][18].

The very large crown compounds like 30-crown-10 or 42-crown-14 use two or more metal ions so that the macrocycle can be held together properly, and the reaction will occur at the right place [17][18]. (I-10)



I-10 Two sodium metal ions in 30-crown-10 cavity

Although the macrocycle is held by the metal cation, the reaction is still statistical. The percentage yield of the products is not very high, not more than 50%.

I-E Liquid Crystalline Polymers and Poly(azomethine)s

Reinitzer was the first one who noticed liquid crystalline behavior in 1888. [28] He noticed that the melt of cholesteryl benzoate was turbid. It did not have a sharp melting point; instead, it had more than one melting state. The compound became a clear liquid at a high temperature at last. He could not explain this phenomenon. After two years, Lehmann also researched these kind of materials, and gave the the name of "liquid crystal" to these materials which have the particular behavior. [29] The first liquid crystalline polymer, poly(γ -benzyl-L-glutamate) was prepared by Elliott and Ambrose in 1950. [30] They prepared slides and examined them by IR and microscope. They found that the polymer was rigid, rod like, and had different crystalline phases. The liquid crystalline polymer field has developed since then.

Adams and his co-workers synthesized the first azomethine [31]. They reacted two benzidine molecules with two terephthaldehydes and two dianisidines to form an azomethine macrocycle with four C=N double bonds. They noticed that the compound had a high melting point (above 275°C). Also they found that the compound

precipitated out from the reaction solution, and did not dissolve in general organic solvents. They tried to make high molecular weight poly(azomethine), but they were not successful, because the polymer precipitated from the reaction solution when the polymer chains grew to a certain length.

Nowadays, people make various different liquid crystalline polymers, including many kinds of poly(azomethine)s.

A polymer can have several different physical states at different temperature ranges. At a high temperature, it is a low viscosity isotropic liquid. At a low temperature, the polymer can be in either crystalline (or partly crystalline) or glassy states. If it is a symmetrical polymer, it will be crystalline or be partly crystalline. If it is an amorphous polymer, it will be glassy.

Liquid crystalline polymers can exist as a low viscosity liquid, while at the same time showing the anisotropic character of a crystalline solid as well under a constant pressure and in a certain temperature range. This special phase is known as liquid crystalline phase [19]. (Fig. I-E1)

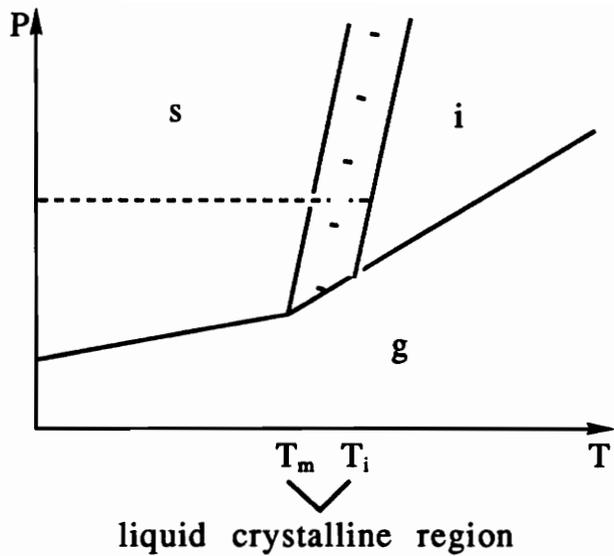
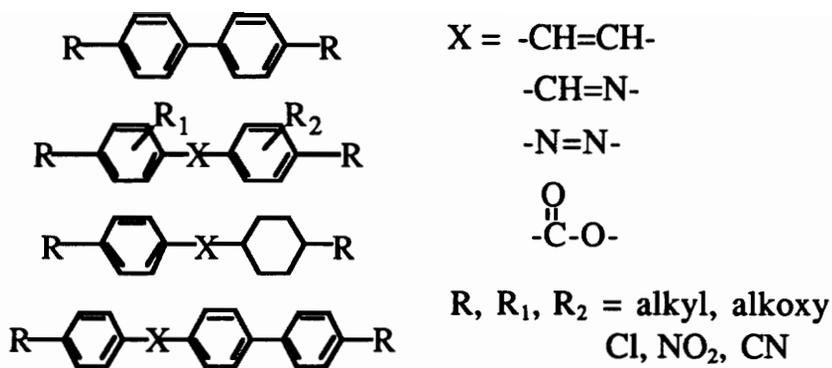


Fig. I-E1

As Fig. I-E1 shows, when the temperature of the polymer is lower than its melting temperature, it shows a three dimensional, long range position-ordered crystalline lattice. At the melting point, it loses most of its long-range positional order, and only has short-range ordering between the molecules. But the long-range positional order of the polymer is not completely lost, and as the temperature increases gradually, the long-range positional order loses one dimension at a time. In the temperature range $T_m < T < T_i$, the polymer exists between the crystalline phase and the isotropic phase. This is the “liquid crystalline phase” of the polymer. [19]

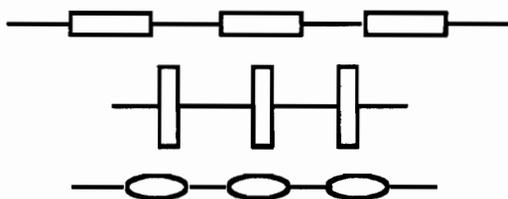
Liquid crystalline polymers contain linear rod or disk-shaped groups which are double bonded and benzene rings in their basic structures (I-11). These molecules are very rigid, and they are not able to be bent. Below the T_m , the long molecules line up in parallel in a three dimensional order to form a crystalline phase. When the temperature rises above T_m , and increases gradually, these long molecules slowly lose their order, and enter an isotropic phase at T_i .



I-11 Mesogenic groups

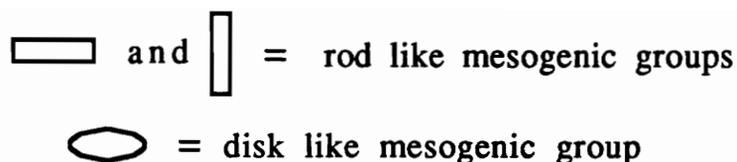
The rod and disk like groups in the molecule are called “mesogenic groups”. These mesogenic groups contain at least two aromatic rings which are connected in the para position. Also they may contain double bonded groups between these rings. The linking groups which are used in liquid crystalline polymers can be imino, azo, azoxy, ester, amine, and vinylene groups. [20]

These liquid crystalline polymers can be arranged into two major groups. When the mesogenic groups are located in the polymer main chain, it is called a main chain liquid crystalline polymer. When the mesogenic groups are located in the side chain, it is called a side chain liquid crystalline polymer. [19] (I-12) (I-13)



I-12 Liquid crystalline main chain polymers





I-13 Liquid crystalline side chain polymers

Since the transitional and rotational motions of these mesogenic groups are different between main chain and side chain liquid crystalline polymers, the physical properties of these two kinds of liquid crystalline polymers are different.

The liquid crystalline polymer chains are very rigid. If the chains line up in a highly ordered manner, they are very strong. Also the higher the molecular weight, the stronger the polymer is. [19][20]

Liquid crystalline polymers have high melting points. Usually the melting point is above 200°C. They are also hard to dissolve in general organic solvents like alcohols, ethyl acetate, acetone, toluene, chloroform, etc.

When substituents are used on the phenyl rings on the main chain, for example, chloro-, bromo-, hydrocarbon, or phenyl groups, the symmetry of the polymer is reduced, and the diameter of the polymer is increased. By using substituents, the T_m of the polymer can be decreased about 60-70°C. [21]

"Flexible spacers" also can decrease the transition temperatures (both T_m and T_i). Usually the "flexible spacers" are the $(CH_2)_n$, or $(CH_2CH_2O)_n$ groups. The transition temperature decreases as "n" increases, and also the mesogenic stability decreases. An even-odd effect is shown by whether "n" is even or odd. The even numbered "flexible spacer" molecules are more symmetrical, and

their transition temperature is higher; the odd numbered "flexible spacer" molecules are less symmetrical, and their transition temperature is lower.[22]

When both "flexible spacers" and "substituents" are used at the same time, the transition temperature can be reduced greatly.

The side chain liquid crystalline polymers have properties similar to the conventional amorphous polymers, but they still show liquid crystalline polymer character. The rigid mesogenic groups of the side chain force the main chain to become ordered in some cases. When the temperature increases, the main chain begins to melt, but the side chain with mesogenic groups can still remain in glassy state. But the T_g and T_m are mainly dependent upon the polymer main chain.

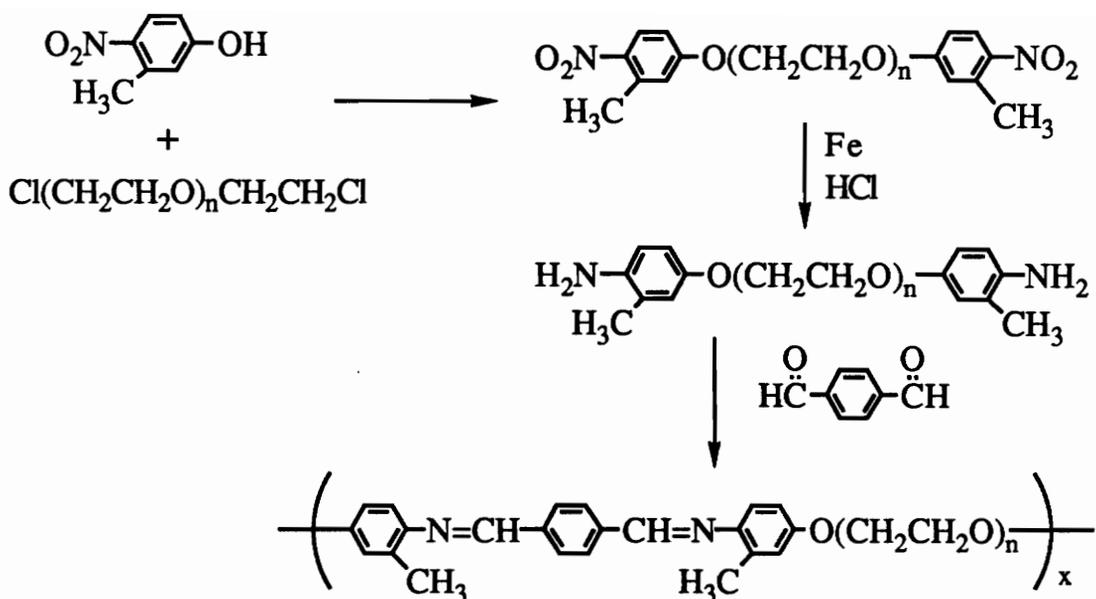
Poly(azomethine) is one type of liquid crystalline polymer. This kind polymer is very rigid and strong. If there is no "substituent" or "flexible spacer" on the chain, T_m will not be observable, because the melting temperature is higher than the decomposition temperature. [23][25] Therefore people put "substituents", "flexible spacers", or both on the main chain of the polymers to improve their properties. When there are "substituents", "flexible spacers", or both on the main chain of the poly(azomethine)s, T_m 's and T_i 's can be observed by DSC and optical microscopy. But the T_m 's are still above 200°C. If too many "substituents" and "flexible spacers" are put onto the polymer chain, the liquid crystalline properties will be lost. [22][23][25]

Poly(azomethine)s do not dissolve in general organic solvents like toluene, alcohols, ethers, acetates, THF, and acetone. Usually they precipitate out from the reaction solution when polymer chains grow to a certain length. [22][23][24][25][27] When a poly-(azomethine) has "substituents" and "flexible spacers" on the

chains, the polymer can dissolve in m-cresol, and dichlorobenzene. But when the same polymer is reprecipitated and dried, it is hard to redissolve in same solvent. [22] If the poly(azomethine) with benzene ring and C=N double bond only has “flexible spacers”, and does not have “substituents” on the chain, it only can dissolve in strong acids like sulfuric acid, methanesulfonic acid, or dichloroacetic acid. [22][23][24][25][26][27] If the poly(azomethine) with a benzene ring and C=N double bond has a “flexible spacer” in the chain, the polymer does not dissolve in any solvent after it is precipitated from the reaction solution. [25] The solubilities of poly(azomethine)s are very low.

I-F Synthetic Methods for Liquid Crystalline Polymers

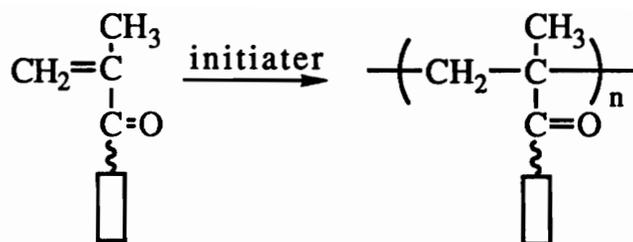
Polycondensation is the common method to synthesize liquid crystalline main chain polymers. Most poly(azomethine)s are synthesized using this method. The reactions can have several steps. “Substituents” and/or “flexible spacers” can be reacted with benzene rings to make the monomers with “substituents” and/or “flexible spacers” first. The polycondensation reaction is the last step to make polymers. Usually the poly(azomethine) is synthesized by reacting terephthaldehyde with diaminophenyl monomers. Here is an example. (Scheme I-f1) [26]



Scheme I-F1 Synthesis of poly(azomethine) with "flexible spacer" and "substituent"

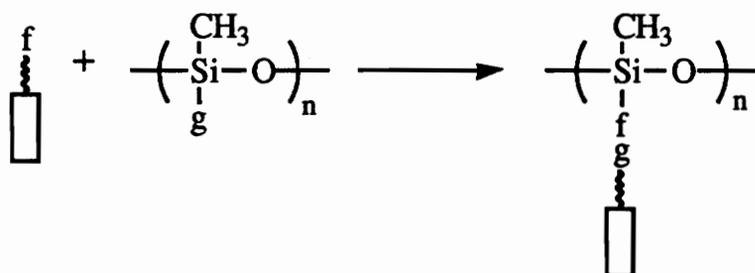
Other main chain liquid crystalline polymers have similar reaction methods as poly(azomethine)s. They just have different monomers. For example, the reactants of polyesters are diacid chloride, and dialcohol; the reactants for polyamides are diacid chlorides and diamines. The reaction temperature is room temperature and above. The polymer will achieve the highest degree of the polymerization at the very end of the reaction, if the polycondensation method is used. Therefore, the reaction time should be long enough to finish the polymerization. Also the purity and the proper stoichiometry of the reactants are very important for the polycondensation reaction.

Most side chain liquid crystalline polymers are synthesized using radical polymerization [19]. (Scheme I-F2) Radical polymerization needs an initiator to start the polymerization. The radical polymerization reaction goes very fast, and it achieves a high degree of polymerization quickly.



Scheme I-F2 Synthesis of side chain liquid crystalline polymer using radical polymerization

Some side chain liquid crystalline polymers are made by substitution reactions [19]. (Scheme I-F3)



Scheme I-F3 Synthesis of side chain liquid crystalline polymer using substitution reaction

Liquid crystalline polymers have special properties, which can be both an advantage and a disadvantage for mankind's technological need. They are rigid and strong. They have high T_m 's, and do not dissolve in general solvents. These properties make the liquid crystalline polymers hard to process. Liquid crystalline polyrotaxanes may be one of the solutions for the processing problems, because this modification will produce property changes in the polymer. After the crown ethers are threaded onto the poly(azomethine) chains, the poly(azomethine)rotaxanes should have lower T_m 's and increased solubilities. The processability and the molecular weight of liquid crystalline polymers should therefore be improved.

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CHAPTER II

CROWN ETHERS

II-A Design of Crown Ethers

To select suitable crown ethers for synthesizing poly-(azomethine)rotaxanes, several concepts need to be considered.

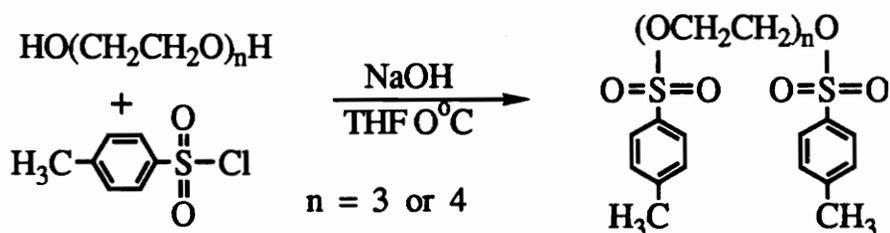
The cavity size of the crown ether is important for synthesizing polyrotaxanes. The cavity size of the crown ether should be larger than the diameter of polymer backbone, so that during the synthesis of polyrotaxane threading can occur. But, on the other hand, if the cavity size of the crown ether is too large, dethreading will easily happen. If the polymer backbone is flexible, the large size of the crown ether can be wrapped around the middle of the polymer chain, so that dethreading will not occur as easily [1]. Thus, for a flexible polymer backbone, a large sized crown ether will be a good choice because it will increase the threading rate. According to the previous reports, the flexibility of crown ether is not very important for synthesizing polyrotaxanes, because the crown ethers usually keep their cavities open unless the size of the crown ether is extremely large. [1] [4] [5] [6]

Poly(azomethine)s have mesogenic groups, so that they are rigid and rod like, and they are not flexible. [2] Therefore, if the size of the crown ether is too large to be blocked, dethreading will happen easily. The large end blocking group, a tris(*t*-butylphenyl)alkyl compound, is designed to block 42 membered rings. If the size of the crown ether is larger than 42 members, the crown ether can go through the large end blocking groups. Then, dethreading can happen easily.

Harrison reported that macrocycles with less than 22 members can not be threaded by 1,10-decandiol [3]. The diameters of the poly(azomethine)s are larger than 1,10-decandiol because of the size of the carbonyl groups and phenyl rings, so that the size of the crown ether should be larger than 22 members.

II-B Results and Discussion, Oligo(ethylene Glycol) Ditosylates

The method of synthesizing crown ethers is the statistical synthetic method. Oligo(ethylene glycol) dichloride or oligo(ethylene glycol) ditosylate are the necessary reactants for synthesizing crown ethers. During the reaction, the oligo(ethylene glycol) reacts with oligo(ethylene glycol) ditosylate or oligo(ethylene glycol) dichloride. Since the tosylate group is a better leaving group, oligo(ethylene glycol) ditosylates are preferred. Tri- and tetra(ethylene glycol) ditosylate syntheses were reported by Inoue and his group in 1984 [7]. Tetra(ethylene glycol) ditosylate was synthesized for making 30-crown-10, and tri(ethylene glycol) ditosylate was synthesized for making 42-crown-14. The reaction method and conditions were the same. The reaction is shown below [7] (Scheme II-B1).



Scheme II-B1 Synthesis of oligo(ethylene glycol) ditosylates

As Scheme II-B1 shows, toluenesulfonyl chloride reacted with tri-, or tetraethylene glycol. The reaction produced HCl as the by-product. NaOH was used as the base which drove the reaction

forward. The solvent was tetrahydrofuran. This was an exothermic reaction, so that the reaction was done in an ice bath at 0°C. Inoue reported that the reaction was stirred for 2 hours [7]. Experimental results showed that if the reaction was stopped in 2 hours, there were some unreacted reactants left, and the percentage yield was not very high (about 80% yield). The reaction time was prolonged to 12 hours. Since this was a two phase reaction, the reaction needed to be stirred very well. A mechanical stirrer was used. After the reaction was finished, 10% HCl, and then NaHCO₃ were added to neutralize the solution. The crude tetra(ethylene glycol) ditosylate was a slightly yellow viscous liquid, and the crude tri(ethylene glycol) ditosylate was a slightly yellow solid.

During the reaction, excess toluenesulfonyl chloride was added. There was unreacted toluenesulfonyl chloride mixed in the products which needed to be separated. From the ¹H NMR spectra, the peaks of reactants were seen. Inoue reported that the unreacted toluenesulfonyl chloride would be converted into toluenesulfonic acid, and washed away by water [7], but the experimental results showed that unreacted toluenesulfonyl chloride could not be washed away by water. The solubility test was tried for toluenesulfonyl chloride, tri-, and tetra(ethylene glycol) ditosylate. The separation was done based on the different solubility of the reactants and the products.

Tetra(ethylene glycol) ditosylate was a viscous liquid. The solubility test showed that toluenesulfonyl chloride dissolved in hexane, and tetra(ethylene glycol) ditosylate did not. The crude tetra(ethylene glycol) ditosylate was washed with hot hexane. Most of the toluenesulfonyl chloride dissolved and was washed away. After the purification, the color of the tetra(ethylene glycol) ditosylate turned lighter, and it became a very pale yellow, almost colorless viscous liquid. The percentage yield was 97.3%. (Inoue reported 83% yield.)

^1H NMR and IR analysis confirmed the compound. (Fig. II-B1, II-B2)

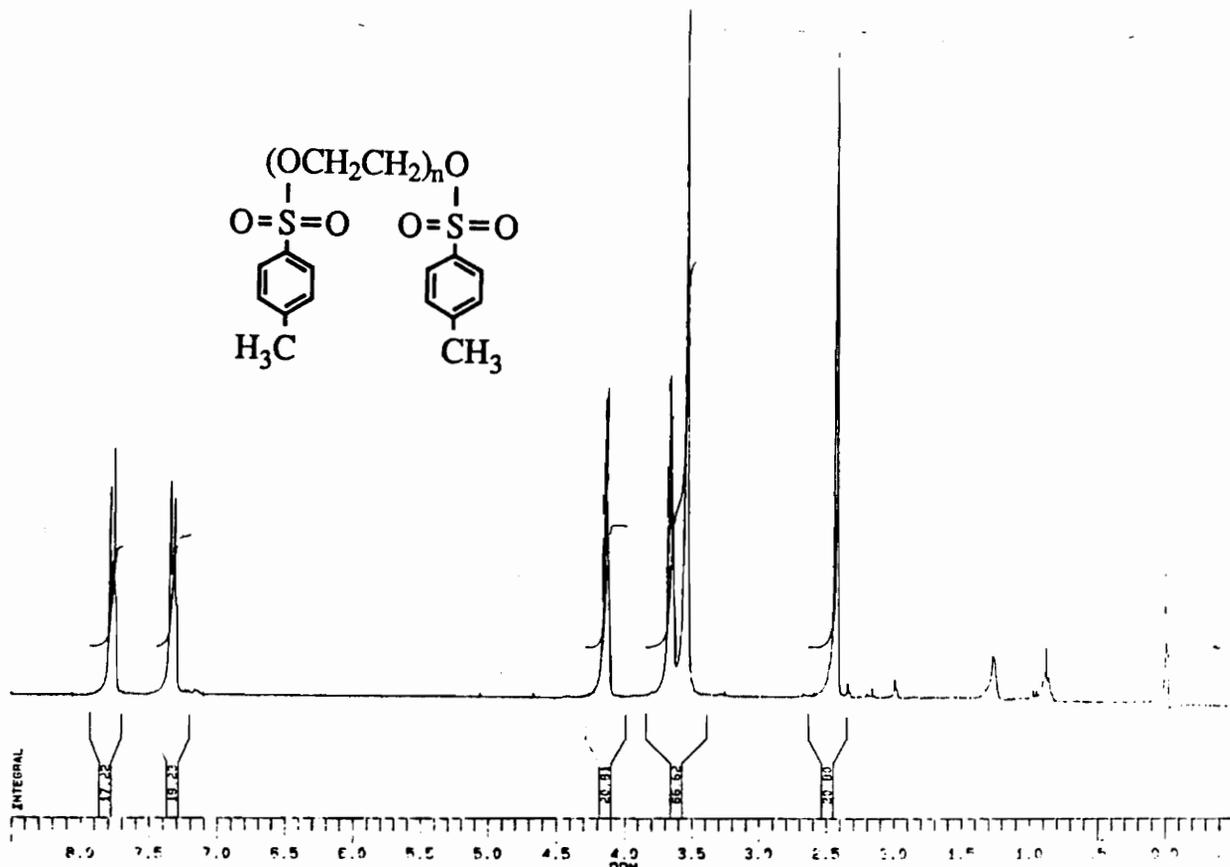


Fig. II-B1 ^1H NMR spectrum of tetra(ethylene glycol) ditosylate in CDCl_3 (ppm)

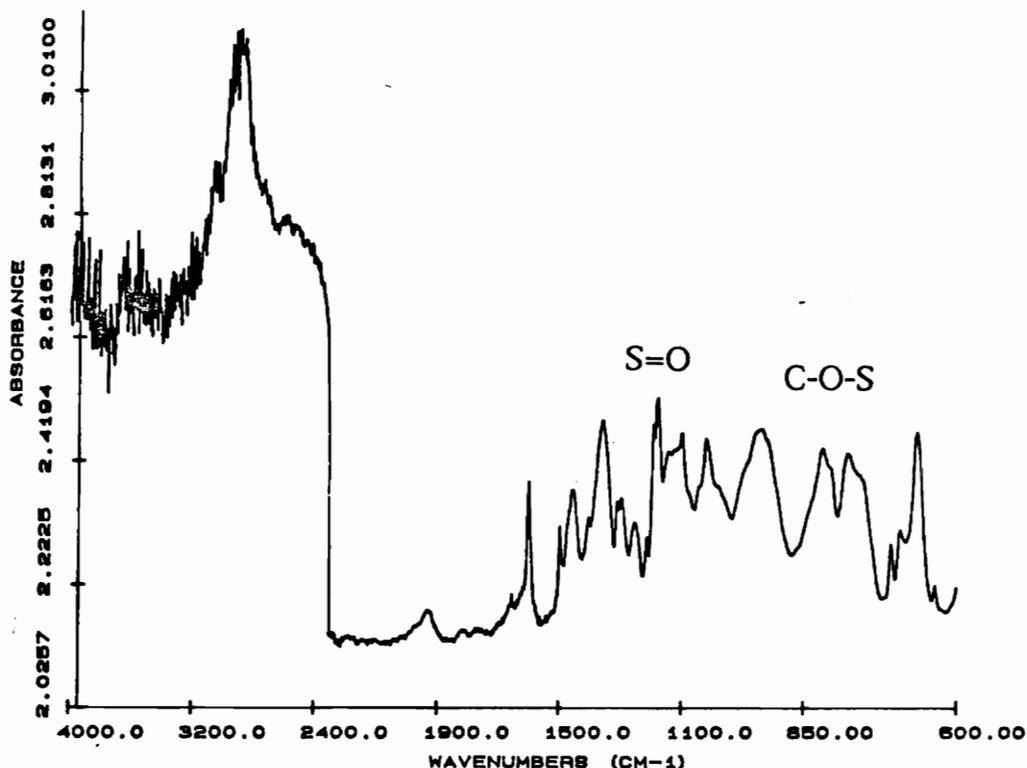


Fig. II-B2 IR spectrum of tetra(ethylene glycol) ditosylate (KBr, cm^{-1})

The crude tri(ethylene glycol) ditosylate was a slightly yellow solid. The unreacted toluenesulfonyl chloride could not be washed away by hot hexane. Tri(ethylene glycol) ditosylate did not dissolve well in most general organic solvents except chloroform and methylene chloride. Recrystallization was done in acetone. Toluenesulfonyl chloride dissolved in hot acetone well. After the recrystallization, the purified tri(ethylene glycol) ditosylate was a colorless crystal. Several recrystallizations were done until the melting point was stable. The final melting point was 83.1-84.9°C.

The percentage yield was 96%. Inoue reported that the the melting point was 80.0-81.0°C, and the percentage yield was 89% [7]. NMR and IR analysis confirmed the product structure. Since the structure of tri(ethylene glycol) ditosylate is similar to tetra(ethylene glycol) ditosylate, the NMR and IR spectra are omitted here.

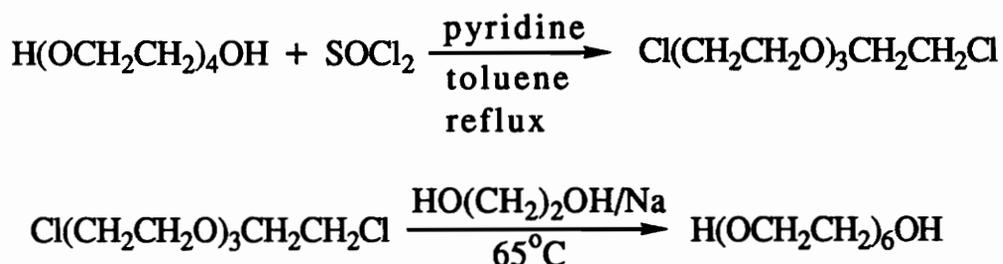
II-C Results and Discussion, Hexa(ethylene glycol)

Hexa(ethylene glycol) is a reactant for synthesizing 30-crown-10. There are two methods to synthesize hexaethylene glycol.

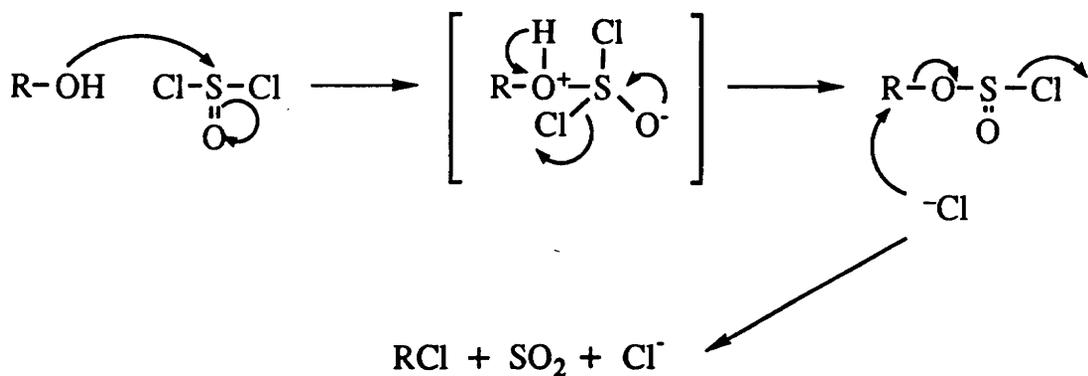
Method 1, sodium method

This synthetic procedure for hexa(ethylene glycol) is from Perry's paper which was published in 1936 [8]. This method of synthesizing hexa(ethylene glycol) includes several steps. (Scheme II-C1)

Tetra(ethylene glycol) dichloride was synthesized first. The reactants were tetra(ethylene glycol) and thionyl chloride. The solvent was toluene. Pyridine was used as the base. The reaction was refluxed for 15 hours. The reaction mechanism is shown in Scheme II-C2 [9].



Scheme II-C1 Synthesis of hexa(ethylene glycol) (sodium method)



Scheme II-C2 Mechanism of synthesizing glycol chloride

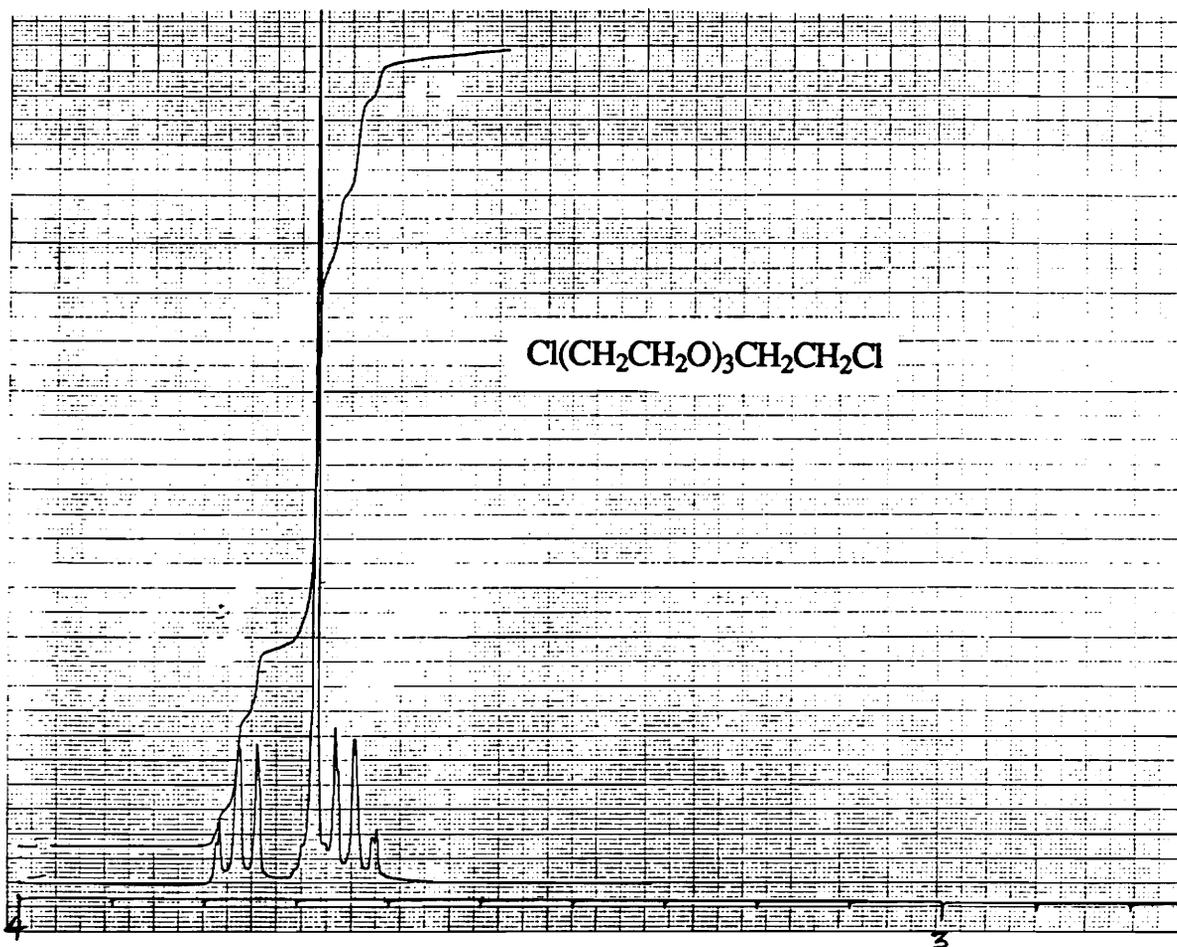


Fig. II-C1 ^1H NMR spectrum of tetra(ethylene glycol) dichloride in CDCl_3 (ppm)

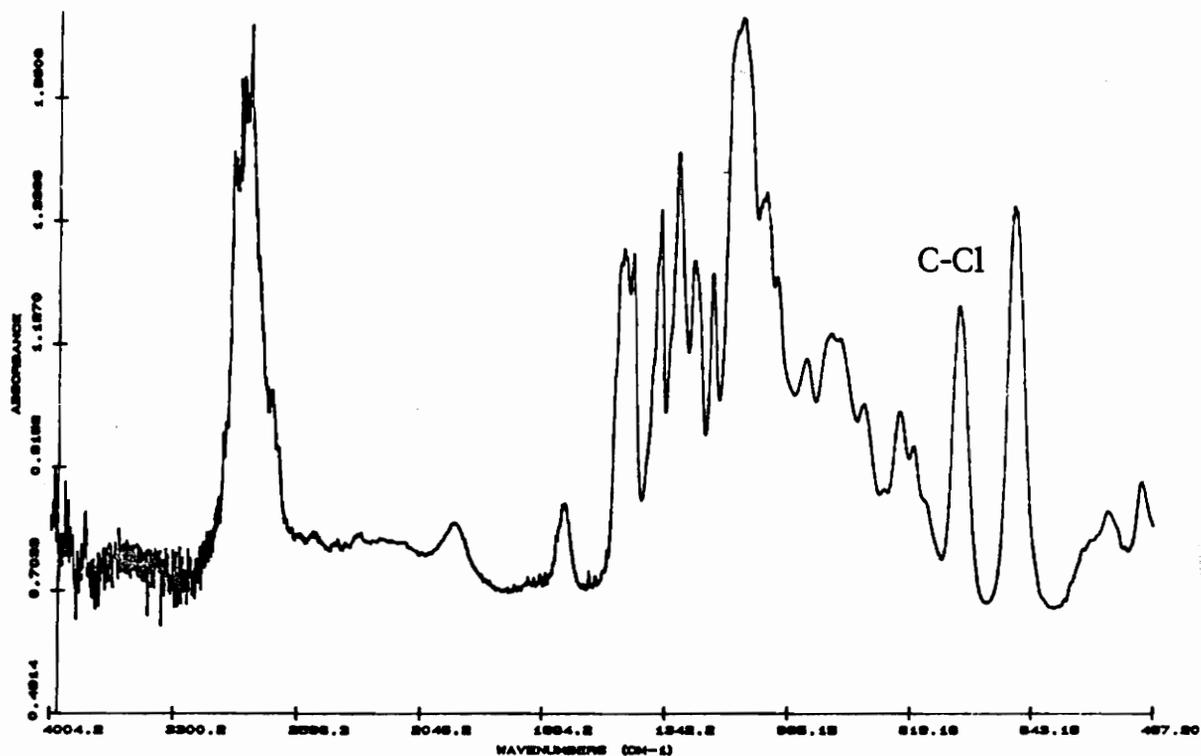


Fig. II-C2 IR spectrum of tetra(ethylene glycol) dichloride (KBr, cm^{-1})

After the reaction was finished, diluted HCl was added to neutralize the solution. The crude product was a yellow oily liquid. The product was purified by vacuum distillation. The purified tetra(ethylene glycol) dichloride was pale yellow oily liquid. The percentage yield was 80%. (Pedersen reported a 92% yield. [9]) ^1H NMR and IR analysis confirmed the product. (Fig. II-C1) (Fig. II-C2)

The second step was making ethylene glycol monosodium salt [10]. Fresh cut sodium was added to ethylene glycol partwise at 65°C. This reaction was moisture sensitive. Before adding the sodium, the ethylene glycol needed to be distilled, in order to remove the water. The reaction was done under nitrogen to prevent moisture absorption. Since the sodium was a very active metal, the reaction was violent. A lot of hydrogen gas was generated during the reaction. To avoid explosion, the sodium pieces needed to be small and added slowly. The reaction temperature needed to be controlled below the sodium melting point, 97.8°C. At the beginning of the reaction, the reaction went fast and violently, and the reaction solution was thin and flowable. As more sodium was added, more salt was formed; the reaction mixture became very thick. A mechanical stirrer was used. The reaction became slower and slower, and the reaction mixture became thicker and thicker. At last even the mechanical stirrer could not stir. Since the reaction became too thick, and no further reaction could occur, only 20% by mole ethylene glycol could react with sodium to form salt. The reaction temperature was increased to 90°C to allow the sodium to react completely.

Tetra(ethylene glycol) dichloride was added to the sodium ethylene glycol salt as the third step. The sodium ethylene glycol salt reacted on the both sides of tetra(ethylene glycol) chloride. The anion on the oxygen on the ethylene glycol attacked the terminal carbons of the tetraethylene glycol chloride. The chloride ion left the carbon, and the product was formed. After the reaction was finished, water was added to destroy the excess sodium and dissolve the NaCl salt. The crude hexa(ethylene glycol) was vacuum distilled at 180°C under 0.25 mm Hg. The purified hexa(ethylene glycol) was a light yellow liquid. The percentage yield was 21%. Perry reported the boiling point of hexa(ethylene glycol) was 166-168°C under 0.015 mm Hg. The percentage yield was

49.75% [10]. ^1H NMR and IR spectra confirmed the product. (Fig. II-C3) (Fig. II-C4)

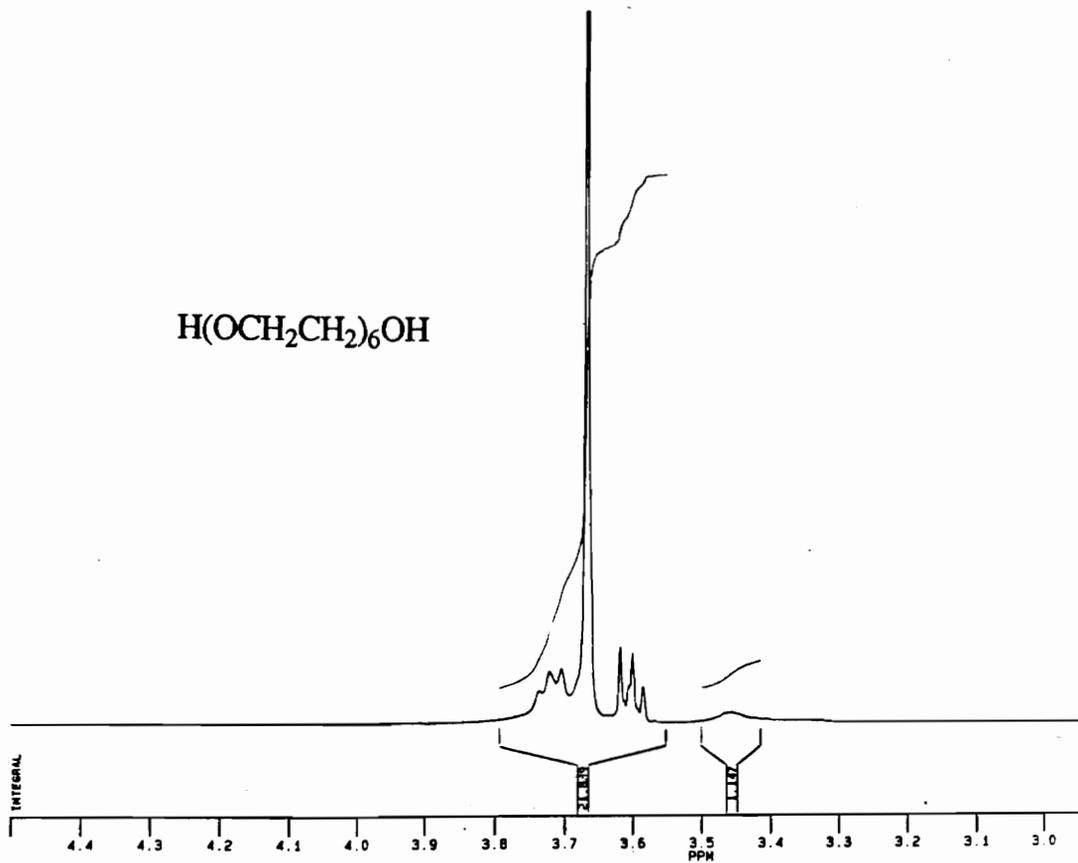


Fig. II-C3 ^1H NMR spectrum of hexa(ethylene glycol) in CDCl_3 (ppm)

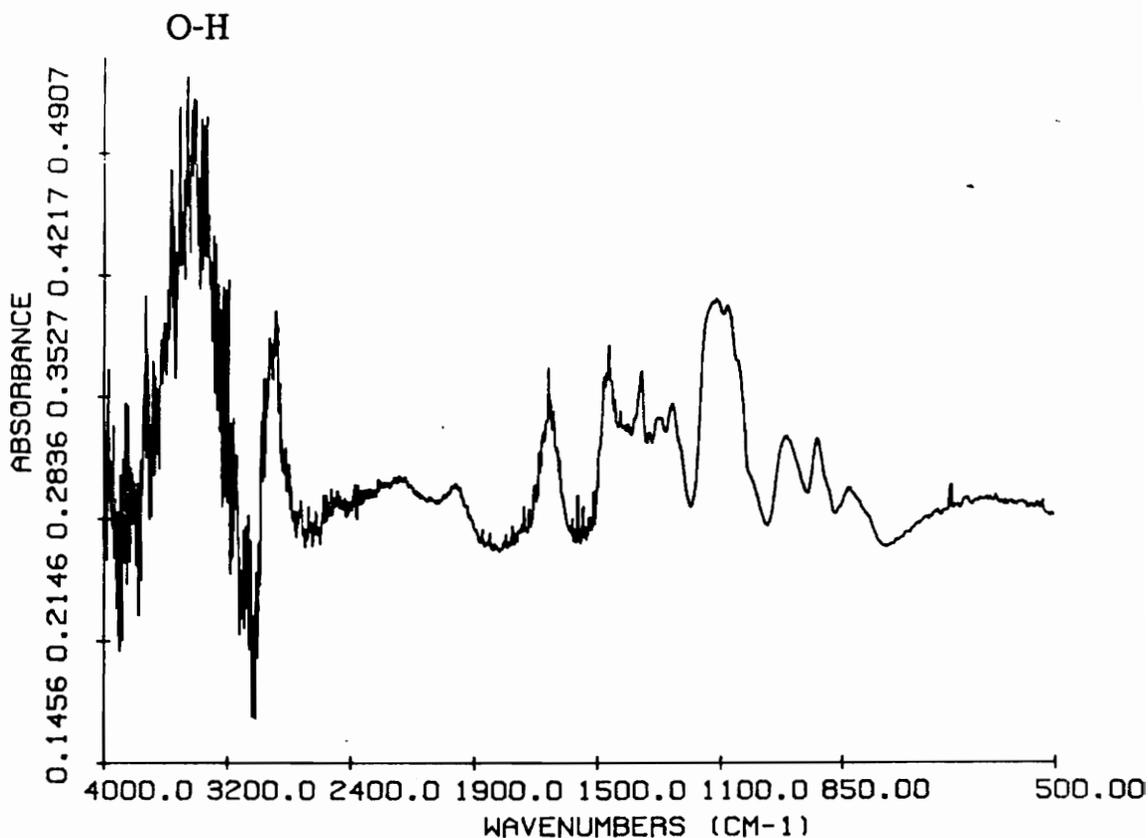
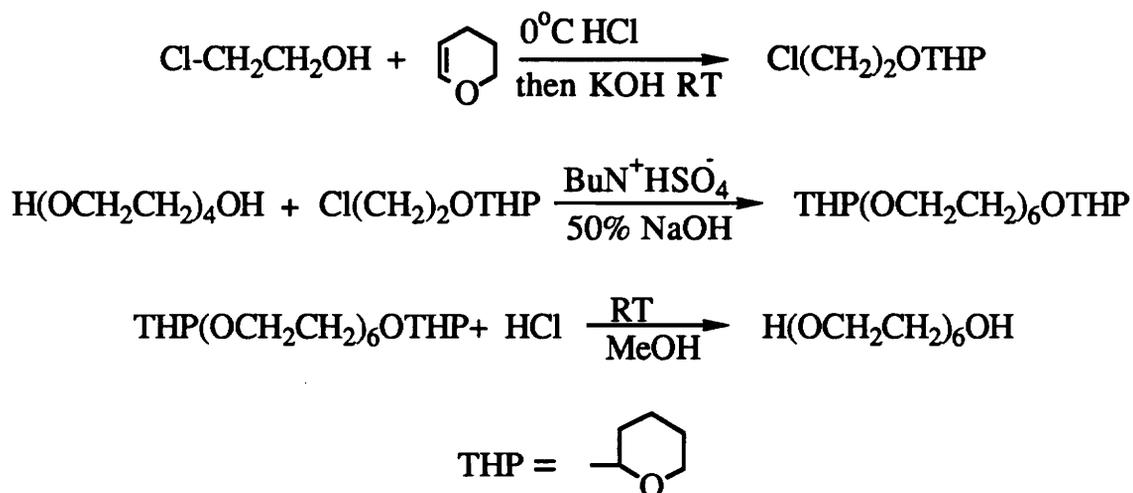


Fig. II-C4 IR spectrum of hexa(ethylene glycol) (KBr, cm^{-1})

Method 2, phase transfer catalyzed method

Synthesizing hexa(ethylene glycol) using the sodium method has several limitations and disadvantages. To make sodium ethylene glycol salt is very difficult. The sodium is a very active metal, and can easily cause an explosion. Although only 20% of the ethylene glycol is reacted and forms the salt, the reaction mixture is very thick and hard to stir. The reaction also becomes very slow when more and more salt is formed. Although the reported percentage yield was 49.75%, the highest percentage yield that we could get

from our experimental results was 29% [1]. For improving these limitations, the phase transfer catalyzed method was used to synthesize hexa(ethylene glycol) [14]. The method also includes several steps. Chloroethanol was protected by tetrahydropyran groups. Then, ClCH₂CH₂OTHP reacted at both ends of tetra(ethylene glycol) to form protected hexa(ethylene glycol). Finally the hexa(ethylene glycol) was deprotected. The details are discussed below. (Scheme II-C2)



Scheme II-C2 Synthesis of hexaethylene glycol (phase transfer catalyzed method)

Protected chloroethanol, ClCH₂CH₂OTHP, was synthesized. [11] [12] [13] 3,4-Dihydro-2H-pyran and 2-chloroethanol were added together along with a few drops of HCl. Since this was an exothermic reaction, the reaction temperature was 0°C (in ice bath). After 20 minutes, the ice bath was removed, and the reaction mixture was neutralized with a base. According to Woods' report [11], a few pellets of sodium hydroxide were added. Our experimental results showed that NaOH would not dissolve in the solution, and the solution could not be neutralized. Cram and his group reported that they added triphenylamine to neutralize the solution because triphenylamine dissolved in the reaction solution. We used

triethylamine which proved a good base to neutralize the solution. The reaction was continuously stirred for 4 hours. After the reaction was finished, the product, $\text{ClCH}_2\text{CH}_2\text{OTHP}$ could be purified by distillation. Woods suggested regular distillation [11], but Cram and Bartsch suggested vacuum distillation. We tried both methods. In the vacuum distillation, the chloroethoxytetrahydropyran boiled at 55°C under 0.5 mm Hg. Cram reported the boiling point of the same compound was $87\text{-}88^\circ\text{C}$ under 0.5 mm Hg [12], and Bartsch reported the boiling point was $97\text{-}99^\circ\text{C}$ under 0.35 mm Hg [13]. In the regular distillation, the chloroethoxytetrahydropyran boiled at 143°C . Woods reported the boiling point of the compound was 146°C [11]. As the boiling points of the reactants and the product were close, (chloroethanol boiled at 129°C , dihydropyran boiled at 86°C , and chloroethoxytetrahydropyran boiled at 143°C) regular distillation is a better choice. If regular distillation is used, the acid in the mixture should be neutralized completely. Otherwise, the solution will decompose and become black. After the distillation, the purified product was a colorless liquid which gave a 94% yield. (Woods reported percentage yield 93% [11], Cram reported a percentage yield of 96% [12], and Bartsch reported a percentage yield of 90% [13].) ^1H NMR and IR analysis confirmed the compound. (Fig. II-C5 and II-C6)

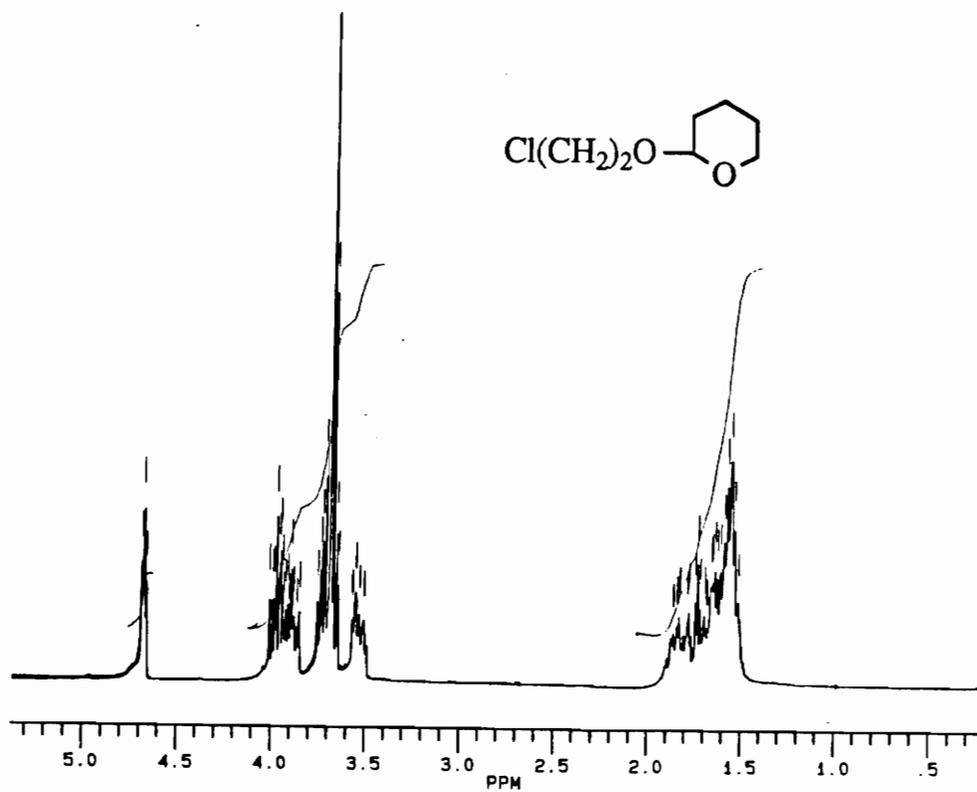


Fig. II-C5 ^1H NMR spectrum of chloroethoxytetrahydropyran in CDCl_3 (ppm)

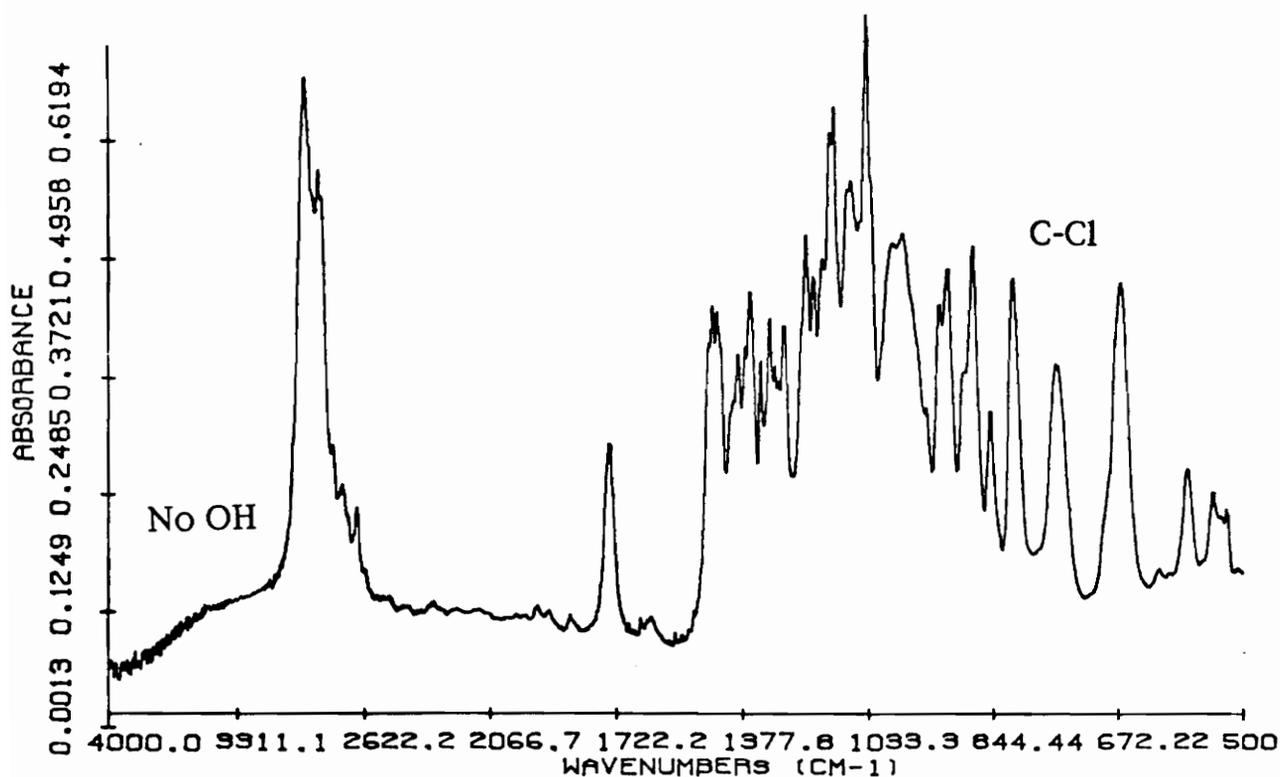


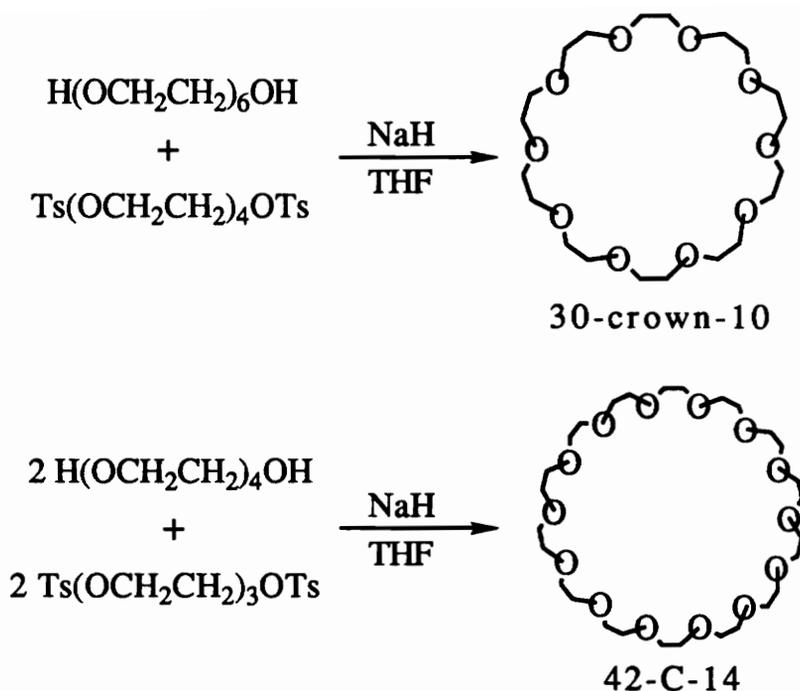
Fig.II-C6 IR spectrum of chloroethoxytetrahydropyran (KBr, cm^{-1})

To make the tetrahydropyran group protected hexa(ethylene glycol) was the second step [14]. Chloroethoxytetrahydropyran and tetraethylene glycol were mixed together. Tetrabutyl ammonium hydrogen sulfate was used as the catalyst, and sodium hydroxide was used as the base. The two phase reaction was stirred at 65°C for 5 days. Bartsch reported the reaction for 3 days. [14] We found that if the reaction ran for 3 days, some tetra(ethylene glycol) molecules only reacted at one side, and some even did not react at all. Therefore the reaction should be long enough to be complete. After 5 days, the reaction mixture turned brown. Then the third step, deprotection, was begun. After extracting the product, methanol was added to the tetrahydropyran group hexa(ethylene glycol).

The deprotection was done in an acidic condition (HCl). After the reaction, the reaction solution was neutralized using NaHCO₃. The crude hexa(ethylene glycol) was a brown-yellow liquid. The crude product still included some impurities like tetra(ethylene glycol), penta(ethylene glycol), and other impurities. Vacuum distillation was used to purify the product. The hexa(ethylene glycol) boiled at 193°C under 0.5 mm Hg. The tetra- and penta(ethylene glycols) boiled at lower temperatures under this vacuum condition. After the purification, the pure hexa(ethylene glycol) was a light yellow liquid. The percentage yield was 91%. Bartsch reported that the percentage yield was 80% [14]. ¹H NMR and IR analysis (Fig. II-C3, II-C4) confirmed the product. Since the ¹H NMR spectra patterns of tetra(ethylene glycol) and penta(ethylene glycol) were similar to that of hexa(ethylene glycol), integration of the peaks needed attention. The integration ratio of the two triplets at 3.6 and 3.72 ppm, and the singlet at 3.67 ppm should be 1:1:4. If the integration ratio was 1:1:2.5, the compound was the mixture of tetra(ethylene glycol) and penta(ethylene glycol). From the spectrum, the singlet at 3.67 ppm for hexa(ethylene glycol) was taller than for tetra- and penta(ethylene glycol).

II-D Results and Discussion, Crown Ethers

The reactions for synthesis of 30-crown-10 and 42-crown-14 are shown below. (Scheme II-D1) [15][16]



Scheme II-D1 Synthesis of crown ethers

Tetra- or hexa(ethylene glycol) and NaH were added to a large amount of THF. Since sodium reacted with ethylene glycol to form a salt, hydrogen gas was formed. Tri- or tetra(ethylene glycol) ditosylate in THF was added dropwise. The reaction was stirred at room temperature for 48 hours. After the reaction was finished, water was added to destroy the excess NaH. The crude product was a brown-yellow liquid.

During the reaction, there were several responses. If one molecule of glycol reacted with one molecule of ditosylate, a small crown was formed. If two molecules of glycol reacted with two molecules of ditosylate, a large crown was formed. If several glycol molecules reacted with several glycol ditosylate molecules to form a long chain, a poly(ethylene glycol) was synthesized. When two crown ethers became attached to each other, a catenane was formed. After the reaction was finished, the product was the mixture of small

crowns, large crowns, catenanes and poly(ethylene glycol). If the reaction was done at room temperature, there would be around 30% small crowns and 30% large crowns. The other 40% would be catenanes, poly(ethylene glycol)s and other impurities. If the reaction was done at the THF boiling temperature, 67°C, the percentage yield of large crown increased to around 50%. The percentage yield of other products was decreased. The reason for this phenomenon may be related to the activation energy.

$$E_a = \Delta H - T \Delta S$$

Since a large crown is formed by four molecules, the synthesis should be more difficult than a small crown which is formed by two molecules. In another words, the activation energy of the large crown may be larger than the activation energy of the small crown.

Since $k = A e^{-E_a/RT}$, then $\ln k = \ln A - E_a/RT$

If we plot $\ln k$ vs. $1/T$, the slope is $-E_a/R$. For the comparison, the plots of small crown and large crown are shown on the same graph. (Fig. II-D1)

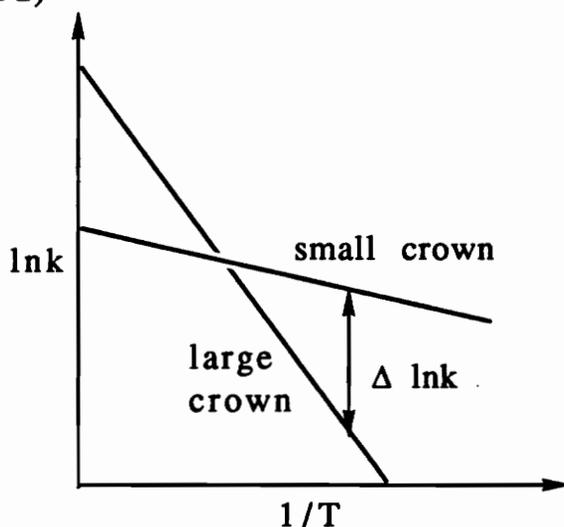


Fig. II-D1 Activation energy graph of crown ether synthesis

Therefore when the temperature is low, the $\Delta \ln k$ is large, the small crown will be easy to form since the E_a of the small crown is small; when the temperature is high, the $\Delta \ln k$ is small, and more large crown will form.

Also on the kinetic side, at low temperature, the shorter chains have shorter end-to-end distance, and have a higher chance to collide. The small crown will be easier to form. When the temperature rises, the molecule's motion becomes more violent, the oligomer chains are pushed apart by the solvent molecules, and the chance to form large crowns is increased. The experimental results are consistent with this idea. During the preparation of 42-crown-14, when the reaction temperature was raised to the boiling temperature of THF, the yield of the large crown, 42-crown-14, almost doubled (from 27% to 40%). The "template effect" has played an important role in the synthesis of crown ethers. Although the high dilution condition makes the probability that the ends of the ethylene glycol and ethylene glycol ditosylate will meet greater than the probability of forming linear poly(ethylene glycol), the yield still can be improved by the "template effect". Since the partially negative oxygen on the glycol and glycol ditosylate and positive metal ions will attract each other, the "template method" can be used to increase the crown ether yield. The metal ion such as Na^+ or K^+ is added to hold the glycol and glycol ditosylate together. Pederson was the first one to report using the template method [8]. Other crown ether reports also used this method to improve the yield [1] [7] [15] [16]. For the large crowns with more than 20 members, there can be more than one metal ion in the cavity of the crown. The scheme of the template method of synthesizing crown ethers, and the structure of the large crown complex is shown in Scheme I-D1 and I-10.

Another fact of the reaction needs to be noted. When tri(ethylene glycol) reacted with tetra(ethylene glycol) ditosylate at room temperature, the percentage yield of 42-crown-14 was about 18%. When the reaction temperature was increased to THF boiling point, 67°C, the percentage yield increased only to 20%. When tetra(ethylene glycol) reacted with tri(ethylene glycol) ditosylate at room temperature, the percentage yield was about 30%. When the reaction temperature was increased to 67°C, the percentage yield increased to 50%. This probably happens because the tetra(ethylene glycol) is the nucleophile. The glycol nucleophile is longer and more acidic, the chain has a greater possibility of attacking the end of the tri(ethylene glycol) ditosylate which has leaving groups. The probability of forming crown ether increases. Inoue and his group also observed this effect. In the synthesis of 20-crown-6, using a longer glycol chain and a shorter glycol ditosylate chain increased the percentage yield from 26% to 42% [7].

After the reaction, the unreacted tri- or tetra(ethylene glycol) ditosylate should be separated from crown ethers first. The crown ethers were very polar, and they dissolved in water. Ditosylates did not dissolve in water. After the reaction, the crude product was poured into water. The undissolved excess ditosylate was separated from the water phase.

Since the crude product was a mixture of small crowns, large crowns, catenanes, and poly(ethylene glycols), separation needed to be done. The boiling point of crown ethers are very high, and the crown ethers decompose at 175-180°C. (Fig. II-D2) Therefore vacuum distillation was not a good method to purify the crown ethers. Some reported information suggested column chromatography [15][17], but this was also not a good separation method for crown ethers. Both silica gel and alumina column separations were tried. The crown ethers were very polar, and they even dissolve well in water. The structures of large crowns, small

crowns, and poly(ethyleneglycol)s were very similar. They showed three very close spots on the TLC plate. Different solvents were tried to separate them. Benzene and other non-polar solvents could not make them move down the column. The polar solvents like chloroform, ethyl acetate, and ethanol could not separate these three close spots.

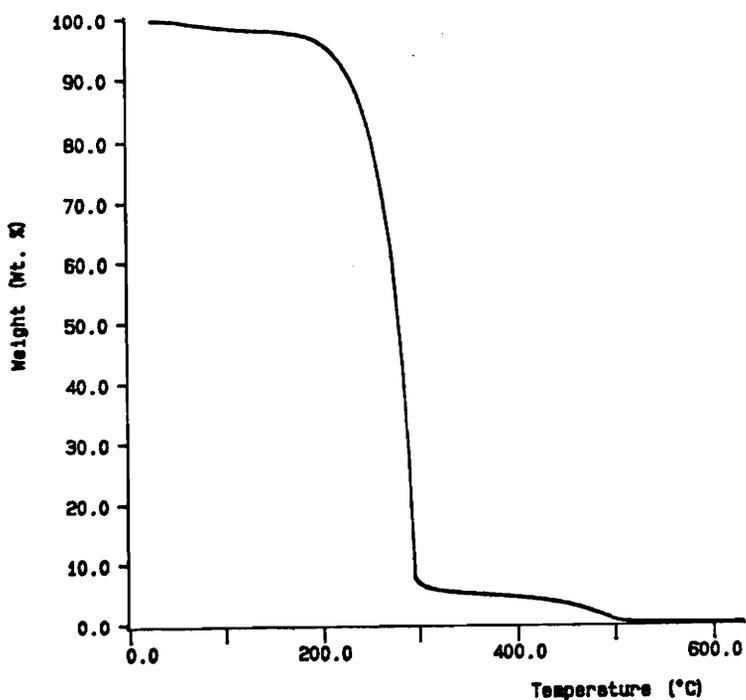


Fig. II-D2 TGA of 42-crown-14 (10°C/min, 25-650°C)

Although column chromatography could not separate the crown ethers, some impurities like salts, and the long chain poly(ethylene glycol) could be separated. The crude product was passed through a 1.5 foot silica gel column, and some impurities were filtered.

Then the short chain poly(ethylene glycol) could be removed by reaction with poly(methacryloyl chloride). Poly(methacryloyl chloride) was made from methacryloyl chloride in THF at 65°C using chain growth polymerization. AIBN was used as the initiator. The product, poly(methacryloyl chloride) was precipitated in hexane. The poly(ethylene glycol) was reacted with poly(methacryloyl chloride) to form polyester in THF. The polyester was precipitated in methanol, and the crown ethers dissolved in methanol. After the poly(methacryloyl chloride) reaction, most of the poly(ethylene glycol) was removed. There was a very small O-H peak at 3555 cm^{-1} in the IR spectrum which could be a water peak. (Fig. II-D3)

Different crown ethers had different solubilities. Crown ethers can be dissolved in polar solvents like water, alcohol, acetone, THF, and ethyl acetate very well. The small crowns like 21-crown-7 also dissolve in non-polar solvents like toluene and hexane, but the big crowns like 60-crown-20 and 42-crown-14 do not. In a mixture of 42-crown-14 and 21-crown-7, most of the 21-crown-7 could be extracted by a non-polar solvent like the mixture of hexane/toluene, 1:1, v/v. 21-Crown-7 showed a singlet at 3.68 ppm in its ^1H NMR spectrum (Fig. II-D4). Mass spectroscopy showed the major peak at a molecular weight of 308. The theoretical molecular weight of 21-crown-7 is 308.3682 (Fig. II-D5). 21-Crown-7 was a yellow oily liquid which gave 23% yield at room temperature reaction and 16% yield at 67°C.

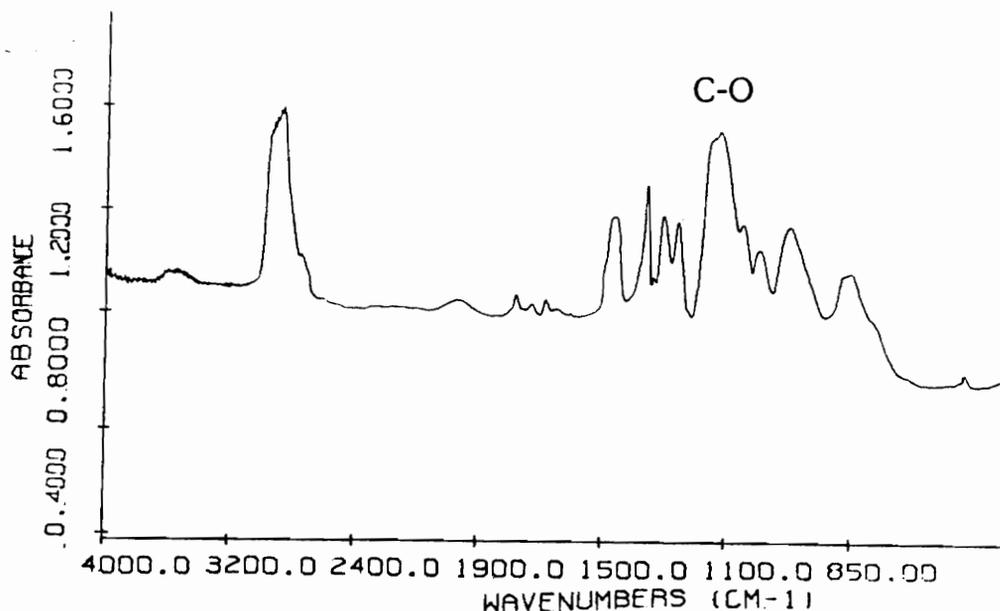


Fig. II-D3 IR spectrum of 42-crown-14 (KBr, cm^{-1})

Low temperature recrystallization was tried. Different size crowns could be recrystallized in different solvents at low temperature. The 60-crown-20 was recrystallized from acetone at 0°C . The recrystallization temperature should not be lower than 0°C . Otherwise some impurities also recrystallized out. The purified 60-crown-20 was a white powder. The percentage yield was 36.8%. The melting point was $57.0\text{-}58.0^{\circ}\text{C}$. Chenevert reported the percentage yield was 26%, and the melting point was $46\text{-}50.5^{\circ}\text{C}$. [15] Shen reported 16% yield, and the melting point was $52.2\text{-}53.9^{\circ}\text{C}$ [1]. Bheda reported 12% yield, and the melting point was $53.5\text{-}55.1^{\circ}\text{C}$ [18]. ^1H NMR showed a singlet at 3.63 ppm. (Fig. II-D6)

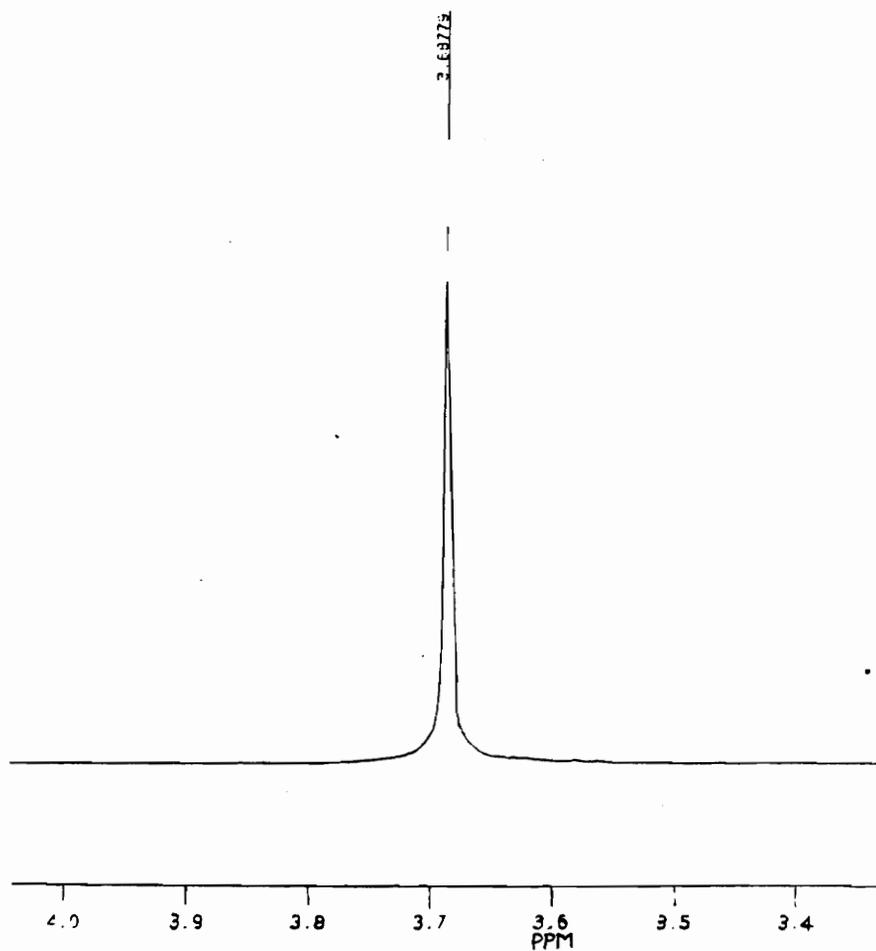


Fig. II-D4 ¹H NMR spectrum of 21-crown-7 in CDCl₃ (ppm)

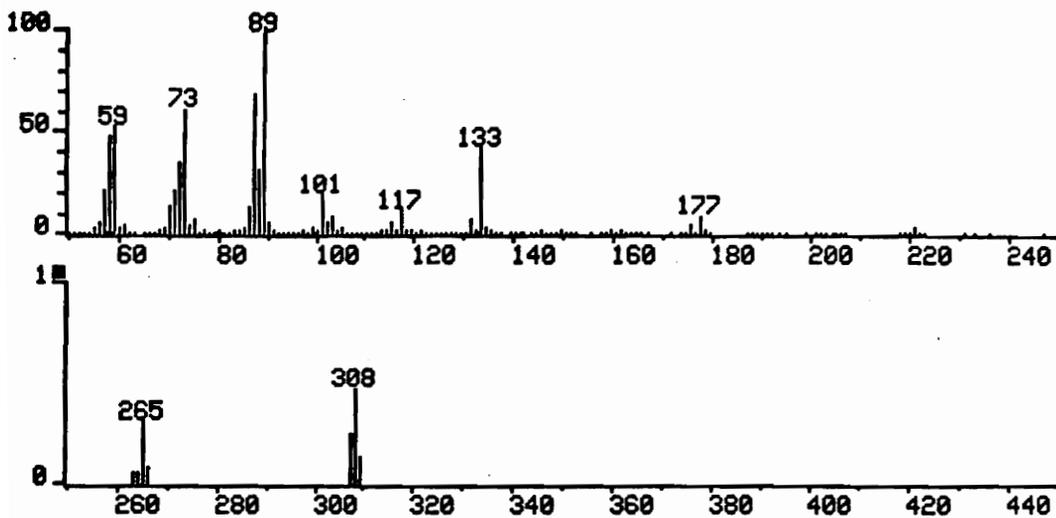


Fig. II-D5 Mass spectrum (DIEI) of 21-crown-7

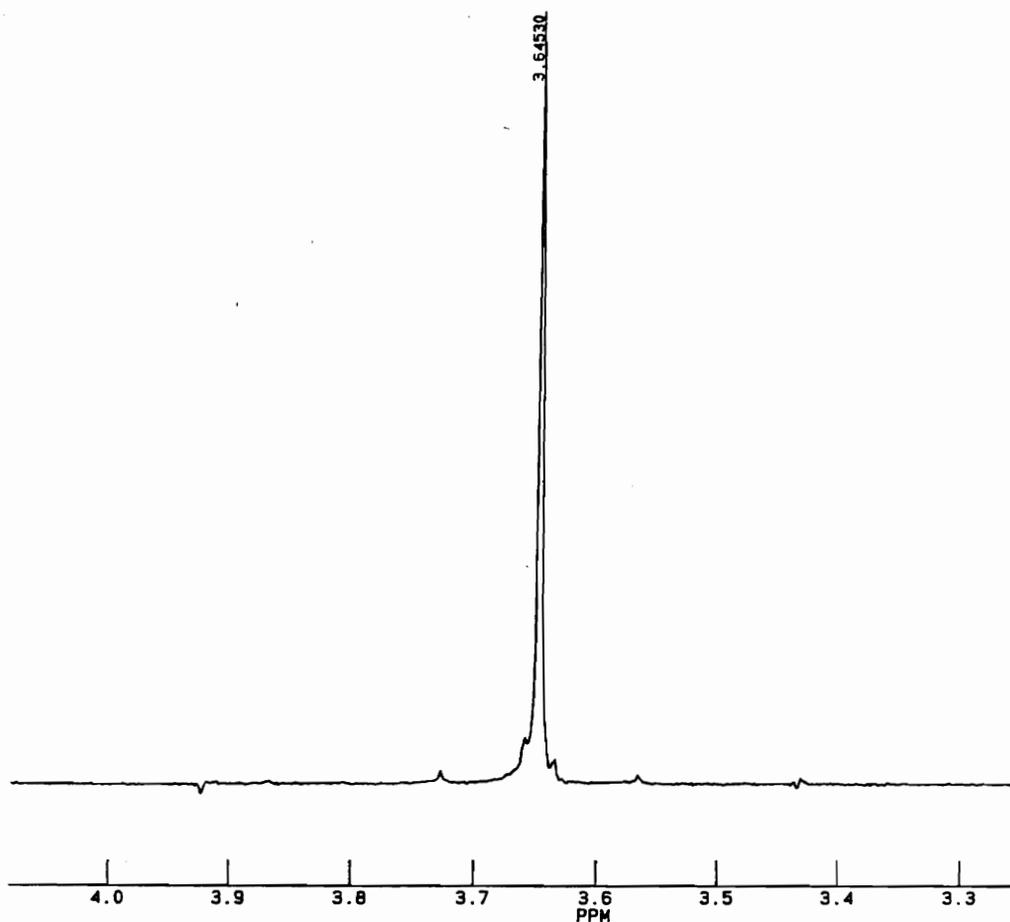


Fig. II-D6 ^1H NMR spectrum of 60-crown-20 in CDCl_3 (ppm)

After most of the 21-crown-7 was extracted by hexane/toluene mixture, the 42-crown-14 was recrystallized from acetone at 0°C . The purified 42-crown-14 was a yellow spherulitic crystal. The percentage yield was 27%, and the melting point was $51.7\text{-}53.3^\circ\text{C}$. When the reaction temperature was increased to THF boiling temperature, 67°C , the percentage yield increased to 40%. Chenevert reported the yield was 20%, and the melting point was $28.5\text{-}31^\circ\text{C}$. [15] Shen reported the yield was 22%, and the melting

point was 49.6-50.4°C [1]. There was a singlet at 3.64 ppm in the ^1H NMR spectrum. (Fig.II-D7) Mass spectroscopy showed a major peak of molecular weight of 617. (Fig. II-D8) The theoretical molecular weight of 42-crown-14 is 616.7364.

The 30-crown-10 was recrystallized from water at 4°C. The mother liquor after the recrystallization of 60-crown-20 was dissolved in hot water, then the solution was set at 4°C. 30-Crown-10 was the only compound that crystallized from the solution as colorless square crystals. The percentage yield was 24.7%. The melting point was 42-43.8°C. Chenevert reported the percentage yield of 30-crown-10 was 55%, and it was oil. [15] Masci reported the percentage was 29%, and the melting point was 33.5-38°C [16]. Bheda reported the melting point was 43.8°C, and 28% yield [18], and Engen did not purify the compound and reported the crude 30-crown-10 was an oil [19]. There was a singlet at 3.66 ppm in the ^1H NMR spectrum.

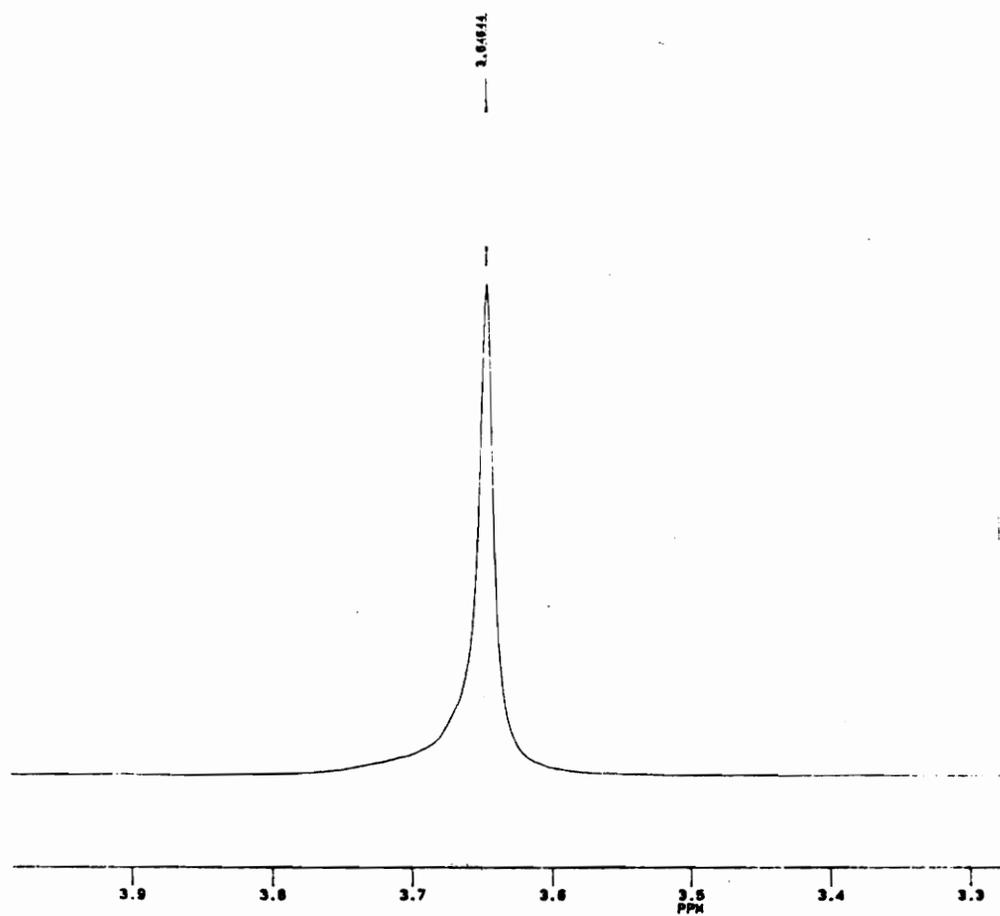


Fig. II-D7 ^1H NMR spectrum of 42-crown-14 in CDCl_3 (ppm)

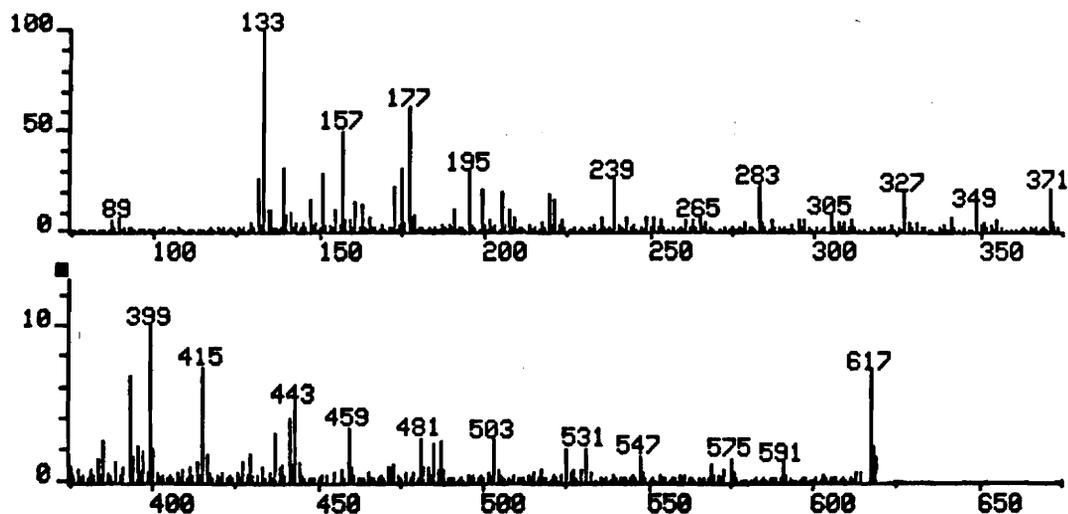


Fig. II-D8 Mass spectrum (DICI) of 42-crown-14

II-E Experimental

Tri(ethylene glycol) (99%), tetra(ethylene glycol) (99%), toluenesulfonyl chloride (98%), ethylene glycol (99%), thionyl chloride (99%), pyridine (99%), sodium metal (99% in kerosene), chloroethanol (99%), sodium hydroxide (99%), 3,4-dihydro-2H-pyran (99%), triethylamine (99%), and tetrabutylammonium hydrogen sulfate (97%) were purchased from Aldrich Chemical Co. and used without further purification. Sodium hydride (60% in mineral oil) was purchased from Aldrich Chemical Co. and was washed with hexane three times before use. Tetrahydrofuran (99%), methanol (97%), ethanol (97%), toluene (99%), and methylene (99%) were purchased from Fisher Scientific Co. and used without further purification.

Melting points were determined on a Haake Buchler capillary melting apparatus and were corrected. The FTIR spectra were recorded from a Nicolet MX-1 FTIR spectrometer. The ^1H NMR spectra were recorded on a Bruker WP 270 MHz instrument. The mass spectra were taken from a VGC 7070E analytical mass spectrometer in Biochemistry Department of Virginia Polytechnic Institute and State University.

Tri- and tetra(ethylene glycol) ditosylates

Tri- or tetra(ethylene glycol), 1 mole, in 450 ml THF was mixed with NaOH, 112 g, (2.8 mole) in 200 ml water. The mixture was cooled to 0°C in an ice bath. A mechanical stirrer was used. Toluenesulfonyl chloride, 400.37 g (2.1 mole), in 800 ml THF was added dropwise. The reaction was stirred for 12 hours in ice bath. After the reaction, 10% HCl was added. The solution was washed with NaHCO_3 . Tetra(ethylene glycol) ditosylate was extracted by toluene; tri(ethylene glycol) ditosylate was crystallized from THF (reaction solution).

Tetra(ethylene glycol) ditosylate was purified by washing with hot hexane, and the percentage yield was 96%. The compound was a pale yellow viscous liquid. The reported yield was 83% [7]. Tri(ethylene glycol) ditosylate was purified by recrystallizing from acetone, and the percentage yield was 97.3%. The compound was colorless crystal. The reported yield was 89%.

Tetra(ethylene glycol) ditosylate: IR (ν/max , cm^{-1}): 666, 772, 819, 918, 1018, 1098, 1177, 1357, 1450, 1496, 1596, and 2870. ^1H NMR (chloroform- d /TMS, ppm): singlet at 2.5 (6H), singlet at 3.5 (8H), triplet at 3.7 (4H), triplet at 4.2 (4H), doublet at 7.4 (4H), and doublet at 7.8 (4H).

Tri(ethylene glycol) ditosylate: IR is similar to tetra(ethylene glycol). ^1H NMR is similar to tetraethylene glycol ditosylate except the integration of the singlet at 3.5 ppm was 4H. The melting point was 83.1-84.9°C. The reported meltin point was 80.0-81.0°C [7].

Tetra(ethylene glycol) dichloride

Tetra(ethylene glycol), 345.3 ml (2 moles), pyridine, 359 ml (4.45 mole), were added to 2 liters of toluene. The mixture was heated to 90°C. Thionyl chloride, 324.6 ml (4.45 mole) was added dropwise. The reaction was refluxed for 15 hours. Water was added to wash the product. The toluene was evaporated. The product was vacuum distilled at 139°C under 1.4 mm Hg. The percentage yield was 80%. The reported yield was 92%, and the reported boiling point was 95°C under 0.4 mm Hg [9]. IR (ν/max , cm^{-1}): 481, 536, 667, 743, 833, 930, 1054, 1123, 1119, 1254, 1303, 1351, 1455, and 2870. ^1H NMR (chloroform- d /TMS, ppm): triplet at 3.65 (4H), singlet at 3.7 (8H), triplet at 3.77 (4H)

Hexa(ethylene glycol) (sodium method)

Ethylene glycol, 550 ml (10 moles), was heated to 65°C under nitrogen. A mechanical stirrer was used. Sodium metal, 92 g (4 moles), was added to the ethylene glycol partwise. The reaction temperature was raised to 90°C when the reaction slowed down. After the sodium reacted with ethylene glycol completely, tetra(ethylene glycol) dichloride, 232 g (1 mole) was added to the sodium ethylene glycol salt dropwise. The reaction was stirred for 15 hours.

Water, 300 ml, was added to the reaction mixture dropwise, and the reaction mixture was stirred for 30 minutes. The NaCl salt was filtered. The crude product was extracted using methylene chloride. The methylene chloride was removed by evaporation. The

hexa(ethylene glycol) was purified by vacuum distillation at 195°C under 0.25 mm Hg, and the purified compound was a light yellow oil. The percentage yield was 21%. Reported yield was 49.7%, and boiling point was 166-168°C under 0.015 mm Hg. IR (ν /max, cm^{-1}): 810, 880, 910, 970, 1010, 1070, 1130, 1220, 1350, 1470, 2820, and 3400. ^1H NMR (chloroform- d /TMS, ppm): triplet at 3.6 (4H), singlet at 3.68 (16H), triplet at 3.73 (4H).

Chloroethoxy tetrahydropyran

4-Dihydro-2H-pyran, 200 ml (2.19 mole) was cooled to 0°C in ice bath, then 2-chloroethanol, 146.8 ml (2.19 mole), was added slowly. HCl, 2 drops, was added. The reaction was stirred for 15 minutes, then the ice bath was removed. The reaction was stirred for another 3 hours at room temperature. Triethylamine, 6 drops, was added. The product was purified by distillation at 142°C under atmosphere pressure. The percentage yield was 96%. The reported boiling point was 146°C, and the yield was 93% [11]. IR (ν /max, cm^{-1}): 570, 600, 670, 710, 850, 870, 890, 950, 1010, 1070, 1150, 1190, 1200, 1210, 1270, 1290, 1300, 1410. ^1H NMR (chloroform- d /TMS, ppm): multiplet at 1.5-1.9 (6H), multiplet at 3.5-3.6 (1H), multiplet at 3.6-3.75 (3H), multiplet at 3.8-4.0 (2H), triplet at 4.7 (1H).

Hexa(ethylene glycol) (phase transfer catalyzed method)

Tetra(ethylene glycol), 97.1 g (0.5 moles), chloroethoxy-tetrahydropyran, 328.68 g (2 moles), and tetrabutyl ammonium hydrogen sulfate, 9.96 g (29.3 mmoles) were added together. Sodium hydroxide, 50% solution, w/w, 533 g solution (6.67 moles), was added dropwise. The two phase reaction was mechanically stirred at 65°C for 120 hours. Water, 500 ml was added. The product was extracted using methylene chloride. The methylene chloride was removed by evaporation. Excess chloroethoxy tetrahydropyran was removed by vacuum distillation.

A mixture of methanol/methylene chloride, 1:1, v/v, 200 ml was added to the THP protected hexa(ethylene glycol). HCl, 30 ml, was added. The deprotection reaction was stirred 4 hours at room temperature. Water, 200 ml was added to the reaction. NaHCO₃ was added to neutralize the solution. The organic phase was separated from the water phase. The solvent was evaporated. The hexa(ethylene glycol) was vacuum distilled at 200°C under 0.7 mm Hg. The yield was 91%. The reported percentage yield was 80%. The reported boiling point was 166-168°C under 0.015 mm Hg [10], and the reported yield was 80% [14]. IR (ν/max, cm⁻¹): 720, 850, 880, 910, 1100, 1220, 1350, 1470, 1600, 2780, 3300. ¹H NMR (chloroform-d/TMS, ppm): triplet at 3.6 (4H), singlet at 3.67 (16H), triplet at 3.72 (4H).

Crown ethers

Tetra-, or hexa(ethylene glycol), 0.3 mole, was dissolved in 2.4 liter of THF. Sodium hydride, 48 g, 60% (1.2 mole), was washed with hexane, and added to the solution. The solution was mechanically stirred. Tri-, or tetra(ethylene glycol) ditosylate, 0.309 mole in 700 ml THF, was added dropwise. The 42-crown-14 reaction was refluxed for 48 hours. The 30-crown-10 reaction was done at room temperature. Water, 800 ml, was added dropwise to the reaction mixture to destroy the excess NaH. THF was evaporated. Excess ditosylate was separated from the water phase by a separatory funnel. Crude crown ether was extracted by methylene chloride.

The crown ether solution was filtered using a 1.5 ft silica gel column. Methylene chloride was used as the solvent. The solvent was evaporated after the filtration.

The mixture of 42-crown-14, 21-crown-7, catenane, and poly(ethylene glycol), 10 g, poly(methacryloyl chloride), 4 g, were added into 250 ml dried THF. The reaction was stirred at room temperature for 15 hours. The polyester was precipitated in to methanol. The purified crown ethers and catenane were dissolved in the methanol.

For the mixture of 30-crown-10, 60-crown-20, catenane, and poly(ethylene glycol), 60-crown-20 was recrystallized from acetone at 0°C. 30-Crown-10 was recrystallized from water at 4°C. The percentage yield of 60-crown-20 was 36.8%, and the percentage yield of 30-crown-10 was 24.7%.

For the mixture of 21-crown-7, 42-crown-14, catenane, and poly(ethylene glycol), 21-crown-7 was extracted by a mixture of toluene/hexane, 1:1, v/v. 42-Crown-14 was recrystallized from acetone.

30-Crown-10, mp. 42-43.8°C, ^1H NMR (chloroform-d/TMS, ppm): singlet at 3.66. The reported melting point was 33.5-38°C [16]. 60-Crown-20, mp. 57-58°C, ^1H NMR (chloroform-d/TMS, ppm): singlet at 3.63. The reported melting point was 53.5-55.1°C [18]. 21-Crown-7, yellow oil, mass spectroscopy (DIEI, mass) 308. ^1H NMR (chloroform-d/TMS, ppm) 3.68. No reported information found about this compound. 42-Crown-14, mp. 51.7-53.3°C, Mass spectroscopy (DICI, mass) 617. ^1H NMR (chloroform-d/TMS, ppm) 3.64. The reported melting point was 44.9-46.7°C.

Poly(methacryloyl chloride)

Methacryloyl chloride, 25 ml (0.25 mole), was poured into 150 ml dried THF. AIBN, 0.5 g (3.76 mmole), was added to the solution. The reaction was refluxed for 15 hours. The product was precipitated in 1 liter of hexane, and dried using a vacuum pump

with NaOH. ^1H NMR (chloroform-d/TMS, ppm) triplet at 1.3, singlet at 1.7, multiplet at 2.3.

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CHAPTER III

END BLOCKERS: TRIBUTYLPHENYLMETHANOL AND ITS DERIVATIVES

III-A Design of The End Blockers

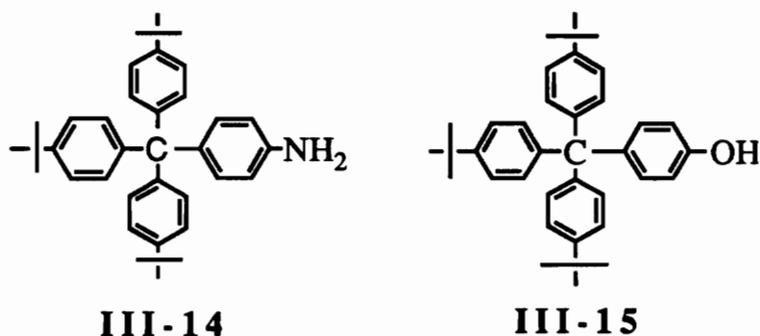
After the crown ethers are threaded on the polymer backbone, and the polyrotaxane is formed, both ends of the polymer need to be blocked by large end groups to prevent the crown ether from sliding off the polymer backbone. Therefore the end blockers need to be larger than the diameter of the threaded crown ether. Most reported information showed that the triphenylmethyl group was used as the end blocker. [1][2][3] Lawrence and Rao used the tetraphenylboron group [4]. These end groups all contain three or four phenyl rings on one atom. People who used these star shaped large end groups reported that these end blockers could block 22-30 membered crown ethers. [1][2][3][5]

The largest crown ether which we used to synthesize rotaxanes is 42-crown-14. The triphenylmethyl group is too small to block 42-crown-14. The tri(p-t-butylphenyl)methyl group was expected to block 42-crown-14. [6][7][8] Thus the tri(butylphenyl)methyl group is a good choice for synthesizing rotaxanes.

Tri(butylphenyl) compounds were synthesized by Marvel and his group in 1941 [9]. He made tri(p-t-butylphenyl)methanol and tri(p-t-butylphenyl)methyl chloride using a Grignard synthesis. We used Marvel's method as the first step of synthesizing end blockers. Since we synthesized different polyrotaxanes with different polymer backbone, the end blockers should have different functional groups. Poly(azomethine)s were synthesized by reacting a bis-phenol with

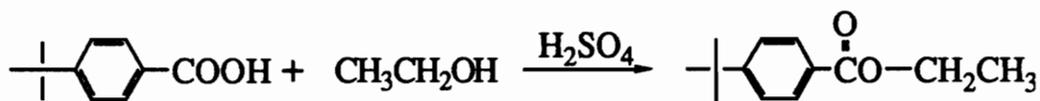
acid chloride monomers; a di(azomethine) was synthesized by reacting a dialdehyde with an aniline. For these system, phenol functional and aniline functional end blockers were synthesized.

p-{Tri(p-t-butylphenyl)methyl}aniline (III-14) and p-{tri(p-t-butylphenyl)methyl}phenol (III-15) are new compounds. No reported information was found for these two compounds.



III-B Results and Discussion, p-{Tri(p-t-butylphenyl)-methyl}aniline and p-{Tri(p-t-butylphenyl)methyl}phenol

Ethyl p-t-butylbenzoate was synthesized as shown in Scheme III-B1



Scheme III-B1 Synthesis of ethyl p-t-butylbenzoate

p-t-Butylbenzoic acid and ethanol reacted to form the p-t-butylbenzoate. The product was a colorless liquid. The percentage yield was 92%. Shen reported 87% yield [7]. IR and ¹H NMR spectra confirmed the compound. (Fig. III-B1)

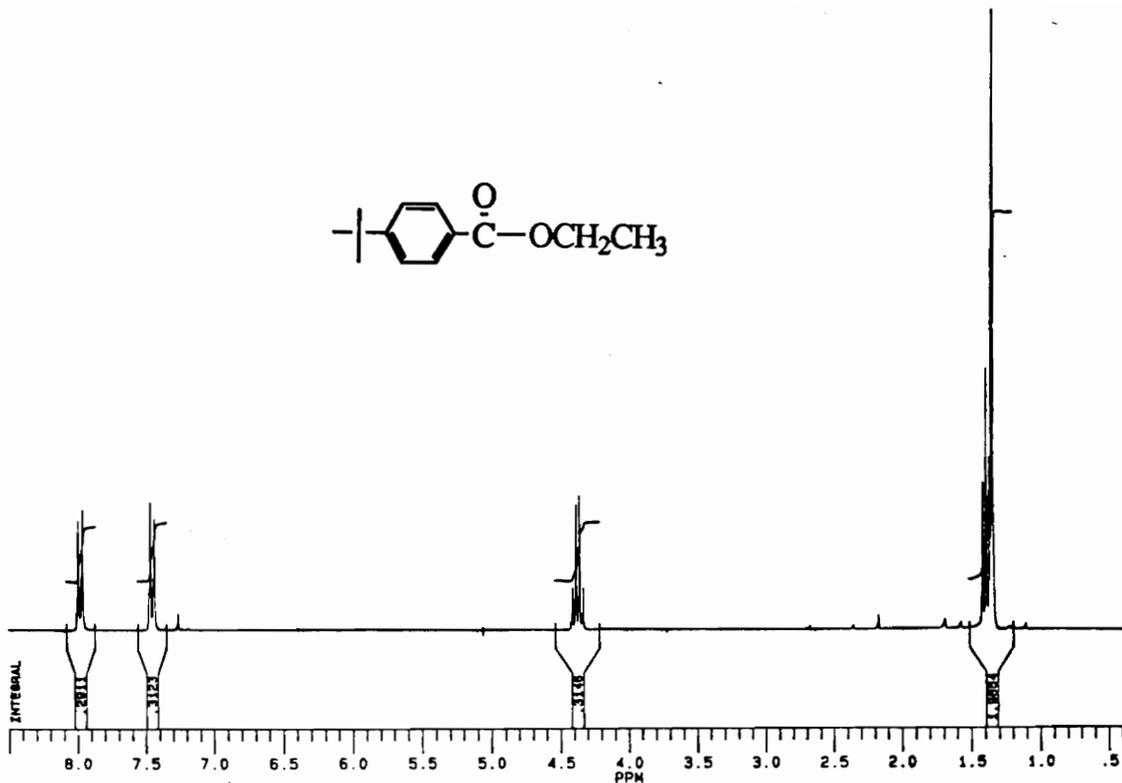
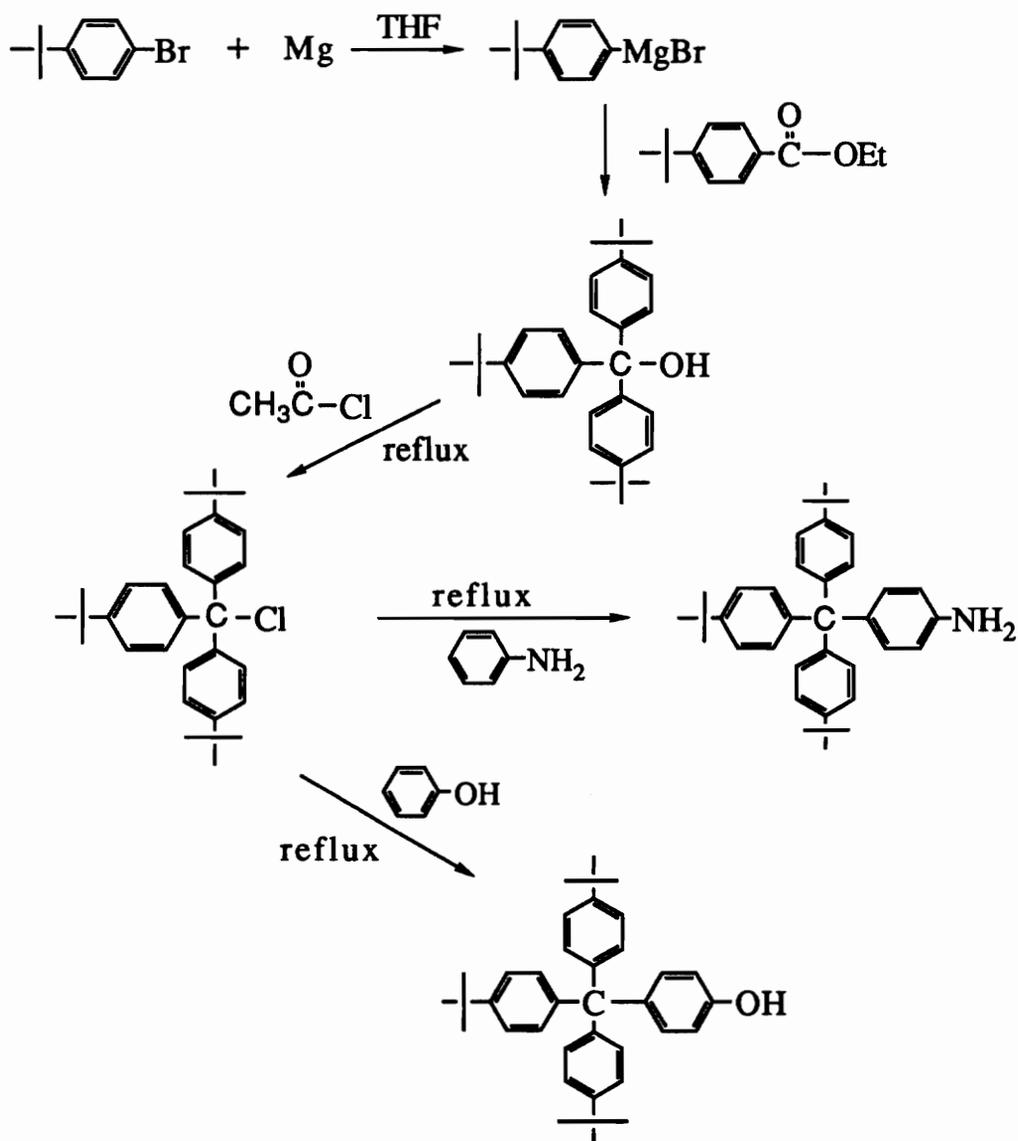


Fig. III-B1 ^1H NMR spectrum of ethyl p-t-butylbenzoate (ppm)

The synthetic schemes for p-{tri(p-t-butylphenyl)methyl}-aniline and p-{tri(p-t-butylphenyl)methyl}phenol are shown below. (Scheme III-B2)

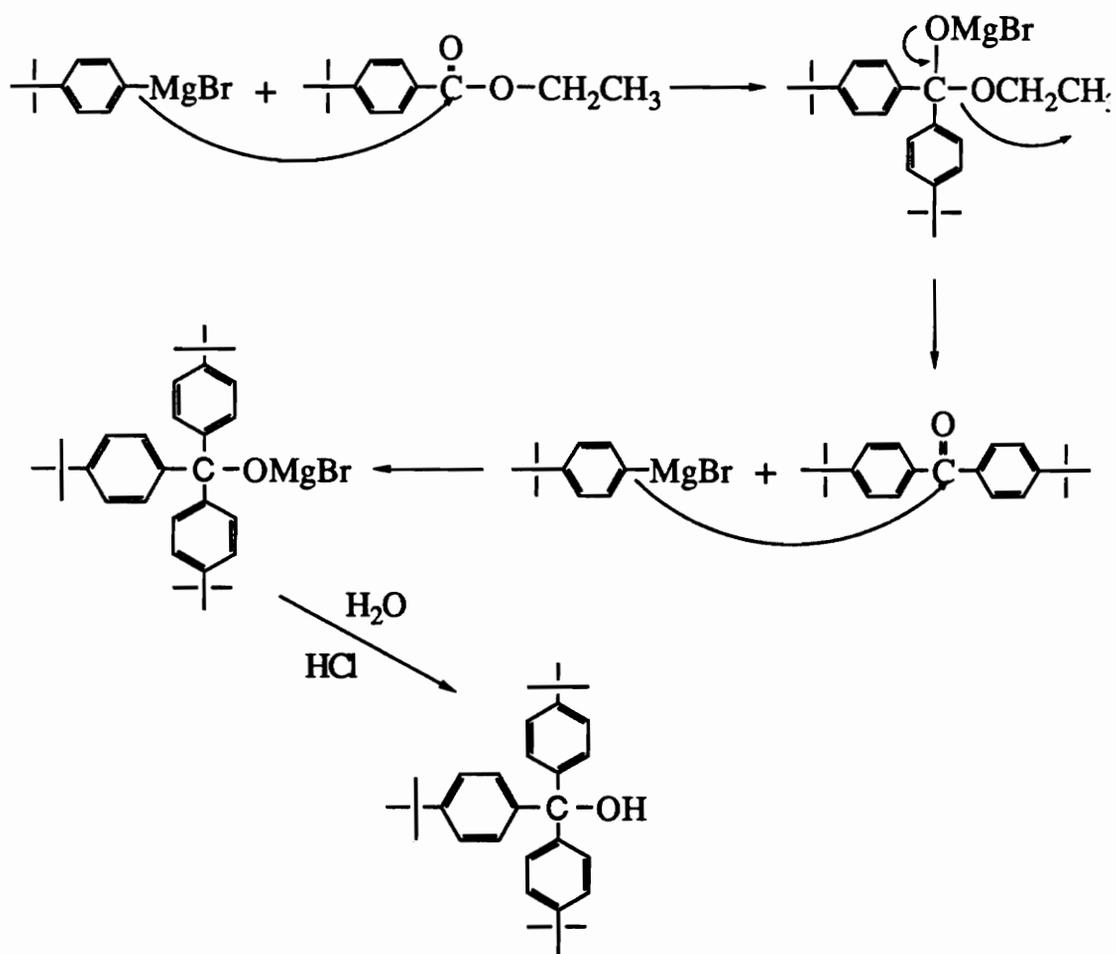
The reaction route is follows. The Grignard reagent was synthesized by reacting p-t-butylphenylbromide with magnesium metal. p-t-Butylphenyl Grignard reagent reacted with ethyl p-t-butylbenzoate to make tri(p-t-butylphenyl)methanol which

further reacted with acetyl chloride to produce p-tri(p-t-butylphenyl)methyl chloride. p-{Tri(p-t-butyl-phenyl)methyl}-aniline or p-{tri(p-t-butyl-phenyl)methyl}phenol were synthesized by reacting p-tri(p-t-butylphenyl)methyl chloride with aniline or phenol.



Scheme III-B2 Synthesis of aniline and phenol functional end blockers

The reaction mechanism for the synthesis of tri(p-t-butylphenyl)methanol is shown in Scheme III-B3.



Scheme III-B3 The mechanism of synthesizing tri(p-t-butylphenyl)methanol

The crude product was a green-yellow solid. After purification, a white solid product, tri(p-t-butylphenyl)methanol was obtained. The percentage yield of the product was 70%. The melting point of the product was 218.9-220.0°C. Marvel reported the percentage yield of the crude product was 96%, and the melting point was 212-213°C [9]. IR (Fig. III-B3) and ^1H NMR analysis confirmed the compound. (Fig. III-B4)

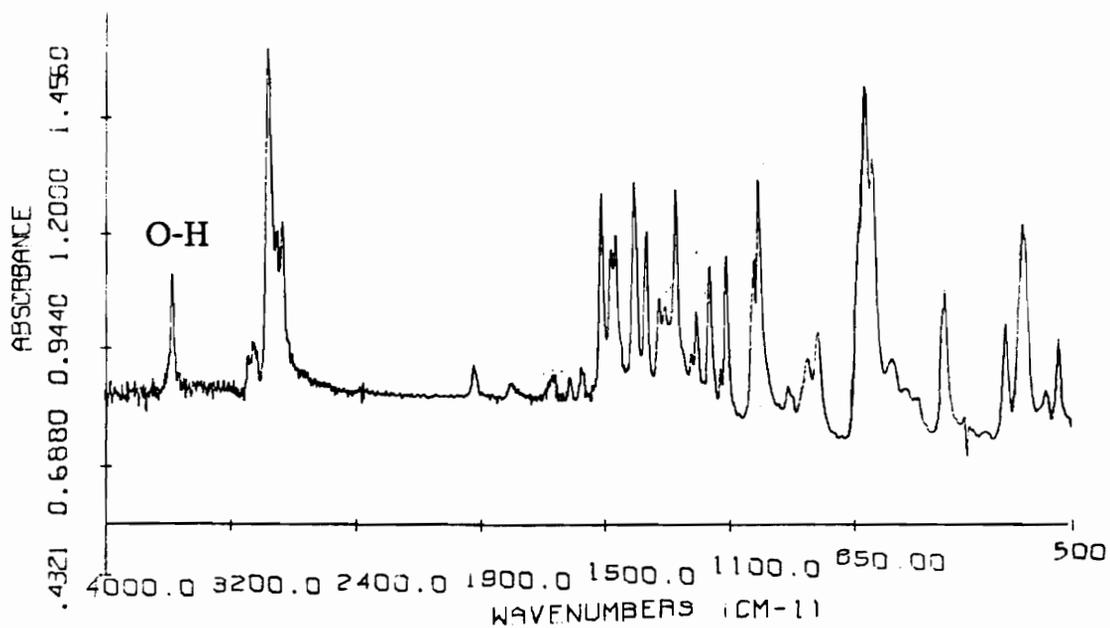


Fig. III-B3 IR spectrum of tri(p-t-butylphenyl)methanol (KBr, cm^{-1})

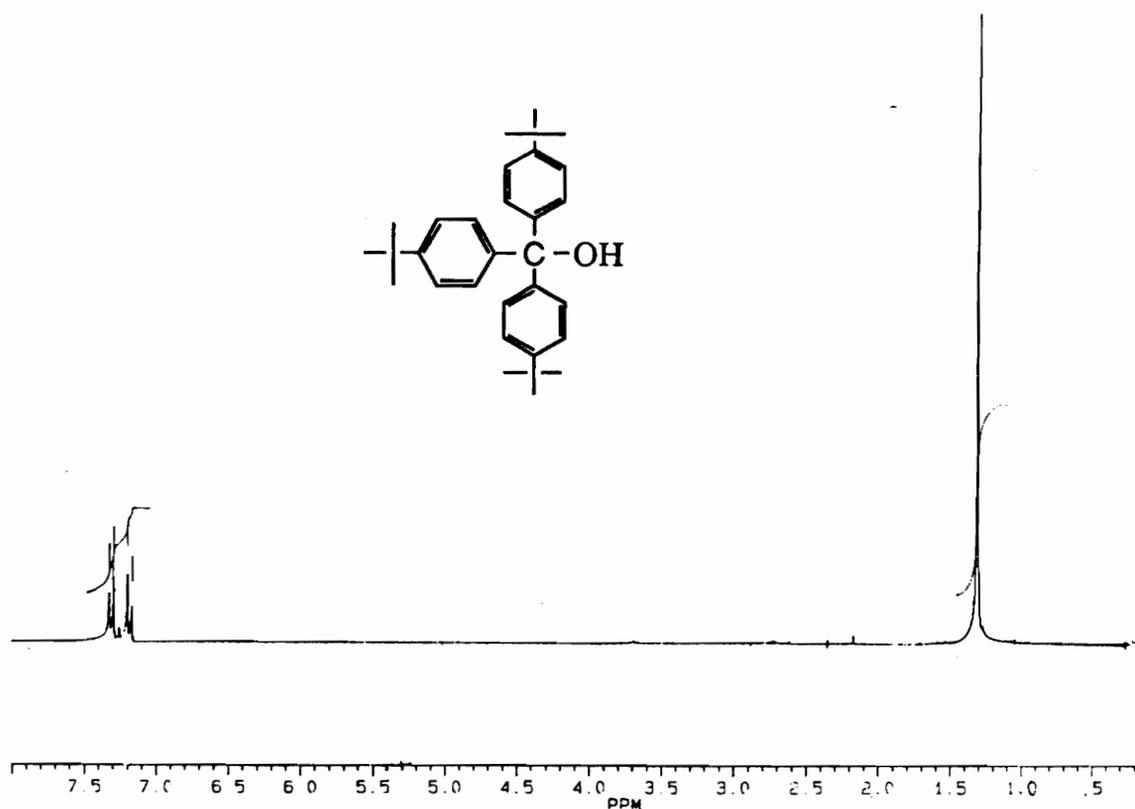
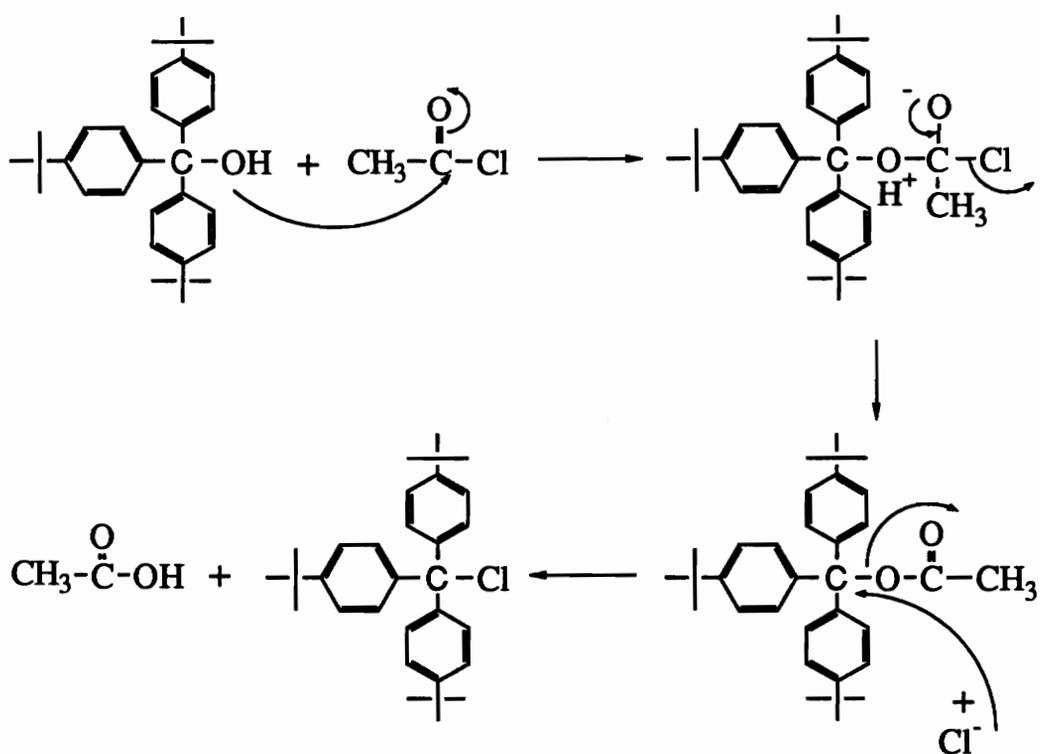


Fig. III-B4 ¹H NMR spectrum of tri(p-t-butylphenyl)methanol (ppm)

The ¹H NMR spectrum showed that the green-yellow impurity was a mixture which needed to be further investigated. The ¹H NMR spectrum of the white impurity which had $R_f=0.61$ on the TLC plate was very similar to tri(p-t-butylphenyl)methanol. The chemical shifts of these two compounds were different. Tri(p-t-butylphenyl)methanol had two doublets at 7.31 and 7.18 ppm, a singlet at 1.3 ppm. The impurity had two doublets at 7.20 and 7.15 ppm, a singlet at 1.26 ppm. The integration ratio in the ¹H NMR spectra of the two compounds was the same. The IR spectral peaks of these two

compounds were very similar. The melting point of the impurity was 195-200.1°C which was lower than tri(p-t-butylphenyl)methanol. The percentage yield of this impurity was around 20-22%. According to the elemental analysis, mass spectroscopy, and the melting point, Mukesh Bheda suggested that the impurity was bis(p-t-butylphenyl)methanol [10] and Sang Hun Lee suggested that the compound was 1,2-hydroxy-1,2-bis(p-t-butylphenyl)ethane [11]. Mass spectroscopy needs to be done to further investigate this compound.

p-Tri(p-t-butylphenyl)methanol was converted to tri(p-t-butylphenyl)methyl chloride by reaction with acetyl chloride. The reaction mechanism is shown below. (Scheme III-B4)



Scheme III-B4 The mechanism of synthesizing tri(p-t-butylphenyl)methyl chloride

Tri(p-t-butylphenyl)methanol was added to acetyl chloride. The reaction was refluxed under nitrogen for 48 hours. The reaction color at first was bright yellow. Later, it became creamy yellow. After the reaction was finished, the excess acetyl chloride was removed by distillation. The percentage yield was 93.9% yield. The melting point was 274.1-276.6°C. Marvel reported that the percentage yield was 16.6%, and the melting point was 259-260°C [9]. The IR spectrum confirmed the compound by a C-Cl peak at 705 cm^{-1} . (Fig. III-B5) The ^1H NMR spectrum of tri(p-t-butylphenyl)methyl chloride was similar to tri(p-t-butylphenyl)methanol.

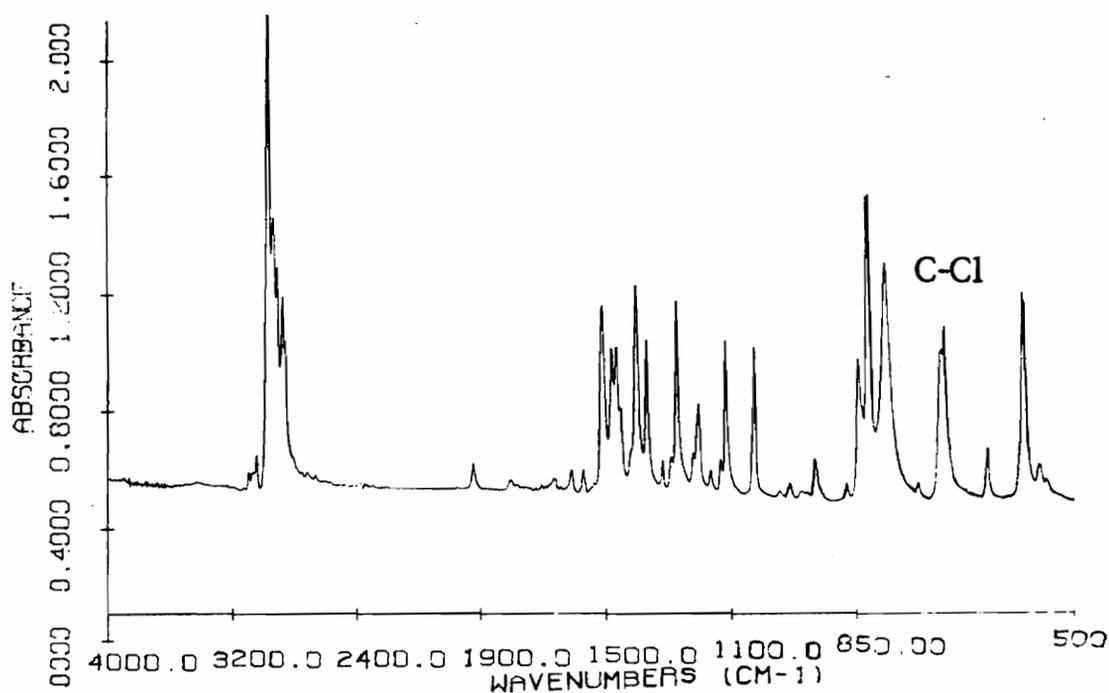
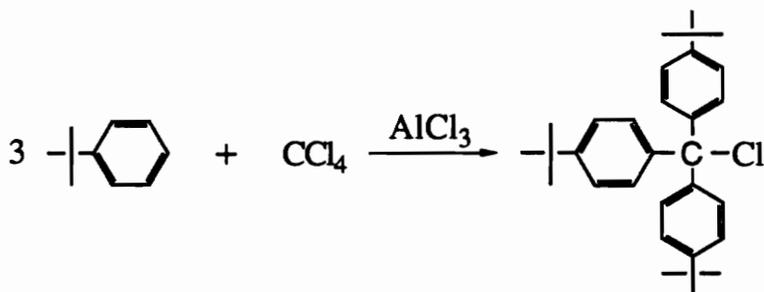


Fig. III-B5 IR spectrum of tri(p-t-butylphenyl)methyl chloride (KBr, cm^{-1})

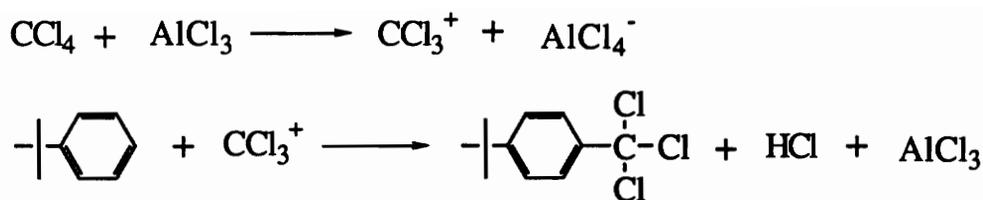
Since the cost of 1-bromo-4-t-butylbenzene was quite high, the Friedel-Crafts reaction was used to synthesize p-tri(p-t-butylphenyl)methyl chloride. I. Vogel's "Practical Organic Chemistry" reported a successful effort to synthesize tri-phenylchloromethane using a Friedel-Craft reaction [12]. The procedure that we used to synthesize tri(p-t-butylphenyl)methyl chloride was similar to the one that Vogel reported. The reaction scheme is shown in Scheme III-B5.



Scheme III-B5 Synthesis of tri(p-t-butylphenyl)methyl chloride
(Friedel-Crafts reaction)

t-Butylbenzene was reacted with carbon tetrachloride to synthesize tri(p-t-butylphenyl)methyl chloride. Aluminium chloride was used as the catalyst. The reaction temperature was 0°C for one hour; then the ice bath was removed, and the reaction was reacted in room temperature for three hours. After the reaction and purification, a white solid was obtained. The melting point was 257-261.2°C which was similar to the reported melting point. (rep. 274.1-276.6°C by myself, 259-260°C by Marvel [9]) The pure product was obtained in 5.6% yield. A brown solid mixture of side product showed four spots on the TLC plate, and the melting point was 221.5-222.0°C. The percentage yield was around 80%.

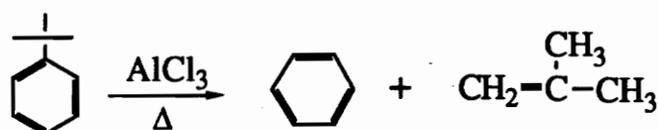
The reaction mechanism was expected [13] to be as shown in Scheme III-B6.



Scheme III-B6 The mechanism of Friedel-Crafts reaction of t-butylbenzene reacts with carbon tetrachloride

This reaction occurred three times to form tri(p-t-butylphenyl)methyl chloride. According to Vogel, the fourth t-butylbenzene would not react with carbon tetrachloride because of steric hindrance. But the fourth t-butylbenzene would react with carbon tetrachloride if the reaction force was large. Because we successfully made p-{tri(p-t-butylphenyl)methyl}aniline and p-{tri(p-t-butylphenyl)methyl}phenol, and t-butylbenzene is more reactive than benzene, the fourth t-butylbenzene can react with carbon tetrachloride to produce tetra(p-t-butylphenyl)methane. Another Friedel-Crafts reaction was tried. The reaction temperature was room temperature; less AlCl₃ was added; the reaction time was reduced to three hours. The percentage yield of p-tri(p-t-butylphenyl)methyl chloride did not increase.

There could be other side reactions. A protodealkylation could happen during the reaction. t-Butylbenzene could be catalyzed by aluminium chloride to form benzene and isobutene [14] as shown in Scheme III-B7.



Scheme III-B7 Protodealkylation reaction of t-butylbenzene

Since dealkylation could happen, the reaction system might become very complicated. The dealkylated benzene could react with carbon tetrachloride to form phenylchloromethane, and t-butylphenylphenylchloromethane. Isobutene could react with carbon tetrachloride to form butylchloromethane. Isobutene also could react with t-butylbenzene to form di-t-butylbenzene. The brown solid was probably a mixture of these products. Since a Friedel-Crafts reaction can have many side products, and the percentage yield of tri(p-t-butylphenyl)methyl chloride was very low, this is not a good choice to synthesize p-{tri(p-t-butylphenyl)methyl}phenol. The Grignard reaction would be the better method.

p-{Tri(p-t-butylphenyl)methyl}aniline was synthesized by reacting tri(p-t-butylphenyl)methyl chloride with aniline at reflux for 24 hours. The procedure was suggested in Mikroyannidis' paper [15], but the product was different. After the purification, the pure product was a white solid in 70.6% yield. There was one spot on the TLC. The melting point was 288.8-291.2°C. There was an N-H peak at 3446 cm^{-1} in the IR spectrum (Fig. III-B6). The $^1\text{H NMR}$ spectrum confirmed the compound (Fig. III-B7). Elemental analysis showed good results (see "experimental" part) Bheda reported that the melting point was 283-286°C, and the percentage yield was 50% [10].

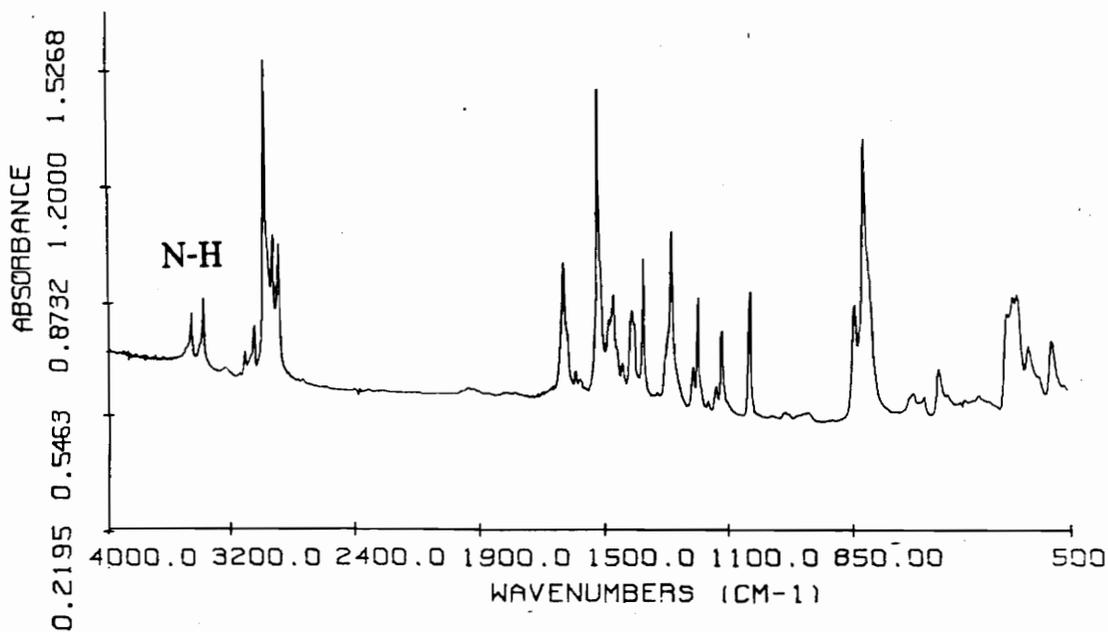


Fig. III-B6 IR spectrum of *p*-{tri(*p*-*t*-butylphenyl)methyl}aniline (KBr, cm^{-1})

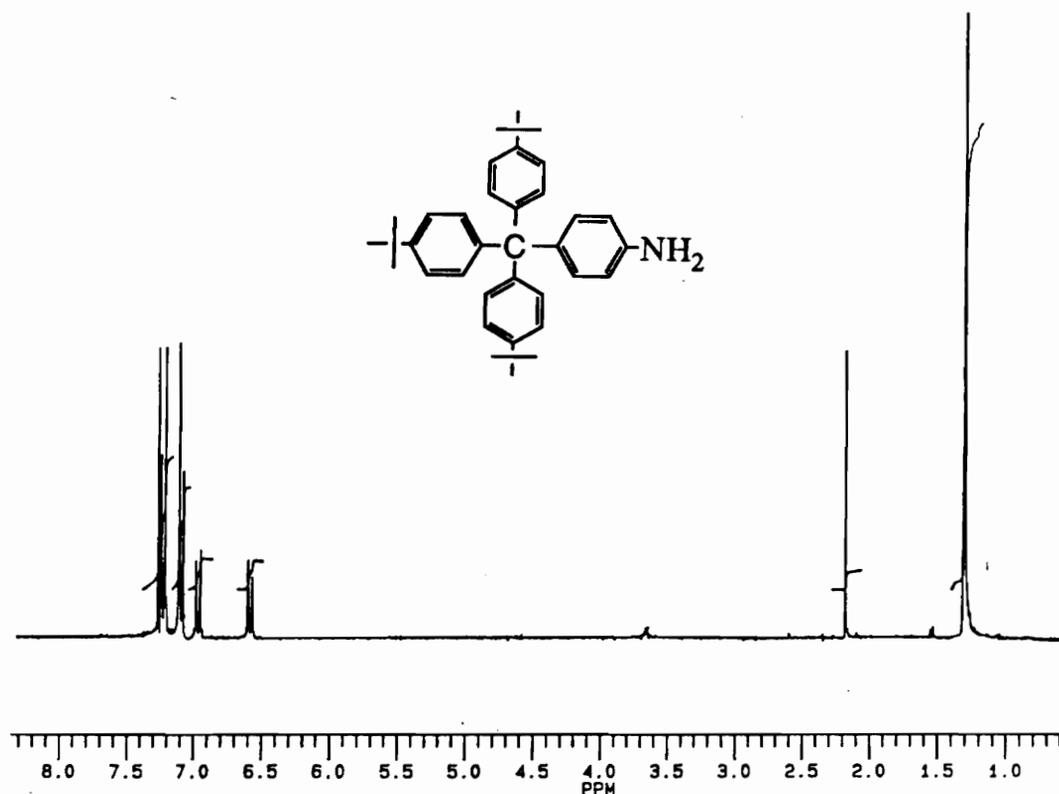


Fig. III-B7 ^1H NMR spectrum of p-{tri(p-t-butylphenyl)methyl}aniline (ppm)

p-Tri{(p-t-butylphenyl)methyl}phenol was similarly synthesized by reacting tri(p-t-butylphenyl)methyl chloride with phenol at 120°C for 24 hours. After the purification, a white solid product, p-tri(p-t-butylphenyl)methylphenol, was obtained in 84% yield. The melting point was $304.2\text{-}306^\circ\text{C}$. There was an O-H peak in the IR spectrum at 3472 cm^{-1} (Fig. III-B8). The ^1H NMR spectrum confirmed the compound (Fig. III-B9). Bheda reported that the percentage yield was 97% and the melting point was $301\text{-}303^\circ\text{C}$ [10].

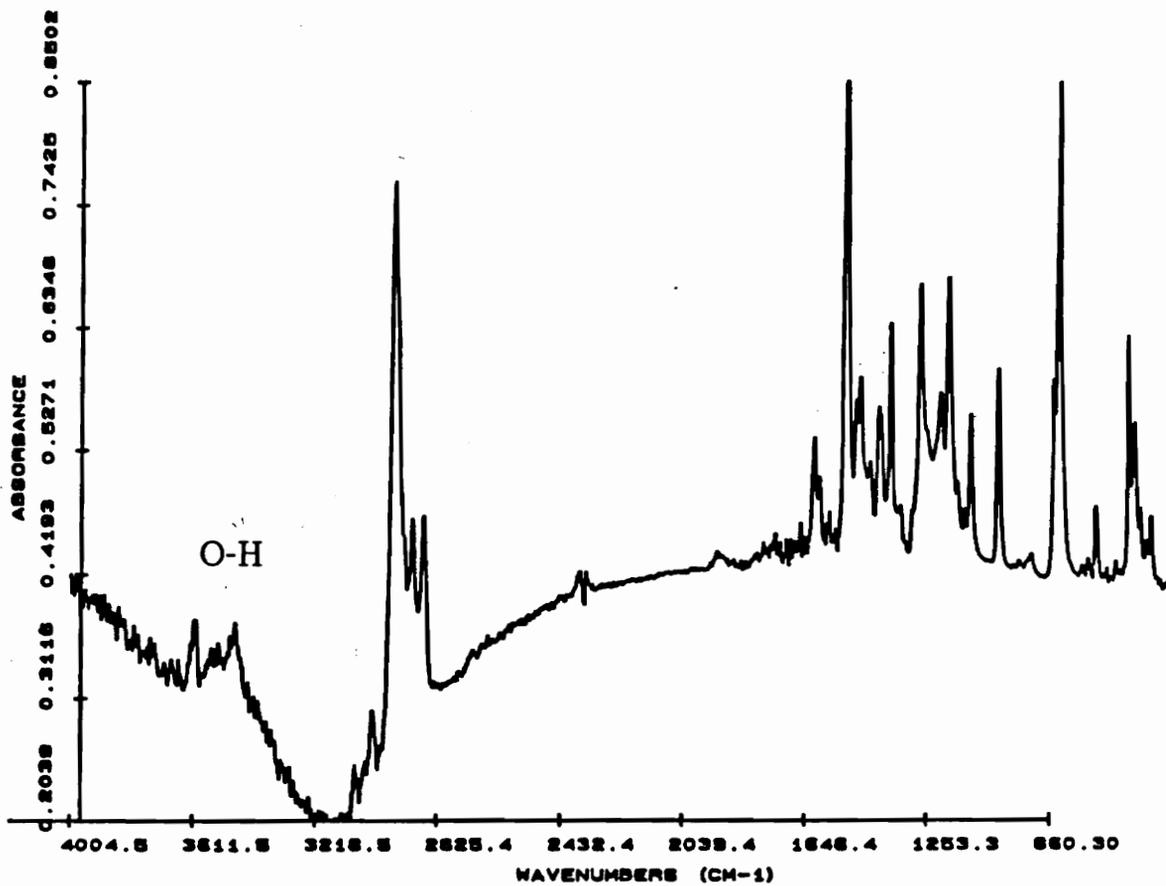


Fig. III-B8 IR spectrum of p-{tri(p-t-butylphenyl)methyl}phenol (KBr, cm^{-1})

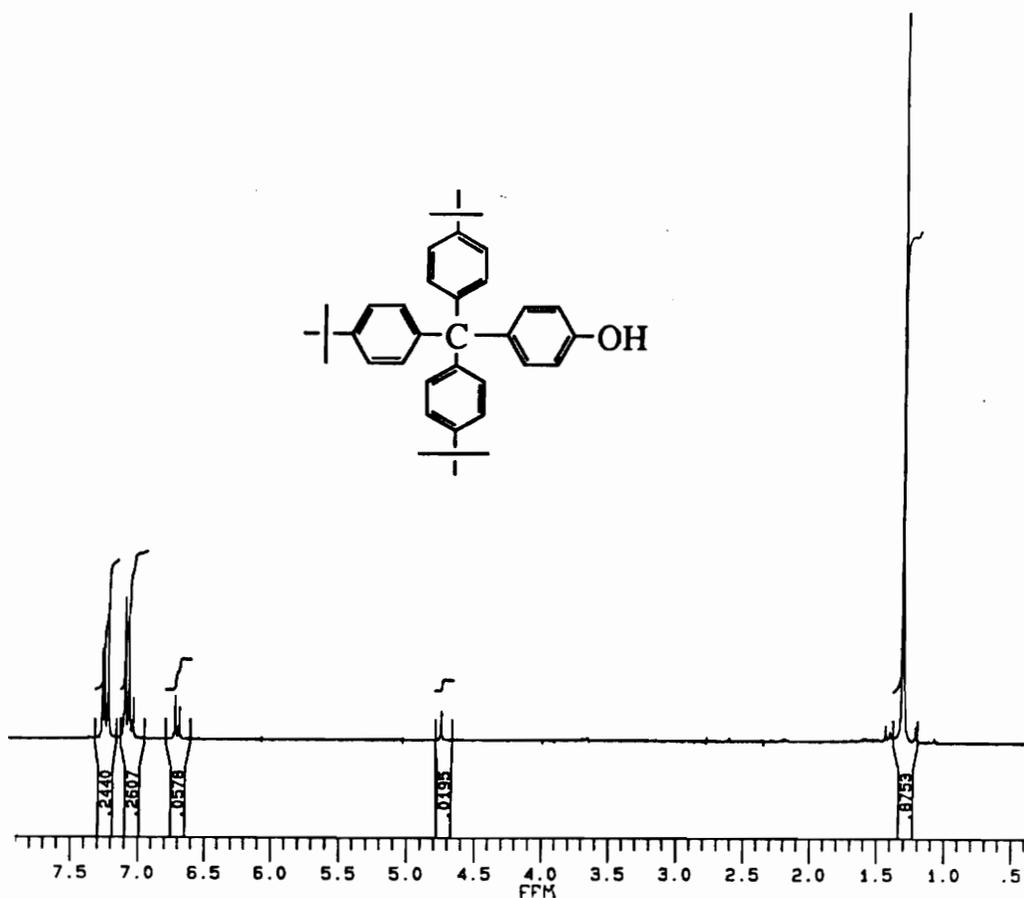


Fig. III-B9 ¹H NMR spectrum of p-{tri(p-t-butylphenyl)methyl}-phenol (ppm)

III-C Experimental

t-Butylbenzoic acid (99%), magnesium metal (99%), 1-bromo-4-t-butylbenzene (99%), iodine (99%), and acetyl chloride (99%) were purchased from Aldrich Chemical Co. and used without further purification. Methanol (97%), ethanol (97%), and phenol (99%) were purchased from Fisher Scientific Inc. and used without further purification. Aniline (99%) was purchased from Fisher Scientific Inc. and was distilled before use. Tetrahydrofuran (99%) was purchased from Fisher Scientific Inc. and was dried with sodium.

Melting points were determined on a Haake Buchler capillary melting point apparatus and were corrected. The FTIR spectra were recorded from a Nicolet MX-1 FTIR spectrometer. The ^1H NMR spectra were recorded from a Bruker WP 270 MHz instrument using tetramethylsilane as the internal standard. The thin layer chromatography was done on Whatman fluorescence UV₂₄₅ 250 μm silica gel plates. The elemental analysis was done by Atlantic Microlab Inc. Norcross, GA.

Ethyl t-butylbenzoate

t-Butylbenzoic acid, 100.1 g (0.56 mole), ethanol, 500 ml (8.70 mole), and sulfuric acid, 50 ml (98%) were added together. p-t-Butylbenzoic acid did not dissolve until the mixture was heated to reflux. The mixture was refluxed for 36 hours. Most of the excess ethanol was removed by rotovapor. The crude product was added slowly to 1 liter iced water. Ethyl t-butylbenzoate was extracted using ethyl acetate. The product was 106.87 g of a colorless liquid, yield 92%. The reported yield was 87% [7]. TLC (hexane/ethyl acetate, 8:2, v/v): 1 spot. Since it was quite pure, the purification was omitted. IR (KBr, ν/max , cm^{-1}): 530, 740, 800, 850, 1040, 1115, 1190, 1279, 1310, 1320, 1430, 1600, 1716, 2820. ^1H NMR (chloroform-d/TMS, ppm): doublet at 8.00 (2H), doublet at 7.45 (2H), quartet at 4.40 (2H), multiplet at 1.30-1.50 (12H)

Tri(p-t-butylphenyl)methanol

Magnesium metal, 13.70 g (0.563 mole), was placed in 200 ml of dried THF with a few iodine flakes. The solution was stirred at room temperature. 1-Bromo-4-t-butylbenzene, 80.00 g (0.375 mole), in 120 ml of dried THF was added dropwise, and iodine helped to start the reaction. Since the reaction was exothermic, a lot of heat was generated when the reaction started. The solution started to boil,

and the color turned gray. When the reaction was proceeding, the amount of magnesium metal diminished. The reaction was stirred for 1 hour after the 1-bromo-4-t-butylbenzene was added. The color of the solution became black-gray when the reaction was done. Ethyl p-t-Butylbenzoate, 37.00 g (0.18 mole) in 120 ml dried THF was added dropwise. The reaction was refluxed for 3 hours, then reacted at room temperature for 12 hours. The color of the reaction turned to green-yellow. The reaction mixture was poured into HCl/water, 1:9, v/v solution. A green-yellow solid was filtered and dissolved in 250 ml methylene chloride. Excess magnesium was filtered. After evaporating the methylene chloride, a green-yellow solid was obtained.

The crude tri(p-t-butylphenyl)methanol showed three spots on TLC plate. This crude product was washed with hot hexane, and the green-yellow impurity was washed away. After washing with hot hexane, the product became a white solid. This white solid was a two compound mixture. One was the impurity which showed a spot on TLC plate at $R_f = 0.61$; another was tri(p-t-butylphenyl)methanol which showed a spot on TLC plate at $R_f = 0.48$. The white solid mixture was recrystallized in cyclohexane at 5°C for several repetitions. The product was purified.

The pure product weighed 56.26 g, 70.0% yield. TLC (hexane/ethyl acetate, 8:2, v/v): 1 spot. Melting point: 218.9-220.0°C. Reported crude yield was 96%, and the melting point was 212-213°C [9]. IR (KBr, ν/max , cm^{-1}): 520, 540, 570, 600, 705, 828, 910, 1005, 1108, 1163, 1204, 1265, 1361, 1402, 1504, 2960, 3609. ^1H NMR (chloroform-d/TMS, ppm): doublet at 7.32 (6H), doublet at 7.20 (6H), singlet at 1.30 (27H).

Tri(p-t-butylphenyl)methyl chloride

Tri(p-t-butylphenyl)methanol, 4.50 g (10.50 mmole) was

added to 40 ml acetyl chloride, and the reaction was refluxed for 48 hours. The excess acetyl chloride was removed by distillation. The product was vacuum dried at room temperature. The product weighed 4.20 g, 93.9% yield. The melting point was 274.1-276.6°C. The reported yield was 259-260°C, and the reported melting point was 16.6% [9]. TLC (hexane/ethyl acetate, 8:2, v/v): 1 spot. IR (KBr, ν/max , cm^{-1}): 570, 620, 705, 800, 830, 850, 910, 1040, 1100, 1200, 1250, 1370, 1410, 1475, 1500, 2800, 2920. ^1H NMR (chloroform-d/TMS, ppm): doublet at 7.33 (6H), doublet at 7.2 (6H), singlet at 1.30 (27H).

p-{Tri(p-t-butylphenyl)methyl}aniline

Tri(p-t-butylphenyl)methyl chloride, 4.20 g (9.39 mmole) was added to 40 ml distilled aniline. The reaction was refluxed for 24 hours. The reaction mixture was precipitated in 300 ml of 10% HCl solution. The crude product was a purple solid which was washed with potassium carbonate solution. The purple solid was dissolved in methylene chloride and filtered through a silica gel filled funnel. The purple-colored impurity remained in the silica gel. The reddish filtrate was precipitated in hexane. A white solid product was obtained. The product was recrystallized from a mixture of toluene/hexane, 3:7, v/v. The product weighed 3.34 g, 70.6% yield. The melting point was 288.8-291.2°C. The reported yield was 50%, and the reported melting point was 283-286°C [10]. TLC (hexane/ethyl acetate, 8:2, v/v, silica gel): 1 spot. IR (KBr, ν/max , cm^{-1}): 520, 590, 770, 1019, 1108, 1183, 1272, 1361, 1402, 1514, 1612, 2810, 2890, 3364, 3439. ^1H NMR (chloroform-d/TMS, ppm): doublet at 7.25 (6H), doublet at 7.13 (6H), doublet at 6.96 (2H), doublet at 6.59 (2H), singlet at 1.30 (27H). Elemental analysis: C 87.82, H 8.93, N 2.98 (theoretical for C, H, and N: C 88.216, H 9.003, N 2.780).

p-{Tri(p-t-butylphenyl)methyl}phenol

Tri(p-t-butylphenyl)methyl chloride, 3.66 g (8.18 mmole), was added to 35 ml phenol. The reaction was heated to 120°C for 24 hours. The reaction mixture was poured into 300 ml of a 5% NaHCO₃ and water solution. A brown powdery solid was obtained. The brown powdery solid was dissolved in methylene chloride and filtered through a silica gel filled funnel. The brown impurity remained in the silica gel. The yellowish filtrate was precipitated into hexane. The white precipitate was the product. The product was recrystallized from a mixture of cyclohexane/toluene, 6:4, v/v. The yield was 3.47 g, 84%. Melting point was 304.2-306°C. The reported yield was 97%, and the reported melting point was 301-303°C [10]. TLC (hexane/ethyl acetate, 8:2,v/v, silica gel): 1 spot. IR (KBr, ν /max, cm⁻¹): 577, 598, 826, 1020, 1110, 1178, 1268, 1365, 1400, 1469, 1510, 1607, 2864, 2899, 2961, 3472, 3603. ¹H NMR (chloroform-d/TMS, ppm): doublet at 7.23 (6H), multiplet at 7.04-7.10 (8H), doublet at 6.70 (2H), singlet at 1.3 (27H).

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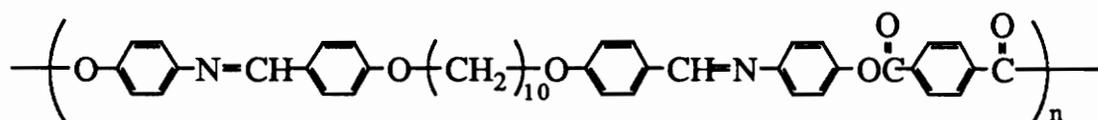
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CHAPTER IV

POLY(AZOMETHINE)S A AND B

IV-A Previous Research on Poly(azomethine)s A and B

Previous research on poly(azomethine)s A (IV-16) and B (IV-17) was reported by Jin and Park in 1987 [1]. These polymers were selected by us as the backbones of polyrotaxanes.



IV-16 Poly(azomethine) A



IV-17 Poly(azomethine) B

According to Jin's report, poly(azomethine)s A and B were synthesized by reacting 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane with terephthaloyl chloride or 1,8-bis(p-chlorocarbonylphenoxy)octane at room temperature for 24 hours, and then heating the reaction solution at 55°C for 2.5 hours. The solvent was N,N-dimethylacetamide (DMAc). Triethylamine was used as the catalyst. The polymers were precipitated in water. [1]

Poly(azomethine)s A and B are liquid crystalline polymers. These polymers contain rod like mesogenic groups. They are rigid and strong. These polymers both have flexible spacers; poly(azomethine) A has a decyl group, and poly(azomethine) B has one decyl group and one octyl group. If the polymers do not have

these flexible spacers, they will precipitate from the reaction solution before their chains grow long enough to form a polymer; also they will be hard to process because of their high T_m and T_i . Jin and Park reported that for poly(azomethine) A, when the flexible spacer was an ethylene group, the last endotherm transition was 286°C , and the T_i was higher than 300°C ; when the flexible spacer was decylene, the T_{last} was 224°C , and the T_i was 257°C . The T_m and T_i of poly(azomethine) B are lower because there are two types of flexible spacers (lower symmetry) in the polymer. But when the flexible spacer was an ethylene group, the T_{last} and T_i were still above 200°C . These polymers are very hard to process because of the very high T_m 's and T_i 's. Jin and park also reported that the transition peaks in the DSC scan were very broad. The last endotherm transition of poly(azomethine) A in the DSC scan was reported, but the T_i could not to be seen in the DSC scan because the polymer decomposed. The T_i of poly(azomethine) B was very weak and broad in the DSC scan, and was hard to determine precisely. The T_i 's were measured with a polarizing microscope.

Jin and and Park reported that the solubility of these poly(azomethine)s was very low. During the reaction, they precipitated from solution, and no longer dissolved in the solvent, which was N,N-dimethylacetamide. They did not dissolve in common solvents like 1,1,2,2-tetrachloroethane, chloroform, phenol, and chlorophenol. These polymers dissolved in dichloroacetic acid. Since the inherent viscosities of these polymers were rather low (around 0.2 dl/g, for 0.5 g/dl in dichloroacetic acid at 45°C), their molecular weights were not very high, in the range of several thousands.

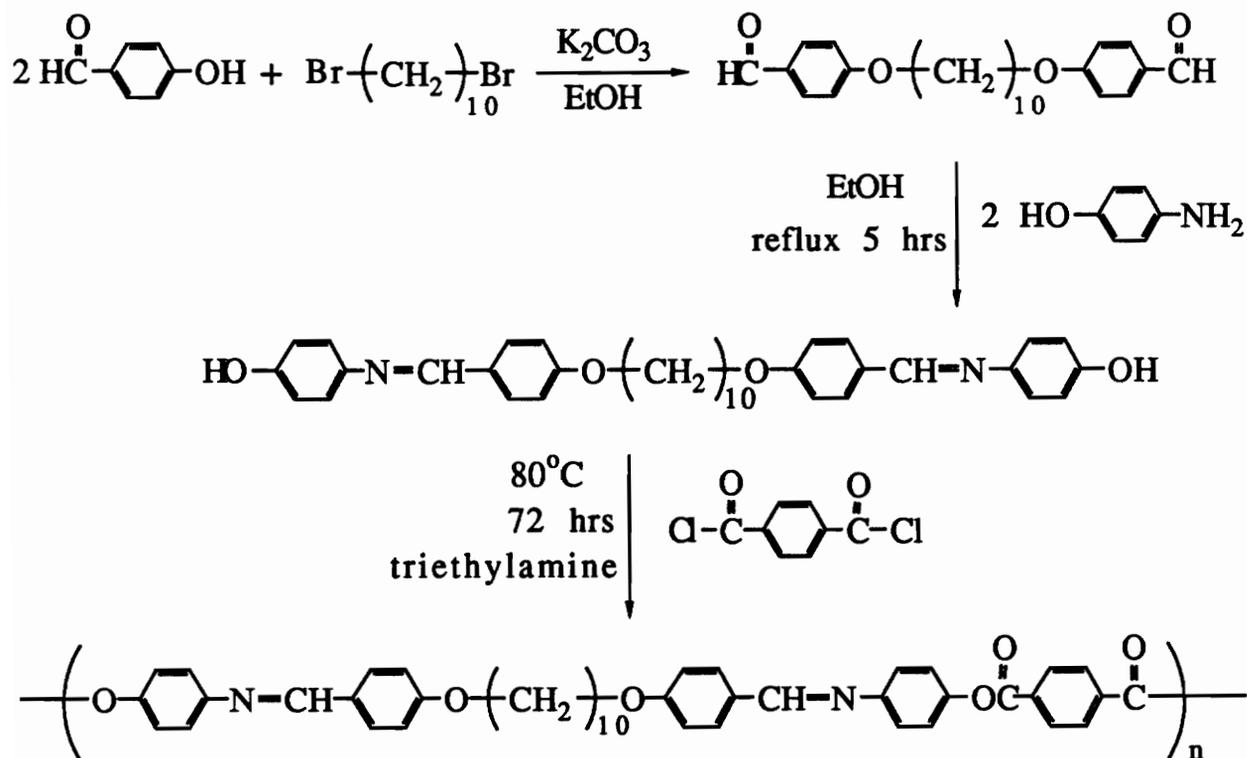
Jin and Park observed typical threaded schlieren textures under the polarizing microscope. Therefore the poly(azomethine)s A and B form nematic phases.

IV-B Results and Discussion, Poly(azomethine)s A and B

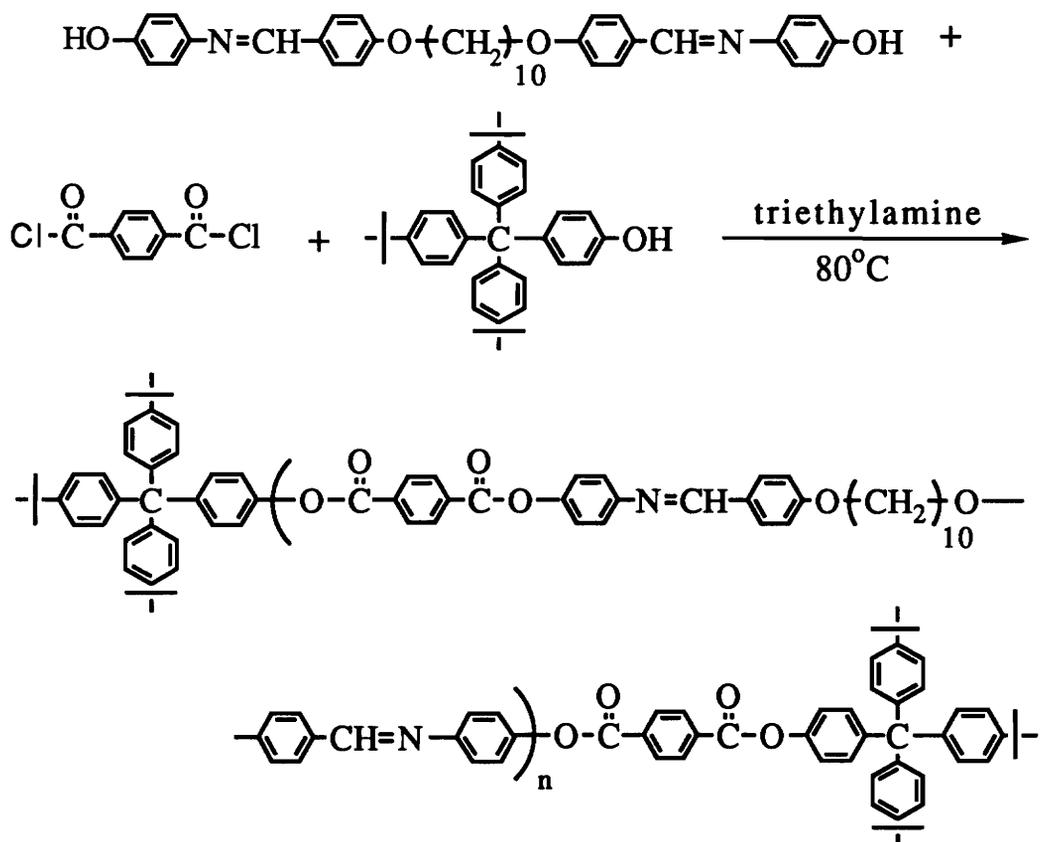
The synthesis of poly(azomethine)s A and B was repeated. Also, since the polyrotaxanes need large end groups at both ends as blocking groups, poly(azomethine) A and B with blocking groups were synthesized.

1. Poly(azomethine) A

The reaction schemes are shown below. (Scheme IV-B1)
(Scheme IV-B2)



Scheme IV-B1 Synthesis of poly(azomethine) A without end blockers



Scheme IV-B2 Synthesis of poly(azomethine) A with end blockers

It took several steps to synthesize poly(azomethine) A and poly(azomethine) A with end blockers.

1,10-Bis(p-formylphenoxy)decane was synthesized by reacting 4-hydroxybenzaldehyde with dibromodecane [2]. The solvent was ethanol, and the catalyst was potassium carbonate. The reaction was stirred at 60°C for 15 hours. The reaction solution was poured into hot water. If the reaction solution was poured into cold water, the product powder would be very fine, and very hard to filter. The water solution with precipitate was cooled to room temperature, and the yellow powdery product was filtered. The melting point was 90.1-92.8°C. The percentage yield was 82.3%. Demus reported the melting point was 78-80°C, and the percentage yield was 72% [2]. IR

and ^1H NMR spectra confirmed the compound. (Fig. IV-B1) (Fig. IV-B2)

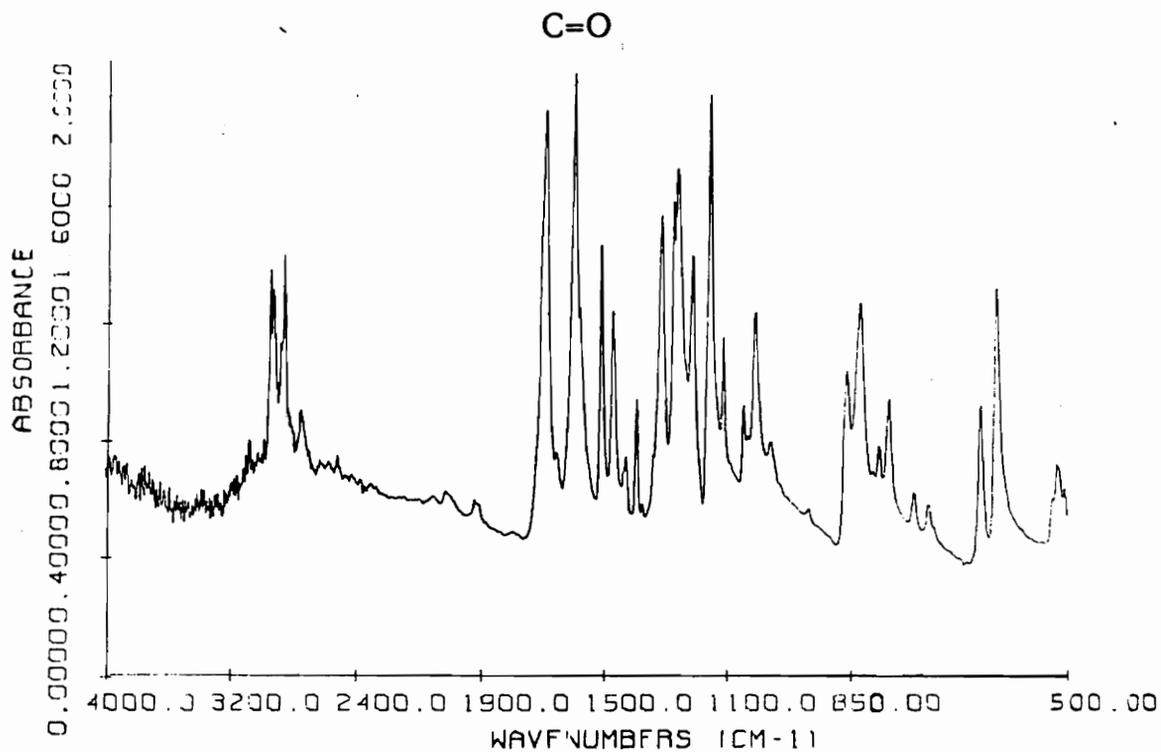


Fig. IV-B1 IR spectrum of 1,10-bis(p-formylphenoxy)decane (KBr, cm^{-1})

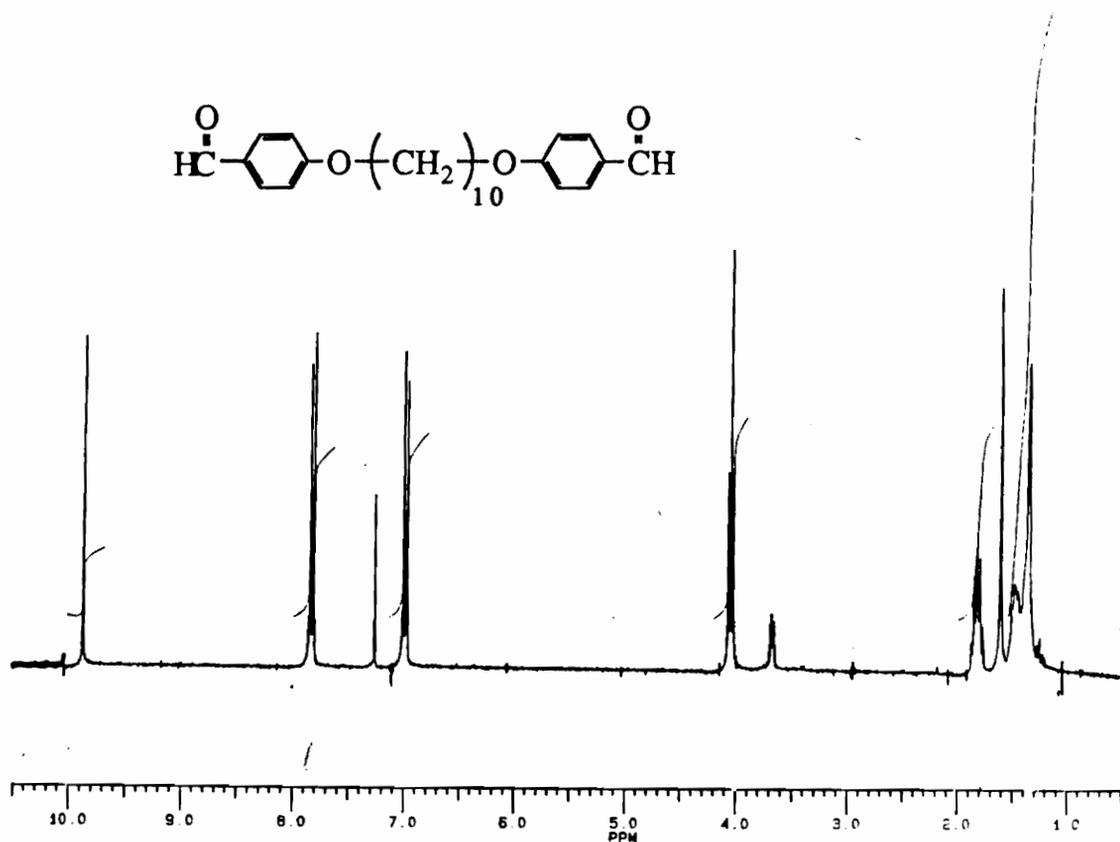
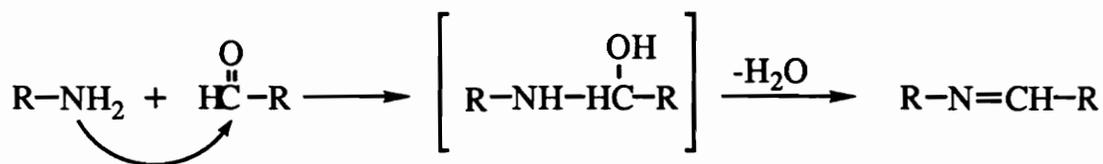


Fig. IV-B2 ^1H NMR spectrum of 1,10-bis(p-formylphenoxy)decane (ppm)

1,10-Bis(p-formylphenoxy)decane reacted with aminophenol to form 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane [1]. The reaction was refluxed in ethanol for 6 hours. The amino group reacted with aldehyde group to form a C=N double bond. The reaction mechanism is shown below. (Scheme IV-B3) Then the reaction solution was cooled in an ice bath. The product, 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane, a light yellow solid, was filtered. The product was recrystallized in 1,4-dioxane, until the melting point was stable. The melting point was 211.0-212.9°C. The percentage yield was 95.5%. Jin and Park reported that the melting

point was 235°C, and the percentage yield was 81% [1]. IR and ¹H NMR spectra confirmed the compound. (Fig. IV-B3) (Fig. IV-B4)



Scheme IV-B3 Mechanism of azomethine reaction

Terephthaloyl chloride was commercially available. Since the polycondensation reaction required very pure reactant, terephthaloyl chloride was recrystallized in cyclohexane. After the terephthaloyl chloride was dissolved in hot cyclohexane, the solution was filtered while it was hot. Terephthaloyl acid was filtered. The pure terephthaloyl chloride recrystallized when the solution reached room temperature. The recrystallization was done several times, until the melting point was stable. The melting point of terephthaloyl chloride was 85.9-86.4°C. The "Handbook of Chemistry and Physics" reports that the melting point of terephthaloyl chloride is 83-84°C [3].

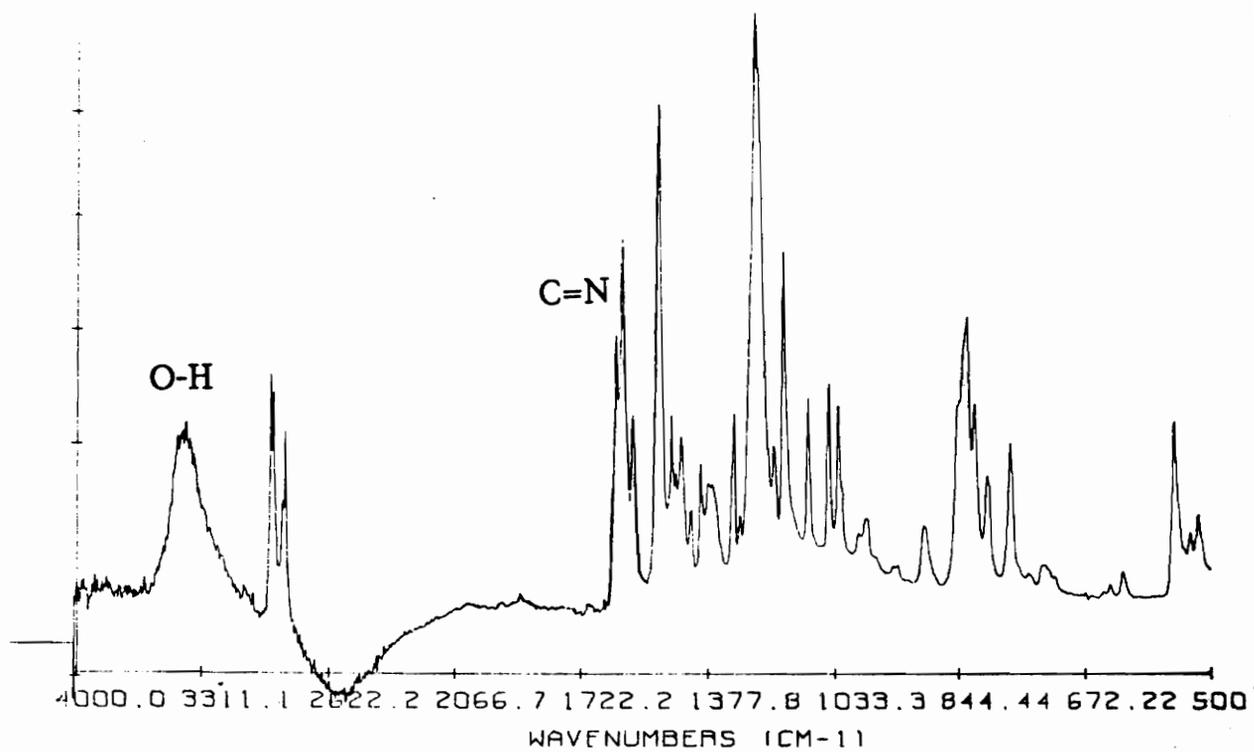


Fig. IV-B3 IR spectrum of 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane

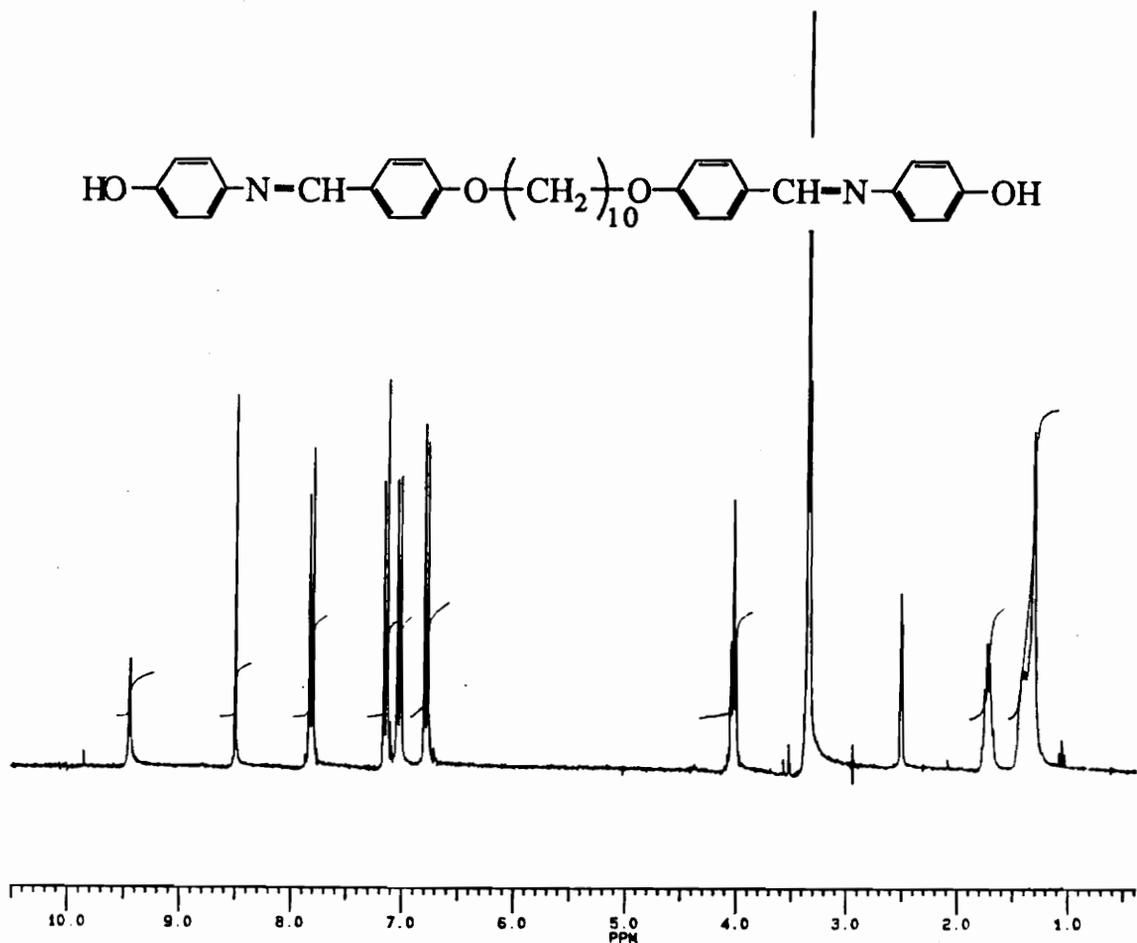


fig. IV-B4 ^1H NMR spectrum of 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane

The poly(azomethine) A was synthesized using a polycondensation reaction. Not only should the reactants be very pure, but also the flask which was used to react the polymer must be very clean and dry. The solvents were distilled. 1,10-Bis(p-hydroxyphenylimino-p-benzylideneoxy)decane was added to DMAc. Triethylamine was added as the catalyst. According to the reported information, the reaction was done at room temperature. But our

experimental results showed that 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane did not dissolve in DMAc at room temperature. The polycondensation reaction had to be done in a homogeneous system. Otherwise the polymerization would not run very well, and the molecular weight of the polymer would not be high. The 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane solution was heated to 65°C, and the reactant started to dissolve. But when the solution cooled to room temperature; the reactant precipitated. Therefore the reaction could not be done at room temperature. The reaction was done at 80°C under nitrogen. After 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane dissolved in DMAc at 80°C, terephthaloyl chloride dissolved in DMAc was added dropwise.

To synthesize poly(azomethine) A with end blockers, p-{tri(p-t-butylphenyl)methyl}phenol was dissolved in DMAc with 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane. The ratio of 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane, terephthaloyl chloride, and p-{tri(p-t-butylphenyl)methyl}phenol was 10:11:2. The degree of polymerization was designed to be 10.

Another reaction was done in the solvent mixture of DMAc and diglyme, 1:1 (v/v), because we wanted to polymerize the poly(azomethine) A in a crown ether solution to make poly(azomethine)rotaxane A. The structure of diglyme is similar to that of the crown ether. If the polymerization could be done in a diglyme solution, it also could be done in a crown ether solution.

During all three reactions described above, half a minute after the terephthaloyl chloride was added, a yellow precipitate formed in the solution. The amount of precipitate increased as the reaction went longer and longer. At last the magnetic stirrer was not able to stir. Then a mechanical stirrer was used. The reaction was stirred at

80°C for 72 hours. The by-product of this reaction was HCl which was trapped by triethylamine. When the reaction was finished, a lot of precipitate had formed in the solution, and the solution became very thick.

The same polymerization of poly(azomethine) A without end blockers was done in pure diglyme solution. But the reaction did not work very well because the pure diglyme is not basic. The product of the reaction did not show liquid crystalline properties; it did not show multi-endothermic transitions in the DSC scan, and the T_m was much lower than reported. The percentage yield of the product was about 67%, which was too low.

After the polymerizations were finished, all of the poly(azomethine) A reaction mixtures were poured into THF, and a yellow solid was filtered (fraction 1). The THF solutions of these poly-(azomethine) A samples were precipitated into methanol. The solution of poly(azomethine) A without end blockers did not show any precipitate in methanol solution; the poly(azomethine) A with end blockers showed a light yellow precipitate in methanol solution (fraction 2). The yellow precipitate was put into THF again; some of the precipitate dissolved in THF, and some of the precipitate stayed at the bottom of the flask and did not dissolve. Even when the THF solution was heated to boiling, there was still precipitate at the bottom of the flask. The process was repeated. The THF solution was precipitated into methanol, and the precipitate was filtered. Then the precipitate was dissolved in THF again. There was always some precipitate at the bottom of the flask, that never dissolved. This meant that some of the poly(azomethine) A which originally dissolved in DMAc and THF would not dissolve back in the same solution. Suematsu and his group also noticed this phenomenon [4]. Although he made different poly(azomethine)s, his poly(azomethin)s

precipitated out of the solution, and would not dissolve back in the same solution.

The poly(azomethine) A without end blockers was washed using ethanol and dried. Since it would not dissolve in general organic solvents like alcohols, acetates, THF, acetone, and benzene, some characterization like NMR, GPC was not able to be done. IR analysis confirmed the compound. (Fig IV-B5) The O-H peak at 3364 cm^{-1} in the IR spectrum was not very large, which meant that the degree of polymerization should not be very low. There was no O-H peak in the IR spectrum of poly(azomethine) A (fraction 2) with end blockers. That meant that end blockers reacted at the both ends of the polymer; there was no phenyl group on the polymer (Fig. IV-B6). The percentage yield was 90% for the poly(azomethine) A made in pure DMAc, and 99.1% for the poly(azomethine) A made in the mixture of DMAc and diglyme. The melting point could not be measured by the melting point apparatus, because the polymer decomposed when the temperature reached above 200°C . Jin and Park reported that the percentage yield of the polymer was 89.3% [1].

The percentage yield of poly(azomethine) A fraction1 was 89%, the fraction 2 was 7.5%. ^1H NMR analysis was done in chloroform for the poly(azomethine) A with end blockers (Fig. IV-B7). The fraction which dissolved in THF also dissolved in chloroform. But the solubility was very low. The result showed that the degree of polymerization of this fraction was 5. This meant that the polymer precipitated from the reaction solution when the degree of polymerization reached 5.

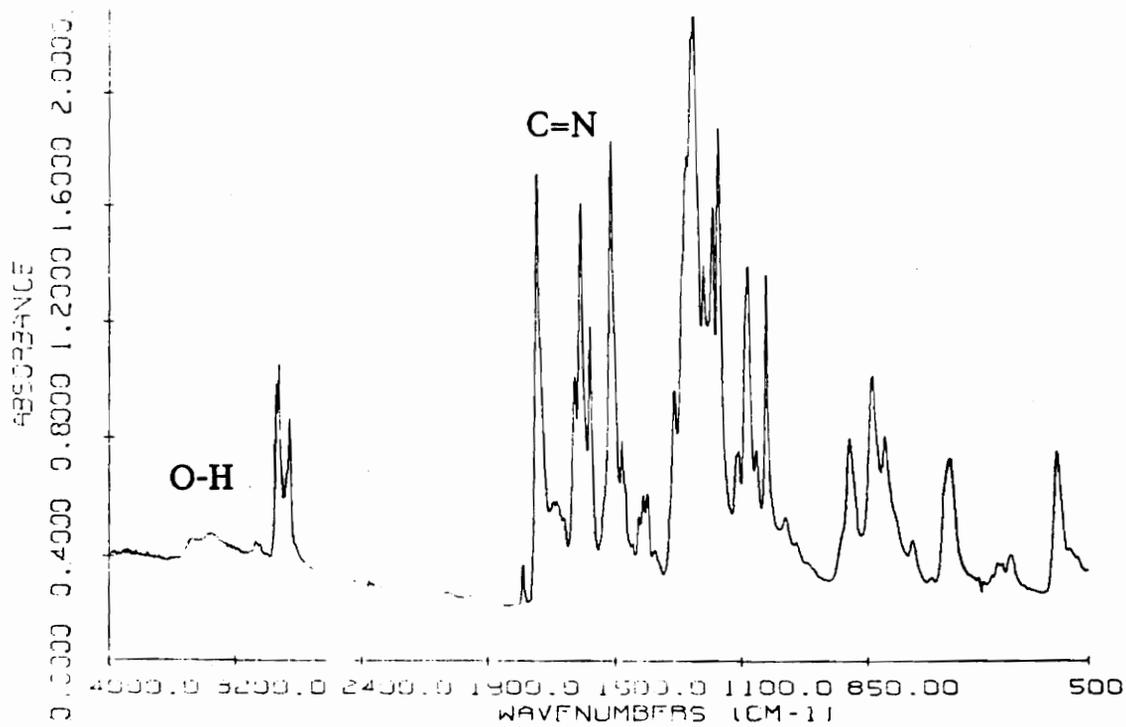


Fig. IV-B5 IR spectrum of poly(azomethine) A without end blockers (KBr, cm^{-1})

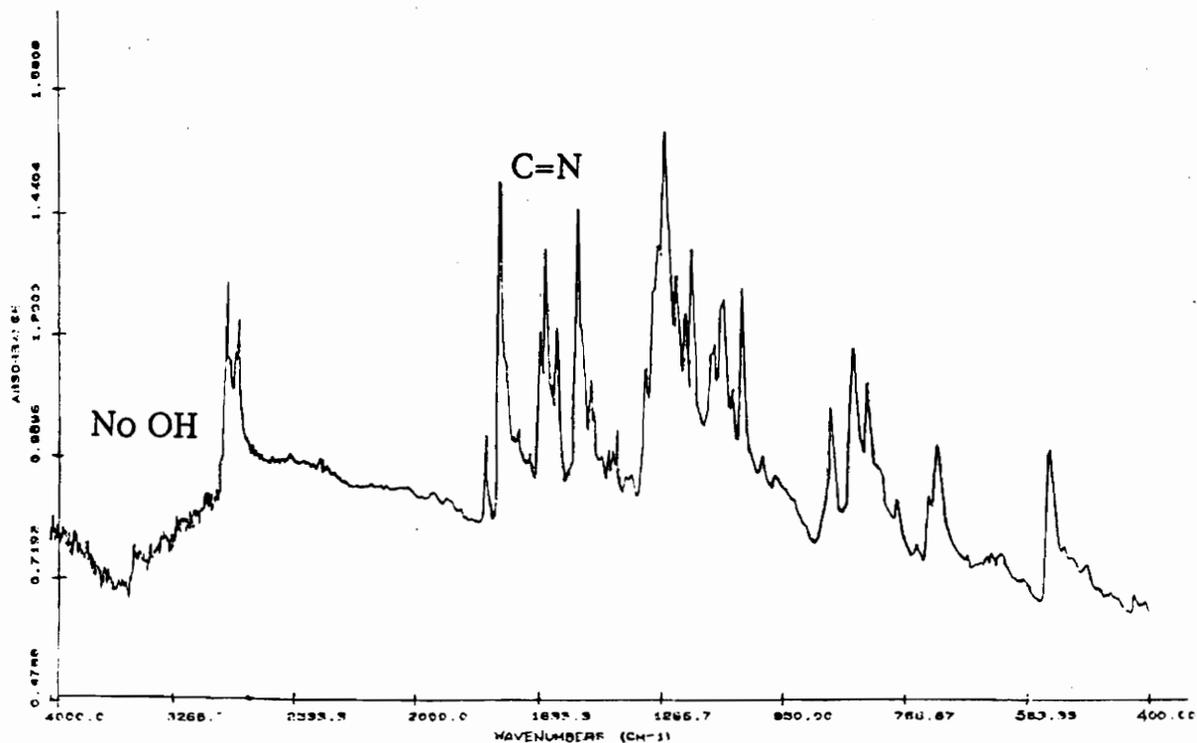


Fig. IV-B6 IR spectrum of poly(azomethine) A with end blockers (fraction 2) (KBr, cm^{-1})

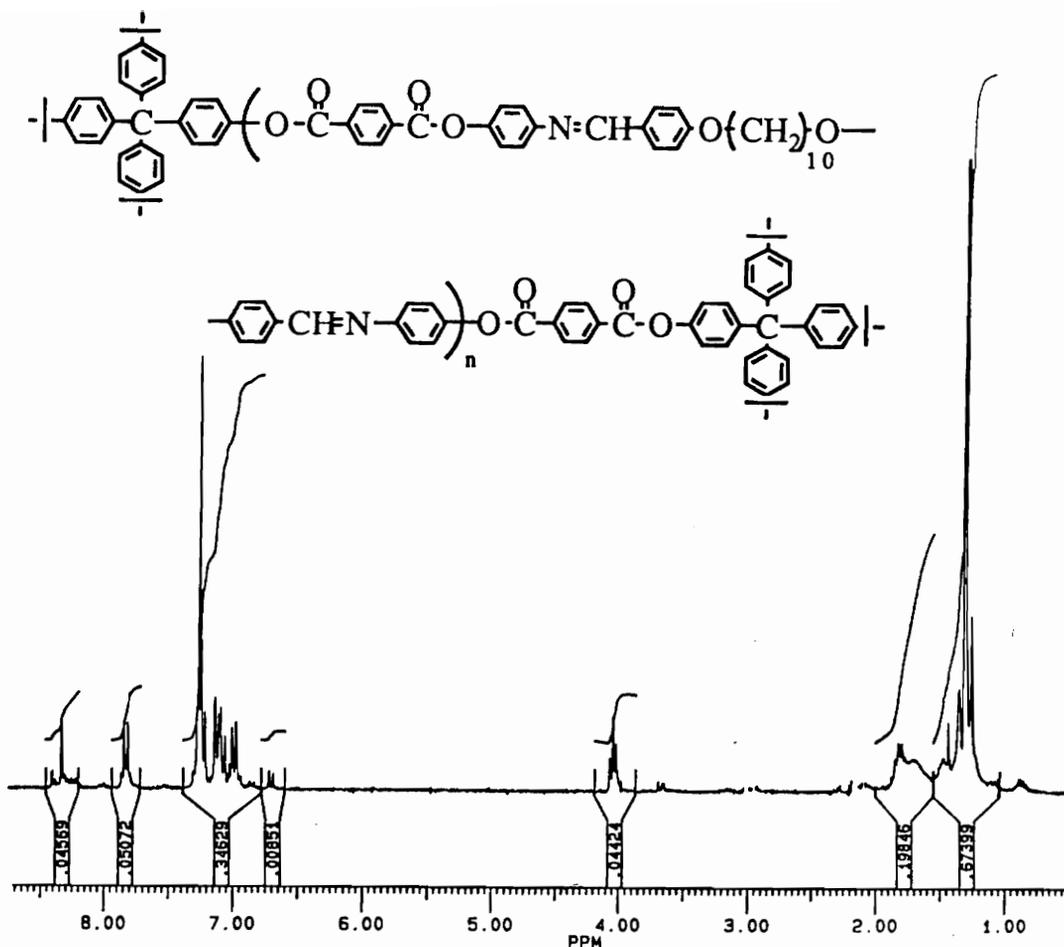
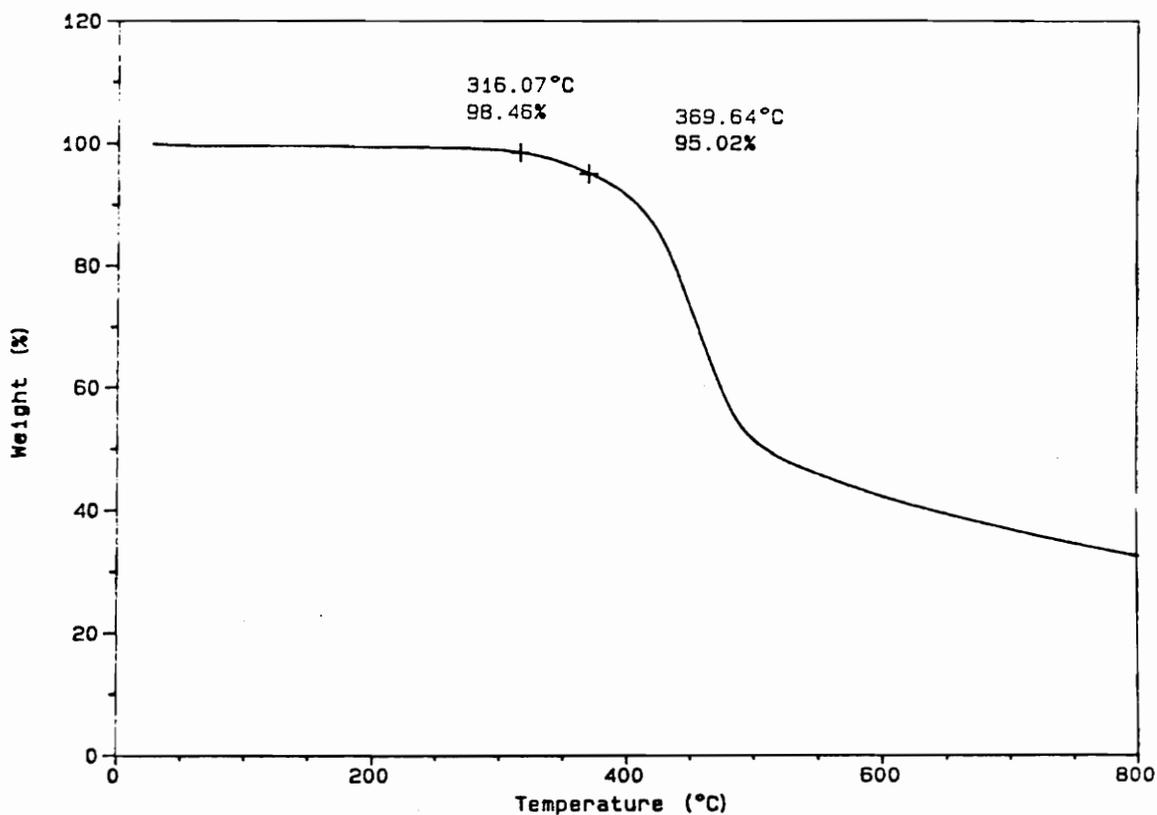


Fig. IV-B7 ¹H NMR spectrum of poly(azomethine) A with end blockers (ppm)

It was not possible to do GPC analysis for poly(azomethine) A. The polymer which precipitated from the reaction did not dissolve in other general organic solvents. The fraction of poly(azomethine) A with end blockers which dissolved in THF also could not be analyzed on the GPC. The reason for this will be discussed in Chapter V.

Thermogravimetric analysis was done for poly(azomethine) A with and without blocking groups. For the poly(azomethine) A without blocking groups, the TGA analysis showed that the % polymer decomposed at 369°C. (Fig. IV-B8) The DSC analysis

showed two endothermic peaks. The first one was at 197°C, and the second one was at 236°C. (Fig. IV-B9) When DSC analysis was done at 5°C per minute, these peaks were not repeatable. In the second heat, these endothermic peaks disappeared. According to Jin and Park's report, the last endothermic transition in the DSC scan was 224°C. Jin and Park did DSC analysis using 20°C per minute. When we used the same heating rate as Jin, the endothermic peaks appeared in the second heating. This meant that with the heating rate of 5°C/minute the polymer had decomposed during heating. Jin and park reported that T_i of 257°C was seen on the polarizing microscope [1], but we were not able to do the optical microscopic analysis, because the polymer did not dissolve in any solvents so that we were not able to make a slide. For the fraction 2 of poly(azomethine) A with end blockers, the sample had 5% decomposition at 300°C in TGA scan. The sample only show a shoulder at 84°C in DSC scan. The low degree of polymerization of the fraction 2 showed low results on the thermal analysis. For the fraction 1 of poly(azomethine) A with the blocking groups, the TGA analysis showed that the 5% polymer decomposed at 185°C, and the DSC analysis did not show any clear endothermic transition. This was because the poly(azomethine) A was destroyed by dichloroacetic acid. Detailed information will be provided in the end of the section B.



**Fig. IV-8 TGA csan of poly(azomethine) A without end blockers
(10°C/min)**

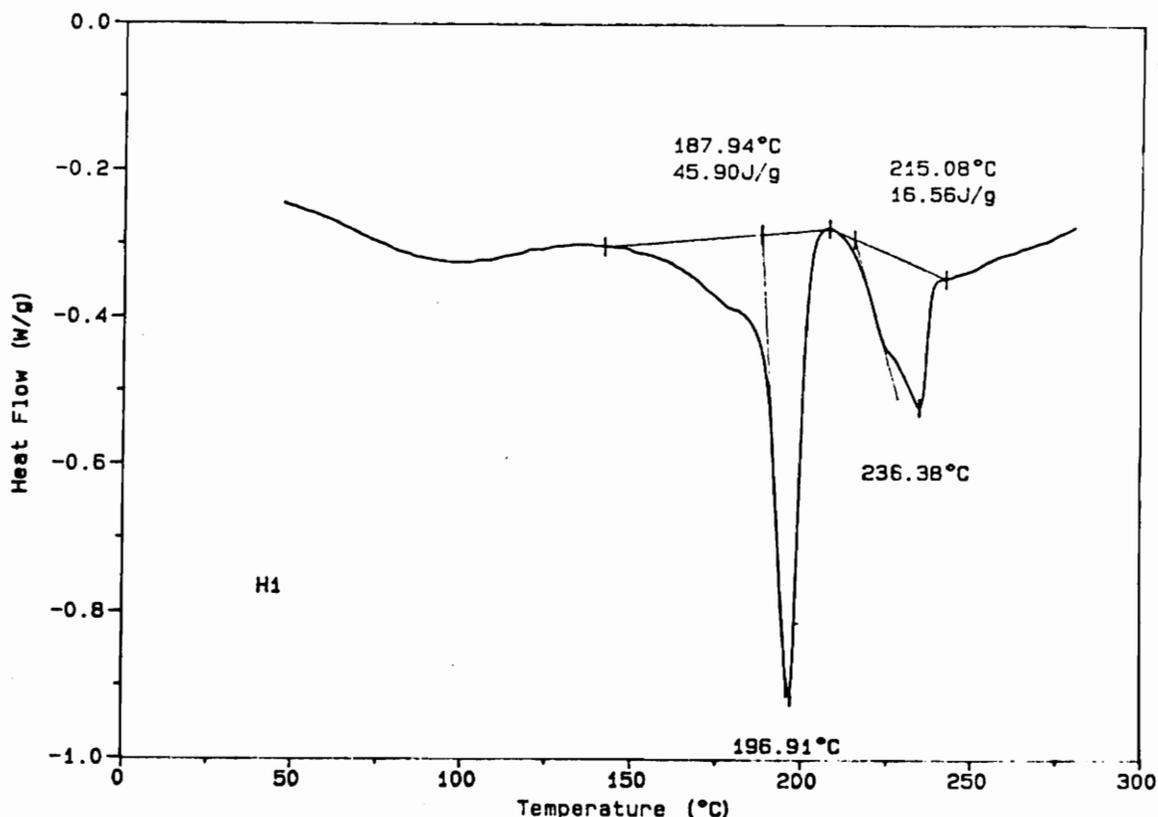
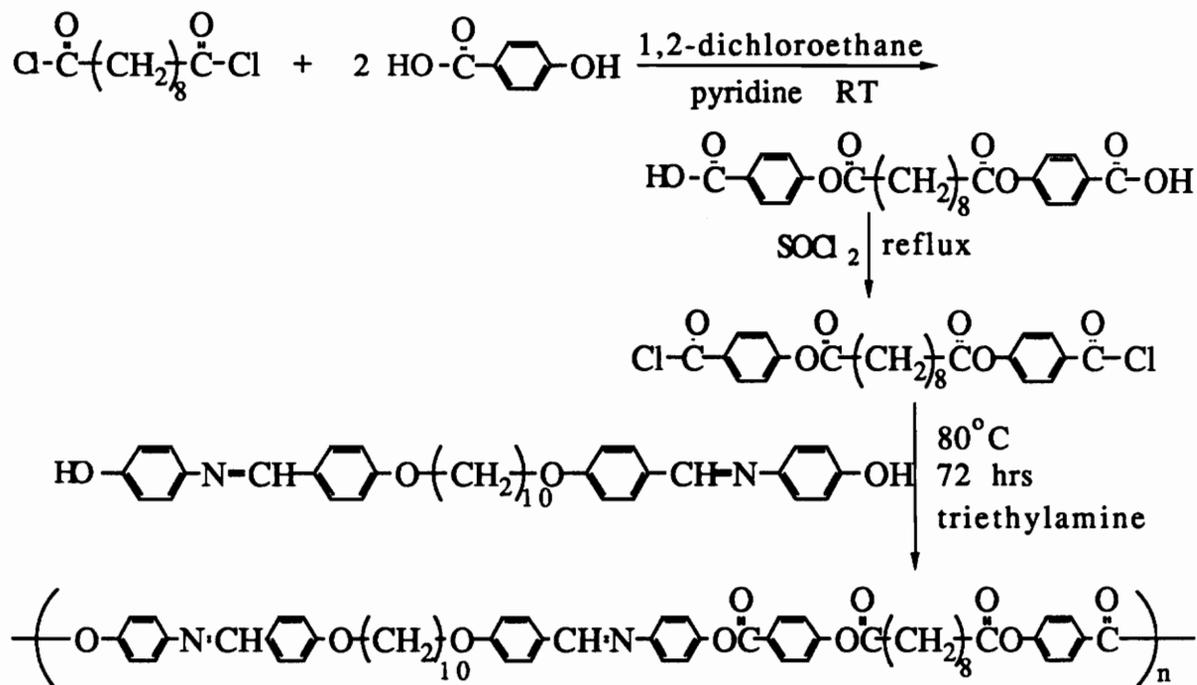


Fig. IV-B9 DSC analysis of poly(azomethine) A without end blocker (20°C/min)

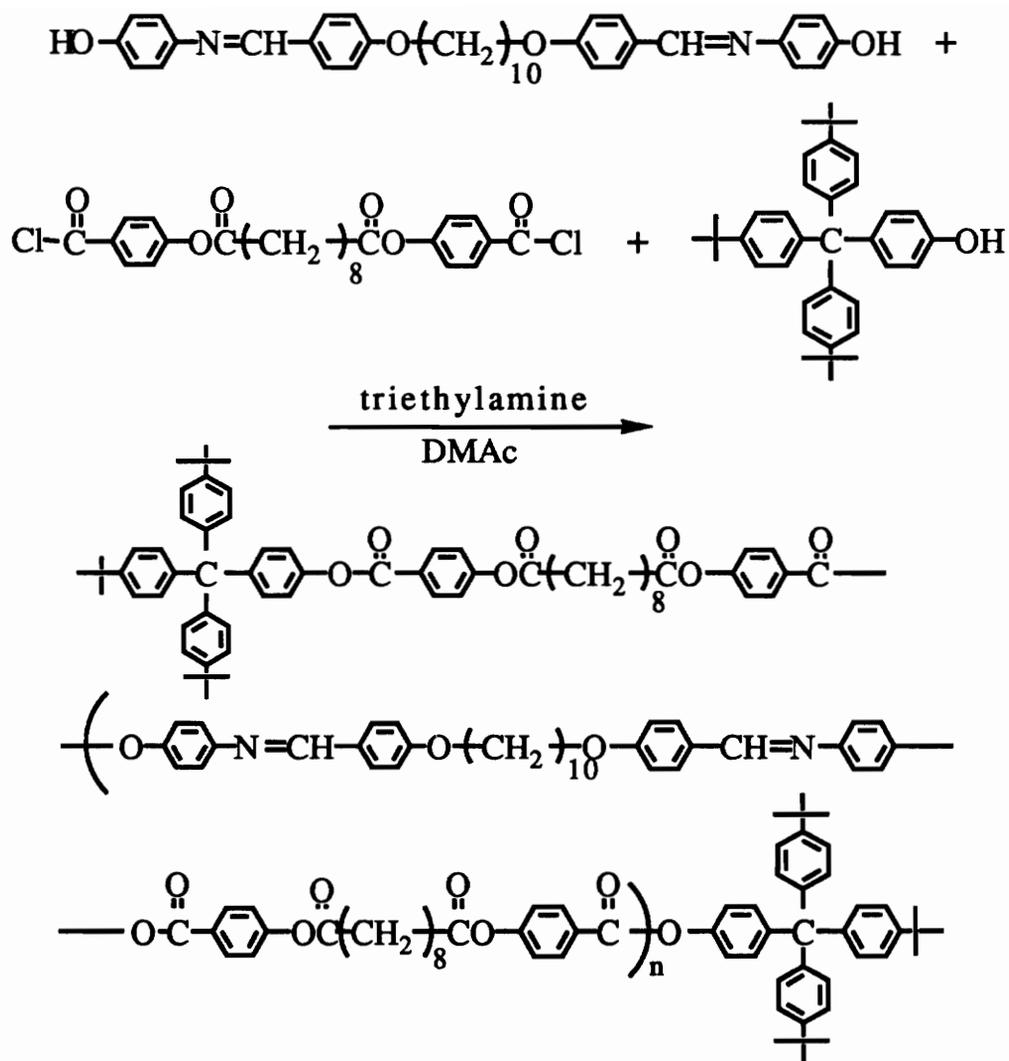
The inherent viscosities were measured for samples of poly(azomethine) A. The solvent was dichloroacetic acid, and the water bath temperature was 45°C. The concentration of the solution was 0.5 g/dl. The results were 0.262 dl/g for poly(azomethine) A without end blockers, and 0.231 dl/g for poly(azomethine) A with end blockers. Jin and Park reported that the inherent viscosity of the same polymer was 0.234 dl/g in the same condition [1]. But these results did not appear to be correct, because poly(azomethine) A decomposes in dichloroacetic acid. Detailed information will be mentioned at the end of section B.

2. Poly(azomethine) B

The reaction schemes for poly(azomethine) B are shown below.
(Scheme IV-B4) (Scheme IV-B5)



Scheme IV-B4 Synthesis of poly(azomethine) B without end blockers



Scheme IV-B5 Synthesis of poly(azomethine) B with end blockers

1,8-Bis(p-chlorocarbonylphenoxy)octane was synthesized as the first step. Sebacoyl dichloride was reacted with p-hydroxybenzoic acid in 1,2-dichloroethane. Pyridine was used as the base. The reaction was stirred under nitrogen for 6 hours. The product, white powdery 1,8-bis(p-carboxyphenoxy)octane, was filtered and washed with methanol, then recrystallized from 1,4-dioxane. The percentage yield was 91.3%. The melting point was 248.1-249.3°C. Jin and Park reported that the percentage yield was

85%, and the melting point was 246-247°C [1]. IR and ¹H NMR spectra confirmed the compound. (Fig. IV-B10) (Fig. IV-B11)

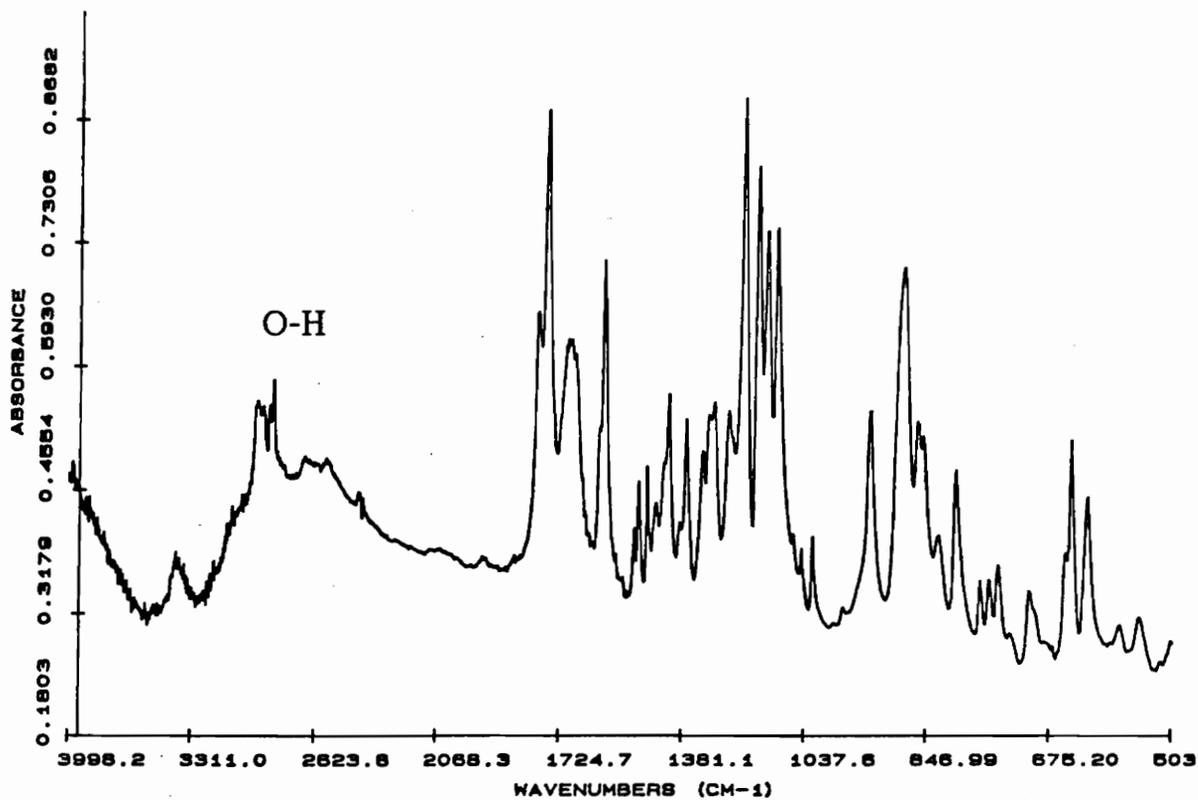


Fig. IV-B10 IR spectrum of 1,8-bis(p-carboxyphenoxy-carbonyl)octane (KBr, cm⁻¹)

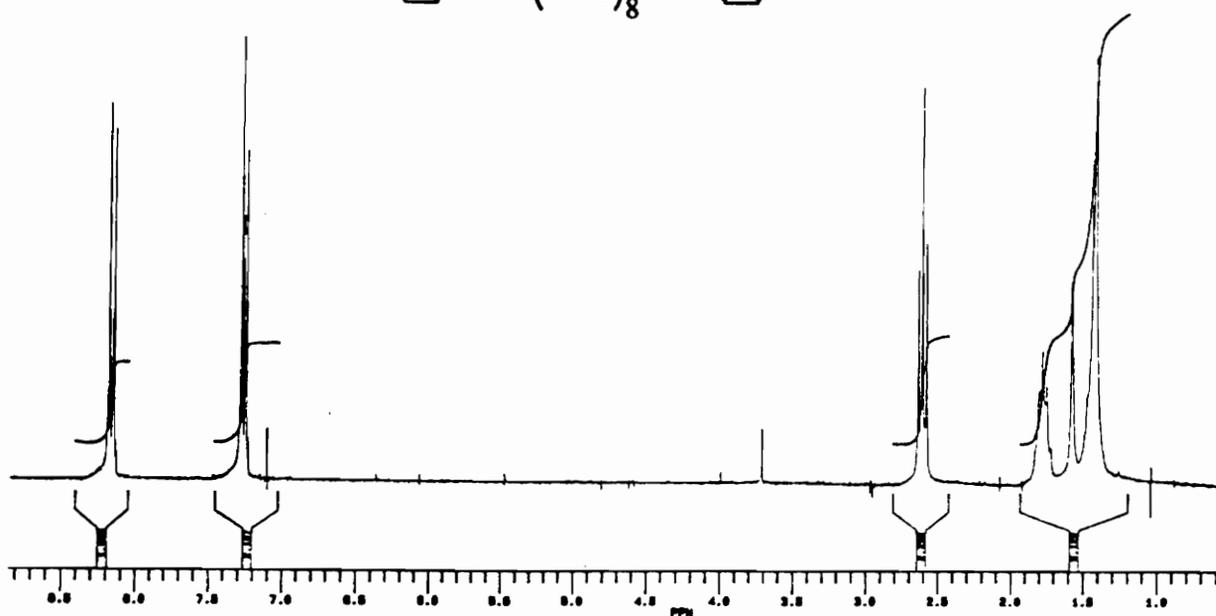
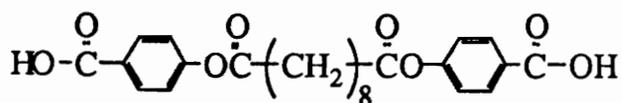


Fig. IV-B11 ^1H NMR spectrum of 1,8-bis(p-carboxyphenoxy-carbonyl)octane (ppm)

1,8-Bis(p-carboxyphenoxy-carbonyl)octane was added to thionyl chloride with a few drops of N,N-dimethylformamide. The reaction was refluxed for 6 hours. The excess thionyl chloride was removed by distillation. A silky, powdery product, 1,8-bis(chloro-carbonylphenoxy-carbonyl)octane, was recrystallized from cyclohexane. After the 1,8-bis(p-chloro-carbonylphenoxy-carbonyl)octane dissolved in hot cyclohexane, the solution was filtered while it

was hot, because the unreacted acid did not dissolve in hot hexane, but the product did. The recrystallization was repeated several times until the melting point of the product was stable. The melting point was 98.3-98.7°C, and the percentage yield was 92%. The IR spectrum confirmed the compound. (Fig. IV-B12) The ^1H NMR spectrum was similar to 1,8-bis(carboxyphenoxy)octane.

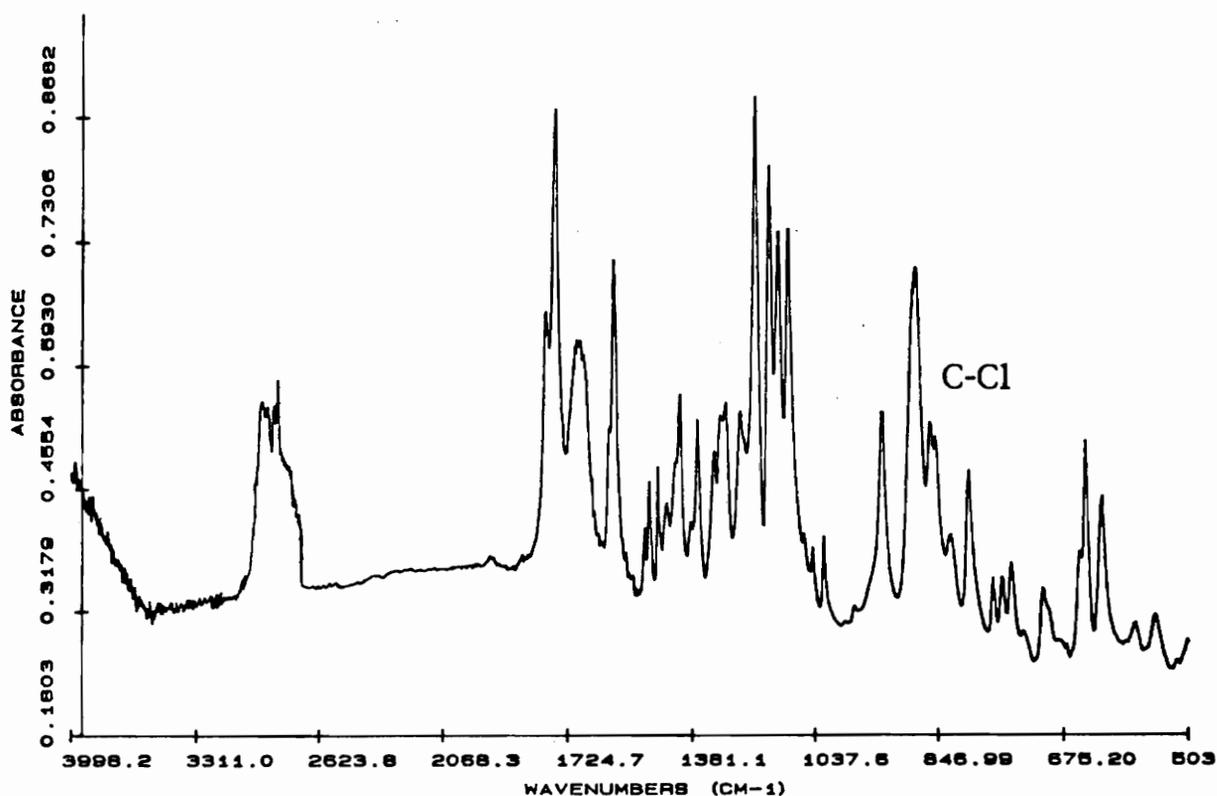


Fig. IV-B12 IR spectrum of 1,8-bis(p-chlorocarbonylphenoxy)octane (KBr, cm^{-1})

Poly(azomethine) B was synthesized by reacting 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane with 1,8-bis(p-chlorocarbonylphenoxy)octane. 1,10-bis(p-hydroxyphenyl-

imino-p-benzylideneoxy)decane was dissolved in DMAc at 80°C under nitrogen. Triethylamine was used as the catalyst. A mechanical stirrer was used. To synthesize poly(azomethine) B with end blockers, the end blocking group, p-tri(p-t-butylphenyl)methylphenol, was added with 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane. The degree of polymerization of poly(azomethine) B with end blockers was designed as 10. DMAc was used as the solvent for one reaction, and the mixture of DMAc/diglyme, 1:1 (v/v), was used as the solvent for another reaction. After 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane completely dissolved in the solvent at 80°C, 1,8-bis(p-chlorocarbonylphenoxy)octane dissolved in DMAc was added dropwise. After half a minute, the solid started to form. The reaction was stirred at 80°C for 72 hours. The by-product of this reaction was HCl which was trapped by triethylamine. The reaction became very thick, and a lot of precipitate formed. After the reaction was finished, the reaction was poured into THF. A light yellow solid was filtered.

A THF solution of the solid was precipitated in methanol. Poly(azomethine) B without end blockers did not give a precipitate in methanol, but poly(azomethine) B with end blockers did give a precipitate in methanol. Poly(azomethine) B with end blockers dissolved in THF, and also dissolved in acetone chloroform, ethyl acetate, etc. But after the product was precipitated out of the solution, it dissolved less and less in the same solvent. ¹H NMR analysis was done for the poly(azomethine) B with blocking groups. From the integration, the degree of polymerization was 3. This means that the polymer precipitated when the degree of the polymerization reached 3. (Fig. IV-B13) Poly(azomethine) B without end blockers did not dissolve in general organic solvents; NMR analysis was not possible. IR analysis confirmed the polymer. (Fig. IV-B14) Since the O-H peak at 3412 cm⁻¹ was quite small, the molecular weight should not be very small. There was no O-H

peaks in the IR spectrum of poly(azomethine) B with end blockers.

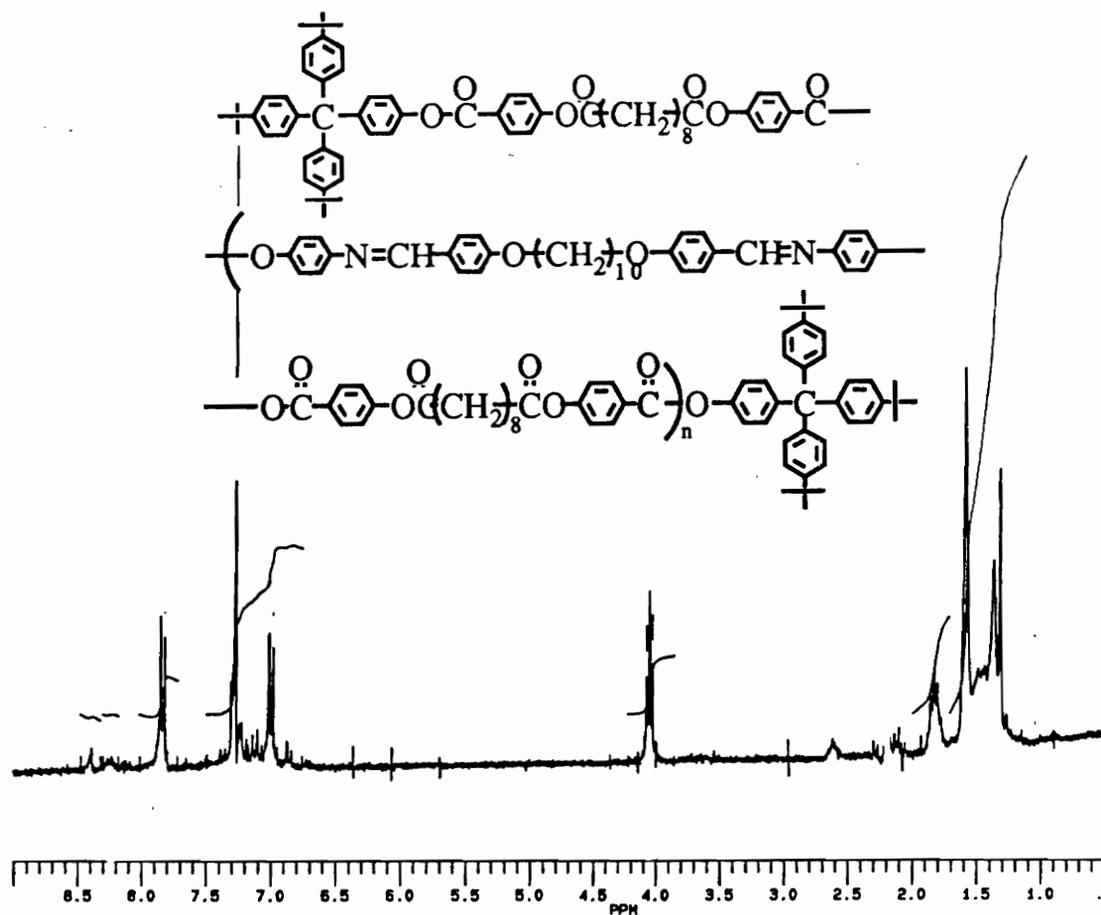


Fig. IV-B13 ^1H NMR spectrum of poly(azomethine) B with end blockers (ppm)

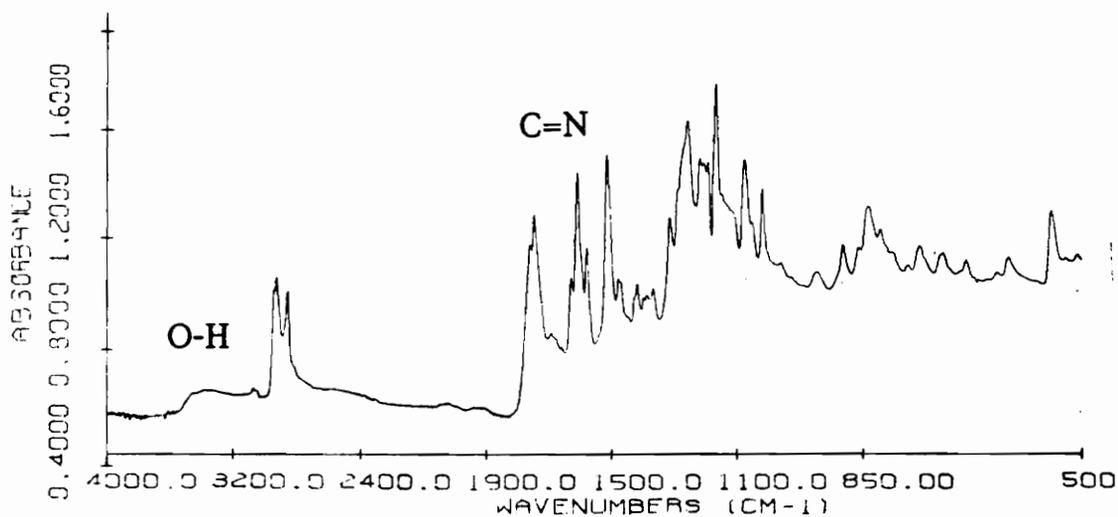


Fig. IV-B14 IR spectrum of poly(azomethine) B without end blocker (KBr, cm^{-1})

The melting point of the polymer could not be measured by the melting point apparatus, because the polymer decomposed when the temperature rose above 200°C . The percentage yield was 86% for the poly(azomethine) B without end blockers, and 88.6% for poly(azomethine) B with end blockers. Jin and Park reported that the percentage yield was 80.1% [1].

The thermal analysis was done on poly(azomethine) B with and without end blockers. The TGA showed that the poly(azomethine) B without end blockers had 5% decomposition at 360°C (Fig. IV-B15), and poly(azomethine) B with end blockers which dissolved in THF

had 5% decomposition at 346°C. In the DSC analysis, when the heating rate was 5°C per minute, there was a shoulder at 123°C, and an endothermic peak at 170°C. But these peaks were not repeatable. When the heating rate was increased to 20°C per minute, there were three endothermic transitions: 108°C, 135°C, and 173°C. These peaks were repeatable (Fig. IV-B16). The polymer decomposed during the slow heating. Jin and Park reported that the last endothermic transition peak in the DSC scan, which they considered a T_m , was at 166°C [1]. The T_i at 181°C, Jin observe under microscope. Since we were not able to make a slide, we were not able to do optical microscopic analysis. The poly(azomethine) B with end blockers which dissolved in THF showed two endothermic transition peaks in DSC scan. One was at 145°C, another was at 215°C. When the heating rate was 5°C per minute, the polymer decomposed during the heating. Therefore, these peaks were not repeatable upon second heating. The poly(azomethine) B with end blockers which did not dissolve in general solvents was destroyed by dichloroacetic acid. A thermal analysis could not be done.

The viscosity of poly(azomethine) B without and with end blockers was measured. The solvent was dichloroacetic acid. The concentration was 0.5 g/dl. The water bath temperature was 45°C. The inherent viscosity was 0.263 dl/g for the sample of poly(azomethine) B without end blocker, 0.256 dl/g for the sample of poly(azomethine) B with end blockers which dissolved in general organic solvents, and 0.249 dl/g for poly(azomethine) B with end blockers which did not dissolve in general solvents. Jin reported that the inherent viscosity was 0.268 dl/g under the same condition [1].

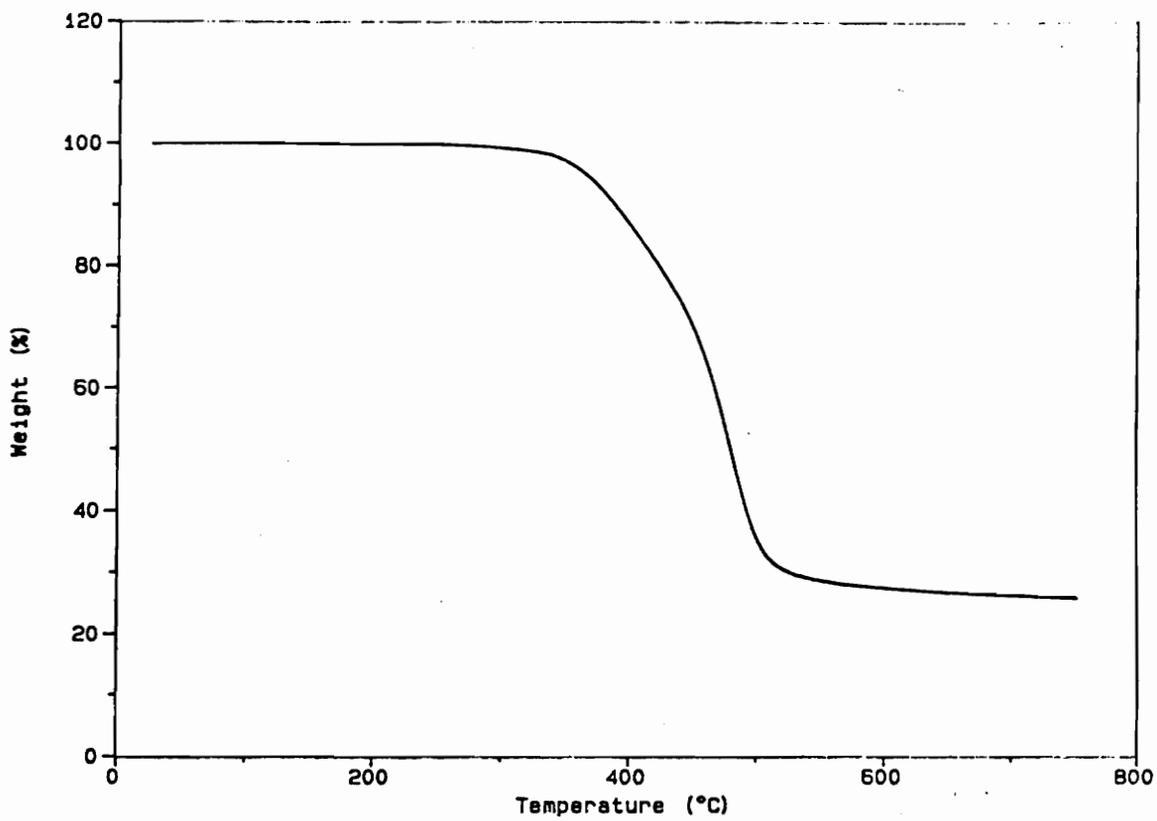


Fig. IV-B15 TGA scan of poly(azomethine) B without end blocker (10°C/min)

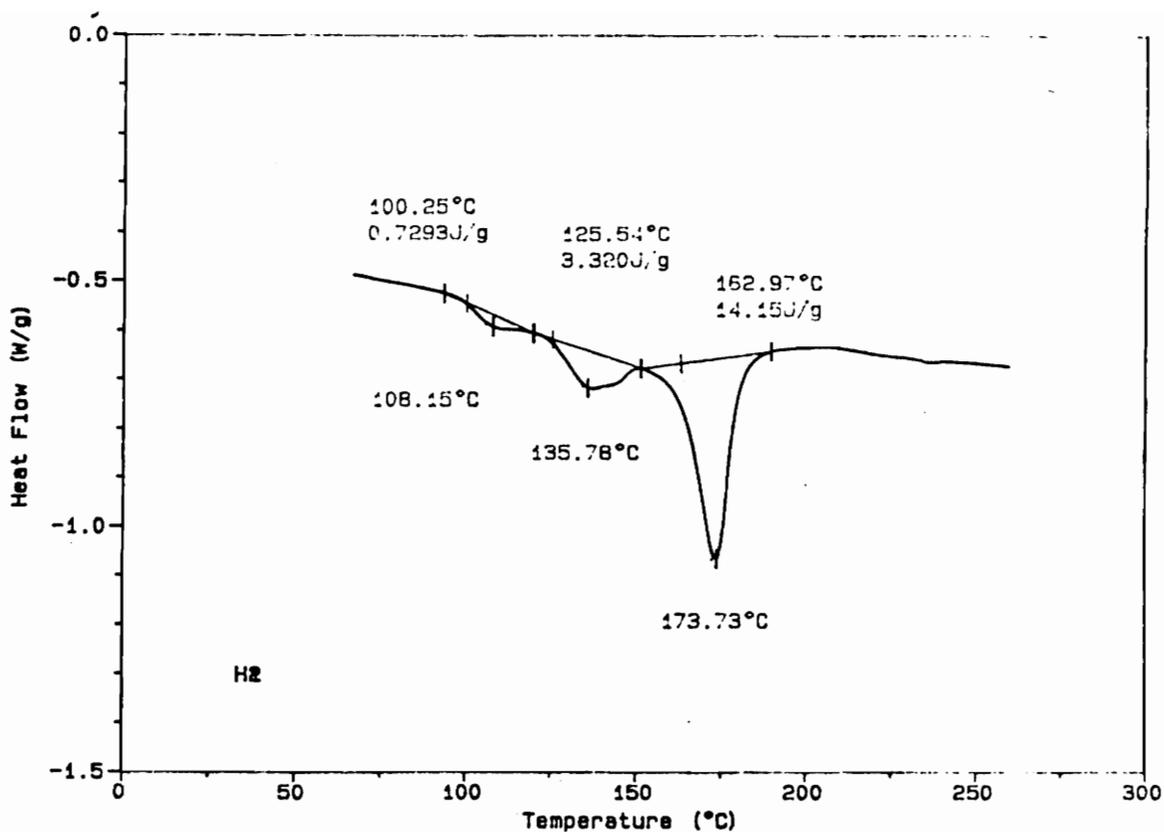


Fig. IV-B16 DSC scan of poly(azomethine) B without end blocker (20°C/min)

We noticed that the viscosity of the different poly(azomethine)s and poly(azomethine)rotaxanes were very similar. Since we noticed that the poly(azomethine) C=N bond was sensitive to acid, a decomposition needed to be considered because of the viscosity results. According to most published papers, poly(azomethine)s only dissolve in strong acids like sulfuric acid, methanesulfonic acid, and dichloroacetic acid. [1][4][5][6][7][8] They measured viscosity in these strong acids. We dissolved 1,10-bis(p-

hydroxyphenylimino-p-benzylideneoxy)decane in dichloroacetic acid. After 15 hours, the solution was precipitated in water. IR and NMR analysis was done on the precipitate. We found the C=O peak in the IR spectrum at 1686 cm^{-1} . The ^1H NMR spectrum was exactly the same as 1,10-bis(p-formylphenoxy)decane. The results confirmed our thoughts. The compound did decompose because the C=N bond broke in strong acid. (Aminophenol was washed away by water.) The poly(azomethine)s decomposed in strong acids instead of dissolving in it.

IV-C Experimental

4-Hydroxybenzaldehyde (99%), 1,10-dibromodecane (99%), aminophenol (99%), p-hydroxybenzoic acid (99%), N,N-dimethylacetamide (99.8%), and 1,2-dichloroethane (99%) were purchased from Aldrich Chemical Co. and used without further purification. Sebacoyl dichloride (99%) was purchased from Aldrich Chemical Co. and was recrystallized from cyclohexane four times. Triethylamine was purchased from Aldrich Chemical Co. and was distilled once before use. Potassium carbonate (99%), ethanol, tetrahydrofuran (99%), pyridine (99%), thionyl chloride (99%), and N,N-dimethylformamide (99%) were purchased from Fisher Scientific Inc. and used without further purification. p-Tri(p-t-butylphenyl)methylaniline and p-tri(p-t-butylphenyl)methylphenol were synthesized (see Chapter III).

The centrifugation was done in a Dynac Centrifuge, Becton, Dickinson & Company. Melting points were determined in a Haake Buchler capillary melting point apparatus and were corrected. Thin layer chromatography was done on Whatman fluorescence UV₂₄₅ 250 μm layer silica gel plate, and DC-Alufolien aluminiumoxid 60 F254 neutral (type E) schichtdicke 0.2 mm layer aluminium gel plate. The FTIR spectra were recorded from a Nicolet MX-1 FTIR spectrometer. The ^1H NMR spectra were recorded from a Bruker WP

270 MHz instrument using tetramethylsilane as the internal standard. Thermogravimetric analysis scans were recorded from a TGA V4.0D DuPont 2100 instrument. Differential Scanning Calorimeter scans were recorded from a DSC V4.0D DuPont 2100 instrument. The viscosity analysis was done in a Cannon 100 B 556 viscometer.

1,10-Bis(p-formylphenoxy)decane

4-Hydroxybenzaldehyde, 24.42 g (0.2 mole), and potassium carbonate, 33.10 g (0.23 mole), were added to 250 ml ethanol. The mixture was stirred under nitrogen at 60°C for 1 hour, until the reactants dissolved in the solvent. 1,10-Dibromodecane, 30.00 g (0.1 mole), in 50 ml hot ethanol was added to the hydroxybenzaldehyde solution dropwise. The reaction mixture was stirred at 60°C under nitrogen for 15 hours. The reaction mixture was precipitated in hot water. The product, a yellow solid which weighed 31.48 g, was filtered. The percentage yield was 82.3%. Melting point: 90.1-92.8°C. The reported yield was 72%, and the melting point was 78-80°C [2]. IR (ν/max , cm^{-1}): 500, 600, 630, 710, 730, 750, 840, 850, 1010, 1030, 1100, 1170, 1210, 1260, 1300, 1410, 1480, 1490, 1550, 1660, 2780, 2820. ^1H NMR (chloroform-d/TMS, ppm): singlet at 9.8 (2H), doublet at 7.8 (4H), doublet at 7.0 (4H), triplet at 4.0 (4H), triplet at 4.8 (4H), multiplet at 1.3-1.4 (12H).

1,10-Bis(p-hydroxyphenylimino-p-benzylideneoxy)decane

1,10-Bis(p-formylphenoxy)decane, 3.82 g (0.01 mole), and aminophenol, 2.18 g (0.02 mole), were added to 100 ml ethanol. The reaction mixture was refluxed for 6 hours. Then the mixture was cooled to 5°C in an ice bath. The product, 5.39 g dark yellow solid, was filtered and recrystallized in 1,4-dioxane. The percentage yield was 95.5%. Melting point: 211.0-212.9°C. The reported yield was 81%, and the melting point was 235°C [1]. IR (ν/max , cm^{-1}): 520,

550, 790, 850, 1050, 1070, 1110, 1140, 1220, 1290, 1380, 1460, 1500, 1570, 1590, 1610, 2710, 2800, 3150, 3420. H^1 NMR (DMSO-d/TMS, ppm): singlet at 9.4 (2H), singlet at 8.5 (2H), doublet at 7.8 (4H), doublet at 7.1 (4H), doublet at 7.0 (4H), doublet at 6.8 (4H), triplet at 4.0 (4H), triplet at 1.7 (4H), multiplet at 1.3-1.4 (12H).

1,8-Bis(p-chlorocarbonylphenoxy)octane

p-Hydroxybenzoic acid, 17.10 g (120 mmole) dissolved in 60 ml pyridine under nitrogen. Sebacoyl dichloride, 14.35 g (60 mmole), in 50 ml 1,2-dichloroethane was added to the p-hydroxybenzoic acid solution dropwise. The reaction was stirred at room temperature for 6 hours. The product, white powdery 1,8-bis(p-carboxyphenoxy-carbonyl)octane, was filtered and washed with methanol, then recrystallized from 1,4-dioxane, 24.24 g, 91.3% yield. The melting point was 248.1-249.3°C. The reported yield was 85%, and the melting point was 246-247°C [1]. 1,8-Bis(p-carboxyphenoxy-carbonyl)octane, 24.24 g (54.78 mmole), was added to 60 g (0.5 mole) thionyl chloride with 10 drops of N,N-dimethylformamide. The reaction was refluxed for 5 hours. The excess thionyl chloride was removed by distillation. The product was recrystallized from cyclohexane. (The solution was filtered hot to remove the unreacted diacid.) The product, 24.16 g, 92% yield, had a melting point of 98.3-98.7°C. No reported information was found for this compound. IR (ν /max, cm^{-1}): 619, 639, 701, 742, 762, 804, 851, 878, 926, 1008, 1111, 1138, 1165, 1199, 1295, 1363, 1411, 1472, 1500, 1595, 1691, 1752, 1779, 2626, 2851, 2940, 3390. H^1 NMR (chloroform-d/TMS, ppm): doublet at 8.1 (4H), doublet at 7.3 (4H), triplet at 2.6 (4H), triplet at 1.8 (4H), multiplet at 1.4 (12H).

Poly(azomethine) A with end blockers, X=10

1,10-Bis(p-hydroxyphenylimino-p-benzylideneoxy)decane, 1.1294 g (2.00 mmole), p-tri(p-t-butylphenyl)methylphenol, 0.2019

g (0.40 mmole), and triethylamine, 0.506 g (5.00 mmole) were added to 30 ml DMAc. The reaction was heated to 80°C. Terephthloyl chloride, 0.4467 g (2.20 mmole), dissolved in 5 ml DMAc was added dropwise. The reaction was stirred at 80°C for 72 hours. The reaction mixture was poured into 200 ml THF. A yellow solid was filtered and washed with ethanol (fraction 1), 1.40 g, 91% yield. The THF solution was precipitated into 1 liter of methanol. The product, a light yellow powder, was collected by centrifugation (fraction 2), 0.1164 g, 7.5% yield. The products were dried in a vacuum oven at 60°C. Fraction 1 was destroyed by dichloroacetic acid. IR of fraction 2 (ν/max , cm^{-1}): 650, 710, 820, 850, 1020, 1070, 1130, 1140, 1250, 1420, 1570, 1600, 1620, 1792, 2820, 2890, 3360. H^1 NMR of fraction 2 (chloroform- d /TMS, ppm): singlet at 8.33, doublet at 7.8, multiplet at 7.3, multiplet at 7.1, doublet at 7.0, triplet at 4.0, triplet at 1.8, multiplet at 1.3. TGA of fraction 2 (10°C/min, 30-750°C, 5% weight lost): 300°C. DSC of fraction 2 (5°C/min, 30-140°C, endothermic transition): 84°C.

Poly(azomethine) B with end blockers, X=10

1,10-Bis(p-hydroxyphenylimino-p-benzylideneoxy)decane, 1.1294 g (2.00 mmole), p-tri(p-t-butylphenyl)methylphenol, 0.2019 g (0.40 mmole), and triethylamine, 0.506 g (5.00 mmole), were added to 30 ml DMAc. The mixture was heated to 80°C. 1,8-Bis(chlorocarbonylphenoxy-carbonyl)decane, 1.0546 g (2.20 mmole) in 5 ml DMAc was added to the reaction mixture dropwise. The reaction was stirred at 80°C for 72 hours. The reaction was poured into 200 ml of THF. A yellow solid was filtered and washed with ethanol (fraction 1), 1.54 g, 72.4 % yield. The THF solution was precipitated into 1 liter methanol. A light yellow solid was collected by centrifugation (fraction 2), 0.3435 g, 16.2 % yield. Fraction 1 was destroyed by dichloroacetic acid. IR of the fraction 2 (ν/max , cm^{-1}): 550, 590, 660, 710, 770, 830, 850, 900, 1010, 1070, 1090, 1251, 1285, 1300, 1350, 1416, 1500, 1540, 1570, 1620, 1744, 2850, 2910,

3412. NMR of the fraction 2 (chloroform-d/max, ppm): singlet at 8.4, multiplet at 7.0-7.2, triplet at 4.0, triplet at 1.8, multiplet at 1.3-1.5. TGA of the fraction 2 (10°C/min, 30-750°C, 2% weight lost) 346°C. DSC of the fraction 2 (5°C/min, 30-270°C, endothermic transitions): 145, 216°C.

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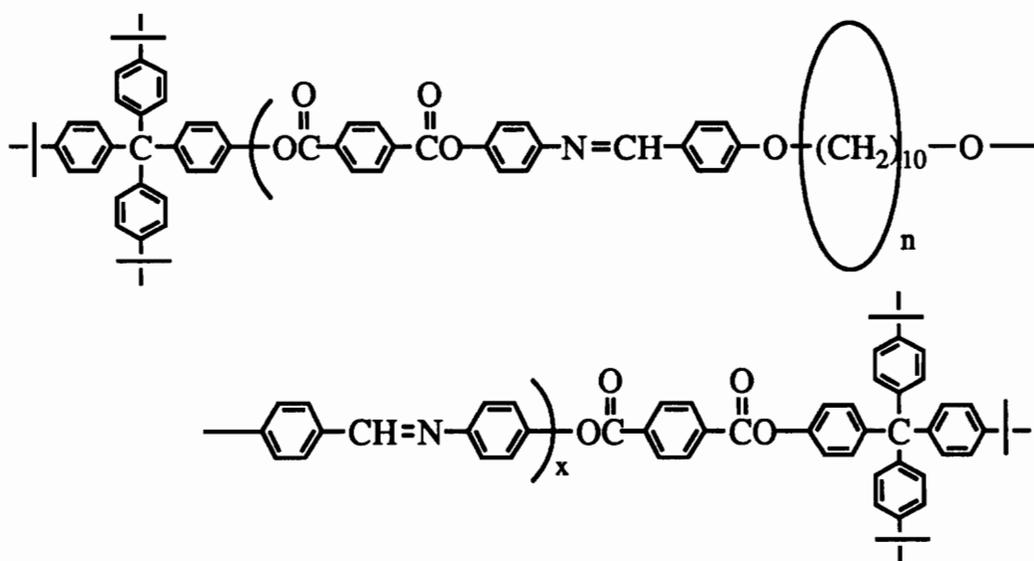
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CHAPTER V

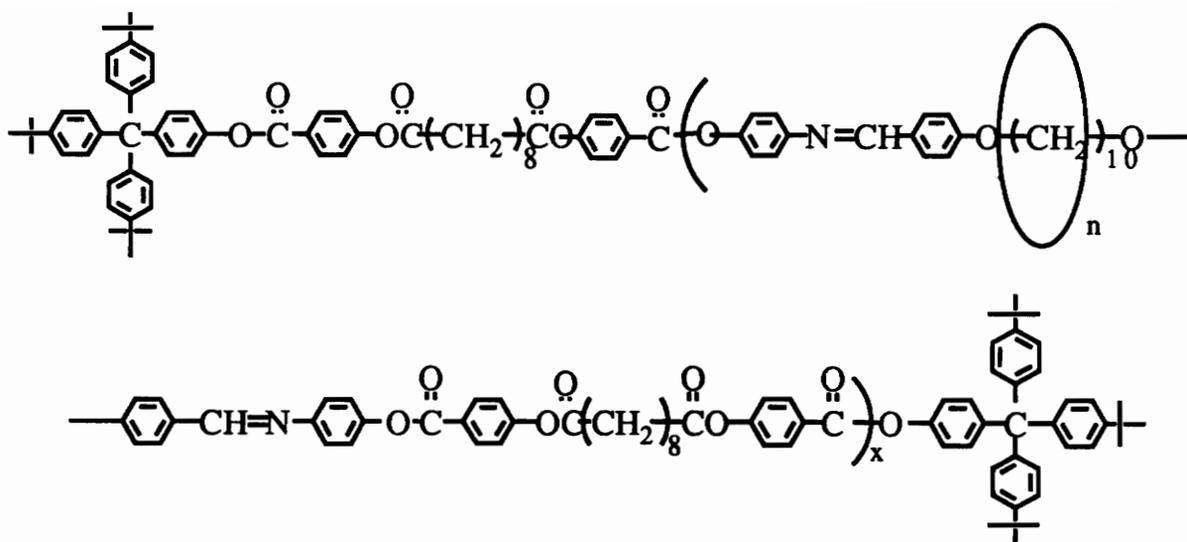
POLY(AZOMETHINE)ROTAXANES

V - A Design of Poly(azomethine)rotaxanes

Poly(azomethine)rotaxanes were synthesized by threading 42-crown-14 onto poly(azomethine) backbones. Poly(azomethine)s were reported by Jin and Park [1]. Poly(azomethine)s are liquid crystalline polymers. They have rod like mesogenic groups. They are rigid and strong. Their molecular weight is not very high because they precipitate out from the reaction solution when the polymers grow to a certain length. Since they have high T_m 's and do not dissolve in general solvents, they are hard to process. To improve their properties, rotaxane formation is a good choice. According to the results with other systems in our group, rotaxane formation will lower the T_m 's and improve the solubilities [2][3][4].



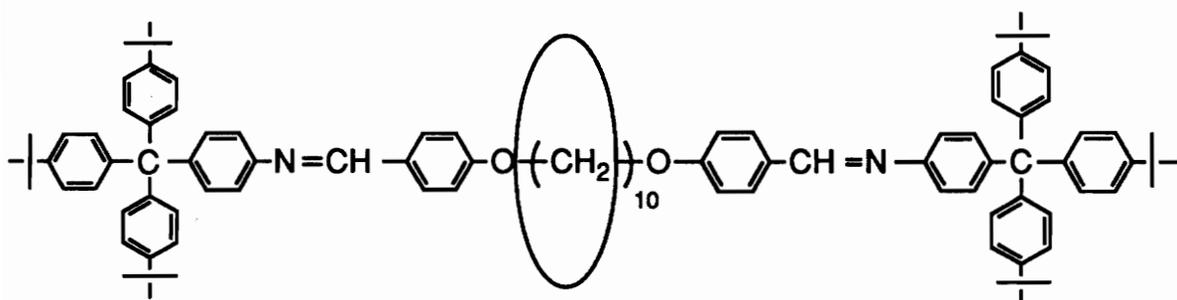
Structure V-16 Poly(azomethine)rotaxane A



Structure V-17 Poly(azomethine)rotaxane B

After the synthesis of poly(azomethine)rotaxanes A and B (Structure V-16 and V-17), the processability of the poly(azomethine)s should be improved.

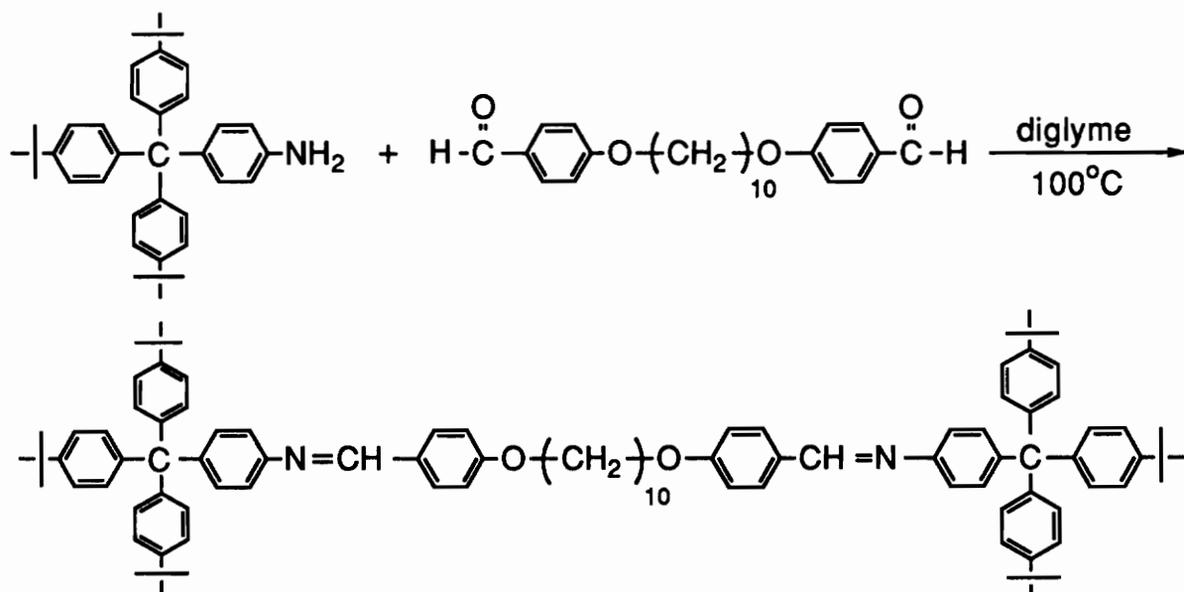
In order to establish the effectiveness of the blocking groups and the threading of 42-crown-14, a monomeric rotaxane, a di(azomethine)rotaxane, was synthesized (structure V-18). 42-Crown-14 is threaded by a short, linear monomer. Both ends of the monomeric rotaxane are blocked by the large end groups. The synthesis of the di(azomethine)rotaxane precedes the preparation of the poly(azomethine)rotaxanes.



Structure V-18 Di(azomethine)rotaxane

V-B Results and Discussion, Di(azomethine)rotaxane

Before synthesizing the di(azomethine)rotaxane, the di(azomethine) with end blockers was synthesized in diglyme. The structure of diglyme is similar to that of the crown ether. If the di(azomethine) can be synthesized in diglyme, it also can be synthesized in the crown ether. The reaction scheme is shown below. (Scheme V-B1)



Scheme V-B1 Synthesis of di(azomethine)

1,10-Bis(p-formylphenoxy)decane and p-{tri(p-t-butylphenyl)methyl}aniline were dissolved in diglyme. The reaction was stirred at 100°C for 6 hours. There was no reported information found for this di(azomethine). The reaction temperature had to be this high at atmosphere pressure, since the by-product of this reaction is water. The reaction can be completed at a lower temperature if under vacuum, and the water was removed. The percentage yield should also be higher.

After the reaction was finished, the reaction mixture was cooled to 5°C in ice bath. A yellow solid was filtered. The crude product was recrystallized in cyclohexane. The percentage yield was 69.1%. The melting point was 278.4-280.1°C. The IR spectrum showed there were two C=N peaks at 1580 and 1605 cm⁻¹. (Fig. V-B1) The ¹H NMR spectrum confirmed the compound. (Fig. V-B2) Elemental analysis also confirmed the compound (see experimental part). The compound showed two spots on a silica gel TLC plate. Actually, the silica gel decomposed the compound. Details will be discussed at the end of section B.

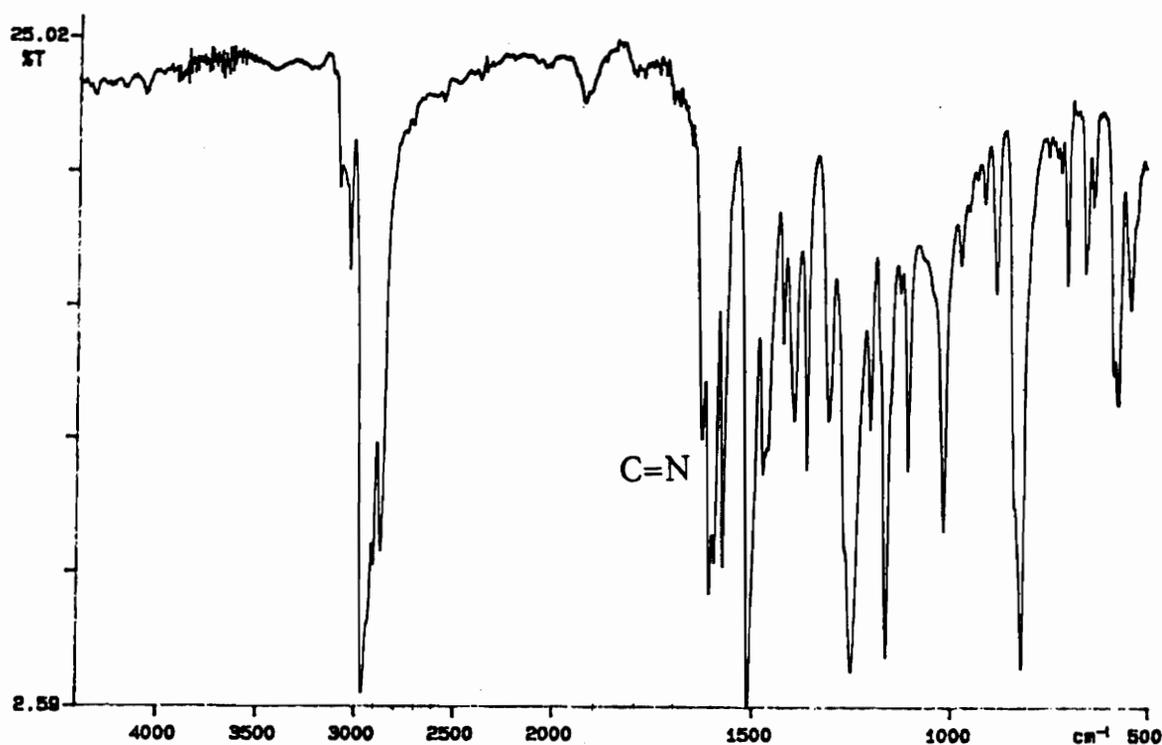


Fig. V-B1 IR spectrum of di(azomethine) (KBr, cm⁻¹)

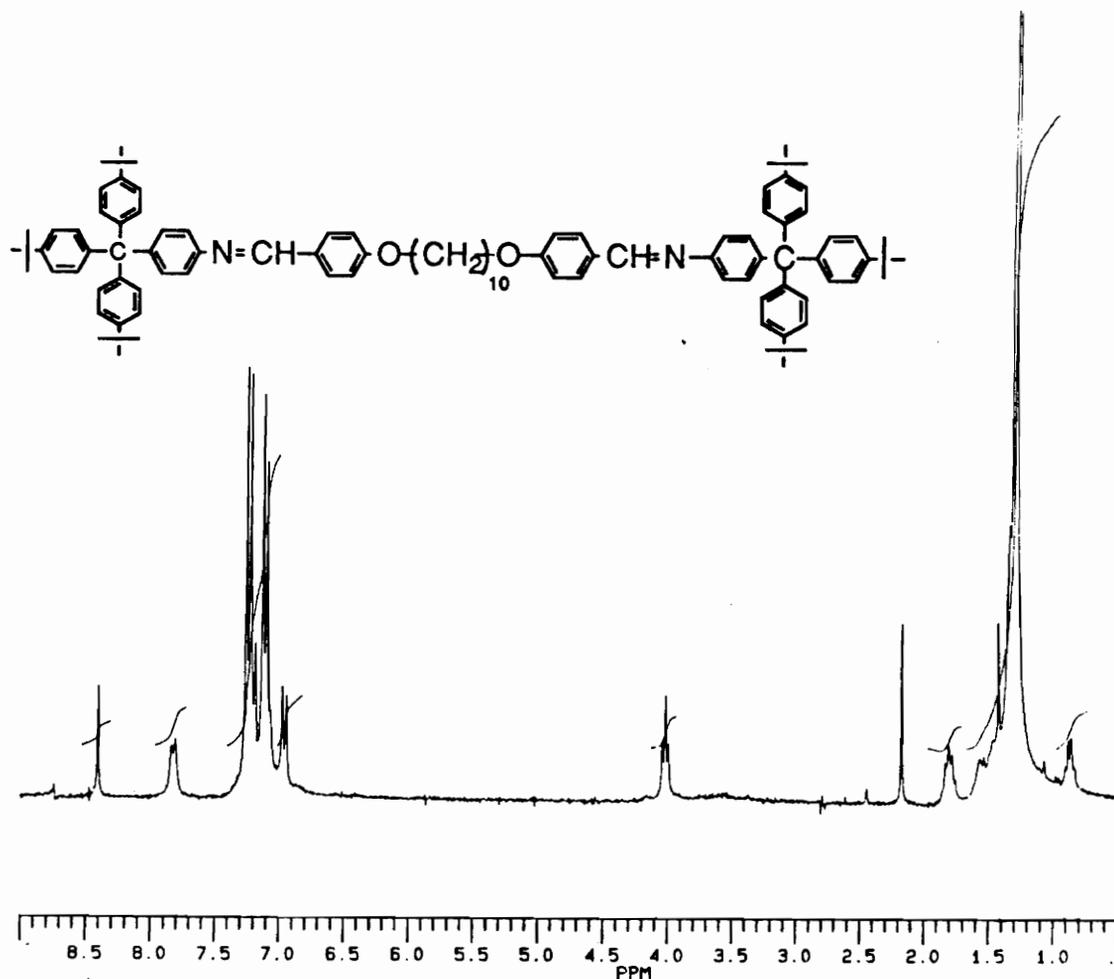


Fig. V-B2 ¹H NMR spectrum of di(azomethine) (ppm)

Thermal analysis was done on the di(azomethine). TGA showed that the di(azomethine) had 5% decomposition at 413°C. (Fig. V-B3) The DSC analysis heating rate was 10°C/minute to 140°C. In the first heating, there was an endothermic transition at 76°C, and an exothermic peak at 119°C. But in the second heating, although the endothermic peak at 79°C reappeared, the sample decomposed during the heating. (Fig. V-B4) Microscopic analysis

was not available, and we could not discover what these peaks were. According to the DSC analysis, we still could conclude that the compound was not thermally stable. From the DSC results of both the di(azomethine) and poly(azomethine)s, a conclusion could be drawn that the azomethine structure is not thermally stable.

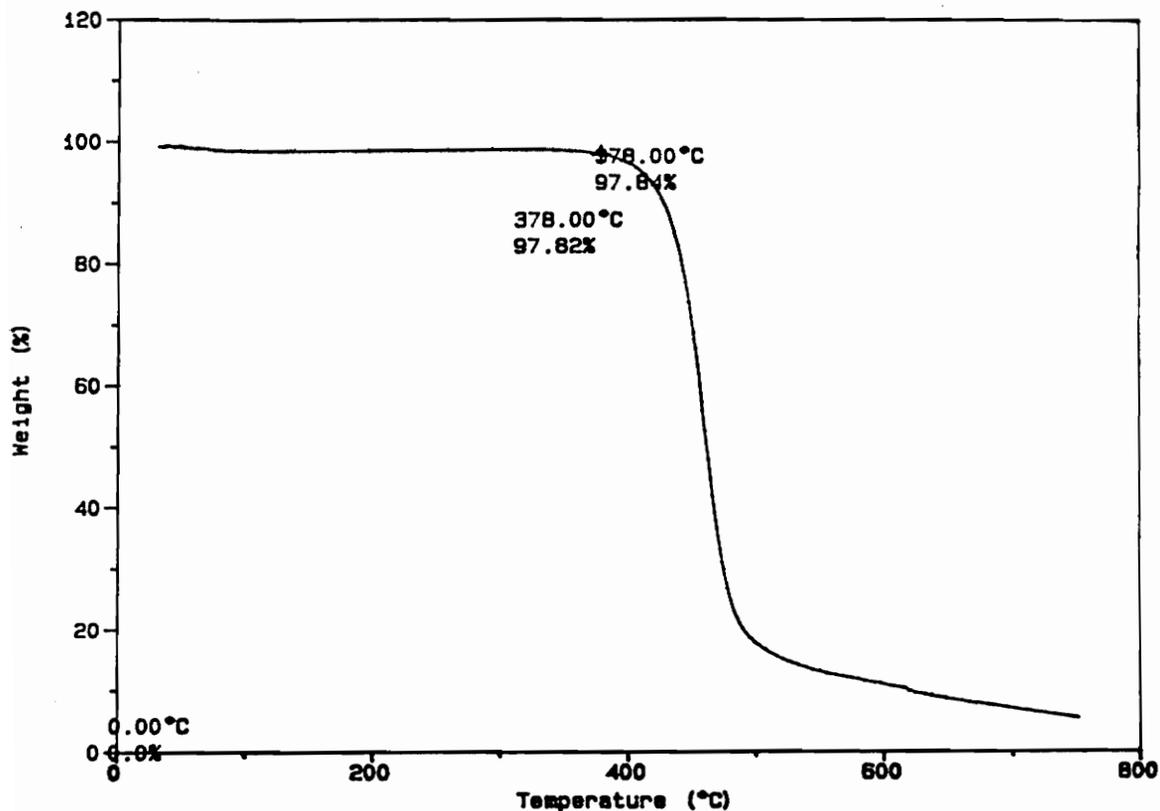


Fig. V-B3 TGA scan of di(azomethine) (10°C/min)

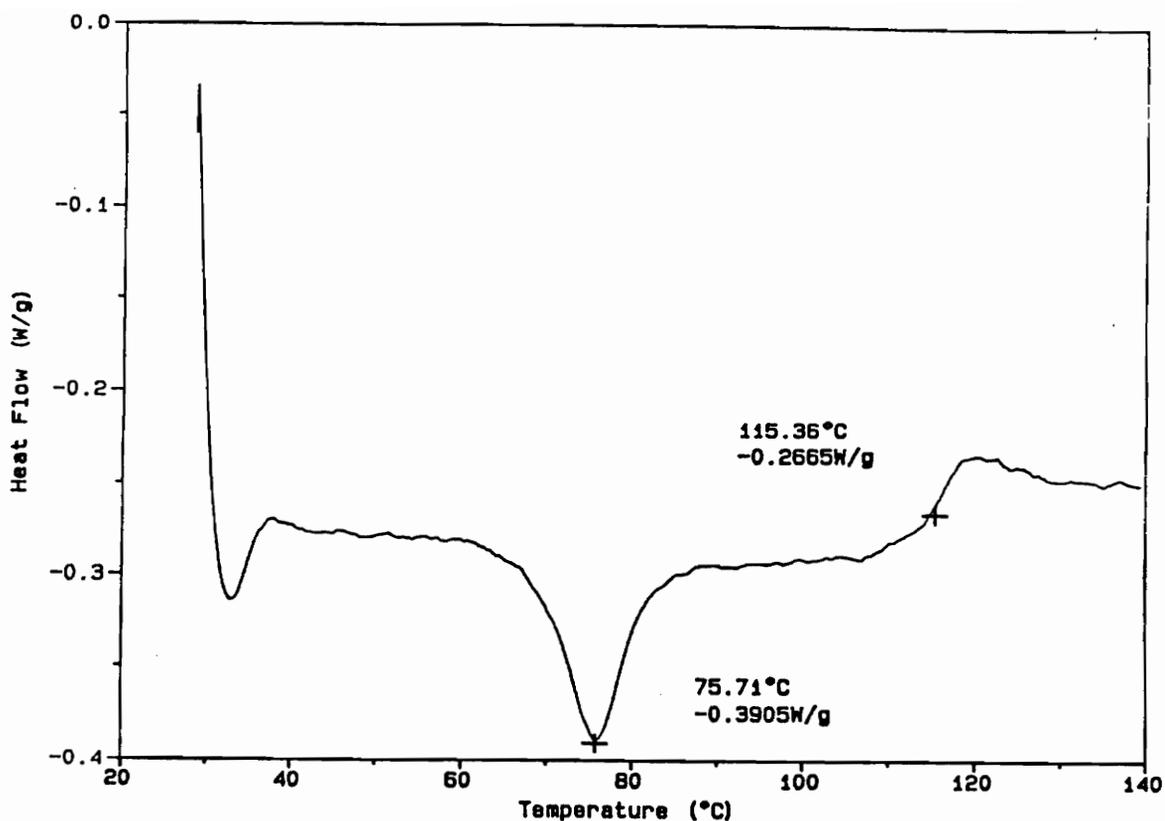
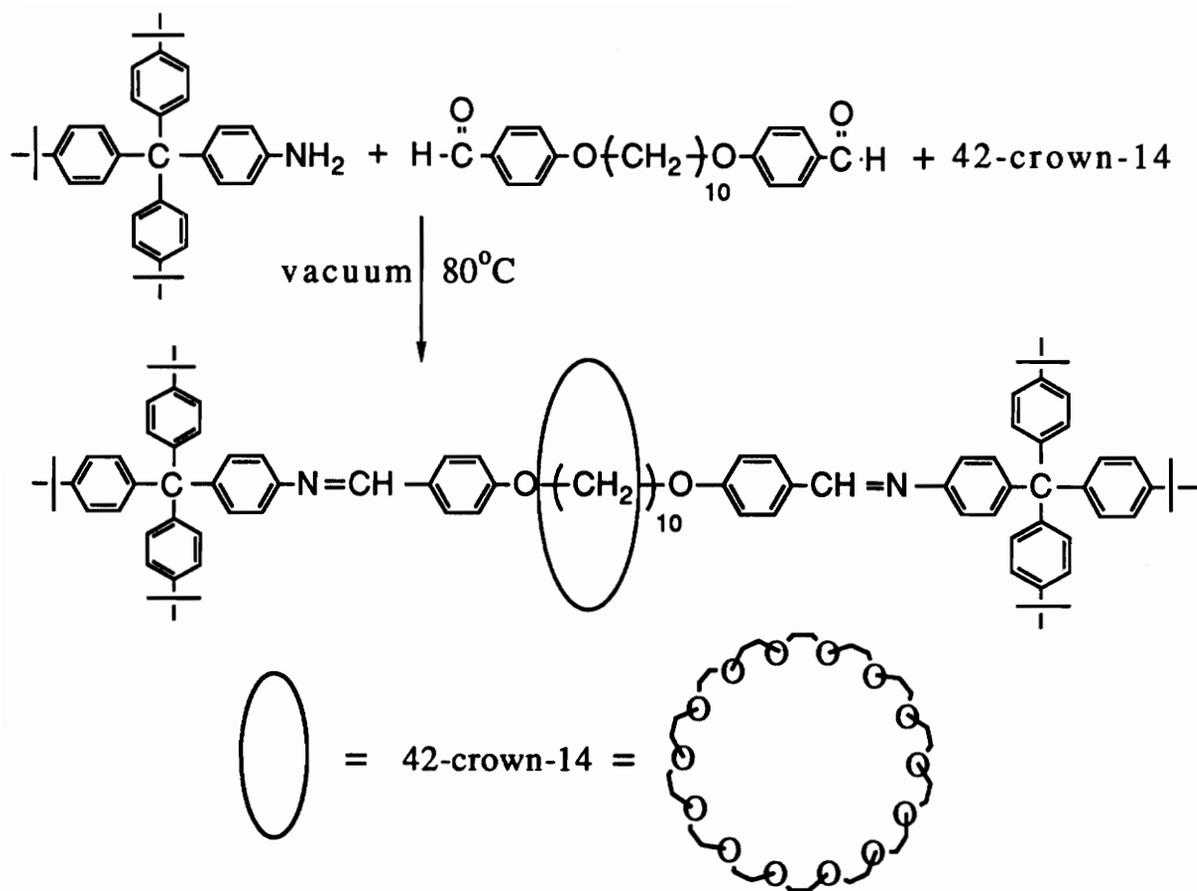


Fig. V-B4 DSC scan of di(azomethine) (10°C/min)

Since the characterization showed that the di(azomethine) could be synthesized in diglyme, the di(azomethine)rotaxane was then synthesized in pure 42-crown-14. (Scheme V-B2)



Scheme V-B2 Synthesis of di(azomethine)rotaxane

1,10-Bis(p-formylphenoxy)decane (2.09 mmole) was added to pure 42-crown-14 (24.30 mmole). The mixture of 1,10-bis(p-formylphenoxy)decane and 42-crown-14 was stirred for 18 hours at 80°C under vacuum. Then p-{tri(p-t-butylphenyl)methyl}aniline (4.34 mmole) in methylene chloride was added dropwise to the reaction mixture. Since the system was under vacuum, the solvent and the by-product, water, were removed very fast. The reaction went very fast. Before all the p-{tri(p-t-butylphenyl)methyl}aniline solution was added, the whole reaction mixture became solid. Therefore the reaction was not completed. The reaction created a yellow wax-like solid in 5 minutes.

The reaction procedure can be improved. 1,10-Bis(p-formylphenoxy)decane and 42-crown-14 mixture can be stirred for 18 hours at 80°C under atmospheric pressure. p-{Tri(p-*t*-butylphenyl)methyl}aniline solution also should be added at atmospheric pressure. The reaction happens quite slowly under atmospheric pressure. After the reactants are mixed together very well, the vacuum pump can be connected. The solvent and the water can be removed, and the reaction will happen fast. Since the reaction mixture turns into a solid, the reaction still may not be complete even though the reactants mix very well. But the percentage yield should be improved when the reactants mix well.

The yellow wax-like solid was dissolved in THF. The solution was precipitated in methanol. Unthreaded 42-crown-14 dissolved in the methanol, and the di(azomethine)rotaxane and the unthreaded di(azomethine) precipitated out. Then the yellow solid, di(azomethine)rotaxane and di(azomethine) mixture, was dissolved in THF and precipitated in methanol again. This precipitation was repeated three times. A yellow solid, a mixture of di(azomethine)rotaxane and di(azomethine), was obtained.

The next step was to separate the di(azomethine)rotaxane and the di(azomethine). The yellow powdery mixture was dissolved in hot toluene. When the solution cooled down, some dark yellow precipitate was obtained. The dark yellow solid was filtered. The toluene filtrate was light yellow, and the toluene was evaporated. A light yellow solid was obtained. ¹H NMR analysis was done on both the dark yellow and light yellow solids. In the spectrum of the dark yellow solid, a large peak at 3.64 ppm was seen. In the spectrum of the light yellow solid, a very small peak at 3.64 ppm was seen. 42-Crown-14 showed a singlet at 3.64 ppm in the ¹H NMR spectrum. The ¹H NMR analysis showed that the dark yellow solid which recrystallized out from toluene was the di(azomethine)rotaxane. The light yellow solid which dissolved in toluene was the di(azomethine).

This recrystallization was done four times so that the di(azomethine)rotaxane and di(azomethine) were separated. In the third and fourth recrystallizations, there was almost nothing dissolved in toluene. The final percentage yield of di(azomethine)rotaxane was 12.0%.

IR analysis was done on the compound. All the functional peaks were shown. There was no carbonyl peak or amine peak and there was a C=N peak at 1607 cm^{-1} . (Fig. V-B5) ^1H NMR analysis was done. (Fig. V-B6) The ratio of 42-crown-14 and the backbone was calculated by integrations of the protons on the decylene group of the backbone and 42-crown-14. Also the ratio of 42-crown-14 and the backbone was calculated by the integration of the protons on the end blockers and 42-crown-14. Both calculation results showed about one crown ether on each backbone. After precipitation and recrystallization four times, there was still one 42-crown-14 on each backbone. We conclude that the 42-crown-14 was threaded by the backbone. We found that relative delay times influenced the NMR integration. The longer the delay time, the more stable was the integration. When the relative delay time was one second or two seconds, the spectra showed different ratios of integrations. After a relative delay time longer than 2 seconds, the integration was constant. Elemental analysis also confirmed the compound (see experimental part).

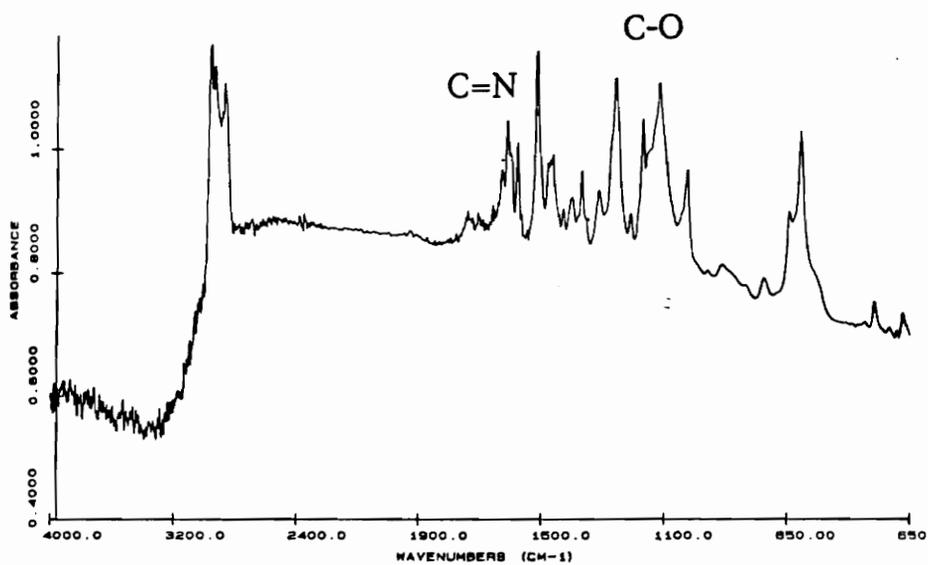


Fig. V-B5 IR spectrum of di(azomethine)rotaxane (KBr, cm⁻¹)

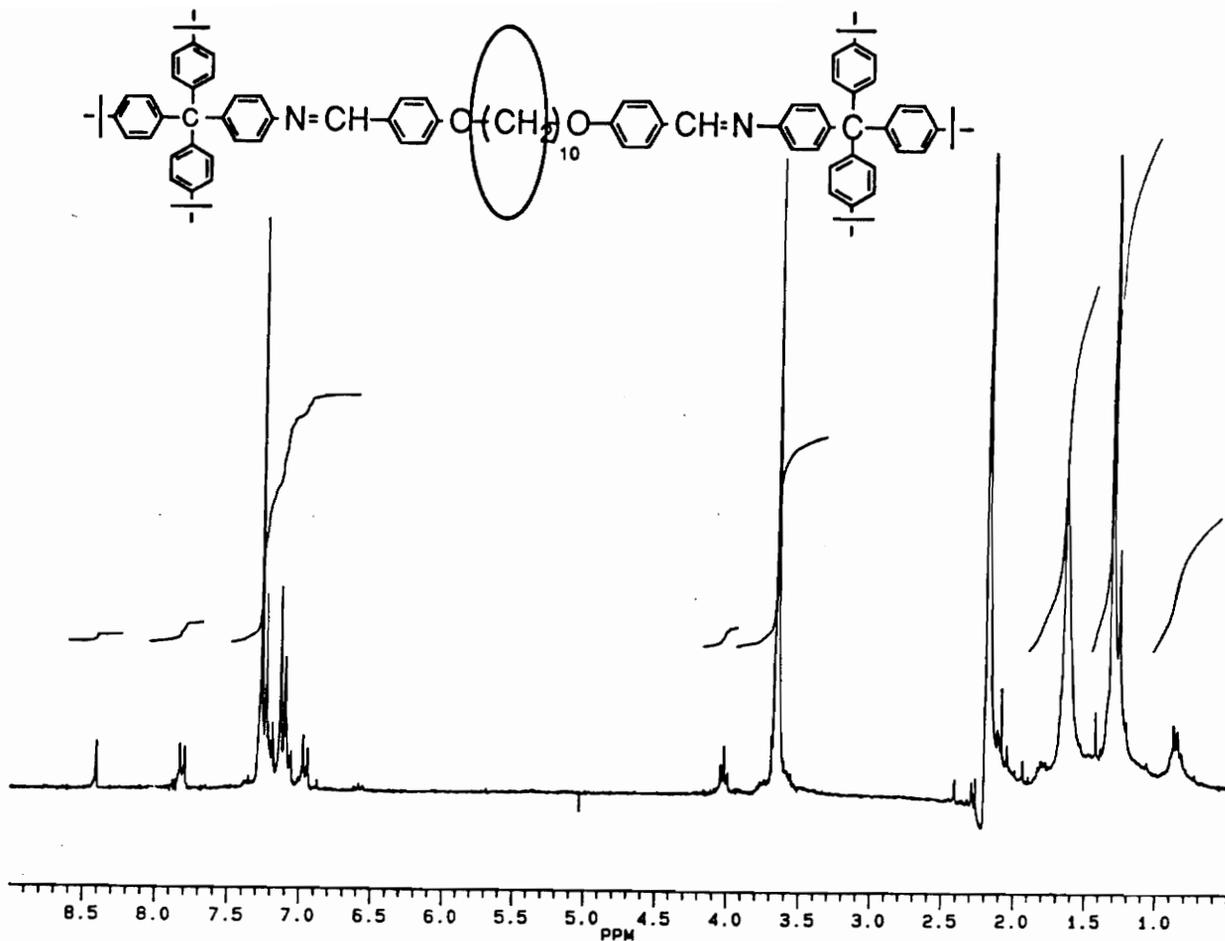


Fig. V-B6 ^1H NMR spectrum of di(azomethine)rotaxane (ppm)

Chromatographic analysis for the di(azomethine)rotaxane was done. The compound showed two spots on a silica gel TLC plate. The spot at the top of the plate was $R_f = 0.92$. The spot near the bottom was $R_f = 0.12$. Silica gel column separation was done. The two fractions were collected. The first fraction had a melting point at 87-90.3°C. ^1H NMR analysis showed that the first fraction was 1,10-bis(p-formylphenoxy)decane. The second fraction had a melting point at 245-252°C. The ^1H NMR analysis showed that the fraction was a mixture of mostly of p-(tri(p-t-butylphenyl)methyl)aniline and a small amount of 42-crown-14. The di(azomethine)rotaxane

had decomposed in the silica gel column. Neutral aluminium gel TLC plate and column were tried with the same result. GPC analysis was tried. The column was neutral, and the solvent was THF. There were three peaks in the chromatogram. 42-Crown-14 and p-{tri(p-t-butylphenyl)methyl}aniline were analyzed by GPC. The results showed that the peak at retention volume 44.5 ml was 42-crown-14. The peak at the retention volume 50 ml was p-{tri(p-t-butylphenyl)methyl}aniline. The di(azomethine)rotaxane also had hydrolyzed in the GPC column. (Fig. V-B7) These results mean that the C=N bond is not stable, and is very easily hydrolyzed.

The melting point range of the compound was very wide, 181-237°C. This melting point already passed the 42-crown-14 decomposition temperature. TGA and DSC analysis were done. The TGA scan showed that the 5% decomposition temperature was at 180°C. (Fig. V-B8) This was the 42-crown-14 decomposition temperature. The heating rate of the DSC analysis was 10°C/minute, from 30-140°C. In the first heat, an endothermic transition at 43°C and a shoulder at 116°C were seen. (Fig. V-B9) But in second heat, the sample was decomposed.

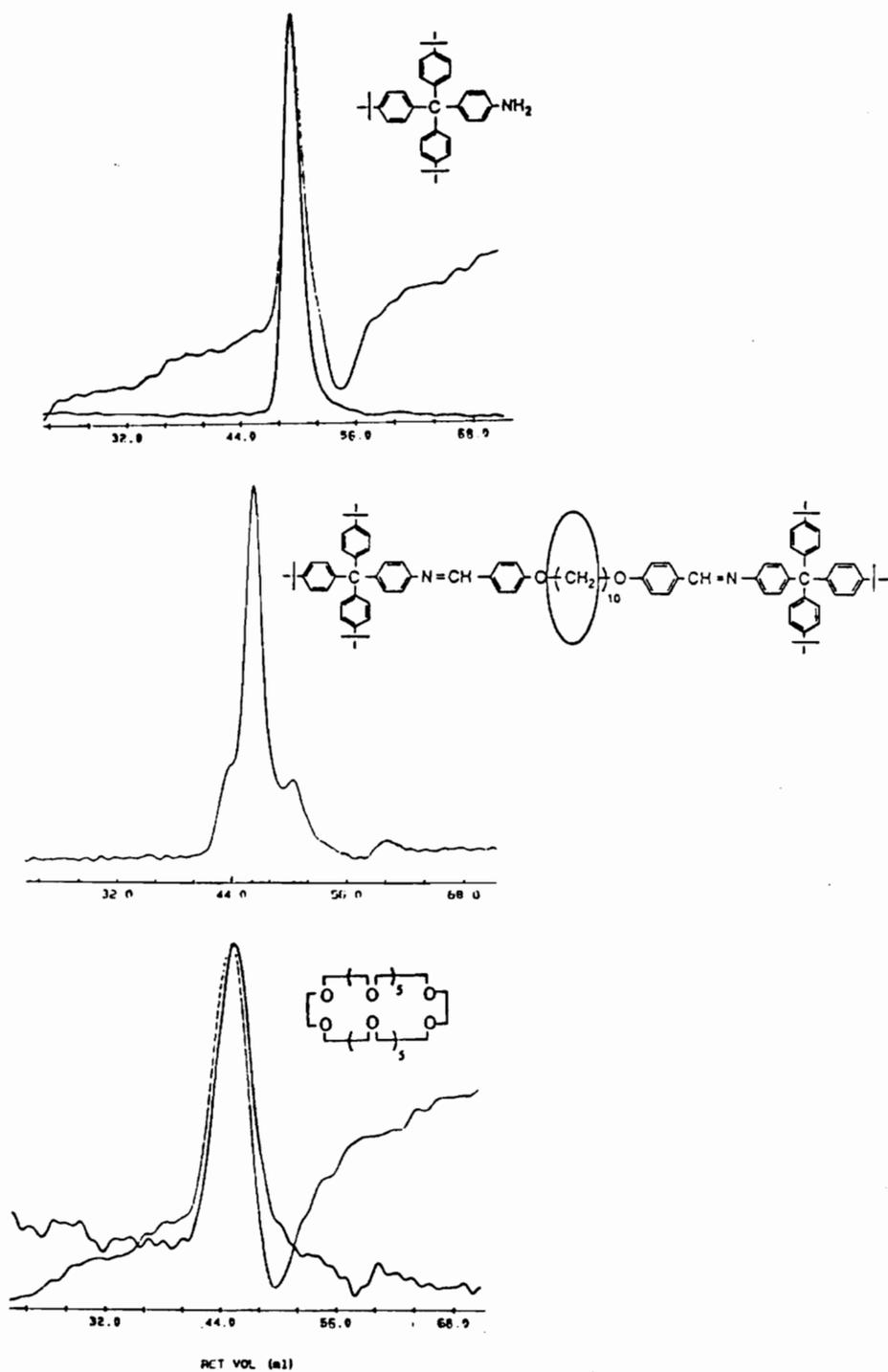


Fig. V-B7 The hydrolysis of di(azomethine)rotaxane in GPC column

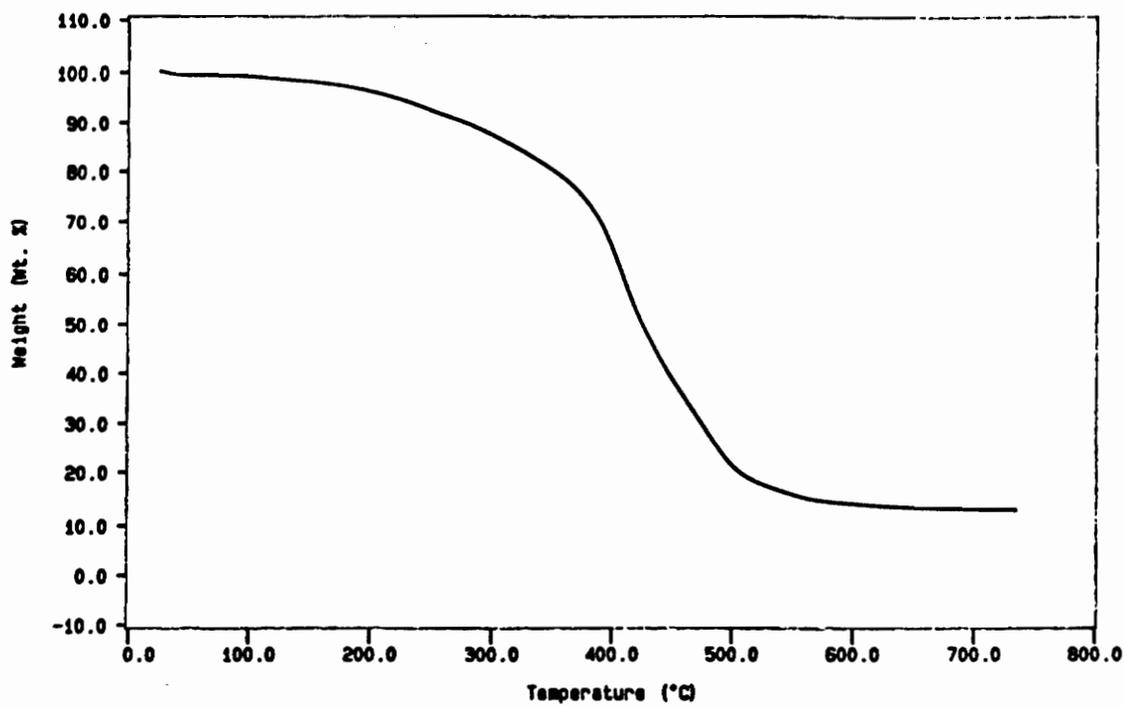


Fig. V-B8 TGA scan of di(azomethine)rotaxane (10°C/min)

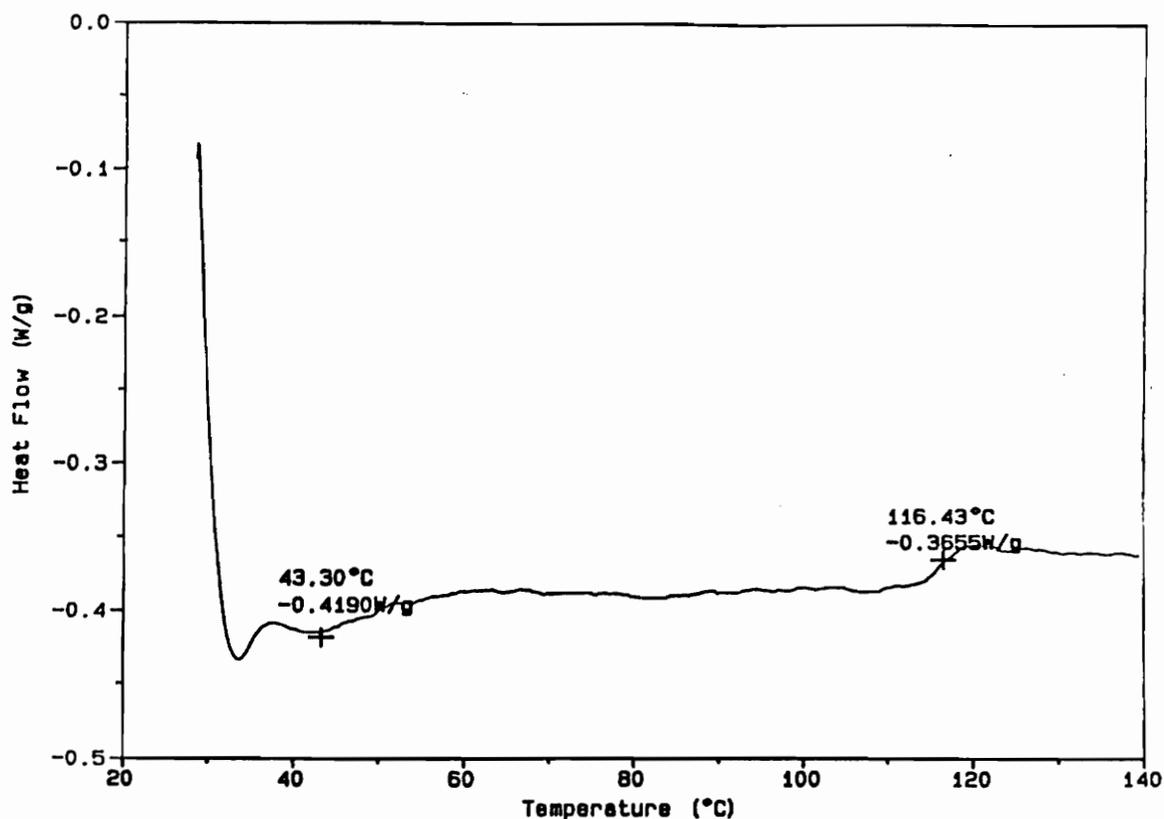
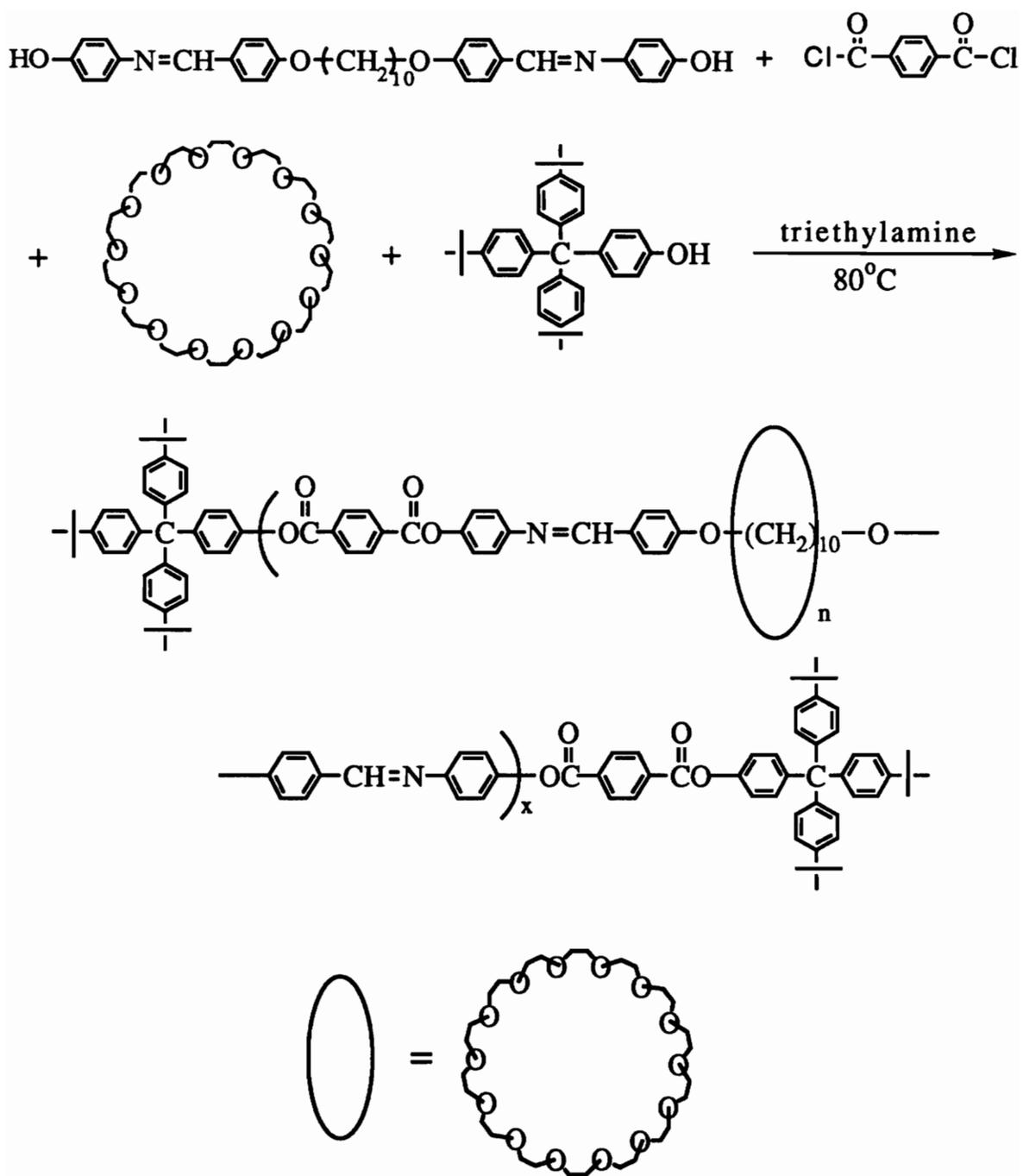


Fig. V-B9 DSC scan of di(azomethine)rotaxane (10°C/min)

HPLC analysis was done on the di(azomethine)rotaxane, but nothing was observed. This result meant that the compound stayed in the silica gel normal phase column and did not come out, and the compound hydrolyzed in the silica gel column.

V-C Results and Discussion, Poly(azomethine)rotaxane A and B

After successfully synthesizing the di(azomethine)rotaxane, poly-(azomethine)rotaxanes A and B were synthesized.



Scheme V-C1 Synthesis of poly(azomethine)rotaxane A

1. Poly(azomethine)rotaxane A

Poly(azomethine)rotaxane A was synthesized by threading 42-crown-14 on the poly(azomethine) A backbone. Poly(azomethine)rotaxane A was a new polymer. The reaction scheme is shown above. (Scheme V-C1)

Poly(azomethine)rotaxane A was synthesized by reacting 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane, and p-{tri(p-t-butyl-phenyl)methyl}phenol (the end blocker) with terephthaloyl chloride in a mixture of 42-crown-14 and DMAc. Triethylamine was used as catalyst. Three reactions were carried out.

For first reaction, the degree of the polymerization was designed as 50. This meant that the mole ratio of 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane, terephthaloyl chloride, and p-{tri(p-t-butylphenyl)methyl}phenol was 50:51:2. 1,10-Bis(p-hydroxyphenylimino-p-benzylideneoxy)decane (2.00 mmole), p-{tri(p-t-butylphenyl)methyl}phenol (0.08 mmole), and triethylamine were added to the mixture of 42-crown-14 (16.21 mmole)/DMAc, 1:1, v/v. The mixture was stirred at 80°C for 15 hours. The solid reactants all dissolved in the solvent so that the reaction system became a clear yellow solution. After stirring 15 hours, some 42-crown-14 was believed to be threaded by the monomers. Terephthaloyl chloride (2.04 mmole) in DMAc was added dropwise. After half a minute of adding terephthaloyl chloride, a yellow solid start to form. The reaction was continued for 72 hours at 80°C. After the reaction was finished, the mixture was poured into water. A yellow solid was filtered. Some unthreaded 42-crown-14 dissolved in the water. The yellow solid was washed with THF, and the THF solution was reprecipitated in methanol. No precipitate was obtained. After the methanol was evaporated, 42-crown-14 was

seen.

This yellow solid did not dissolve in general solvents like chloroform, methylene chloride, DMF, THF, toluene, ketone, acetate, and alcohol. Since the polymer precipitated from the reaction solution, and did not dissolve in general solvents, the degree of polymerization might be designed too high.

Thus, in the second reaction the degree of polymerization was designed as 20. The mole ratio of 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane, terephthaloyl chloride, and p-tri(p-t-butylphenyl)methylphenol was 20:21:2. The reaction condition was the same. After the reaction was finished, the reaction mixture was poured into THF. A yellow solid was filtered. The THF filtrate was precipitated in methanol. A light yellow precipitate was obtained. The light yellow solid was collected by centrifugation. Free 42-crown-14 dissolves in methanol. The light yellow solid was dissolved in THF and reprecipitated in methanol. The precipitation was done four times. For the last two times, there was no macrocycle found in methanol.

The light yellow solid also could be dissolved in chloroform, methylene chloride, acetone, and ethyl acetate. ^1H NMR analysis was done on this light yellow solid. The degree of polymerization was calculated by the ratio of the integrations of the protons on the end blockers, and the decylene group. The average degree of polymerization was 11. The ratio of the repeating unit to 42-crown-14 was calculated by the ratio of the integration of the protons on the end blockers to 42-crown-14, and decylene group to 42-crown-14. There was one 42-crown-14 for every ten repeating units. The weight percentage of 42-crown-14 to polymer backbone was 7.43%. The percentage yield of this fraction was 23.1%.

The fraction which precipitated from the reaction solution did not dissolve in general organic solvents. This yellow solid was washed with THF many times to wash away the free 42-crown-14. The percentage yield of this fraction was 78.2 %.

Since the maximum degree of polymerization of this polyrotaxane was 11, another reaction in which the degree of polymerization was designed to be 10 was done. 1,10-Bis(p-hydroxyphenylimino-p-benzylideneoxy)decane (2.00 mmole), p-{tri(p-t-butylphenyl)methyl}phenol (0.40 mmole), 42-crown-14 (16.21 mmole), DMAc (20.00 ml), and triethylamine (0.70 ml) were added together and stirred at 80°C. After the mixture dissolved, terephthaloyl chloride (2.20 mmole) in DMAc was added dropwise. Other reaction conditions were the same as mentioned above. After the washing and precipitation, two fractions were obtained. The first fraction, a yellow solid 66.4% yield, precipitated out from the reaction solution. It did not dissolve in general solvents. The second fraction, a light yellow solid with 17.2% yield, dissolved in solvents like chloroform, methylene chloride, acetone, and ethyl acetate, etc. It dissolved slightly in toluene and propanol.

The second fraction was dissolved in THF and precipitated into methanol four times. For each precipitation, ¹H NMR analysis was done. the ratio of 42-crown-14 to the number of the repeating units was calculated. The results was listed in the table below. (Table V-C1)

Table V-C1 The ratio of the number of the backbone repeating units to 42-crown-14 units in poly(azomethine)rotaxane A

ppt. in MeOH (THF solution)	42-c-14 : backbone units (x/n=8)
1	1 : 1.75
2	1 : 7.43
3	1 : 8.11
4	1 : 8.23

For the last two precipitations, the content of 42-crown-14 was similar. This result meant that after two precipitations, most free 42-crown-14 had been removed because it dissolved in methanol. The threaded 42-crown-14 units were blocked by the blocking group and could not be washed away by methanol. After the fourth precipitation, there was one 42-crown-14 for about every eight repeating units. The weight percentage of 42-crown-14 was 9.12%. The ^1H NMR also showed that the degree of polymerization was 10 which was the designed number. From the ^1H NMR spectrum, all protons on the backbone, end blockers, and 42-crown-14 were seen. (Fig. V-C1)

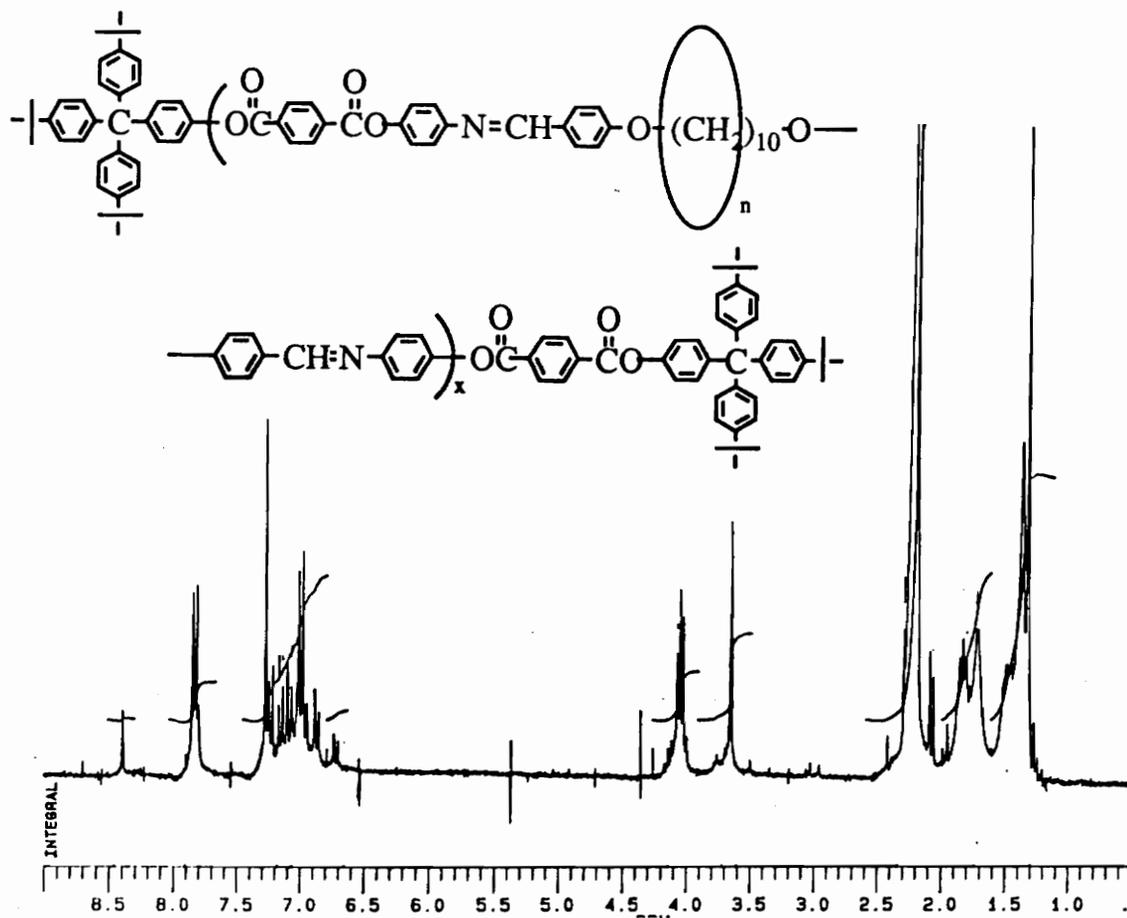


Fig. V-C1 ^1H NMR spectrum of poly(azomethine)rotaxane A
($x=10$, $x/n=8.2$) (ppm)

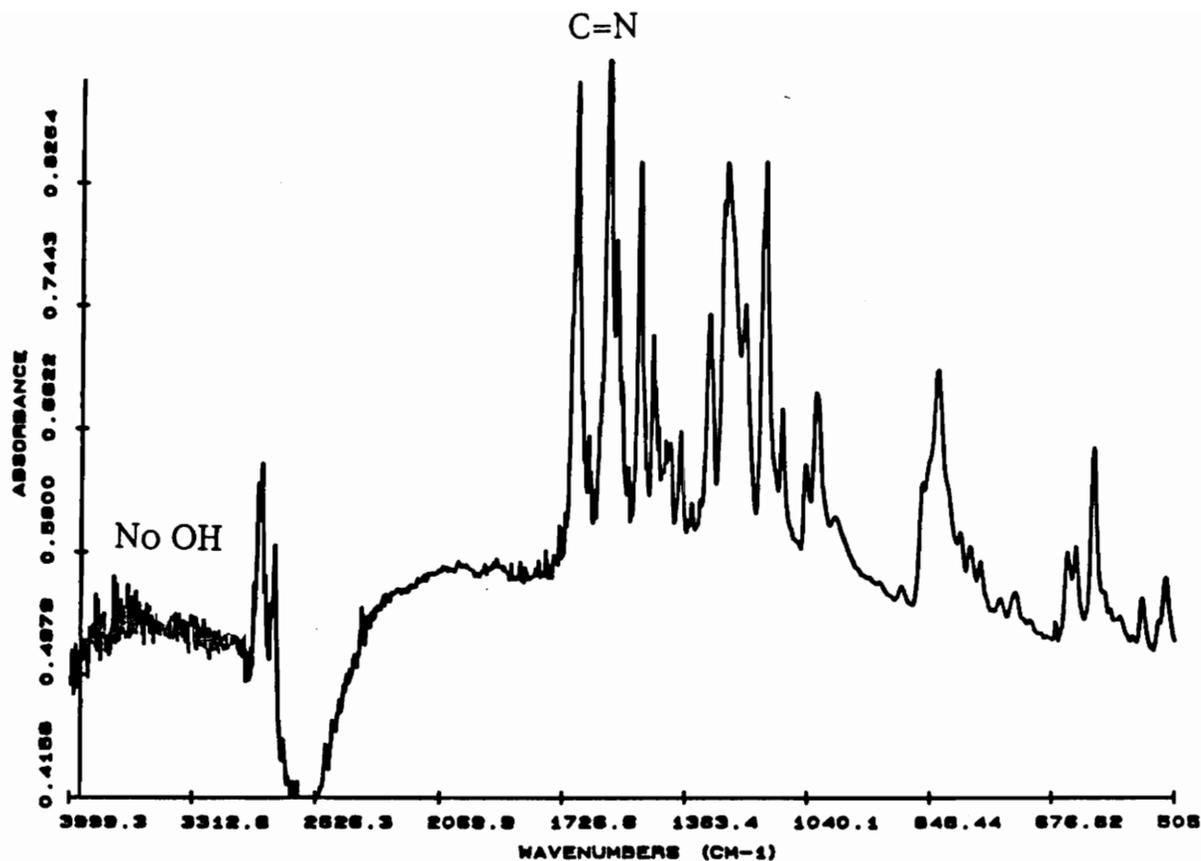


Fig. V-C2 IR spectrum of poly(azomethine)rotaxane A ($x=10$, $x/n=8.2$) (KBr, cm^{-1})

The result of IR analysis is shown above. All the functional peaks were there. The result confirmed the compound. (Fig. V-C2)

The second fraction of poly(azomethine)rotaxane A was recrystallized from toluene two times. From its ^1H NMR spectrum, the poly(azomethine)rotaxane A which recrystallized from the solution was the same as the poly(azomethine)rotaxane A which

dissolved in toluene. These two fractions had the same peaks and the same integration. Nothing could be separated.

When the viscosity measurement was tried, the samples were dissolved in dichloroacetic acid. The inherent viscosity of fraction 1 was 0.243 dl/g (0.5 g/dl, 45°C water bath), and it was 0.237 dl/g for fraction 2 in the same condition. The viscosity result of poly(azomethine) A was 0.233 dl/g in the same condition. Also the reported inherent viscosity was 0.234 dl/g in the same condition. These results were very similar. Therefore we think that the polymer is hydrolyzed in dichloroacetic acid. We did a test to prove the hydrolysis (see section B in Chapter IV).

Thermal analysis was done on all three poly(azomethine)-rotaxanes with different degrees of polymerization. Since the results are similar, only the thermal analysis of the third reaction ($X=10$) is discussed here.

TGA was done for the sample of the first fraction of poly(azomethine)rotaxane A ($x=10$, $x/n=8$). The 5% decomposition temperature of this polymer was 375°C. This temperature was similar to the decomposition temperature of poly(azomethine) A without 42-crown-14. DSC analysis was done for this fraction. The heating rate was 10°C/minute. The temperature range was 25-280°C. The spectrum showed 4 endothermic transition peaks at 46, 185, 204, 236°C. The last thermal transition temperature was similar to poly(azomethine) A without 42-crown-14, although the poly(azomethine) A only had 2 endothermic transitions. These thermal transition peaks did not reappear on the second heating. This meant that the polymer decomposed during heating. This fraction behaved similarly to poly(azomethine) A without 42-crown-14.

TGA at a heating rate of 10°C/minute showed that the second fraction of poly(azomethine)rotaxane A ($x=10$, $x/n=8$) had 5% decomposition at 275°C. This temperature was similar to the 42-crown-14 decomposition temperature. (Fig. V-C3) DSC analysis was done. The heating rate was 5°C/minute. The temperature range was from 30-160°C, and the sample was then cooled down to 30°C. The heating was repeated two times. In the first heating, two endothermic transitions were seen. One was at 73°C, and another was at 121°C. These peaks reappeared on the cooling line at lower temperatures. One appeared at 53°C, and another appeared at 91°C. These peaks were repeatable on the second and third heats. On the second heat, three endothermic transitions were seen. They were at 67, 73, and 123°C. On the cooling line of the second heat, they appeared at 50, 53, 89°C. (Fig. V-C4) On the third heat, these three transitions were at the same three temperatures as in the second heat. The last endothermic transition appeared at 123°C, which was around 100°C lower than the last endothermic transition in the DSC scan of poly(azomethine) A reported by Jin and Park [1].

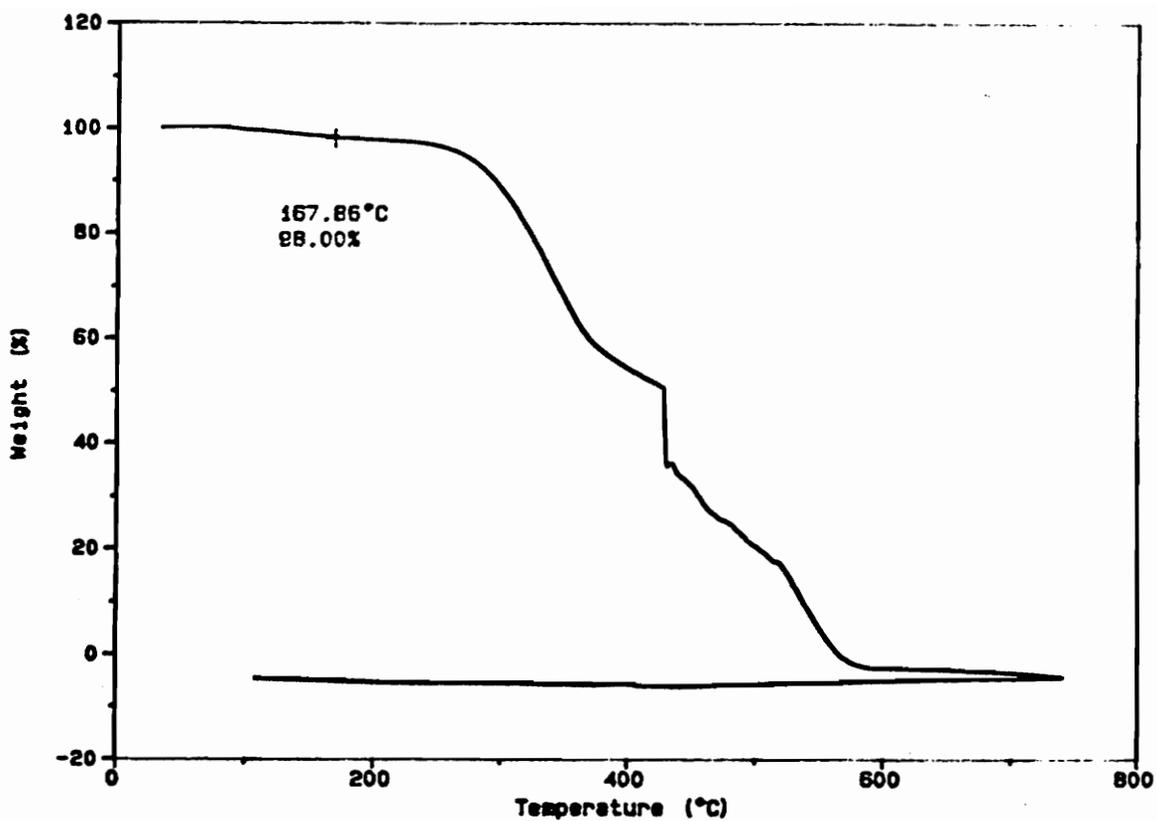


Fig. V-C3 TGA scan of the second fraction of poly(azomethine)rotaxane A ($x=10$, $x/n=8.2$) which dissolved in THF ($10^{\circ}\text{C}/\text{min}$)

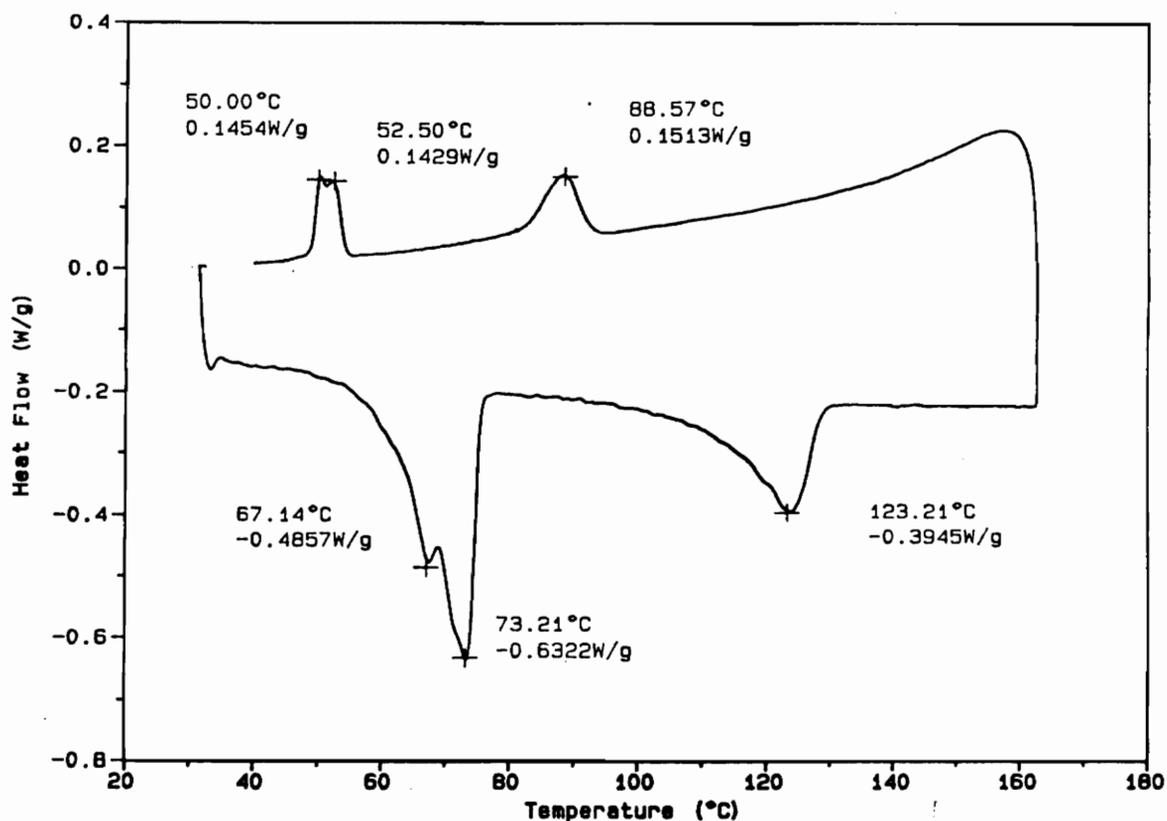


Fig. V-C4 DSC scan of the second fraction of poly(azomethine)rotaxane A ($x=10$, $x/n=8.2$) which dissolved in THF ($5^{\circ}\text{C}/\text{min}$)

Polarizing microscopic analysis was done for the second fraction of poly(azomethine)rotaxane A. At room temperature, the structure was a crystalline solid. When the temperature rose to 80°C , the structure started to change. The bright and dark structure started to become larger. When the temperature was between 80-

100°C, the structure showed liquid crystalline behavior because disclination lines were seen. The mesophase was nematic. When we pressed the slide, the structures moved. When the temperature rose above 100°C, the liquid crystalline structure disappeared. On the dark background, bright rod and flowery crystal-like structures were seen. These crystals were not liquid crystals. When the temperature rose to 130°C, the crystals all disappeared. The polymer reached the isotropic phase. The polymer showed two different phases, and was a mixture of 2 different structures. Since there were 2 compounds in the polymer, the isotropic thermal transition peak in the DSC scan was very broad (102-130°C) When the sample was cooled to 96°C, these bright rod and flowery crystals started to reappear. Most of these rod and flowery structures appeared at 90°C. When the temperature reached 74°C, the liquid crystalline structure was observed, because the disclination lines reappeared. When the temperature reached 54°C, the polymer was back to crystals. When the heating was repeated, these phase changes were repeatable.

From what we have seen under the polarizing microscope, we can make the following conclusions. (1) The polymer which is between 80-100°C is liquid crystalline, and the mesophase is nematic. (2) The rod and flowery structures between 100-130°C are not liquid crystalline. (3) The polymer is a mixture of two different materials. These two compounds are probably the threaded polyrotaxane and the unthreaded short chain oligomer. Since they have very similar solubilities, it is very hard to separate them.

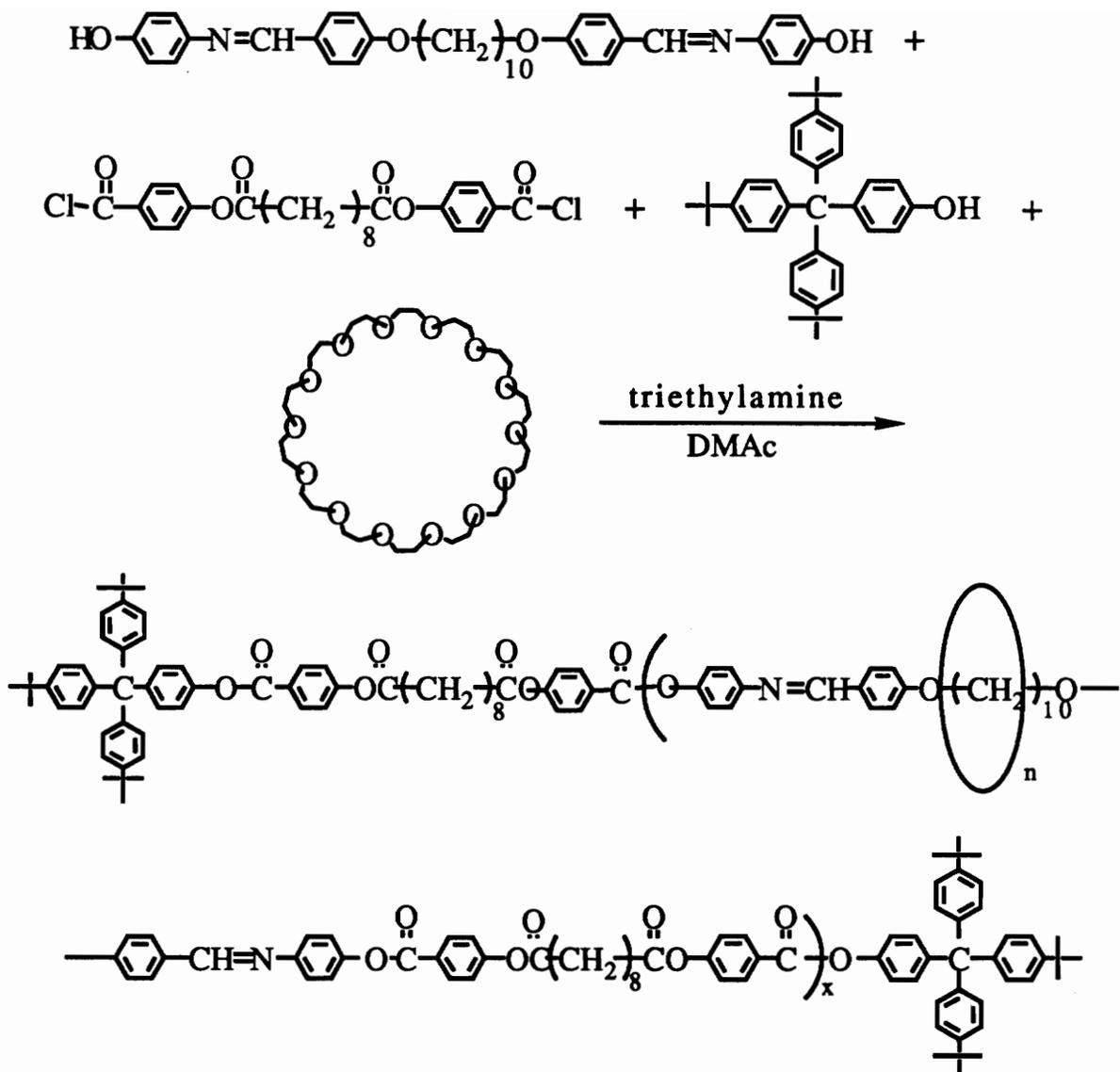
Viscosity analysis could not be done in dichloroacetic acid because the poly(azomethine) backbone is hydrolyzed in the acid. Since the second fraction of the polyrotaxane could be dissolved in some solvents like methylene chloride, THF, acetone, and ethyl acetate, the viscosity analysis could be done in these solvents. But since most of the poly(azomethine)rotaxane sample was destroyed

by dichloroacetic acid, there was not enough sample to do viscosity analysis. More poly(azomethine)rotaxane A had to be made. GPC analysis was also not possible because the poly(azomethine) backbone was hydrolyzed in the GPC column.

For future work, increasing the crown ether content of the polymer is very important. The polymerization could not be done in a pure crown ether solution because the crown ether was not basic enough. The poly(azomethine)rotaxane A had to be polymerized in the mixture of crown ether and DMAc. The mole ratio of crown ether to DMAc could be increased in order to increase the crown content.

2. Poly(azomethine)rotaxane B

Poly(azomethine)rotaxane B was synthesized by threading 42-crown-14 on the poly(azomethine) B backbone. Poly(azomethine)rotaxane B is also a new material. The degree of polymerization was designed as 10. The reaction scheme is shown below. (Scheme V-C2)



Scheme V-C2 Synthesis of poly(azomethine)rotaxane B

Poly(azomethine)rotaxane B was synthesized by reacting 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane (2.00 mmole) and p-{tri(p-t-butylphenyl)methyl}phenol (0.40 mmole) with 1,8-bis(p-chlorocarbonylphenoxy)octane (2.20 mmole) in the mixture of 42-crown-14 (16.21 mmole) and DMAc (20 ml). 1,10-Bis(p-hydroxyphenylimino-p-benzylideneoxy)decane and

p-{tri(p-t-butylphenyl)methyl}phenol were added to the mixture of 42-crown-14 and DMAc, 1:1, v/v. Triethylamine was added as the catalyst. The mixture was stirred at 80°C for 15 hours under nitrogen. 1,8-Bis(p-chlorocarbonylphenoxy)octane dissolved in DMAc was added to the mixture dropwise. One minute after the 1,8-bis(p-chlorocarbonylphenoxy)octane solution was added, a yellow precipitate was formed in the reaction solution. The reaction was continuously stirred for 72 hours at 80°C under nitrogen. A lot of yellow solid precipitated out of the solution. After the reaction was finished, the reaction mixture was poured into THF. A brown-yellow solid was filtered and washed with THF. This brown-yellow solid was fraction 1. The percentage yield was 73%. This fraction did not dissolve in general organic solvents.

The THF filtrate was precipitated into methanol. A light yellow solid was obtained. The unthreaded 42-crown-14 dissolved in methanol. The light yellow solid (fraction 2) was collected by centrifugation, and dissolved in THF again. The THF solution was precipitated into methanol 4 times. Each time, the precipitate was analyzed by ¹H NMR, and the ratio of 42-crown-14 to polymer backbone repeating units was calculated. The results are shown below. (Table V-C2)

Table V-C2 The ratio of the number of the backbone repeating units to 42-crown-14 in poly(azomethine)rotaxane B

ppt. in methanol (THF solution)	42-c-14 : backbone units (x/n=8)
1	1 : 2.16
2	1 : 3.56
3	1 : 8.41
4	1 : 8.33

From the table, we can see that the ratio of 42-crown-14 to backbone repeating units was similar to poly(azomethine)rotaxane A, one 42-crown-14 every 8.3 repeating units. This meant that after two precipitations, most of the unthreaded 42-crown-14 had been removed by dissolution in methanol. The threaded 42-crown-14 was blocked by the end blockers during the precipitation. Since the mole ratio of 1,10-bis(p-hydroxyphenylimino-p-benzylideneoxy)decane to 42-crown-14 was the same for poly(azomethine)rotaxanes A and B, the ratio of the number of the 42-crown-14 units to backbone repeating units was very similar (1 to 8.23 for poly(azomethine)rotaxane A and 8.33 for poly(azomethine)rotaxane B). Because when 1,10-bis(hydroxyphenylimino-p-benzylideneoxy)decane and 42-crown-14 were added together and stirred, the threaded and the unthreaded 42-crown-14 reached an equilibrium. After the polymerization, the ratio of the 42-crown-14 units and the backbone repeating units suppose to be certain.

The degree of polymerization was calculated from the integration of protons on the end blockers and decylene group in the ^1H NMR spectrum. The average degree of polymerization was 10. This was the intended value. (Fig. V-C5) IR analysis was done. All the functional peaks are seen. (Fig. V-C6) Beside THF and chloroform, this fraction (fraction 2) also dissolved in other general solvents like methylene chloride, acetone, and ethyl acetate. It dissolved slightly in toluene and propanol. The percentage yield of fraction 2 was 11%.

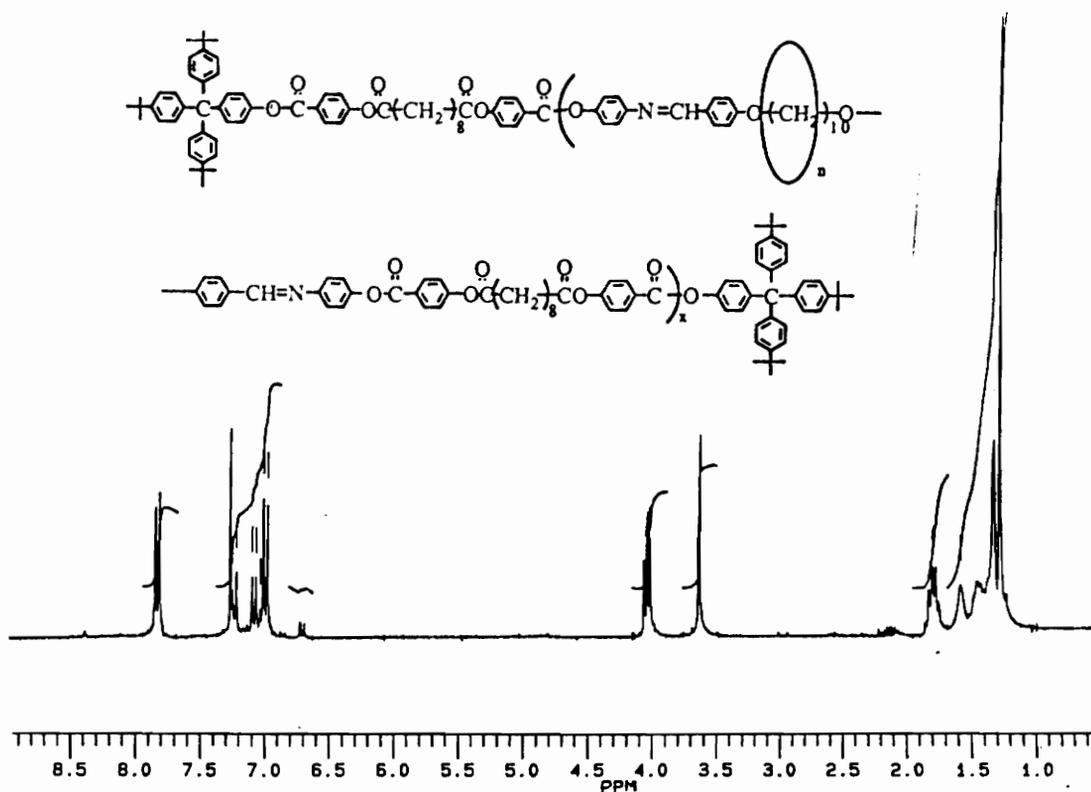


Fig. V-C5 ^1H NMR spectrum of poly(azomethine)rotaxane B
($x=10$, $x/n=8.3$) (ppm)

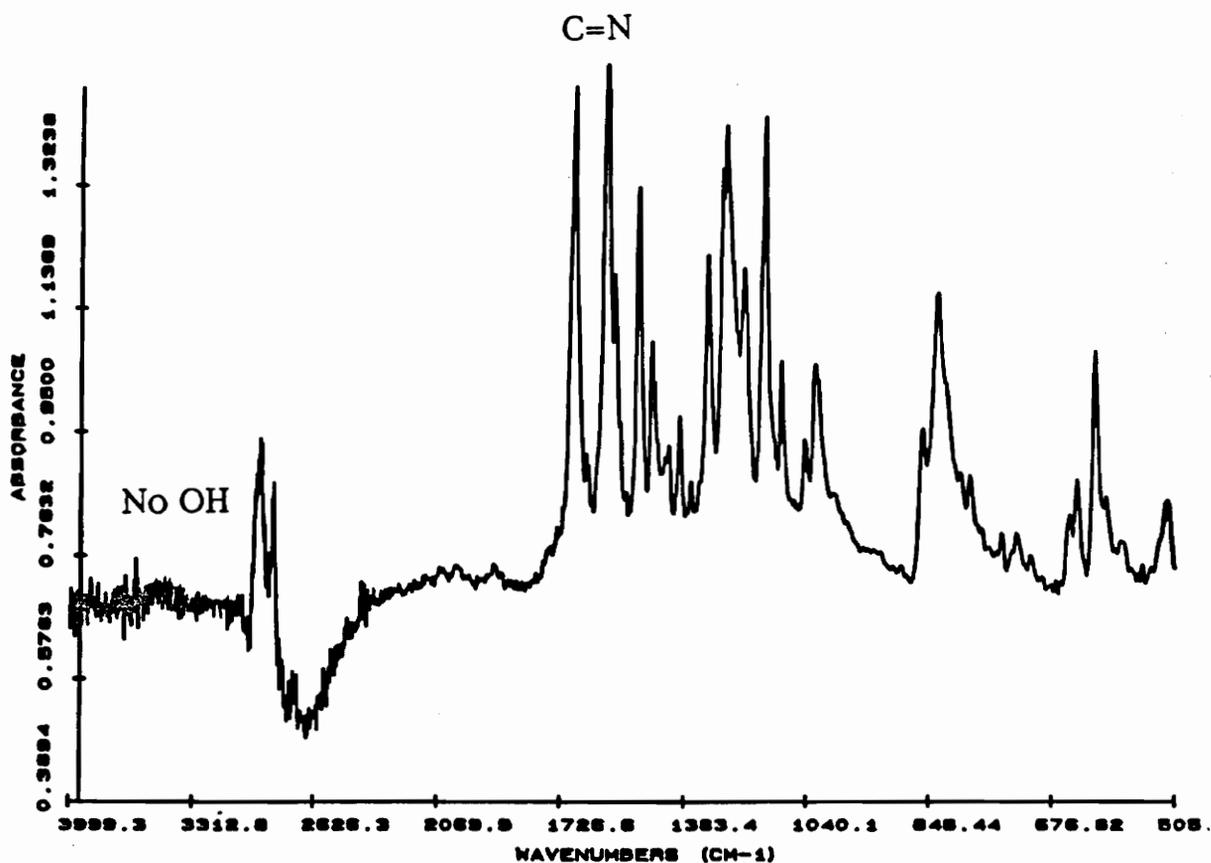


Fig. V-C6 IR spectrum of poly(azomethine)rotaxane B
($x=10$, $x/n=8.3$) (KBr, cm^{-1})

Since the poly(azomethine) backbone decomposed in dichloroacetic acid, the viscosity results in dichloroacetic acid were not meaningful. THF or chloroform could be used as the solvent for of the viscosity analysis for fraction 2. But since most of the poly(azomethine)rotaxane B sample was destroyed by dichloroacetic acid, more polymer needs to be made for a viscosity analysis.

Thermal analysis of poly(azomethine)rotaxane B was done. The second fraction had a 5% decomposition at 280°C. (Fig. V-C7) The first fraction sample was destroyed by dichloroacetic acid, so TGA and DSC analysis could not be done. DSC analysis was done on fraction 2. (Fig. V-C8) The temperature range was 30-160°C. The heating rate was 5°C/minute. There were three endothermic transitions. They were at 66, 72, 103°C. On cooling, 2 exothermic transition peaks were seen. They are at 51 and 68°C. These endothermic and exothermic transitions were repeated at the second and third heating. On the second and third heating, the three endothermic transitions were at 68, 72, and 95°C. On the second and third cooling, the two exothermic transitions were at 51 and 68°C. Jin and Park reported that poly(azomethine) B had the last endothermic transition at 166°C [1]. The last endothermic transition peak of poly(azomethine)rotaxane B was about 70°C lower than that of poly(azomethine) B.

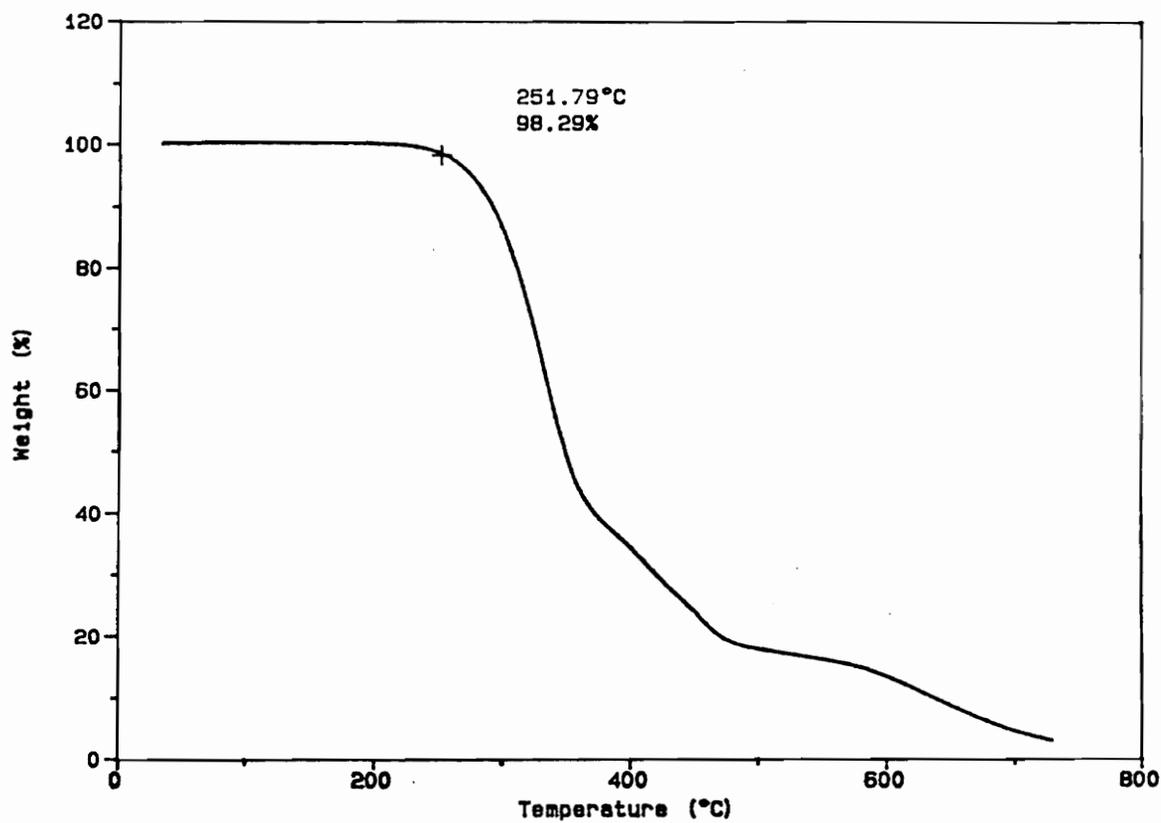


Fig. V-C7 TGA scan of poly(azomethine)rotaxane B (X=10, x/n=8.3) (10°C/min)

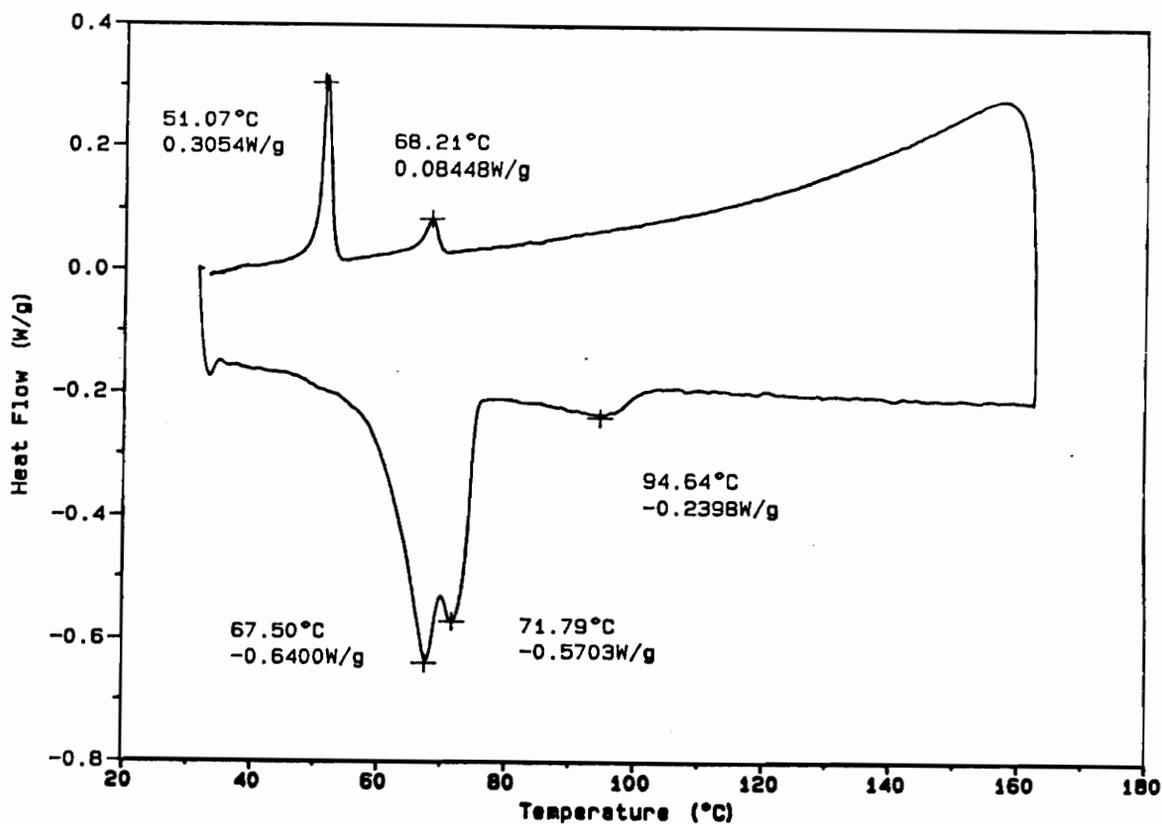


Fig. V-C8 DSC scan of poly(azomethine)rotaxane B ($x=10$, $x/n=8.3$) ($5^{\circ}\text{C}/\text{min}$)

Polarizing microscopic analysis was done for poly(azomethine)rotaxane B. At room temperature, the sample was a crystalline solid. When the temperature rose to above 70°C , some large bright spots appeared which meant that some structures had started to melt. When the temperature was between $70\text{-}98^{\circ}\text{C}$, the sample was in a liquid crystalline phase. When the slide was pressed, the structure moved like in liquid. Disclination lines were seen which meant that the phase was nematic. When the

temperature rose to 98°C, some structures completely melted to an isotropic phase, but some rod like structures were still seen. When the temperature rose above 160°C, some decomposed structures were seen. These decomposed structures could be 42-crown-14 which has a decomposition temperature of around 170°C. These rod-like structures melted at 198°C. When the temperature rose to 200°C, all the structures melted. The sample was in an isotropic phase. When the sample was cooled to 154°C, the rod like structure and the droplets of the decomposed material reappeared. When the sample was cooled under 90°C, some crystalline structure started to grow. In the range of 50-70°C, the sample showed the liquid crystalline phase again. When the temperature was under 50°C, the sample was a crystalline solid again. If the heating was repeated, the sample showed the same behavior as mentioned above. The difference was that the decomposed droplets appeared at 98°C. These decomposed droplets were formed during the first heat. Although in the isotropic state the sample showed one phase, it still could be a mixture of the long threaded poly(azomethine)rotaxane B and the short unthreaded poly(azomethine) B with similar solubilities. These rod-like structures might be unthreaded poly(azomethine) chains because they have high isotropic temperature which was higher than the reported isotropic temperature 181°C [1].

The microscopic analysis confirmed the liquid crystalline nature of the polyrotaxanes. But the reaction method could be improved by increasing the ratio of 42-crown-14 to DMAc as the solvent for synthesizing poly(azomethine)rotaxane A and B in order to increase the crown ether content.

V-D Recovery of 42-crown-14

After synthesizing poly(azomethine)rotaxanes, unthreaded 42-crown-14 could be recovered. After the first precipitation of poly(azomethine)rotaxanes, the poly(azomethine)rotaxane solid was collected by centrifugation. The methanol centrifugate contained mostly unthreaded 42-crown-14. The centrifugate was filtered through a silica gel filled filter funnel. Then the silica gel was washed with methanol. The methanol was evaporated, and the crude 42-crown-14 was recrystallized from acetone three times at 0°C. A yellow solid 42-crown-14 was obtained. IR and ¹H NMR analysis showed that the recovered 42-crown-14 was quite pure. Around 50-56% 42-crown-14 could be recovered.

V-E Experimental

N,N-dimethylacetamide (99.8%), and diglyme (99%) were purchased from Aldrich Chemical Co. and were used without further purification. Tetrahydrofuran (99%), methanol (98%), and toluene (99%) were purchased from Fisher Scientific Inc. and were used without further purification. Triethylamine (99%) was purchased from Aldrich Chemical Co. and was distilled once before use. Terephthaloyl chloride was purchased from Aldrich Chemical Co. and was recrystallized from cyclohexane before use. p-{Tri(p-t-butylphenyl)methyl}aniline (see Chapter III), p-{tri(p-t-butylphenyl)-methyl}phenol (see Chapter III), 1,10-bis(p-formyl-phenoxy)decane (see Chapter IV), 1,10-bis(p-hydroxyphenylimino-p-benzylidene-oxy)decane (see Chapter IV), 1,8-bis(chlorocarbonylphenoxy-carbonyl)octane (see Chapter IV), and 42-crown-14 (see Chapter II) were synthesized.

The centrifugation was done in a Dynac Centrifuge, Becton, Dickinson & Company. Melting points were determined in a Haake Buchler capillary melting point apparatus and were corrected. Thin

layer chromatography was done on Whatman fluorescence UV₂₄₅ 250 μm layer silica gel plate, and DC-Alufohlen aluminiumoxid 60 F254 neutral (type E) schichtdicke 0.2 mm layer aluminium gel plate. The viscosity analysis was done in a Cannon B 556 viscometer. The FTIR spectra were recorded on a Nicolet MX-1 FTIR spectrometer. The ^1H NMR spectra were recorded on a Bruker WP 270 MHz instrument using tetramethylsilicane as the internal standard. Thermogravimetric analysis scans were recorded with a TGA V4.0D DuPont 2100 instrument. Differential Scanning Calorimeter scans were recorded using a DSC V4.0B DuPont 2100 instrument. Gel permeation chromatogram were recorded with Waters 150-C ALC/GPC instrument. Elemental analyses were done by Atlantic Microlab Inc. Norcross, GA

Di(azomethine)

1,10-Bis(p-formylphenoxy)decane, 0.10 g (0.26 mmole), and p-{tri(p-t-butylphenyl)methyl}aniline was added to 10 ml diglyme. The reaction was stirred for 6 hours at 110°C. The reaction mixture was cooled to 5°C in an ice bath. A yellow powdery product, di(azomethine), was filtered. The product was recrystallized in cyclohexane. The final product weighed 0.243 g, 69.1% yield. Melting point: 278.4-280.1°C. Elemental analysis: C 86.15, H 8.32, N 2.15 (Theoretical calculated for C, H, N: C 86.86, H 8.63, N, 2.06). IR (ν/max , KBr, cm^{-1}): 550, 580, 640, 690, 800, 870, 1010, 1105, 1162, 1205, 1249, 1310, 1360, 1375, 1420, 1480, 1508, 1575, 1605, 1613, 1802, 2840, 2970, 3020. ^1H NMR(chloroform-d, ppm): singlet at 8.43 (2H), doublet at 7.82 (4H), multiplet at 7.00-7.41 (24H), triplet at 4.02 (4H), quintet at 1.83 (4H), triplet at 1.30 (46H). TGA (Du Pont, 10°C/min, 30-750°C): 2% decomposition at 413°C. DSC (Du Pont, 10°C/min, 30-140°C, endothermic transitions): 76, 115°C.

Di(azomethine)rotaxane

1,10-Bis(p-formylphenoxy)decane, 0.80 g (2.09 mmole), was dissolved in 42-crown-14, 15 g (24.32 mmole), at 80°C. The mixture was stirred at 80°C for 18 hours under vacuum. p-{Tri(p-t-butylphenyl)methyl}aniline, 2.20 g (4.34 mmole), in 7 ml methylene chloride was added dropwise. The reaction became a wax-like solid was in 5 minutes. The wax-like solid dissolved in THF and precipitated in methanol and recrystallized from toluene. The di(azomethine)rotaxane was a yellow solid, 0.494 g, 12.0% yield. Melting point: 181-238°C. Elemental analysis: C 75.93 H 8.96 N 1.28 (theoretical calculated for C, H, N: C 76.79 H 8.80 N 1.42). IR (ν /max, KBr, cm^{-1}): 660, 710, 820, 840, 1060, 1108, 1166, 1251, 1303, 1362, 1467, 1507, 1572, 1605, 1624, 2780, 2840. ^1H NMR (chloroform-d, ppm): singlet at 8.41 (2H), doublet at 7.82 (4H), multiplet at 7.10-7.26 (24H), doublet at 6.94 (4H), triplet at 4.02 (4H), singlet at 3.64 (56H), quintet at 1.77 (4H), triplet at 1.30 (46H). TGA (10°C/min, 30-750°C): 5% decomposition at 180°C. DSC (10°C/min, 30-140°C, endothermic transitions): 43, 116°C.

Poly(azomethine)rotaxane A (x=50)

1,10-Bis(p-hydroxyphenylimino-p-benzylideneoxy)decane, 1.1294 g (2.00 mmole), p-{tri(p-t-butylphenyl)methyl}phenol, 0.04038 g (0.08 mmole), triethylamine, 0.70 ml (5.00 mmole), 42-crown-14, 10.000 g (16.21 mmole), and 15 ml DMAc were added together. The reaction mixture was stirred at 80°C under nitrogen for 15 hours. Terephthaloyl chloride, 0.4142 g (2.04 mmole), dissolved in 5 ml DMAc were added dropwise. The reaction was continuously stirred for 72 hours. After the reaction was finished, the reaction mixture was poured into 200 ml of water. A yellow precipitate was filtered and washed with THF. The water filtrate was evaporated, and 42-crown-14 was found. The THF filtrate was precipitated in methanol, and no precipitate was formed. The

methanol solution was evaporated, and 42-crown-14 was found. The yellow precipitate weighed 0.625 g, 41% yield. IR (ν/max , KBr, cm^{-1}): 547, 716, 821, 842, 878, 1018, 1075, 1166, 1215, 1250, 1510, 1574, 1602, 1623, 1743, 1785, 2835, 2950. TGA ($10^\circ\text{C}/\text{min}$, 30-750 $^\circ\text{C}$, 5% decomposition): 346 $^\circ\text{C}$. DSC ($10^\circ\text{C}/\text{min}$, endothermic transitions, first heating): 193, 220, 236, 250 $^\circ\text{C}$. The sample decomposed after the first heating.

Poly(azomethine)rotaxane A (X=20)

1,10-Bis(p-hydroxyphenylimino-p-benzylideneoxy)decane, 1.1294 g (2.00 mmole), p-{tri-(p-t-butylphenyl)methyl}phenol, 0.10095 g (0.20 mmole), triethylamine, 0.70 ml (5.00 mmole), 42-crown-14 10 g (16.21 mmole), and 15 ml DMAc were added together. The reaction mixture was stirred at 80 $^\circ\text{C}$ under nitrogen for 15 hours. Terephthaloyl chloride, 0.4263 g (2.1 mmole), in 5 ml DMAc was added dropwise. The reaction was continuously stirred for 72 hours. After the reaction was finished, The reaction mixture was poured into 100 ml THF. A brown-yellow solid was filtered and washed with THF (fraction 1). The THF filtrate was precipitated in 1 liter of methanol. A yellow solid was collected by centrifugation, and recrystallized from toluene (fraction 2). Percentage yield: 1.2002 g, 78.2% yield (fraction 1); 0.5078 g, 23.1% (fraction 2). IR of fraction 2 (ν/max , KBr, cm^{-1}): 545, 720, 832, 844, 880, 1015, 1065, 1123, 1215, 1256, 1510, 1580, 1630, 1644, 1730, 2833, 2921. ^1H NMR of fraction 2 (chloroform-d, ppm): singlet at 8.38, doublet at 7.84, multiplet at 6.87-7.28, triplet at 4.03, singlet at 3.64, quintet at 1.83, and multiplet at 1.3-1.6. TGA ($10^\circ\text{C}/\text{min}$, 30-750 $^\circ\text{C}$, 5% decomposition), fraction 1: 213 $^\circ\text{C}$; fraction 2: 302 $^\circ\text{C}$. DSC ($10^\circ\text{C}/\text{min}$, endothermic transitions): fraction 1 (25-160 $^\circ\text{C}$), 45, 48, 53 $^\circ\text{C}$; fraction 2 (25-250 $^\circ\text{C}$), 68, 111 $^\circ\text{C}$. The samples decomposed after the first heating.

Poly(azomethine)rotaxane A (X=10, x/n=8.2)

1,10-Bis(p-hydroxyphenylimino-p-benzylideneoxy)decane, 1.1294 g (2.000 mmole), p-{tri(p-t-butylphenyl)methyl}phenol, 0.2019 g (0.400 mmole), triethylamine, 0.70 ml (5.00 mmole), 42-crown-14, 10.000 g (16.210 mmole), and 15.00 ml DMAc were added together. The reaction mixture was stirred at 80°C under nitrogen for 15 hours. Terephthaloyl chloride, 0.4467 g (2.200 mmole), dissolved in 5.00 ml DMAc was added dropwise. The reaction was continuously stirred for 72 hours. After the reaction was finished, the reaction mixture was poured into 100 ml of THF. A brown-yellow solid was filtered and washed with THF (fraction 1). The THF filtrate was precipitated in 1 liter of methanol. A yellow solid was collected by centrifugation, and was recrystallized from toluene (fraction 2). Percentage yield: 0.9002 g, 66.4% yield (fraction 1); 0.2646 g, 17.2% yield (fraction 2). IR of fraction 2 (ν /max, KBr, cm^{-1}): 510, 540, 614, 648, 839, 1010, 1044, 1112, 1160, 1214, 1262, 1317, 1392, 1426, 1474, 1508, 1597, 1685, 2852, 2934. ^1H NMR of fraction 2 (chloroform-d, ppm): singlet at 8.38, doublet at 7.84, multiplet at 6.86-7.26, triplet at 4.04, singlet at 3.64, quintet at 1.81, multiplet at 1.3-1.6. TGA (10°C/min, 30-750°C, 5% decomposition): fraction 1, 375°C; fraction 2, 275°C. DSC (endothermic transitions, 5°C/min): fraction 1 (30-295°C), heating: 46, 184, 203, 235°C; fraction 2 (30-160°C), heating: 67, 73, 123°C, cooling: 89, 53, 50°C. Polarizing microscopic analysis: see "Results, and discussion" part.

Poly(azomethine)rotaxane B (X=10, x/n=8.3)

1,10-Bis(p-hydroxyphenylimino-p-benzylideneoxy)decane, 1.1294 g (2.00 mmole), p-{tri(p-t-butylphenyl)methyl}phenol, 0.2019 g (0.40 mmole), 42-crown-14, 10.000 g (16.21 mmole), triethylamine, 0.700 ml (5.00 mmole), and DMAc, 15.00 ml were added together. The mixture was stirred at 80°C under nitrogen for 15 hours. 1,8-Bis(chlorocarbonylphenoxy)octane, 1.0546 g

(2.2 mmole), dissolved in 5 ml DMAc was added dropwise. The reaction was continuously stirred at 80°C under nitrogen for 72 hours. After the reaction was finished, the reaction mixture was poured into 100 ml THF. A brown-yellow solid was filtered and washed with THF (fraction 1), 1.5632 g, 73% yield. The THF filtrate was precipitated in 1 liter methanol. A yellow precipitate was collected by centrifugation (fraction 2), 0.2366 g, 11% yield. IR of fraction 2 (ν/max , KBr, cm^{-1}): 510, 614, 642, 833, 850, 1017, 1044, 1112, 1153, 1213, 1262, 1317, 1392, 1474, 1508, 1576, 1597, 1686, 2860, 2941. ^1H NMR of fraction 2 (chloroform-d, ppm): singlet at 8.39, multiplet at 6.73-7.26, triplet at 4.04, singlet at 3.64, quintet at 1.80, multiplet at 1.30-1.60. TGA (10°C/min, 30-750°C, 5% decomposition): (fraction 1 was destroyed by dichloroacetic acid), fraction 2: 280°C. DSC (5°C/min, 30-160°C, endothermic transitions): fraction 2, heating: 68, 72, 94°C; cooling: 86, 51°C. Polarizing microscope analysis: see "Results, and discussion" part.

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CHAPTER VI

CONCLUSIONS

VI-A Crown Ethers

Crown ethers, 30-crown-10, 60-crown-20, 42-crown-14, and 21-crown-7 have been synthesized by reacting oligo(ethylene glycol)s with oligo(ethylene glycol) ditosylates in highly diluted tetrahydrofuran with NaH as the base and template metal. Each reaction product include two types of crown ethers, two molecule combination crowns and four molecule combination crowns. The later has twice the ring size of the former one. High reaction temperature favors the four molecule combination crown, and low temperature favors the two molecule combination crown. The crown ethers can be purified by recrystallization from non-polar or polar solvents at -20-0°C. The overall yields of crown ethers are from 16-40%.

VI-B End Blockers

The end blockers, p-{tri(p-t-butylphenyl)methyl}aniline and p-{tri(p-t-butylphenyl)methyl}phenol are synthesized. The Grignard reaction is a good method to synthesize p-tri(p-t-butylphenyl)-methanol. Then, p-tri(p-t-butylphenyl)methanol is converted to its derivatives, p-{tri(p-t-butylphenyl)methyl}aniline and p-{tri(p-t-butylphenyl)methyl}phenol. The largest size crown ether which these end blockers can block is 42-crown-14.

VI-C Poly(azomethine)s A and B

Poly(azomethine)s A and B syntheses have been repeated, and poly(azomethine)s A and B with end blockers have been synthesized. These liquid crystalline polymers have high T_m 's and low solubilities. They precipitated out from the reaction solution with degrees of polymerization of 3-5. They did not dissolve in general organic solvents. They can be easily hydrolyzed in strong acids, silica, aluminium gel columns, and GPC columns, and they are thermally unstable.

VI-D Di(azomethine)rotaxane and Poly(azomethine)-rotaxanes A and B

Di(azomethine)rotaxane has been synthesized in pure 42-crown-14 with 12% yield, one crown ether per compound. Poly(azomethine)rotaxanes A and B have been synthesized in 42-crown-14/DMAc solution. Each reaction produced two fractions. Fraction 1 (yield of 66-78%) did not dissolve in general organic solvents. Fraction 2 (yield of 11-23%) dissolved in some general solvents. The degree of polymerization of the fraction 2 was increased to 10 (compare to the poly(azomethine)s A and B). There is one crown for every eight repeating units. The T_m 's of poly(azomethine)rotaxanes (fraction 2) are lowered by 70-100°C. The solubilities of poly(azomethine)rotaxanes A and B were increased. The processability of poly(azomethine)rotaxanes is thereby increased.

VITA

JEAN Y. SZE

Jean Y. Sze is a native of Shanghai China. When she graduated from the high school during the culture revolution, she was not able to enter a university to continue her education. She was assigned to work in a radio factory where she worked as an electronic technician, draftswoman, engineering assistant, and advertising designer.

In 1980, she entered Shanghai Conservatory of Music (evening school) to study Zheng performance and received a BM degree. At the same time, she performed in West Shanghai Workers Chinese Orchestra.

In 1984, Jean got a chance to come to The United States. Since then, her life was completely changed. She studied in College of St. Elizabeth in New Jersey and got a bachelor degree on chemistry and music composition. She began her graduate study in polymer chemistry at Virginia Tech in 1988, and successfully synthesized poly(azomethine)rotaxanes, new novel polymer compounds. Jean got her master degree in 1992.

During her studying in Virginia Tech, Jean was an active musician, a Zheng performer and a composer in New River Valley and Roanoke area.