Chapter 1

Literature Review

1.1 Introduction

1.1.1 Topologies of conventional polymer

A *polymer* is a high molar mass molecule constructed from small units called *monomers*. To be a monomer, a molecule has to possess functionality, 2 or more reactive groups. These monomers, "building blocks", are converted to polymers by polymerization. In addition to chemical composition, topology is a main factor in determining polymer properties.[1,2] Depending on how small units are connected, conventional polymers can be classified into cyclic, linear, branched and crosslinked (network) polymers as depicted in Figure 1.1.[1]

Compared to its linear counterpart, a cyclic polymer without chain ends, a closed form of a linear polymer, often has characteristic properties such as low hydrodynamic volume and low viscosity.[3,4]

Linear polymers with two chain ends can be divided into homopolymers consisting of a single type of repeat unit, and copolymers containing two or more different types of repeat units. In addition to its chemical composition, molecular weight and polydispersity, which determine the properties of a homopolymer, the fashion of connection between different repeat units also contributes to the final properties of a copolymer. For example, alternating and random copolymers are single phase materials and their properties are the average of those of corresponding homopolymers. By changing the ratio of the two repeat units, their properties, e.g., glass transition temperatures, can be deliberately adjusted. On the other hand,

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[1] Frechet, J. M. *Science* **1994**, *263*, 1710.

[2] (a) Gibson, H. W. In *Large Ring Molecules*, Semlyen, J. A. ed., J. Wiley and Sons, New York, **1996**, 191-262. (b) Philp, D.; Stoddart, J. F. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154-1196. (c) Amabalino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725-2828. (d) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843-945.

[3] Semylen, J. A., ed. *Cyclic Polymers* Elsevier Applied Science, New York, **1986**.

[4] McKenna, G. B.; Hosteltter, B. J.; Hadjichristidis, N.; Fetters, L. J.; Plazek, D. J. *Macromolecules* **1989**, *22*, 1834.

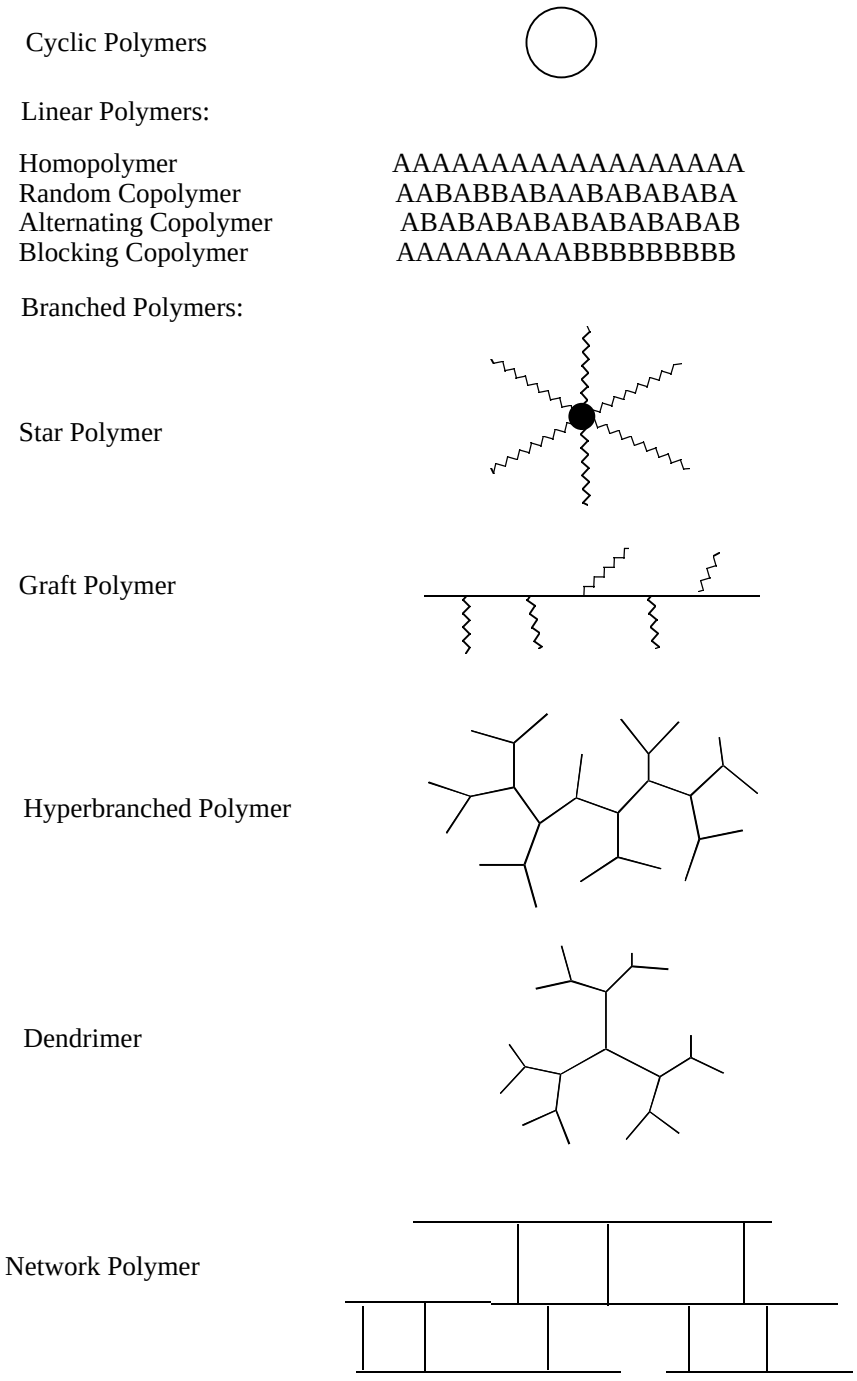


Figure 1.1 Various topologies of conventional polymers

if different block segments are not compatible with each other, a block copolymer will show phase separation behavior and thus can be viewed as a chemically linked polymer alloy; this often brings about unique properties, e.g., two glass transition temperatures.[5,6]

Branched polymers have more than two chain ends per molecule. In a star polymer, a number of polymeric chains radiate from a common branching point and thus the number of chain ends per molecule is equal to its number of arms (number of branches). Relative to a linear polymer, the globular shape of a star polymer contributes to its low radius of gyration and low intrinsic viscosity, depending on arm number.

A graft polymer consists of main chain and pendant chain. If the pendant chain is long enough and is not compatible with the main chain, the graft polymer will exhibit phase separation in the solid state and can be used as a compatiblizer for polymer blends of those homopolymers compatible with the pendant chain and the main chain, respectively.[1,7]

A hyperbranched polymer is prepared from AB_2 monomers (A and B are reactive groups) by one step polymerization but is not well defined in terms of its structure, molecular weight and polydispersity. A dendrimer, prepared from an AB_2 monomer by multiple steps, is a monodisperse and structurally perfect material. Both the branched polymers and the dendrimers adopt condensed globular shapes; this introduces new properties, e.g., low melt viscosity, low intrinsic viscosity and surface functionality. These materials can be used as compatiblizers for polymer blends, rheology control agents to improve polymer processibility, surface modification agents and drug delivery.[1,8,9,10]

Crosslinked polymers are three dimensional macromolecules. They are insoluble in any solvent and infusible.[5] The properties of network polymers are controlled by crosslinking density, e.g., the higher the density is, the higher glass transition temperature the

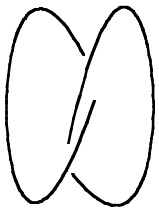
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[5] Riess, G. *Principles of Polymerization* 3rd Ed., John Wiley & Sons, Inc., New York, **1991**.
[6] Noshay, A.; McGrath, J. E. *Block Copolymers: Overview and Critical Survey,* Academic Press, Inc., New York, **1977**.
[7] Meier, D. J. ed., *Block Copolymers: Science and Technology,* MMI Symposium Series, Harwood Academic Publishers, **1983**.
[8] Dvornic, P. R.; Tomalia, D. A. *Curr. Opinion Coll. Interface Sci.* **1996**, *1*, 221-235.
[9] Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *"Dendritic Molecules"*, VCH Publishers, Weinheim, Germany, **1996**.
[10] Fréchet, J. M. J. *J. Macromol. Sci. Pure Appl. Chem.* **1994**, *A31*, 1627.

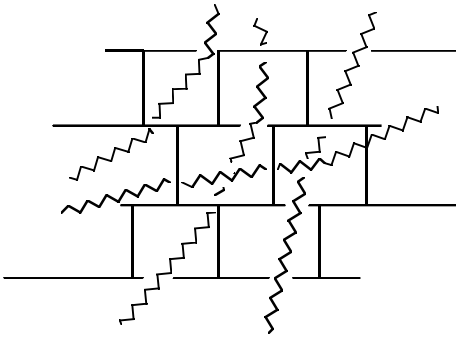
polymer has. Because of their excellent solvent resistance and thermostability, crosslinked polymers are widely used for coatings, adhesives and reinforcing materials in composites. However, they are not reprocessible.

1.1.2 Mechanically linked polymers

In addition to the above-mentioned covalent polymers, there are other different topological polymers, i.e., mechanically linked polymers; this was first suggested in the early 1960's by Frisch and Wassermann.[11] Catenane **1.1**, consisting of two interlocked macrocycles,[2,11] represents this novel structure at the small molecular level. Interpenetrating polymer networks (IPN) **1.2**, prepared by polymerization of one monomer in the presence of another preformed crosslinked polymer or by simultaneous polymerization of two different monomers by different mechanisms,[5] are examples of such polymer topology. Based on **1.1**, imaginative scientists conceived related polymeric analogies, polycatenanes **1.3** and **1.4**.[2]

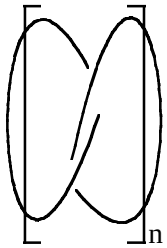


1.1

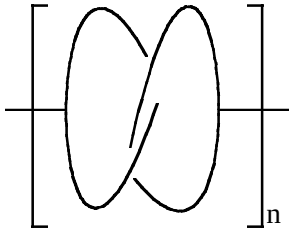


1.2

[11] Frich, H. L.; Wassermann, E. J. *J. Am. Chem. Soc.* **1961,** *83,* 3789.

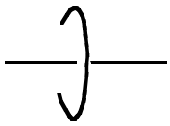


1.3

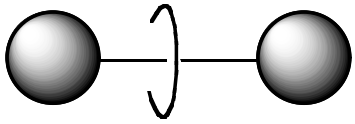


1.4

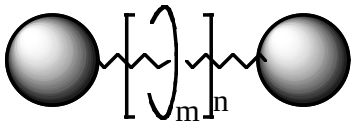
A monorotaxane, prepared by threading a cyclic species onto a small linear molecule, was first addressed by Wassermann.[12] In terms of its thermostability, it can be defined as pseudorotaxane **1.5**, in which two components can dissociate from each other by external forces, and real rotaxane **1.6**, in which the cyclic moiety is constrained between blocking groups (BG), and can not slip off the linear component unless one or more chemical bonds is/are broken.[2]



1.5



1.6



1.7

The polymeric analog of **1.5** and **1.6** is polyrotaxane **1.7**, in which the cyclic moieties are threaded onto a polymeric backbone. Since no covalent bond exists between the two components of **1.7**, it is a molecular composite. Its new topology yields its unique properties, a novel concept for modification of conventional polymers.[2]

Different types of polyrotaxanes were conceived, depending on how the cyclic and linear units are connected, and are summarized in Figure 1.2.[2] According to the location of the rotaxane unit, polyrotaxanes can be defined as main chain systems (Figure 1.2A', A", A'", B' and B"), in which the rotaxane unit is a main chain component, and side chain systems (Figure 1.2C', C", D' and D"), in which the rotaxane unit is located in the side chain.

[12] Wassermann, E. J. *J. Am. Chem. Soc.* **1960**, *82*, 4433.

Or by stability toward dethreading, they can be classified as polypseudorotaxanes (Figure 1.2A", B", C" and D") without blocking groups (BG), in which the mechanical linkages can be disassociated by some external forces, and true polyrotaxanes (Figure 1.2A', A'", B', C' and D') with BG at the linear end or as in-chain units, in which the two components can not be separated from each other unless one or more covalent bonds is/are broken.

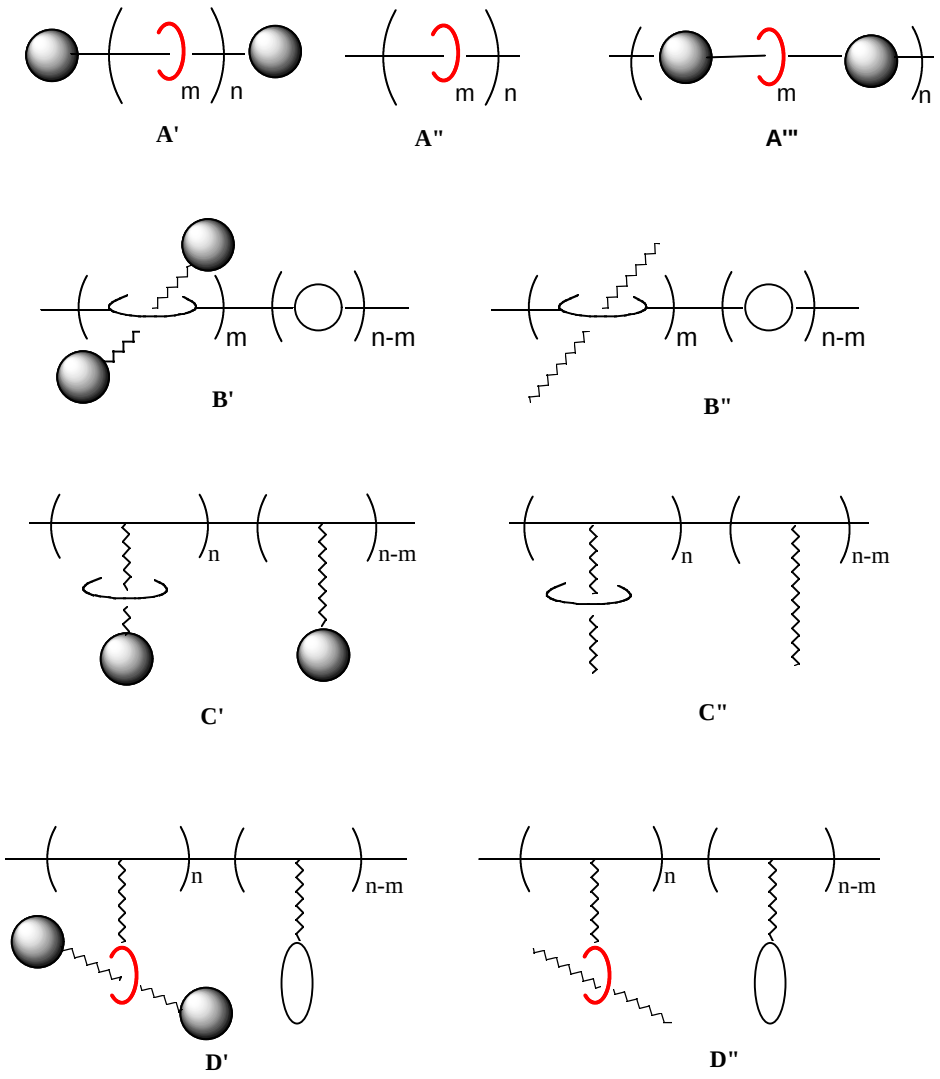


Figure 1.2. Various types of main chain and side chain polyrotaxanes

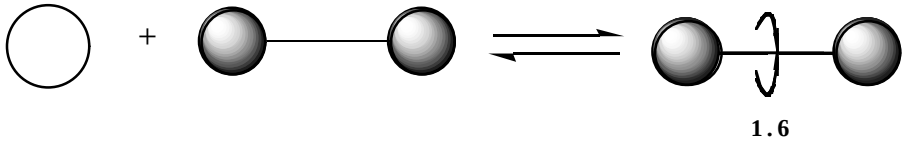
In last couple of decades, significant progress has been made in the supramolecular field. In following sections, recent developments in rotaxane and polyrotaxane areas are reviewed.

1.2 Monorotaxanes

Since the first monorotaxanes were reported in 1967 by Harrison and Harrison[13] by a statistical approach and by Schill and Zollenkopf[14] by a chemical conversion method, significant advances have been made in this specific area; this progress is summarized here and divided into subsections based on the driving forces for threading.

1.2.1. Statistical threading.

Statistical threading is an approach by which the formation of rotaxane is based on a purely statistical process without any apparent attractive force between the linear species and the cyclic molecules; this was first demonstrated in 1967.[2, 13] In this early work, Harrision also introduced the slippage concept (Scheme 1.1), a process for the cyclics to slip over blocking groups (BG) nearly matching the cavity size as shown for **1.6**. It was also revealed that the yield of rotaxane by statistical threading depended on the size of macrocycle; the larger the size was, the higher the yield was. Compared to other methods, however, the statistical method is not very effective in the preparation of rotaxanes because ΔH is nearly zero or so and ΔS is always negative toward threading.[2]

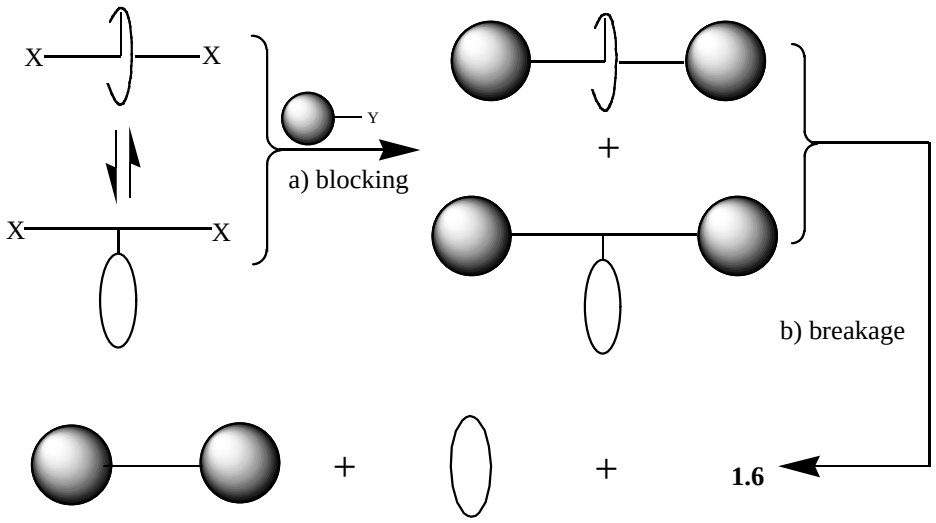


Scheme 1.1 The slippage threading process

[13] Harrison, I. T.; Harrison, S. *J. Am. Chem. Soc.* **1967**, *89*, 5723.
[14] (a) Schill, G.; Zollenkopf, H. *Nachr. Chem. Techn.* **1967**, *79*, 149. (b) Schill, G.; Luttringhaus, A. *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 546.

1.2.2 Chemical conversion

The chemical conversion method for the preparation of rotaxanes was introduced by Schill et al. in the 1960's.[14] The basic idea is described in Scheme 1.2. First the cyclic molecule was chemically bonded to the linear species bearing reactive groups X. Then its reaction with monofunctional BG afforded an intermediate in which the cyclic was constrained between BG. Finally, the chemical bond between the linear units and the cyclic moiety underwent a cleavage reaction to give rotaxane **1.6**. This strategy always involves multiple steps and thus is time consuming and not effective in terms of overall yield.



Scheme 1.2 Chemical conversion method

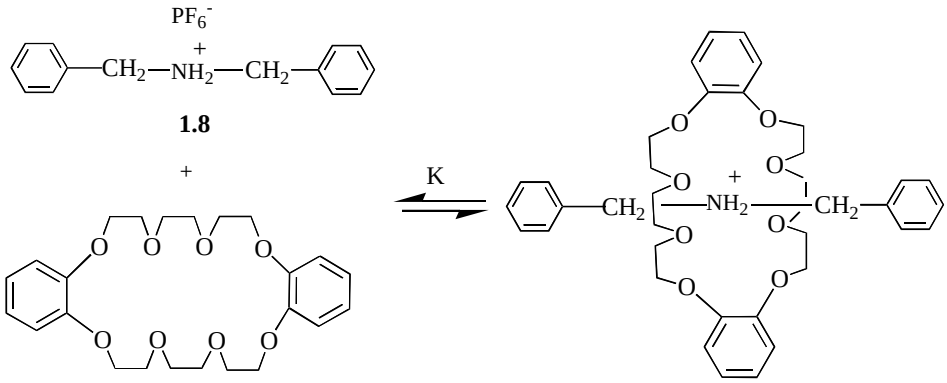
1.2.3 Threading driven by enthalpy

Threading driven by enthalpy is different from the statistical method in that there is an intermolecular attractive force between the linear species and the cyclic to derive a negative ΔH value toward threading. Therefore, relative to the statistical method, this approach is usually more effective and gives higher yields. Different types of attractive forces have been used in rotaxane synthesis: hydrogen bonding, metal-ligand complexation, π-π stacking, hydrophilic-hydrophobic interaction and combinations of these forces.

Hydrogen bonding

It is well known that crown ethers can complex with metal ions through ion-dipole interaction and form hydrogen bonds with acidic protons such as NH, OH, and ammonium ions.[15,16] However, it was not until recently that scientists started to utilize this interaction to prepare various non-covalent supramolecules, rotaxanes.

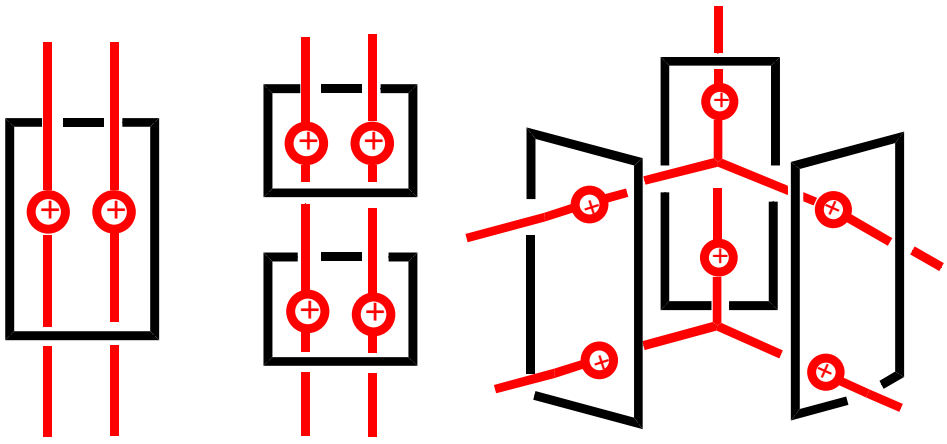
Stoddart and coworkers prepared pseudorotaxane **1.10** without BG at the ends of the linear species by hydrogen bonding of dibenzo-24-crown-8 (DB24C8) (**1.9**) and ammonium molecules **1.8**.[17] The formation of the rotaxane was directly proved by X-ray crystal structure and mass spectroscopy. The complexation constant between **1.8** and **1.9** varied from 360 to 27000 L/mol, depending on solvent.[17a] In order to prevent disassociation of **1.10**, BGs were incorporated at both ends and a dumbbell thermostable rotaxane of type **1.6** was obtained.[17b]



The authors also prepared a rotaxane with two cyclic molecules threaded per linear component bearing two ammonium sites with a yield of 10 %.[17b] DB24C8 can only accommodate one linear species because of its small cavity. Bis-para-phenylene-34-crown-

[15] Pedersen, C. *J. Am. Chem. Soc.* **1967**, *89*, 7017.
[16] Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. *Chem. Rev.* **1991**, *91*, 1721.
[17] (a) Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 709. (b) Ashton, P. R.; Glink, P. T.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 729.

10 (BPP34C10) has a much larger cavity. Indeed, it was found that BPP34C10 can accommodate two ammonium linear molecules per cavity. Thus much more complicated and elegant rotaxanes, double threaded **1.11** (2 to 1 complex), double threaded and double encircled **1.12** (2 to 2 complex) and interwoven supramolecular cage **1.13** (3 to 2 complex), were obtained with BPP34C10 as the cyclic and mono-, di- and tri- ammonium molecules as the linear species, respectively.[18] These results demonstrated the importance of molecular recognition in synthetic chemistry directed toward supramolecular systems like those encountered in natural systems.

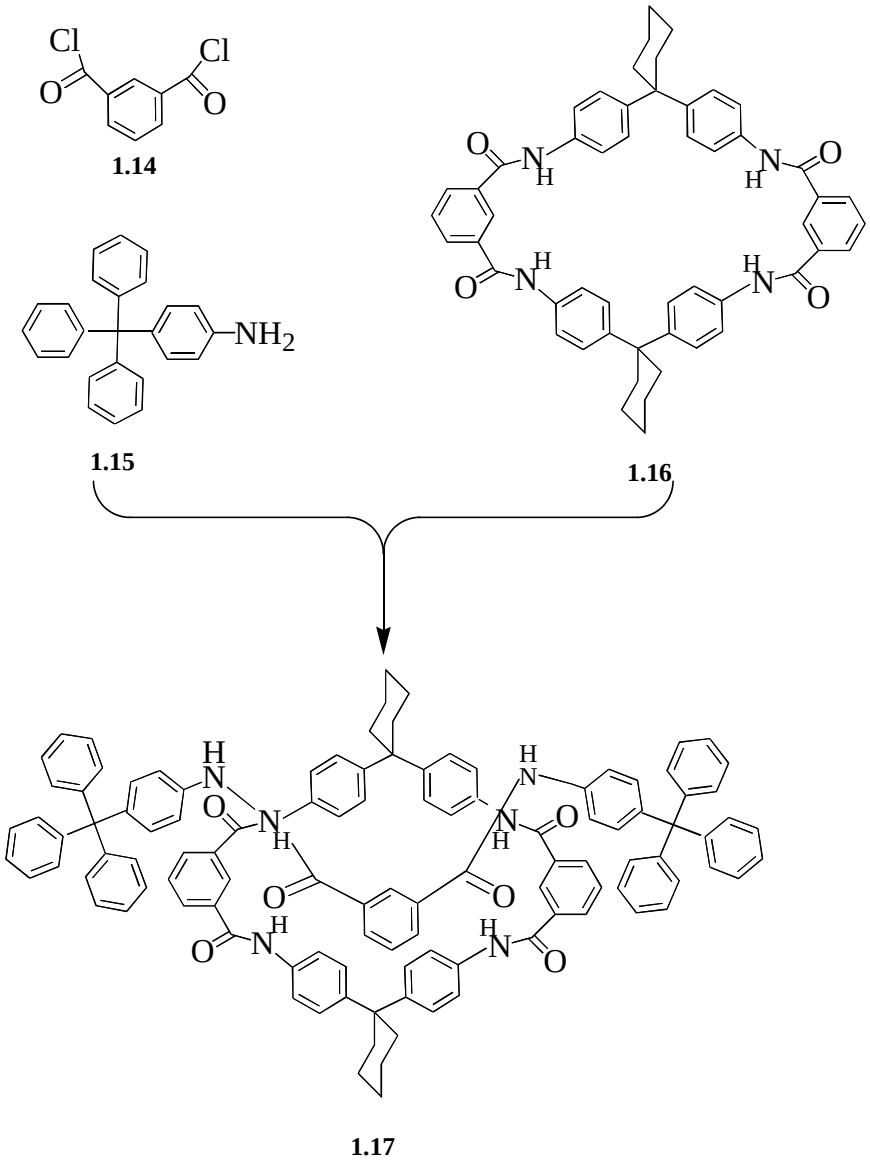


1.11 **1.12** **1.13**

In 1995, Vögtle et al. synthesized a monorotaxane based on hydrogen bonding between amide groups of a cyclic species and a reactive NH group of a linear species.[19] Hydrogen bonding between the NH_2 group of monofunctional BG **1.15** and cyclic amide **1.16** was the initial driving force for threading.

[18] (a) Glink, P. T.; Schoavo, C.; Stoddart, J. F.; Williams, D. J. *Chem. Commun.* **1996**, 1483. (b) Ashton, P. R.; Collins, A. N.; Mattew, C. T. F.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; Williams, D. J. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 58.

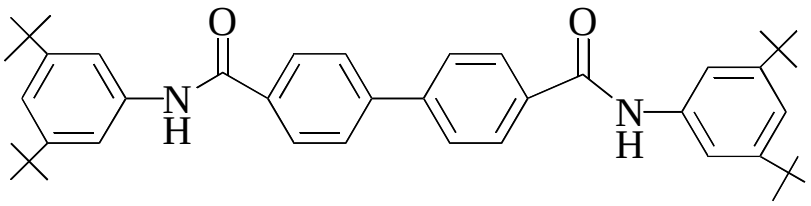
[19] For review: Jager, R.; Vögtle, F. *Angew. Chem. Int. Ed. Engl* **1997**, *36*, 930.



1.14 **1.15** **1.16** **1.17**

After the formation of the amide linkage from the reaction of acid chloride **1.14** and the amine group of **1.15**, the hydrogen bonding between the -CONH- of the linear species and the amide linkage of the cyclic **1.16** provided a retaining force to prevent dissociation before both ends had been blocked. By varying the structure of diacid chloride, different but very similar rotaxanes were also prepared. Moreover, the slipage threading approach (Scheme 1.1) was also employed in the preparation of amide-based rotaxanes by a “brief melting”

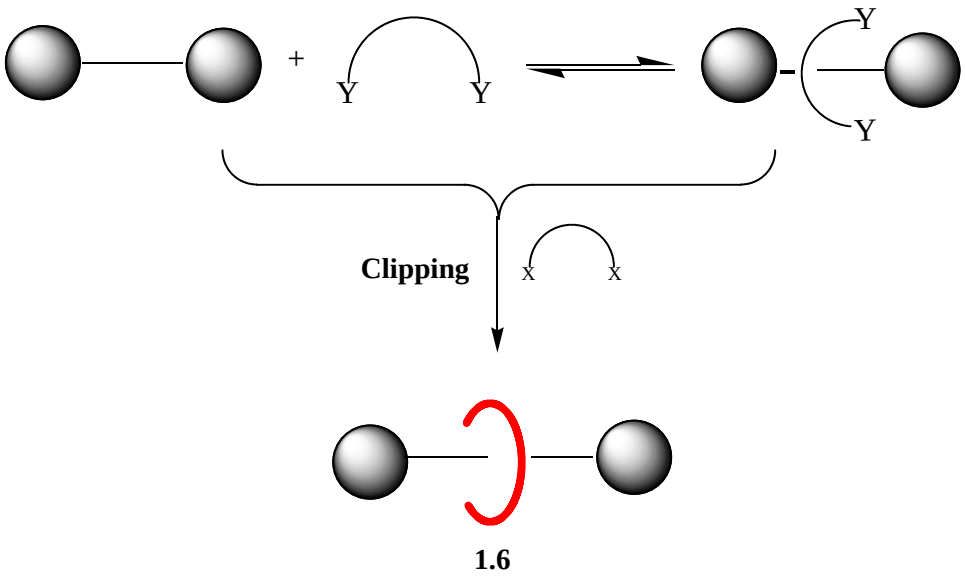
procedure.[19,20] To be suitable for this approach, the size of the bulky end group should be slightly smaller that that of a fully opened cyclic for threading to occur at a high temperature but sterically bulky enough to provide slow dethreading at room temperature so that enough time is available for separation and characterization. The cyclics in the resultant rotaxane can dissociate from the linear units but at a slower rate and thus the rotaxane is metastable . In this case, compound **1.18** was used as the linear molecule and **1.16** as the cyclic. The rotaxane formation was again driven by H-bonding between the amide groups of these two components.



1.18

Leigh and coworkers successfully prepared rotaxanes of type **1.6** by H-bonding between amide NH and carbonyl oxygen groups through a very interesting approach, a clipping method as depicted in Scheme 1.3; this is cyclization in the presence of a dumbbell shaped molecule.[21] In order to achieve high yield, a strong driving force between dumbbell molecules and one or both cyclic precursors is essential because the probability of the cyclization taking place around a linear species is very low by pure statistics. Based on their previous study of catenane systems,[19] these authors recognized that **1.20** can form hydrogen bonds with carbonyl oxygen atoms and thus **1.19** was deliberately designed to hydrogen bond with **1.20** to afford intermediate **1.21**. Consequently, the closure of **1.20** in **1.21** by reaction with diacid chloride **1.22** gave rotaxane **1.23**.

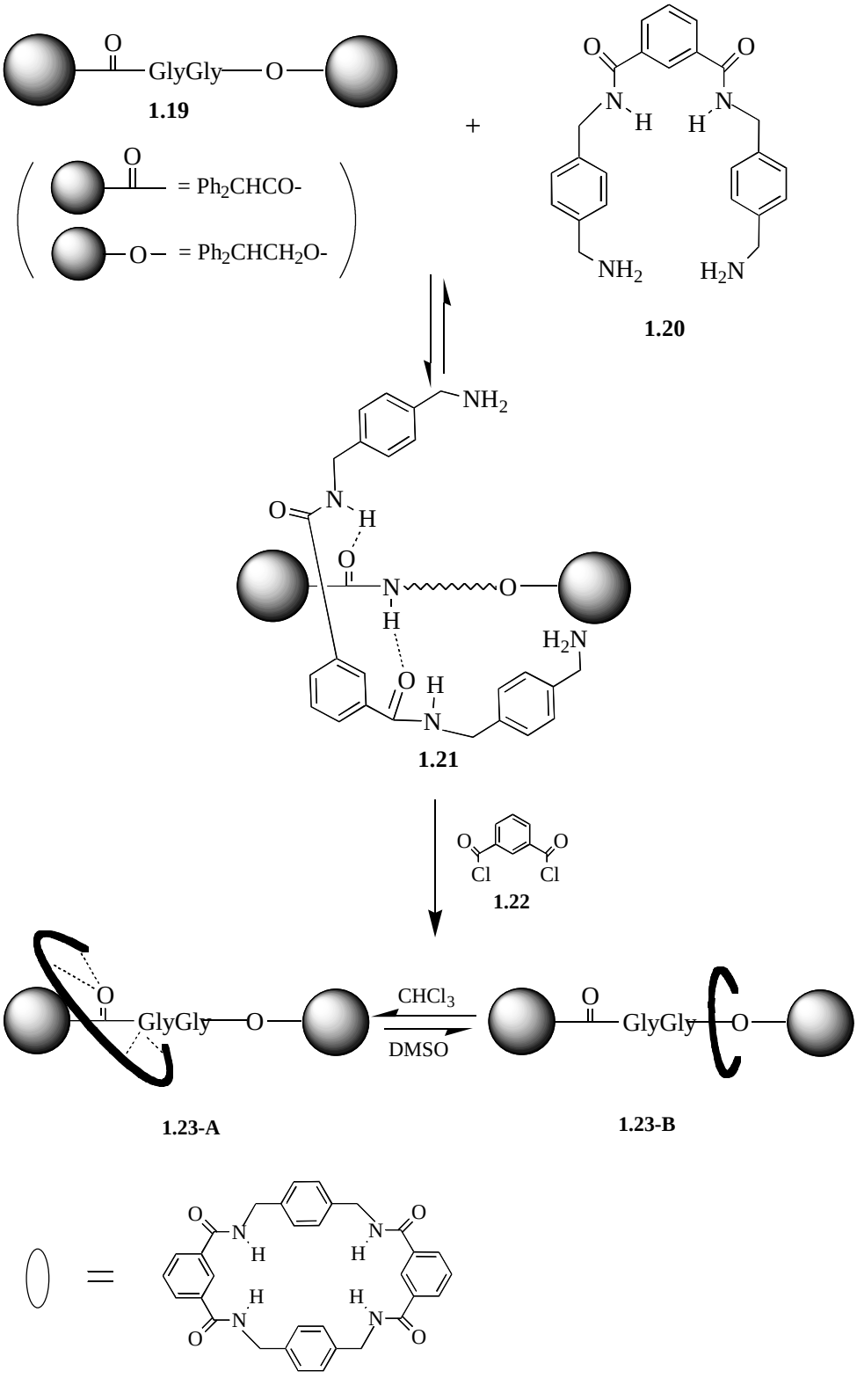
[20] Handel, M.; Plevoets, M.; Gestermann, S.; Vogtle, F. *Angew. Chem. Int. Ed. Engl.* **1997**, *109*, 1199.
[21] Leigh, D. A.; Murph, A.; Smart, J. P.; Slawin, A. M. Z. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 728.



1.6

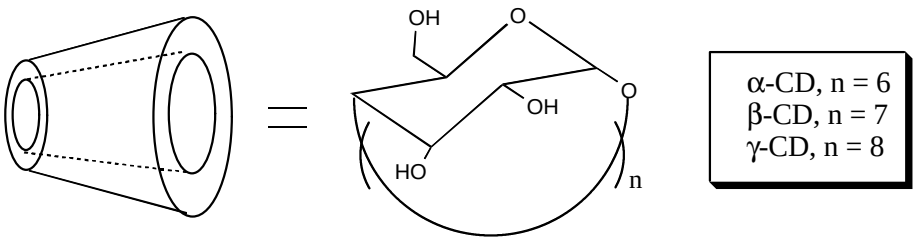
Scheme 1.3. Clipping approach

In practice, it is not necessary to prepare **1.20**. **1.23** was directly prepared by the cyclization of m-xylyldiamine and diacid chloride **1.22** in the presence of **1.19** in a yield of 34 %.[21] In addition, the authors also found that intra-annular H-bonding exists between the threaded cyclics and the linear units in **1.23**. By the proper choice of solvent, the location of the ring was controlled: **1.23-A** in chloroform or **1.23-B** in DMSO; this was proved by proton NMR study. Thus **1.23** was a molecular shuttle.


GlyGly
O
1.19
= Ph2CHCO-
= Ph2CHCH2O-
+
1.20
1.21
1.22
CHCl3
DMSO
1.23-A
1.23-B

Hydrophilic-hydrophobic interaction

Cyclodextrins (CD) can form inclusion complexes with small molecules by hydrophilic-hydrophobic interations.[22] Wenz et al. designed a compound bearing BG at one end, a hydrophilic moiety at the other end and a hydrophobic moiety in-between. The compound complexed with β-CD to give a pseudorotaxane which further reacted with another monofunctional BG to afford a CD-based rotaxane of type **1.6**.[23a] A similar approach was used by Kaifer and Isnin for an α-CD-based rotaxane with a smaller backbone.[23b]

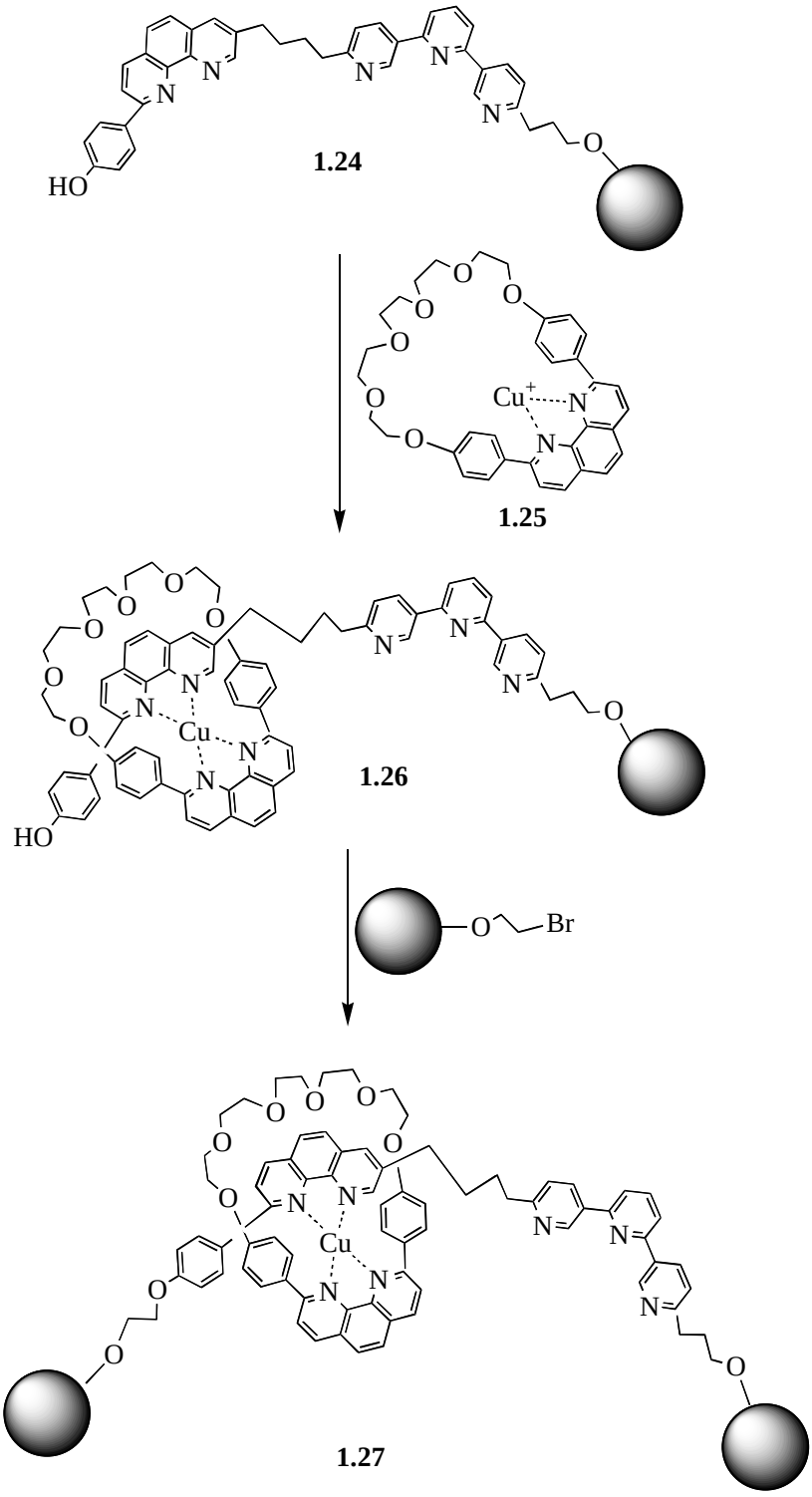


Cyclodextrins' structure and shape

Metal-ligand complexation

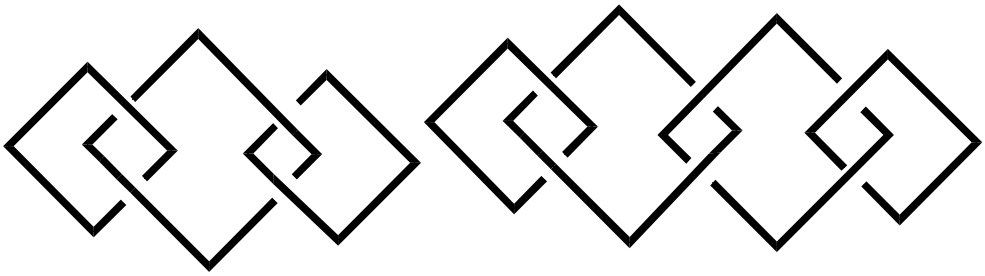
Metal-ligand complexation, especially the complexation between copper (I) and 1,10-phenanthroline (*phen*) derivatives, has been widely employed in Sauvage's group for the preparation of catenanes and molecular knots.[24] Recently, this mechanism was applied in rotaxane synthesis.[25] **1.24** bearing both a host site, a *phen* moiety, and BG complexed with a guest, *phen*-based cyclic **1.25** through Cu^{+}. The complex **1.26** reacted with a bromide BG to produce a thermostable rotaxane **1.27**. The yield of the last step was 40 %; the high yield is expected as metal-ligand complexation is very strong. Similarly, a *phen* linear molecule with both ends bearing reactive groups, e.g., OH, complexed with cyclic **1.25**, too, and the

[22] Review: Szejtli, J. *Cyclodextrin Technology* in *Topics in Inclusion Science* (Ed: Davies, J. E.), Kluwer, Dordecht, **1988**.
[23] (a) Wenz, G.; Bey, E. v. d.; Schmidt, L. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 783. (b) Isnin, R.; Kaifer, A. E. *Pure & Appl. Chem.* **1993**, *65*, 495.
[24] Chasmbron, J.-C.; Dietrich,-Buchecker, C. O.; Sauvage, J.-P. *Comprehensive Supramolecular Chemistry , Vol. 9;* (Ed: Lehn, J. M.) Pergamon Press: Oxford, 1996, 43.
[25] Gavina, P.; Sauvage, J.-P. *Tetrahedron Lett.* **1997**, *38*, 3521.

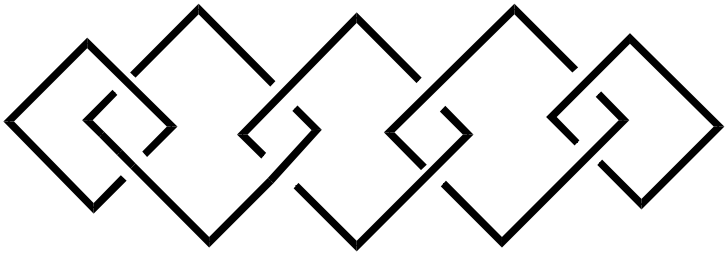

HO
1.24
Cu+
1.25
Cu
HO
1.26
Br
Cu
1.27

complex intermediate underwent cyclization by reaction with difunctional monomers, e.g., tetra(ethylene glycol)-dibromide, to give different catenanes.[24] In addition to simple rotaxanes and catenanes, a lot of very elegant molecular knots were also built by similar approaches. After the desired structures were obtained, products were usually demetallized by applying large excesses of a competitive complexation agent to afford true non-covalent supramolecules.[24]

Self assembly: π-π stacking/charge transfer accompanied by hydrogen bonding and dipole-dipole interaction



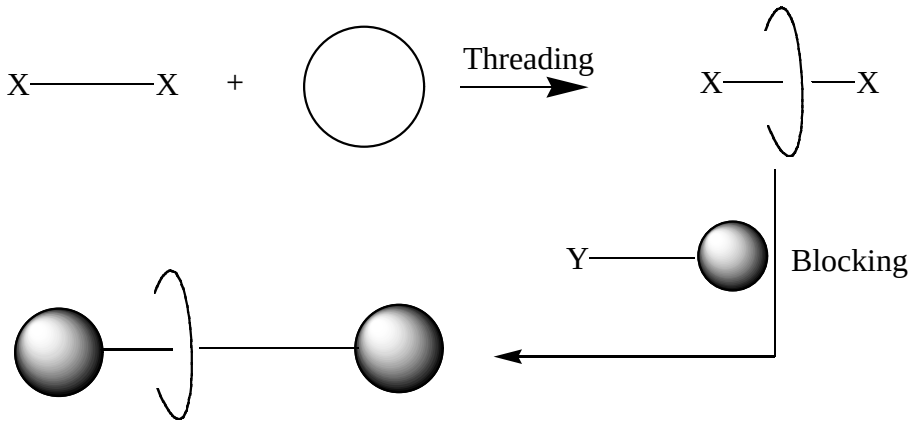
1.28 **1.29**



1.30

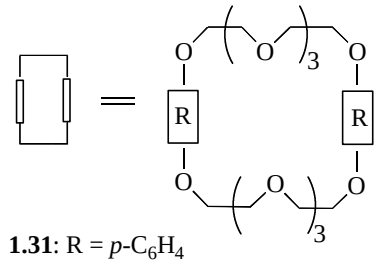
In the late 80's, Stoddart's research group reported the complexation between bisphenylene-based crown ethers (electron rich, donor) and N,N'-bipyridinium salt (electron poor, acceptor).[2c] The association constants were in range of 100 to 1000, depending on solvent, temperature and chemical compositions of the crown ethers. The strong association is a result of combinations of π-π stacking/charge transfer, hydrogen bonding and dipole-dipole interaction. Since then, this complexation has become an effective path for construction of supramolecules. Numerous catenanes,[2c] e.g., [2]catenane **1.1**, [3]catenane

1.28, [4]catenane **1.29** and [5]catenane **1.30** (olympiadane), and rotaxanes have been reported.[2c] However, the following section only concentrates on the recent developments in the rotaxane area related to the present work.



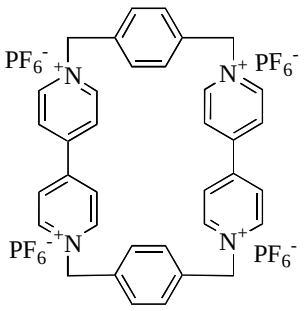
Scheme 1.4 Threading/blocking method

Slipping (Scheme 1.2), clipping (Scheme 1.3) and two-step (threading/blocking) approaches (Scheme 1.4) were employed to synthesize different rotaxanes. As expected, blocking groups were always used to either totally prevent dethreading for the clipping method or to slow down dethreading for the slipping method. For self assembly to occur, the combination of linear and cyclic components often complies to a pair rule, electron-rich/electron-poor, e.g., linear bipyridinium salt vs. phenylene-based crown ethers **1.31**, **1.32** and **1.33** or linear hydroquinone derivative vs. biparaquat cyclophane **1.34**.



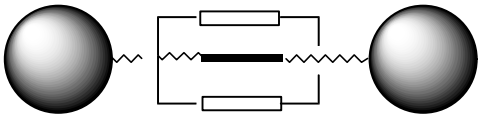
1.31: R = *p*-C_6H_4
1.32: R = *m*-C_6H_4

1.33: R =

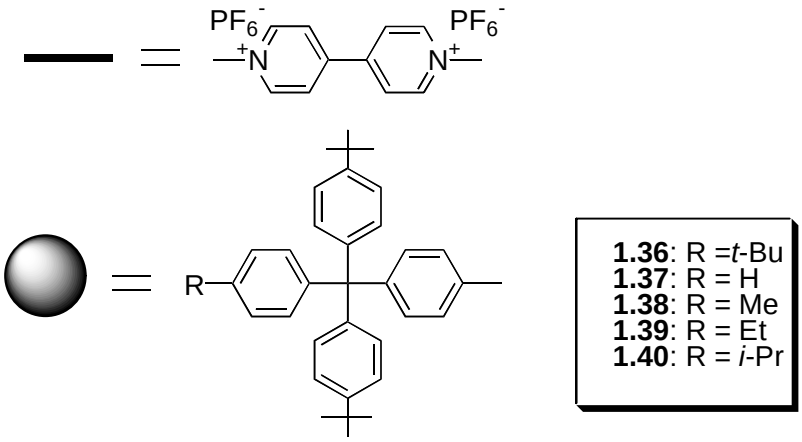


1.34

Rotaxane **1.35** was prepared by threading/blocking approach with **1.36** as the blocking group and **1.31** as the cyclic with yield of 26 %.[26] Similar rotaxanes were also obtained by the slippage approach with different blocking group at the ends. To use the slippage approach, group R in the blocking group was found to be critical. If R was *i*-Pr, no product was obtained. However, **1.35** was prepared in a yield of about 50 % when R was H, Me, or Et. Not surprisingly, the cyclics in these rotaxanes can dethread in DMSO upon heating but only slowly (2 hrs at 100 ^{o}C), and thus these rotaxanes are metastable. By a similar approach, [3]rotaxanes (two cyclics per linear), [4]rotaxanes (three cyclics per linear) were also synthesized with linear molecules bearing two and three bipyridinium moieties between BG.[26] Other interesting rotaxanes are dendritic analogs **1.41**, **1.42**, and **1.43**. They were prepared by a similar approach depicted in Scheme 1.4 with **1.36** as the blocking group.[27]

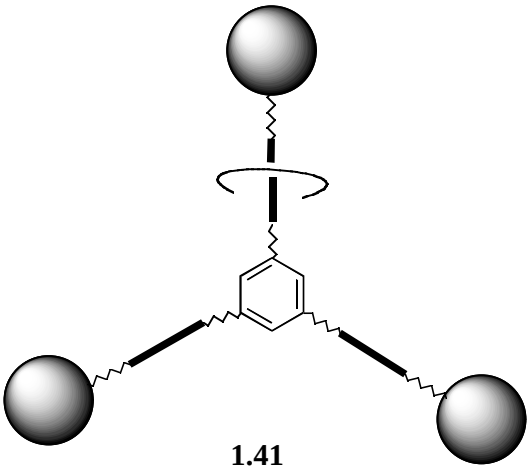


1.35

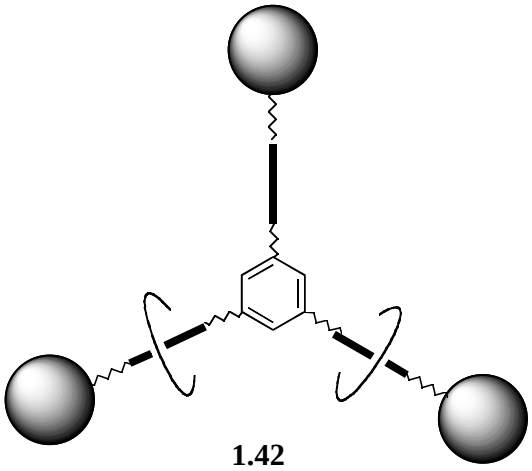


[26] Ashton, P. R.; Ballardini, R.; Balzani, V.; Belohradsky, M.; Gandolfi, M. T.; Philp, D.; Prodi, L.; Raymo, F. M.; Reddington, M. V.; Spencer, N.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1996**, *118*, 4931.

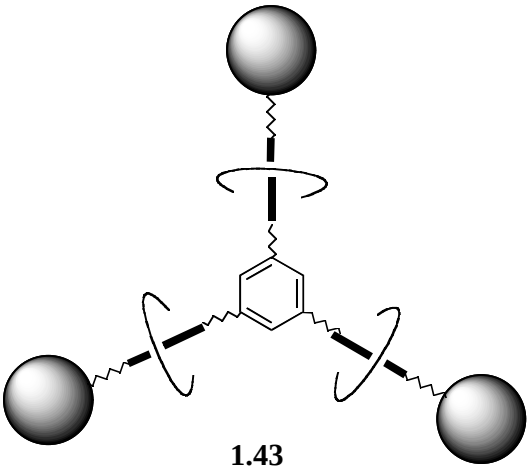
[27] Amabilino, D. B.; Ashton, P. R.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1995**, 751.



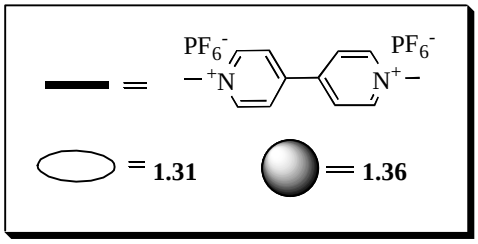
1.41



1.42

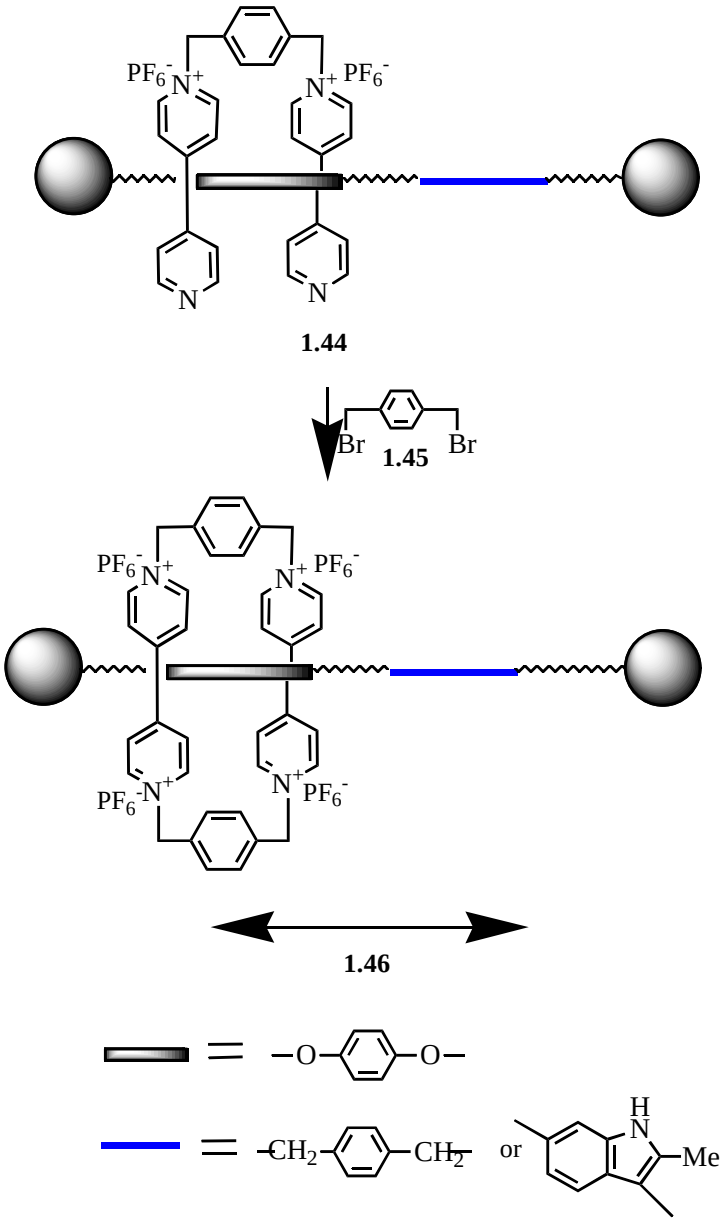


1.43



By introducing different host sites in same linear molecule, molecular shuttles **1.46** were also successfully prepared by clipping the complex intermediate **1.44** with dibromide **1.45**. Because hydroquinone is more electron-rich than other donor host sites, the cyclic in **1.46** spends more time at this site; this was proved by proton NMR studies.[28]

[28] Ashton, P. R.; Bissell, R. A.; Spencer, N.; Stoddart, J. F.; Tolley, M. S. *Synlett.* **1992**, (a) 914; (b) 919 and (c) 923.



1.3 Polyrotaxanes

The concept of a monorotaxane, a non-covalent molecular interconnection, was also applied in the polymer area to prepare its polymeric analog, polyrotaxane. As it is defined, a polyrotaxane is constructed simply by incorporating the rotaxane moiety into a polymer. Because there is no covalent bond between the linear and cyclic components, a polyrotaxane can be viewed as a composite at the molecular level. As shown in Figure 1.2, there are

different types of polyrotaxanes, main chain and side chain polyrotaxanes based on the location of rotaxane moiety, or polypseudorotaxanes and true polyrotaxanes based on their thermostability. Because of its new architecture, a polyrotaxane often exhibits new properties different from conventional polymers. Significant advances have been made in this area over the last decade. The following section is designed to give an overview about the progress; it is divided as cyclodextrin-based, crown ether-based and other cyclic-based polyrotaxanes.

1.3.1 Cyclodextrin-based polyrotaxanes

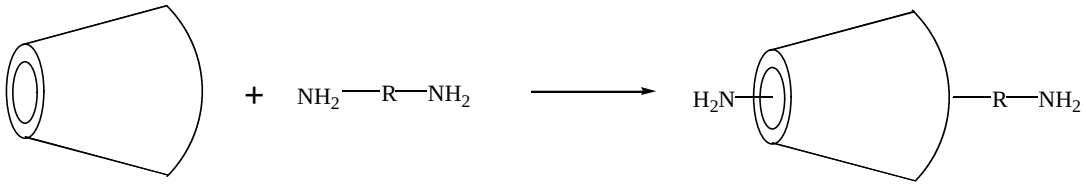
The inclusion complexes of cyclodextrins (CD) with different linear molecules by hydrophilic-hydrophobic interactions provide a strong driving force for threading and afford polyrotaxanes with high threading efficiency.[2] Therefore, CDs have become one of the most common cyclics used in polyrotaxanes.

The CD-based polyrotaxanes reported in 1975 by Otaga were main chain polyrotaxanes of type A" (Figure 1.2), in which β-CD was the cyclic and polyamides were the linear backbones.[29] CD was threaded onto the diamine monomer to afford difunctional rotaxanes **1.47** by mixing both components in water. Interfacial or solution polymerization of **1.47** with diacid chloride gave poly(amide rotaxane)s **1.48** with different backbones. Interestingly, the resultant polyrotaxanes were even soluble in hot water; it was explained by the polarity of the cyclic. However, the extent of threading was not defined and the molecular weight was low.

A couple of years later, Maciejewski also reported a β-CD-based poly(vinylidene chloride rotaxane) by radiation polymerization of a reactive monomer, a complex of CD and vinylidene chloride.[30] After purification, a threading efficiency (m/n value, the average number of cyclic per repeat unit) of 0.34 was achieved. Therefore, the loss of cyclic occurred during purification of the polyrotaxane, boiling in a mixture of hexane and water.

---

[29] Ogata, N.; Sanuim, K.; Wada, J. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *14*, 459.
[30] a) Maceiejewski, M. *J. Macromol. Sci. Chem.* **1979**, *A18(1)*, 77. b) Maciejewski, M.; Gwizdowski, A.; Peczak, P.; Pietrak, A. *J. Macromol. Sci. Chem.* **1979**, *A13(1)*, 87.

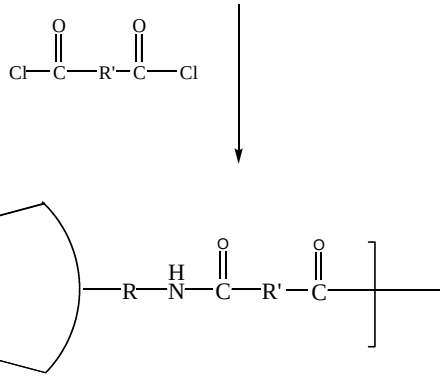


β-CD

1.47

R = $(CH_2)_6$, *m*-$CH_2C_6H_5CH_2$ or *p*-$CH_2C_6H_5CH_2$

R' = *m*-C_6H_5 or *p*-C_6H_5



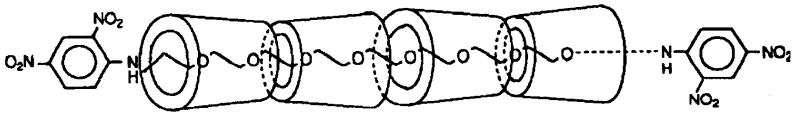
1.48

While these two papers dealt with polypseudorotaxanes without BG at chain ends, Ogino and coworkers prepared a thermostable CD-based polyrotaxane using metal complexes as stoppers.[31] It was found that a linear molecule had to have certain length for threading to occur.

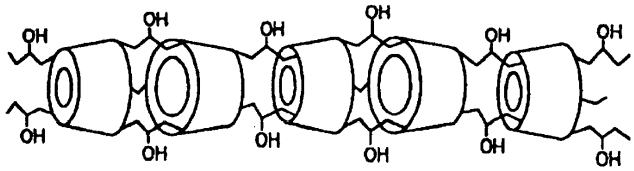
More recently, Harada and coworkers found that CD strongly complexed with various polymeric backbones including poly(ethylene oxide),[32] poly(propylene oxide)[33] and polyisobutylene[34] and thus corresponding polyrotaxanes were prepared simply by mixing a solution of CD and the backbone. Interestingly, the cavity size of CD was found to be a main factor to determine whether threading can occur or not. While one α-CD was threaded onto every two repeat units in poly(ethylene oxide), it was too small for polyisobutylene. On the

[31] Ogino, H.; Ohata, K. *Inorg. Chem.* **1984**, *23*, 3312.
[32] a) Harada, A.; Kamachi, M. *Macromolecules* **1990**, *23*, 2821. b) Harada, A.; Li, J.; Kamachi, M. *Nature* **1992**, *356*, 325.
[33] a) Harada, A.; Okada, M.; Li, J.; Kamachi, M. *Macromolecules* **1995**, *28*, 8406. b) Harada, A.; Kamachi, M. *J. Chem. Soc. Chem. Commun.* **1990**, 1322.
[34] Harada, A.; Li, J.; Suzuki, S.; Kamachi, M. *Macromolecules* **1993**, *26*, 5267.

other hand, every two propylene oxide units complexed with one β-CD but not with α-CD because the cyclic was too small. Moreover, evidence for formation of rotaxane structures, e.g., chemical shift changes of CD upon threading, was also demonstrated. To prevent threaded CD from slipping off the backbone, dinitrophenyl amino moieties were introduced at the chain ends as BG by reaction of dinitrofluorobenzene with the amino end groups of PEO-based polypseudorotaxanes to afford polyrotaxane **1.49**.[32] **1.49** was further reacted with epichlorohydrin in a basic solution to give a tubular structure in which the adjacent CDs were linked together by bridges.[35] Upon cleavage of BG, the linear polymer was removed to afford a molecular "nanotuble" **1.50**.



1.49



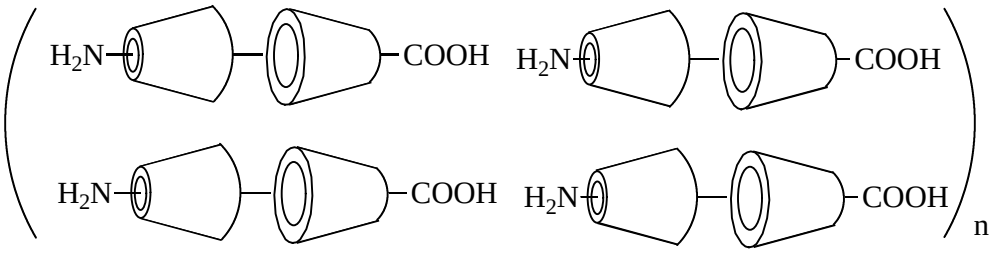
1.50

Wenz and Keller reported α-CD-based polyrotaxanes with poly(iminoundeca-methylene) and poly(iminotrimethylene iminodecamethylene) as backbones by mixing a solution of the corresponding polyammonium ions with CD.[36] The threading process was monitored by proton NMR spectra and viscosity change. The time required for threading varied significantly with the number of methylene moieties between amine groups, from a couple hours to weeks; the slow rate was explained by a hopping process. An individual CD had to find a chain end to thread. Once threaded, it had to move toward the middle of chain to regenerate the site for next ring. This process also explained a slow equilibrium in a dialysis study; disassociation of threaded CD from backbone was slow and not complete even

[35] Harada, A.; Li, J.; Kamachi, H. *Nature* **1993**, *364*, 516.
[36] Wenz, G.; Keller, B. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 197.

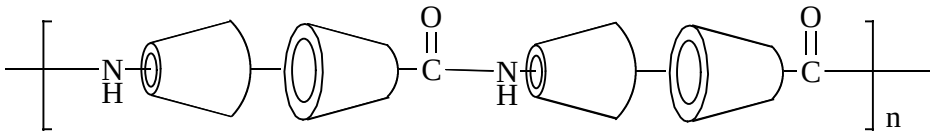
after two weeks. In 1995, Yui et al. demonstrated that this process can be used for controled release.[37]

Steinbrunn and Wenz recently reported poly(amide/CD rotaxane)s **1.52**.[38] First, CD was threaded onto an α,ω-amino acid in water to give monorotaxanes **1.51**. Based on NMR study, two CD molecules were found to be incorporated per linear molecule for 11-aminoundecanoic acid. The X-ray powder pattern indicated that these rotaxanes stacked like a channel in solid state; this provided a basis for solid state polymerization of **1.51**. Indeed, solid polycondensation of **1.51** at about 200 ^{o}C afforded polymeric materials **1.52**. Very interestingly, these polyamides were soluble in water because of the hydrophilic nature of CD. Therefore, the results demonstrated that polyrotaxanes indeed can provide an effective route to modify conventional polymers.



1.51

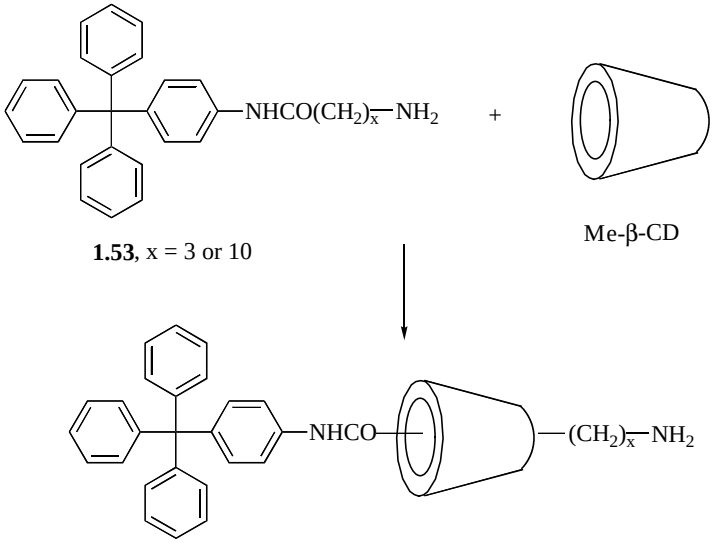




1.52

[37] Ooya, T.; Mori, H.; Terano, M.; Yui, N. *Macromol. Rapid Commun.* **1995**, *16*, 259.
[38] Steinbrunn, M. B.; Wenz, Gerhard *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2139.

In addition to the above main chain polyrotaxanes, CD was also successfully used for the preparation of side chain polyrotaxanes of type C (Figure 1.2). In 1991, Ritter and coworkers reported such a polyrotaxane for the first time.[39] First, 2,6-di-*O*-methyl β-CD was threaded onto a monofunctional BG **1.53** in water or chloroform to afford a monorotaxane **1.54**. **1.54** was characterized by mass spectroscopy and NMR. The isolated intermediate **1.54** was then reacted with a preformed copolymer **1.55** based on poly(methyl methacrylate) in organic solvents to derive side chain polyrotaxanes **1.56**.



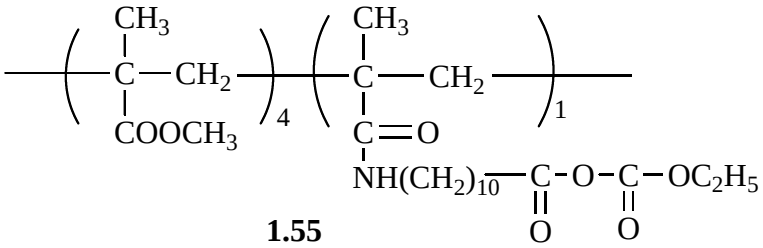
1.53, x = 3 or 10

1.54, x = 3 or 10

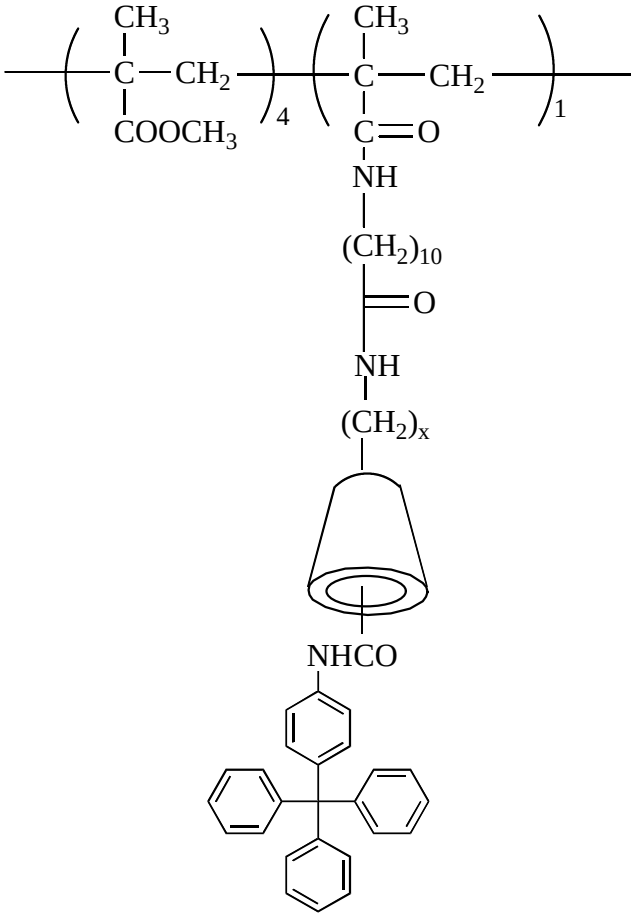
Later on, activated poly(ether-ether-ketone) and poly(ether sulfone) were also chosen as backbones for the corresponding side chain polyrotaxanes.[40] The preparation method was the same as for **1.56** except that the pendant reactive moiety, a carboxylic acid, was introduced at the alkylidene group of the bisphenol units of the backbones. The further extension of the above method derived a new structural side chain polyrotaxane **1.57** called poly(tandem rotaxane), in which two cyclic were threaded per pendant group.[41] The resultant

[39] Born, M.; Ritter, H. *Macromol. Chem. Rapid Commun.* **1991**, *12*, 471.
[40] a) Born, M.; Ritter, H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 309. b) Born, M.; Ritter, H. *Angew. Chem. Int. Ed. Engl.* **1996**, *8*, 149.
[41] Born, M.; Rotter, H. *Adv. Mater*. **1996,** *8*, 149.

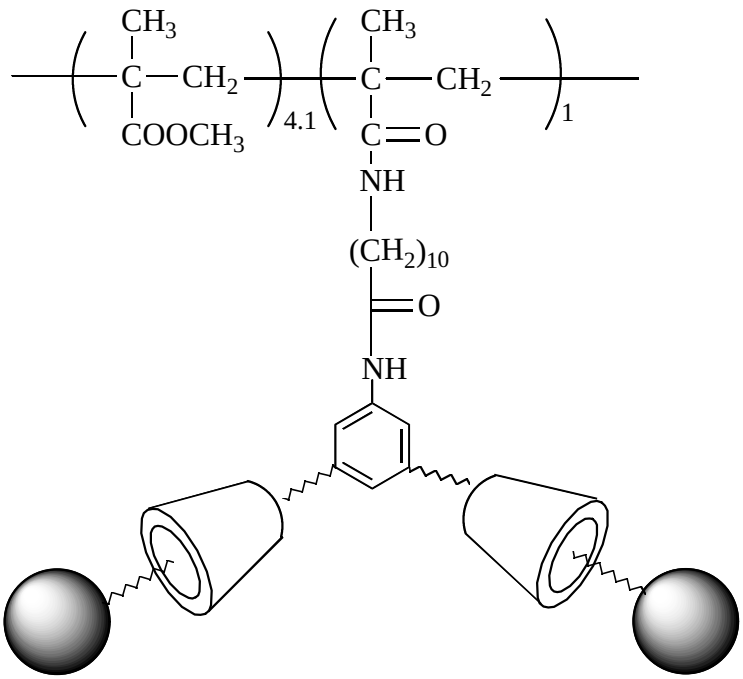
polyrotaxane had a glass transition temperature higher than the corresponding backbone because threaded CD increased the rigidity of the polymer chain; this again demonstrated that conventional polymers can be modified by the formation of polyrotaxanes.



1.55 + **1.54**



1.56



1.57

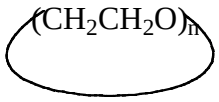
1.3.2 Crown ether-based polyrotaxanes.

As one of most common cyclics used in polyrotaxanes, crown ethers can complex with different metal ions and form hydrogen bonds with acidic protons, e.g., -OH and -NH; this provides the necessary driving force for the formation of polyrotaxanes.[16] Because these crown ethers are soluble in almost any organic solvent and even in water for aliphatic ones, they are compatible with various polymerization conditions and thus broaden the scope of polyrotaxanes in terms of synthesis methods and types of backbones. Also their good solubility insures an easy purification procedure; unthreaded species can be easily removed by precipitation.[2,42]

Different crown ethers, 30-crown-10 (30C10), 42-crown-14 (42C14), 48-crown-16 (48C12) and 60-crown-20 (60C20) were successfully employed in various polyrotaxane

[42] Gibson, H.; Marand, H. *Adv. Mater*. **1993**, *5*, 11.

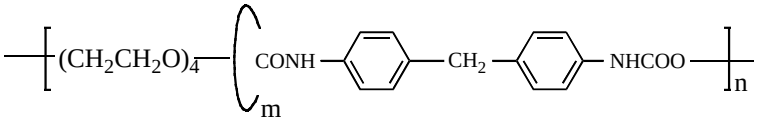
syntheses including polyurethane, polyester, polystyrene, polyamides and poly(arylene ether)s.[42-50]



30C10: n = 10 **42C14**: n = 14
48C16: n = 16 **60C20**: n = 20
18C6: n = 6

Crown ethers

Poly(urethane crown ether rotaxane)s **1.58** were reported in 1994. They were prepared by solution polycondensation using crown ether as solvents.[43] Without any BG,

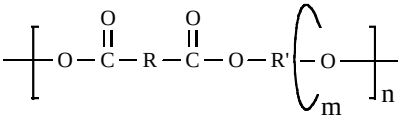


1.58

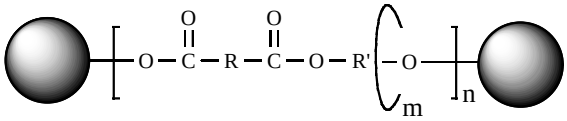
1.58 were main chain polypseudorotaxanes. They were purified by multiple precipitations into a solvent good for the crown ethers but poor for the backbone. The effective removal of unthreaded cyclics was demonstrated by a model study based on 18-crown-6 (18C6) whose size is too small to thread. The authors also recognized that threading efficiency was affected by two factors: ring size and the feed ratio of the cyclic vs. diol monomer; the larger the ring was and the higher the ratio was, the higher the threading efficiency was. While the hydrogen bonding between the crown ethers and OH groups of diol monomers may be a driving force for threading, a statistical threading model and statistical calculation method for the equilibrium constant were applied in this paper. Indeed, the data from the studies of ring size

[43] Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.* **1994**, *116*, 537.
[44] Marand, E.; Hu, Q.; Gibson, H. W.; Veytsman, B. *Macromolecules* **1996**, *29*, 2555.
[45] Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc.* **1995**,*117*, 852.
[46] Gibson, H. W.; Liu, S.; Gong, C.; Ji, Q.; Joseph, E. *Macromolecules,* **1997**, *30*, 3711.
[47] Gibson, H. W.; Liu, S. *Macromol. Symp.* **1996**, *102*, 55. [48] Bheda, M. C. *Ph.D. Dissertation* Virginia Polytechnic Institute and State University, **1992**.
[49] a) Engen, P. T. *Ph.D. Dissertation*, Virginia Polytechnic Institute and State University, **1991**. b) Lee, S.-H. *Ph.D. Dissertation*, Virginia Polytechnic Institute and State University, **1996**.
[50] Gibson, H. W.; Engen, P.T.; Lee, S. H.; Liu, S.; Marand, H.; Bheda, M. C. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1993**, *34(1)*, 64.

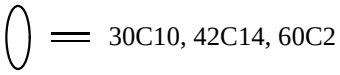
and the feed ratio effects did not afford a conclusion about the threading mechanism. It was also found that the resultant polyrotaxanes had better solubility than backbones; some of them were even soluble in water! Moreover, these polyrotaxanes had only one glass transition temperature and thus were molecular composites. While the authors did not address the role of intraannular hydrogen bonding between the threaded crown ether and the in-chain NH groups, this was elucidated by Marand et al.[44]



1.59



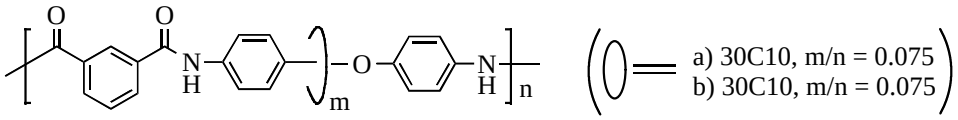
1.60



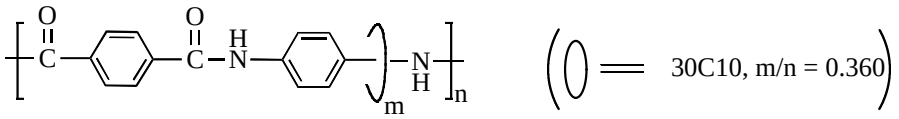
Similarly, poly(ester crown ether rotaxane)s **1.59** were also prepared using crown ethers as solvents by diacid chloride and transesterification methods.[45] In order to prevent dethreading, BG's were incorporated at chain ends to afford thermostable polyrotaxanes **1.60**. As revealed in the preparation of poly(urethane rotaxane)s, the larger the ring was, the higher the threading efficiency was. Different from poly(urethane rotaxane)s **1.58**, **1.59** and **1.60** with polyester backbones exhibited two melting temperatures corresponding to those of the crown ether and the backbone; this was attributed to the fact that threaded cyclic can move along the backbone because no apparent interaction between the backbone and the cyclics exists.

Attempting to prove hydrogen bonding to be the driving force for crown ether-based polyrotaxanes, more detailed studies in terms of threading efficiency (m/n) were performed with polyester backbones.[46,47] In summary, the following relationships were found: m/n a)

was independent of the length of monomer; b) increased with the ring size; c) increased with the feed ratio of the cyclic vs. diol monomer and d) did not change with polymerization temperature. However, these results could still not give any conclusions about the threading mechanism because the lack of temperature dependence was contrary to H-bonding theory while other results were in agreement with the hypothesis. Based on dethreading studies, polypseudorotaxanes **1.59** were found to be very stable; the dethreading rate was 1.0×10^{-2} %/day; the random coil conformations of the polymers may be the cause. A common method for CD-based polyrotaxanes, threading cyclic onto preformed polymer, was also tested in this system, but only very little was threaded (m/n = 1.3×10^{-2} for 42C14). Despite the fact that the crown ethers in the polyrotaxanes **1.59** and **1.60** were already occupied by the backbone, they still complexed with different metal ions, Na^+, K^+, Ca^{++} and Cs^+. This result is very important because it implies new applications for polyrotaxane as metal ion transport or separation materials. In terms of the properties, the intrinsic viscosities and the melt viscosities of these polyrotaxane were measured. Compared to the backbone, polyrotaxanes had lower absolute melt viscosity because of less entanglement but higher intrinsic viscosity because of increased hydrodynamic volume.



1.61



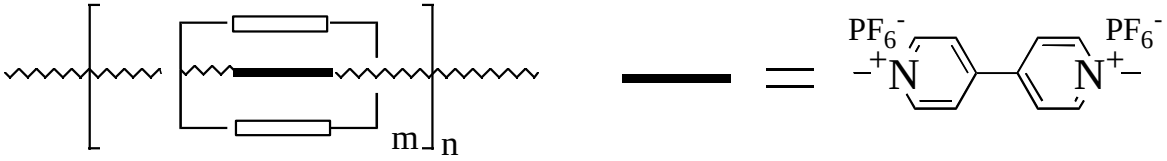
1.62

Polyamide rotaxanes **1.61** were reported by Bheda and Gibson with 30C10 or 60C10 as the cyclic from polymerization of isophthalic acid and bis(p-aminophenyl)ether.[48] Threading efficiency was lower compared to polyurethane and polyester systems. They also prepared a polyrotaxane **1.62** with Kevlar backbone by reaction of terephthalic acid and p-

phenylenediamine in the presence of 30C10. According to solid state NMR, m/n reached 0.36 (57 % by weight)! However, because these polyrotaxanes were not soluble in common solvents, unthreaded cyclic was removed only by washing. Thus some detected cyclics may be the trapped species.

By free radical polymerization, a family of polystyrene rotaxanes[49] and polyacrylonitrile rotaxanes[50] were synthesized using various crown ethers. To prevent dethreading, a bulky azo initiator was used which incorporated BG at the chain ends. These backbones provided no attractive forces for the crown ethers and thus threading was purely statistical. As expected, threading efficiency was low relative to polycondensation systems.

As demonstrated by Stoddart's group, bisphenylene-based crown ether can complex with 4,4'-bipyridinium salts. This complex was utilized in the construction of polypseudorotaxane **1.63** using BPP34C10 as the cyclic and a copolyurethane bearing bipyridinium moiety as the backbone. This was the first example of a self assembly derived polyrotaxane.[51]



1.63

More recently, poly(arylene ether) rotaxanes were prepared using 42C14 as cosolvent.[52] The complex between the metal counter ions and the crown ether was believed to be driving force for effective threading. However, rotaxanation did not improve the solubility of the polymer.

[51] Gibson, H. W.; Liu, S.; Shen, Y. X.; Bheda, M. C.; Lee, S.-H.; Wang, F *NATO ASI Series*, Kluwer Acad. Pub., Dordrect, the Netherlands, Series C, Vol. 456 **1995**, pp. 41.
[52] Xie, D. *Ph.D. Dissertation*, Virginia Polytechnic Institute and State University, **1997**.

1.3.3 Other cyclics-based polyrotaxanes

Hodge et al. studied the complexation of tetracationic cyclophane cyclobis(paraquat-phenylene) **1.34** with several preformed polymers bearing hydroquinol ether linkages in acetone; this leads to polypseudorotaxanes similar to **1.63**.[53] Since the complexation was governed by equilibrium, as expected, threading efficiency increased at lower temperature according to a proton NMR study; an m/n value of 0.94 was reached at -40 ^{o}C despite of the existence of electrostatic repulsion between adjacent threaded cyclophanes. Resorting to proton NMR techniques, Parsons et al. studied a similar system in more detail in terms of the threading process and molecular motion.[54] They found that some cyclophanes exchanged rapidly between the polymer chain ends and solution relative to the NMR time scale while some were locked on polymer chain. These two papers demonstrated that self assembly provided a very strong driving force for threading and was important in polyrotaxane synthesis. However, the above work only dealt with solution state and no solid state properties of the polyrotaxanes were reported.

Metal-ligand complexation was also employed for polyrotaxane synthesis.[55] In this paper, the authors attached a pyrrole moiety at both ends of a linear species bearing a phenanthroline moiety in-between. Then the linear molecule was complexed with a *phen*-based cyclic **1.25** through Co^{++} to afford a reactive monorotaxane. By grafting the preformed monorotaxanes with pyrrolic nuclei, a polymeric network was obtained by electropolymerization and thus the cyclic was trapped in the network. Interestingly, in this network, Co^{++} can still dissociate from the polymer and then the polymer can reassociate with Cu^{+}. This reversible metal exchange process was readily monitored by cyclic voltammetry.

1.4 Summary and conclusions.

As noted in the above sections, rotaxanes and polyrotaxanes, non-covalent supramolecules, have drawn great interest from scientists world-wide. They are novel in

[53] Owen, J.; Hodge, P. *J. Chem. Soc., Chem. Commun.* **1997**, 11.
[54] Mason, P. E.; Parsons, I. W.; Tolley, M. S. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2238.
[55] Kern, J.-M.; Sauvage, J.-P.; Bidan, G.; Billon, M.; Divisia-Blohorn, B. *Adv. Mater.* **1996**, *8*, 580.

terms of both topology and ultimate properties relative to chemically bonded small molecules and polymers.

Various monorotaxanes have been prepared by statistical, chemical conversion and templating approaches. Since no attractive force exists between a linear species and the cyclic components, as expected, the statistical approach is not feasible in terms of yield. Chemical conversion always involves multiple steps and thus is time consuming.

Templating methods can be divided into sub-classes according to the sources, including hydrogen bonding, metal-ligand complexation, hydrophilic-hydrophobic interaction and self assembly. All these interactions provide strong driving forces for threading and are effectively applied for the preparation of monorotaxanes by different procedures, threading/blocking, slipping and clipping.

Polyrotaxanes, side chain and main chain, or polypseudorotaxane and true polyrotaxanes, are the polymeric analogs of monorotaxanes. CD and crown ethers have been the most common cyclics successfully threaded onto polymeric backbones. Only a few polyrotaxanes are based on other macrocycles, e.g., phenanthroline-based cyclics and bisparaquat cyclophane.

While the threading mechanism of CD-based polyrotaxanes was understood to be inclusion complexation, that of crown ether-based polyrotaxanes based on polycondensation methods remained unsolved; the threading efficiency dependencies on the feed ratio of the cyclic vs. diol monomer, the length of monomer and the ring size were in agreement with hydrogen bonding theory but the lack of temperature dependence was contrary to the hypothesis but rather compatible with a statistical mechanism.

Most of the CD-based polyrotaxanes were prepared by threading CD onto a preformed polymer because CD is only soluble in polar solvents or water and not compatible with lots of polymerization conditions. On the other hand, aliphatic crown ethers are soluble in water and most organic solvents (except hexane for larger crown ethers). Therefore, they have broadened the scope of polyrotaxanes in terms of both polymerization conditions and types of backbones. However, they were always threaded as solvent onto polymeric backbones during polymerization.

Because of their novel topologies, polyrotaxanes often exhibit different properties from conventional polymers. It was noticed that solubility, intrinsic viscosity, melt viscosity, glass transition, melting temperature and phase behavior can be altered by the formation of polyrotaxanes. The detailed changes are related to both the properties of the threaded cyclics and the backbone and the threading efficiency.

While various polyrotaxane types were conceived, to date, only polyrotaxanes of type A and type C were reported (Figure 1.2). Since the properties of a polymer are always related to its structure, new polyrotaxanes of type B and type D are worth study; this may provide more interesting results about the relationship of the properties vs. structures. In addition, so far, polyrotaxanes have been restricted to linear backbones. Thus exploring the possibility of extension of this concept into three dimensional polymeric materials, hyperbranched and cross-linked polymers, is interesting and important in terms of the construction of new structures and inducing new properties.

Chapter 2
Research Objectives and Scopes

The objectives of this research are to identify the threading and dethreading mechanisms for crown ether-based polyrotaxanes, apply these mechanisms for the construction of new topological polymers, design and prepare new types of main chain, side chain and three dimensional network polyrotaxanes by self assembly and synthesize other crown ether-based polyrotaxanes with versatile backbones.

The syntheses of new diol and diacid chloride blocking groups as well as their derived polyester rotaxanes with 30C10 as the cyclics are described in Chapters 3-5. By using these BG to decrease or diminish dethreading during polymerization and comparing with those systems without BG or with monofunctional BG, threading and dethreading mechanisms are explored for crown ether-based systems. New spectroscopic evidences for the formation of polyrotaxanes are also reported.

To study the effect of in-chain hydrogen bonding sites, e.g., NH, on the threading process, polyurethane rotaxanes are prepared by both polymerization using the crown ethers as solvent and threading the crown ethers onto a preformed polyurethane; this is described in Chapter 6. The microstructures and the properties of the resultant polyrotaxanes are also discussed in the section.

By applying the threading mechanism elucidated in Chapters 3-6, the synthesis of hyperbranched and crosslinked poly(methyl methacrylate crown ether)s and poly(urethane crown ether)s, by a pendant group modification reaction of a preformed poly(methacryloyl chloride) with a monohydroxy crown ether and by polymerization of a dihydroxy crown ether and diisocyanate, respectively, are reported in Chapters 7-8. Controlling the polymer topology and polydispersity by polymerization conditions is also demonstrated.

With the complexation of metal ion and crown ethers, some poly(arylene ether/“42C14”rotaxane)s were prepared and described in Chapter 9. Interestingly, the threaded crown ethers were very mobile at room temperature as proved by CP ^{13}C solid state

NMR spectra; this findings provides basis for understanding mechanical and thermal properties of these materials.

New main chain polyrotaxanes were constructed by self assembly of a polymeric crown ether, poly(sebacate crown ether), and a linear 4,4’-bipyridinium salt in solution. The factors governing threading efficiency are also studied. In addition, by a self assembly process, a three dimension polyrotaxane, an interpenetrating network from two preformed polymers bearing 4,4’-bipyridinium salt moieties and crown ether units, respectively, is explored. The reversibility of the structure is also studied by varying the solvent system and temperature. The results are presented in Chapter 10.

Chapter 3

A Diol Blocking Group-based Poly(ester/crown ether rotaxane)s

3.1 Introduction

Polyrotaxanes are new polymeric materials with novel architectures in which macrocycles are threaded onto a linear polymeric backbone.[1] Upon introduction of different cyclic molecules, the properties of a polymer are expected to be altered on purpose. Two main classes of polyrotaxanes have been widely studied in recent decades; cyclodextrin-based[2-4] and crown ether-based.[5-9]

Preparation of different crown ether-based polyrotaxanes is one of the main goals we are pursuing.[5-9] The most popular method employed in our lab is polycondensation with a crown ether as solvent (Scheme 3.1).[6,7] By this approach, different polyrotaxanes **3.4**, e.g., polyester[7] and polyurethane[6] rotaxanes with 30C10, 42C14 and 60C20 as macrocyclic components were obtained. Since threaded crown ether molecules can move along the polymeric backbone, they can slip off the backbone during the preparation period, especially while the polymer is of low molecular weight. Therefore, different monofunctional bulky

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[1] a) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843-945. b) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.*, **1995**, *95*, 2725-2828. c) Philp, D.; Stoddart, J. F. *Angew. Chem. Int. Engl.* **1996**, *35*, 1154-1196. d) Gibson, H. W. in *Large Ring Molecules*; Semlyen, J. A., ed.; J. Wiley and Sons: New York, **1996**, 191-262.

[2] a) Li, J.; Harada, A.; Kamachi, M. *Polym. J.* **1994**, *26*, 1019. b) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1994**, *27*, 4538. c) Harada, A.; Okada, M.; Li, J.; Kamachi, M. *Macromolecules*, **1995**, *28*, 8406.

[3] a) Born, M.; Ritter, H. *Angew. Chem. Int. Engl.* **1995**, *34*, 309-311. b) Born, M.; Ritter, H. *Adv. Mater.* **1996**, *8*, 149-151. c) Born, M.; Ritter, H. *Macromol. Rapid Commun.* **1996**, *17*, 197-202.

[4] a) Weickenmeier, M.; Wenz, G. *Macromol. Rapid. Commun.* **1996**, *17*, 731-736. b) Steinbrunn, M. B.; Wenz, G. *Angew. Chem. Int. Engl.* **1996**, *35*, 2139-2142.

[5] Gibson, H. W.; Marand, H. *Adv. Mater.* **1993**, *5*, 11.

[6] Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.* **1994**, *116*, 537.

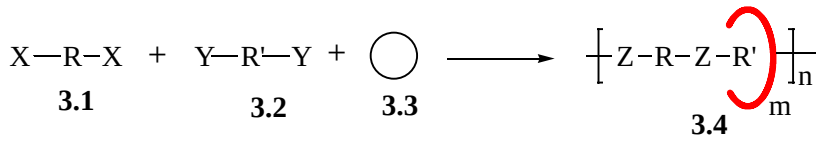
[7] Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc.* **1995**, *117*, 852.

[8] Loveday, D.; Wilkes, G. L.; Bheda, M. C.; Shen, Y. X.; Gibson, H. W. *J Macromol. Sci.* **1995**, *A32(1)*, 1.

[9] Marand, E.; Hu, Q.; Gibson, H. W.; Veytsman, B. *Macromolecules*, **1996**, *29*, 2555.

"blocking groups" (BGs) were prepared[10] to lower the extent of dethreading and thus increase threading efficiency (m/n values). Using these BGs, polyrotaxanes of type **3.6** (Scheme 3.2) were prepared and had an average m/n value indeed higher than that without BG.[7] However, the molecular weight of polymer is limited by introduction of these BGs and dethreading can still occur during the polymerization period because of the existence of some macromolecules with only one end blocked (**3.6a**) and/or no end blocked (**3.4**) as shown in Scheme 3.2. Additionally, in both polyrotaxanes **3.4** and **3.6**, threaded macrocycles can accumulate to form a separate phase.[7]

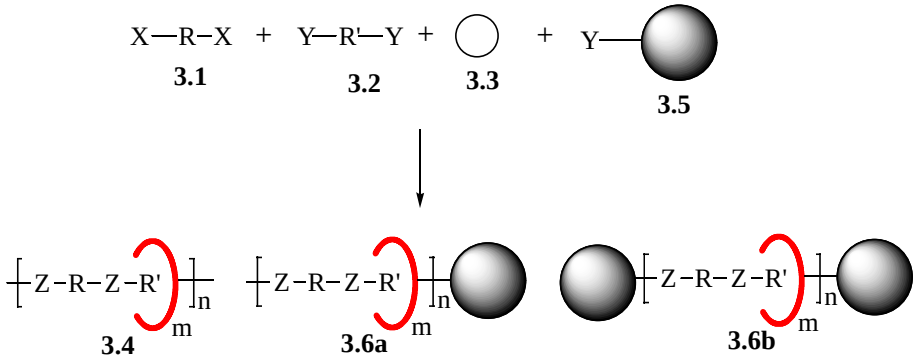
Scheme 3.1



3.1 **3.2** **3.3** **3.4**

Where X + Y = Z, e.g., X = COCl, Y = OH and Z = COO;
3.3: macrocycles, e.g., 30C10; **3.4**: polyrotaxane

Scheme 3.2



3.1 **3.2** **3.3** **3.5**

3.4 **3.6a** **3.6b**

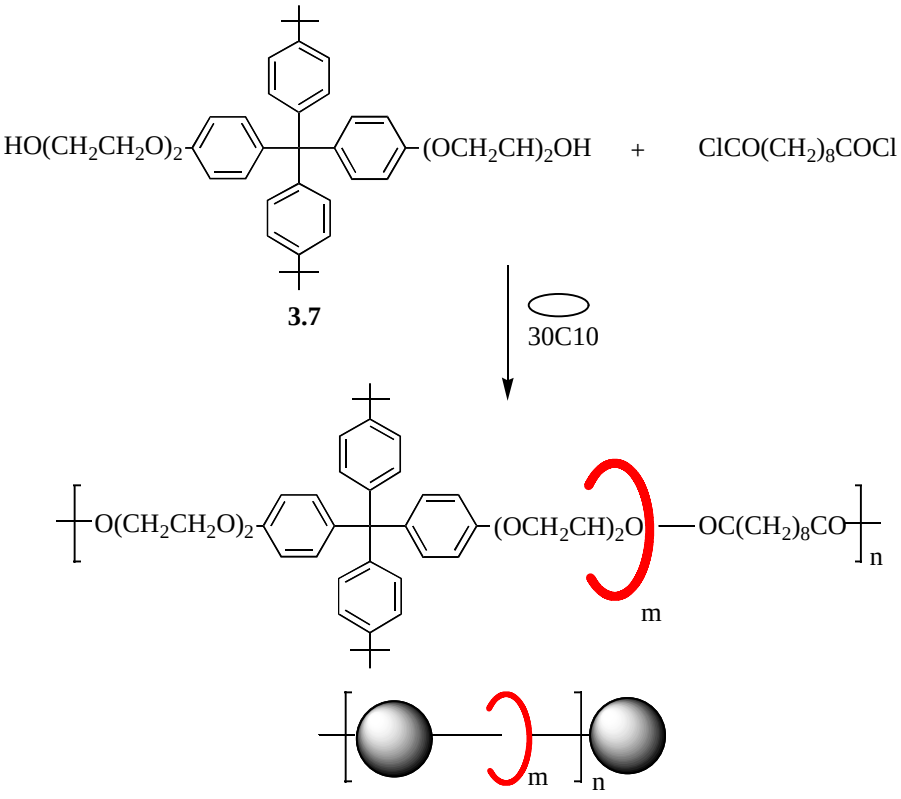
Where X + Y = Z, e.g., X = COCl, Y = OH and Z = COO;
3.3: macrocycles, e.g., 30C10; **3.4**: polyrotaxane

In this chapter, I report the synthesis and characterization of a new difunctional blocking group (diol BG **3.7**) and its derived polyrotaxane **3.8** with a novel architecture, in which threaded macrocycles are confined between stoppers (Scheme 3.3). In addition, the

[10] Gibson, H. W.; Lee, S.-H.; Engen, P. T.; Lecavalier, P.; Sze, J.; Shen, Y. X.; Bheda, M. *J. Org. Chem.* **1993**, *58*, 3748.

dependencies of m/n values of polyrotaxane **3.8** on the polymerization temperature and the feed ratio of the cyclic vs. diol monomer were studied.

Scheme 3.3



3.8: m/n > 0
3.9: m/n = 0

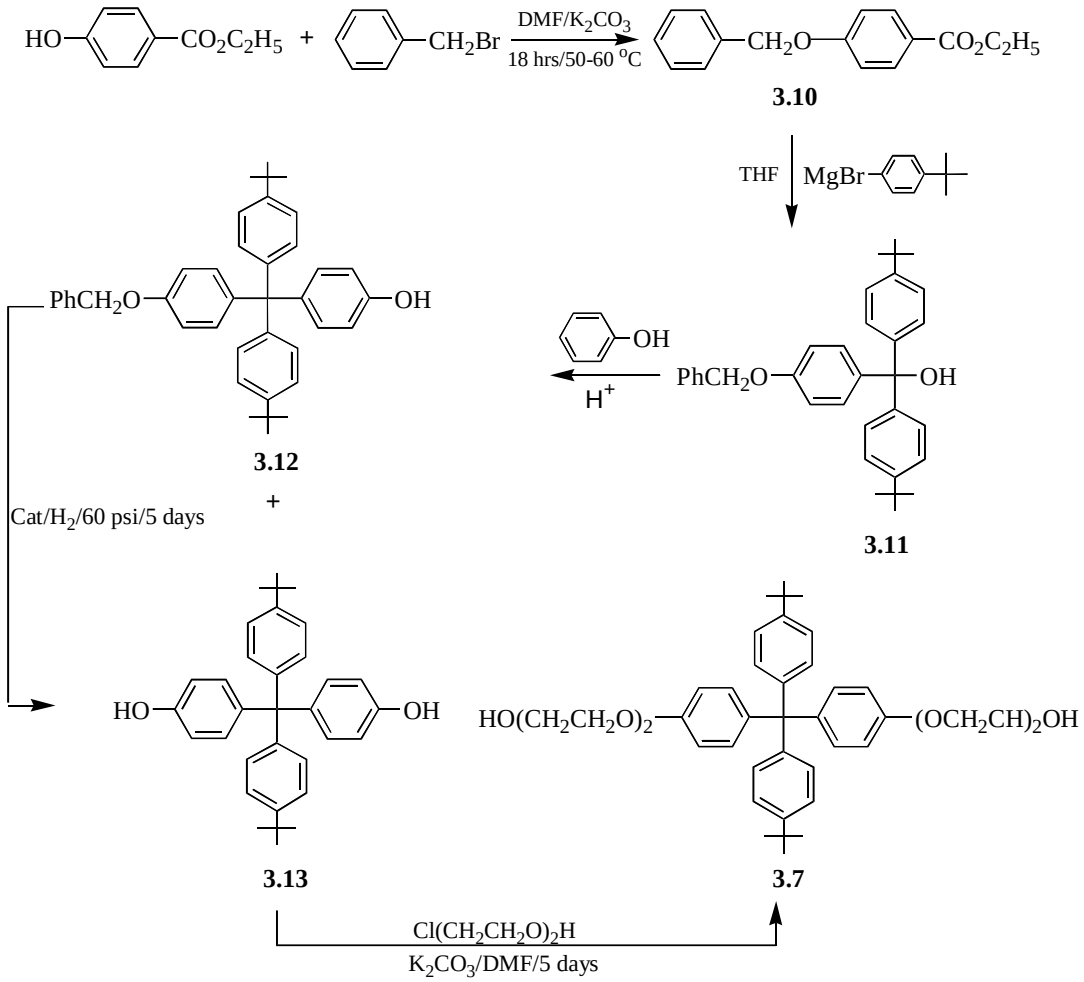
3.2 Results and discussion

3.2.1 Synthesis of diol functionalized blocking group 3.7

Diol BG **3.7** was synthesized by a five step approach shown in Scheme 3.4. The first step was to protect the hydroxyl group of ethyl 4-hydroxybenzoate with benzyl bromide in DMF solution, using excess potassium carbonate as base. **3.10** was obtained in 79% yield. **3.10** was converted to tertiary alcohol **3.11** by a Grignard reaction. In this case, to initiate the reaction, heating the system is needed due to the low reactivity of *p*-bromo-*tert*-

butylbenzene and further refluxing is necessary to increase the reaction rate.[10] **3.11** was purified by recrystallization with yield of 62%.

Scheme 3.4



Following the approach used by Mikroyannidis in the preparation of bis(*p*-hydroxyphenyl)diphenylmethane[11] and later by us with other difunctional BGs,[12] compound **3.11** underwent Friedel-Crafts reaction by refluxing in a large excess of phenol with acid as a catalyst. Because of the steric effect, only the para substitution product was formed. Interestingly, in addition to compound **3.12** (34 %), deprotected product **3.13** was obtained

[11] Mikroyannidis, J. A. *Eur. Polym. J.* **1995,** *10*, 895.
[12] Liu, S.; Shen, X. Y.; Gibson, H. W. *J. Org. Chem.* **1995**, *60*, 3155.

with a fairly high yield (28%). The *in situ* deprotection of the benzyl ether group in this reaction is probably due to an acid induced ether cleavage and/or ether exchange since a large excess of phenol exists in the system. **3.12** was quantitatively deprotected by hydrogenation with Pd/C as catalyst.[13] The structure of compound **3.13** is analogous to that of bisphenol-A. It can be used for the preparation of poly(arylene ether rotaxane)s.

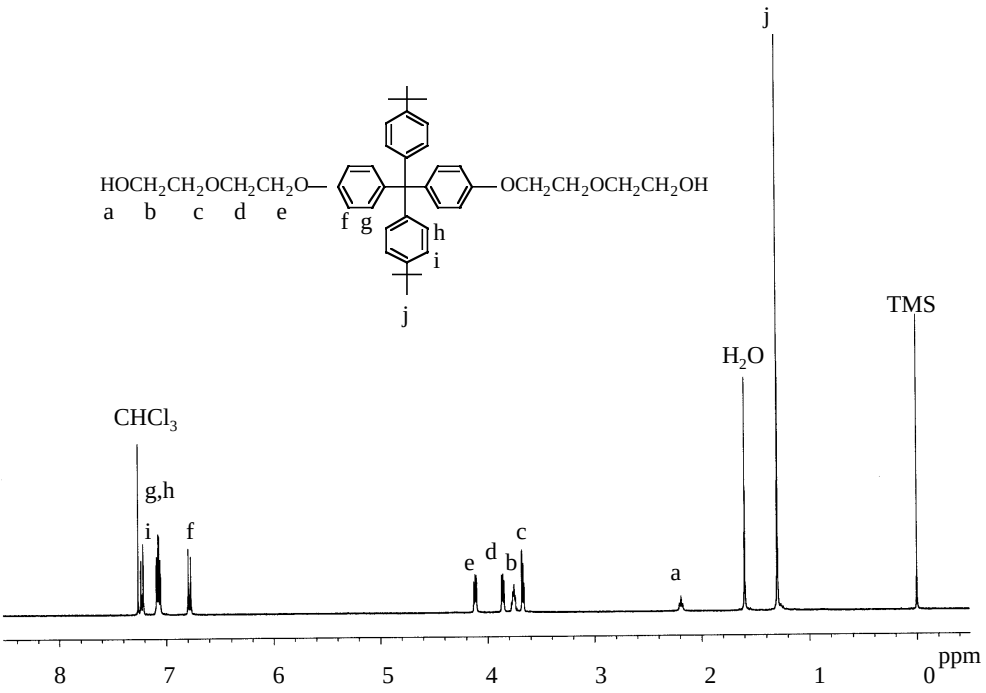


Figure 3.1 The 400 MHz proton NMR spectrum of diol BG 3.7 in $CDCl_3$ at 25 °C

I also wish to have an aliphatic hydroxyl-terminated difunctional BG. Therefore, **3.13** was allowed to react with an excess of 2-(2-chloroethoxy)ethanol in DMF at 70-80 °C, using potassium carbonate as a base, to afford diol BG **3.7** in 63% yield. All new compounds were identified by ^{13}C NMR, ^{1}H NMR (Figure 3.1 for **3.7**), melting point and elemental analysis. Harrison investigated the steric influence of various monofunctional blocking groups and found that tris(*p-tert*-butylphenyl)methanol could constrain macrocycles comprised of up to

[13] Carpino, L. A.; Han, G. Y. *J. Org. Chem.* **1972**, *37*, 3404.

42 methylene groups.[14] Therefore, compound **3.7** is large enough to block 30C10 and thus its derived polyester rotaxanes were studied.

3.2 Synthesis and characterization of diol BG-based polyrotaxanes 3.8

Polyrotaxane **3.8** was synthesized by a polycondensation with 30C10 as solvent (Scheme 3.3). Unthreaded 30C10 was removed by three precipitations from THF solution into water.

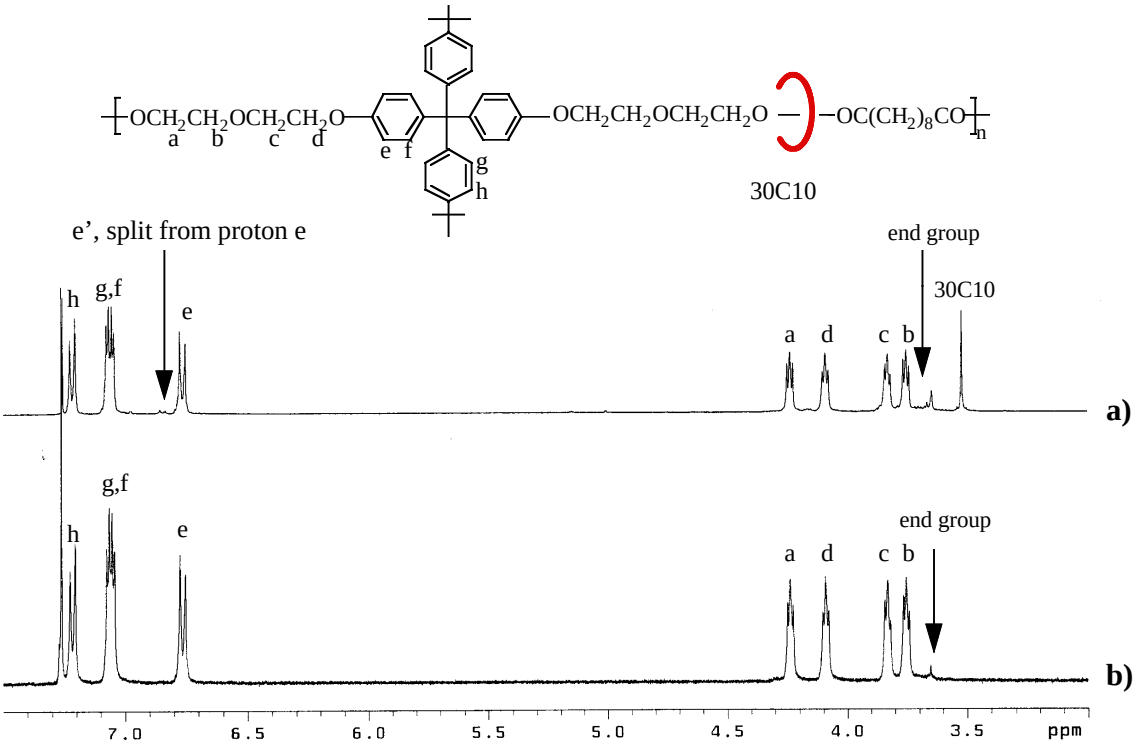


Figure 3.2 The 400 MHz proton NMR spectra of a) top, polyrotaxane **3.8** and b) bottom, model polyester **3.9** in $CDCl_3$ at 25 °C

Surprisingly, compared to that of model polymer **3.9**, a new signal (δ3.52) appeared instead of the signal (δ3.67) of free 30C10 in the ^{1}H NMR spectrum of **3.8** (Figure 3.2). Since no chemical shift change has been previously reported for polyrotaxanes based on aliphatic crown ethers,[5-9] how do we explain the new peak? To answer this question, we hydrolyzed the polyrotaxane by refluxing it in a basic solution. The dried reaction products

[14] a) Harrison, I. T.; Harrison, S. *J. Am. Soc. Chem.* **1967**, *89*, 5732. b) Harrison, I. T. *J. Chem. Soc., Chem. Commun.* **1972**, 231. c) Harrison, I. T. *J. Chem. Soc., Perkin Trans. I* **1974**, 301.

were extracted with chloroform to separate the neutral compounds from sebacic acid potassium salt. As shown in the proton NMR spectrum of neutral hydrolytic products (Figure 3.3, middle), the free 30C10 signal (δ3.67) returned and the δ3.52 signal disappeared, which indicated that the new signal in polyrotaxane **3.8** was indeed due to threaded 30C10. In addition, by extracting the neutral hydrolytic products with hexane, pure 30C10 was recovered (75%) (Figure 3.3, top).

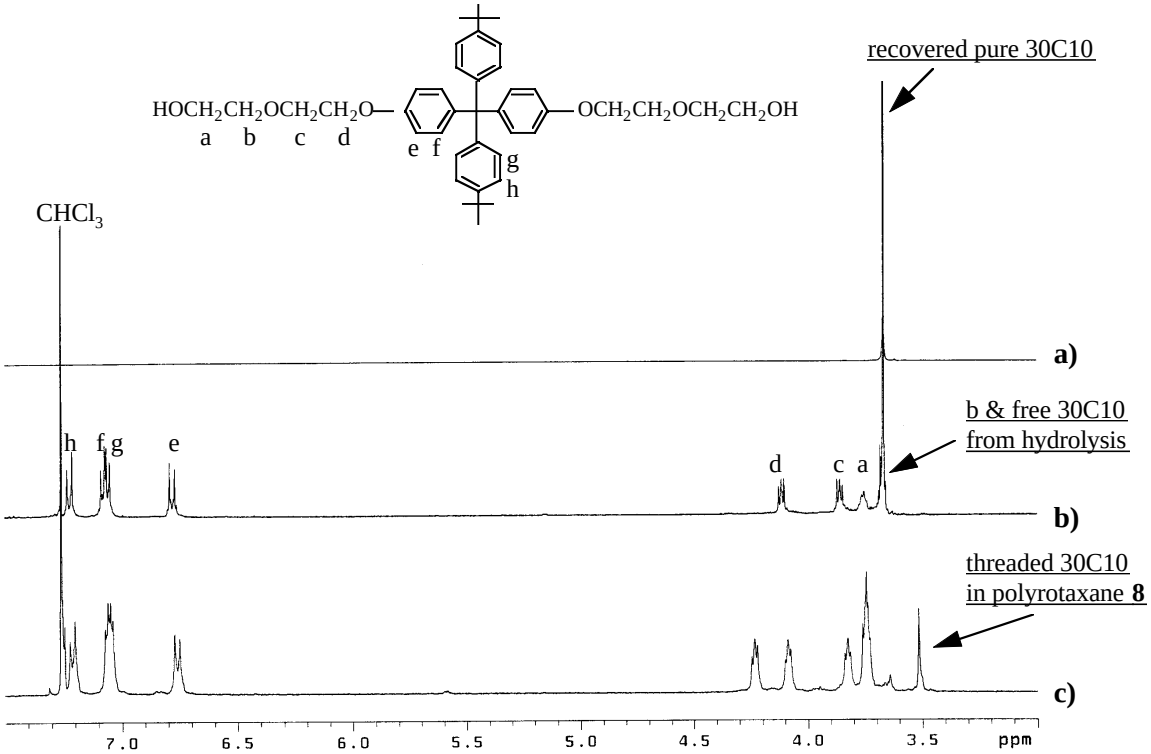


Figure 3.3 The 400 MHz proton NMR spectra of a) top, recovered 30C10, b) middle, the neutral hydrolytic products and c) bottom, polyrotaxane **3.8** in $CDCl_3$

What causes the upfield shift of the protons of 30C10 in polyrotaxane **3.8**? According to the COSY spectrum of polyrotaxane **3.8** (Figure 3.4), there is no interaction between the δ3.52 peak and any peaks of the polymer backbone, which eliminates the possibility that the signal is from the protons of groups chemically bonded to the backbone. Thus the only possible reason is the existence of some through-space interaction.

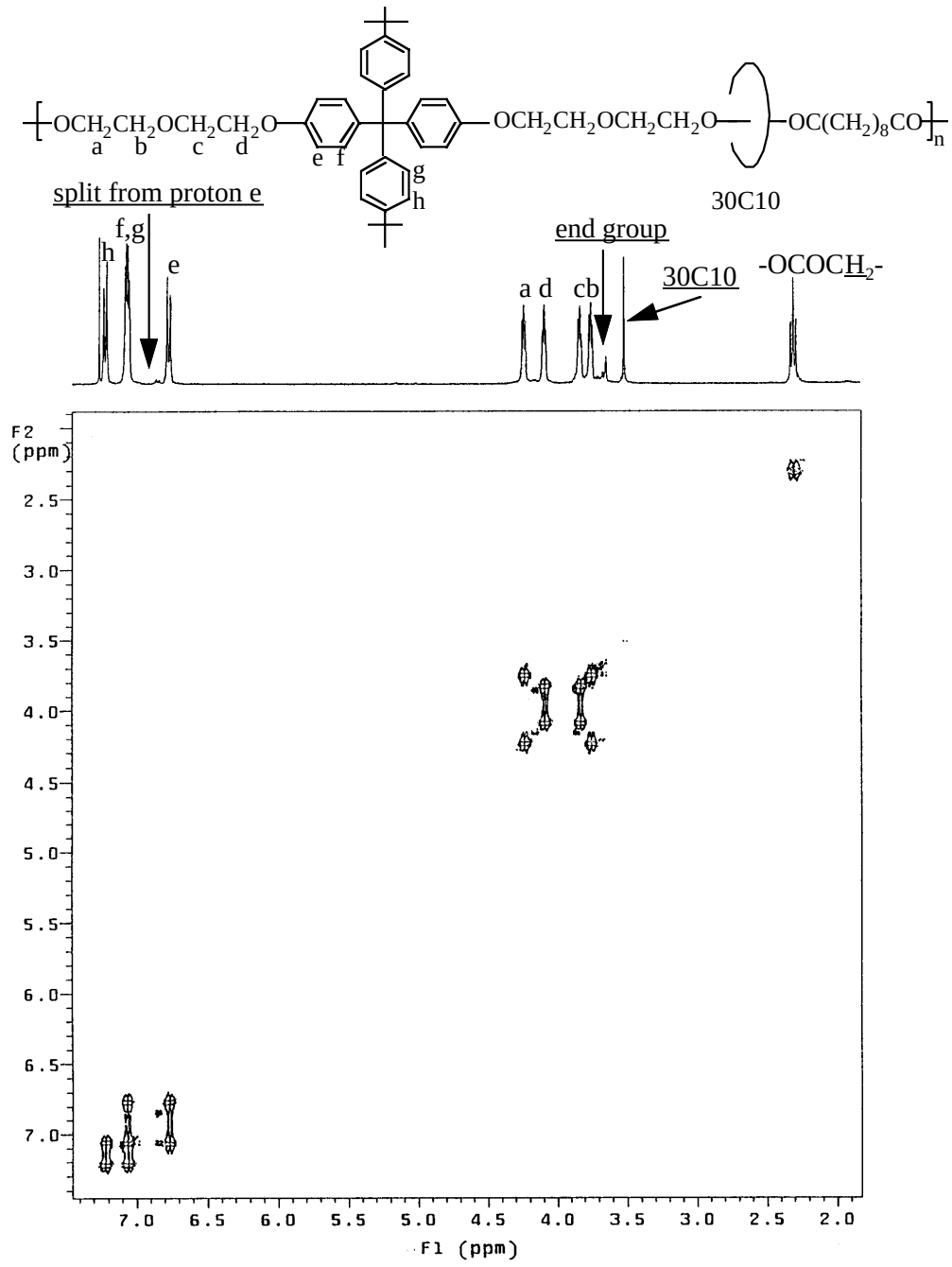


Figure 3.4 400 MHz proton 2D COSY spectrum of polyrotaxane 3.8 in $CDCl_3$

The NOESY spectrum of the polyrotaxane (Figure 3.5) did show that the signals a' and b' (hidden in multiplet for b and c) in the aromatic region of the polymer backbone correlate with threaded 30C10. Apparently, the observed correlation results from the shielding of

aromatic electrons in the diol BG unit via the ring current effect, resulting in upfield shift of 30C10 and splitting of proton a and b. Therefore, the novel structure of the diol BG-based polyrotaxane (Scheme 3.3) brought us new tools to prove the formation of polyrotaxanes.

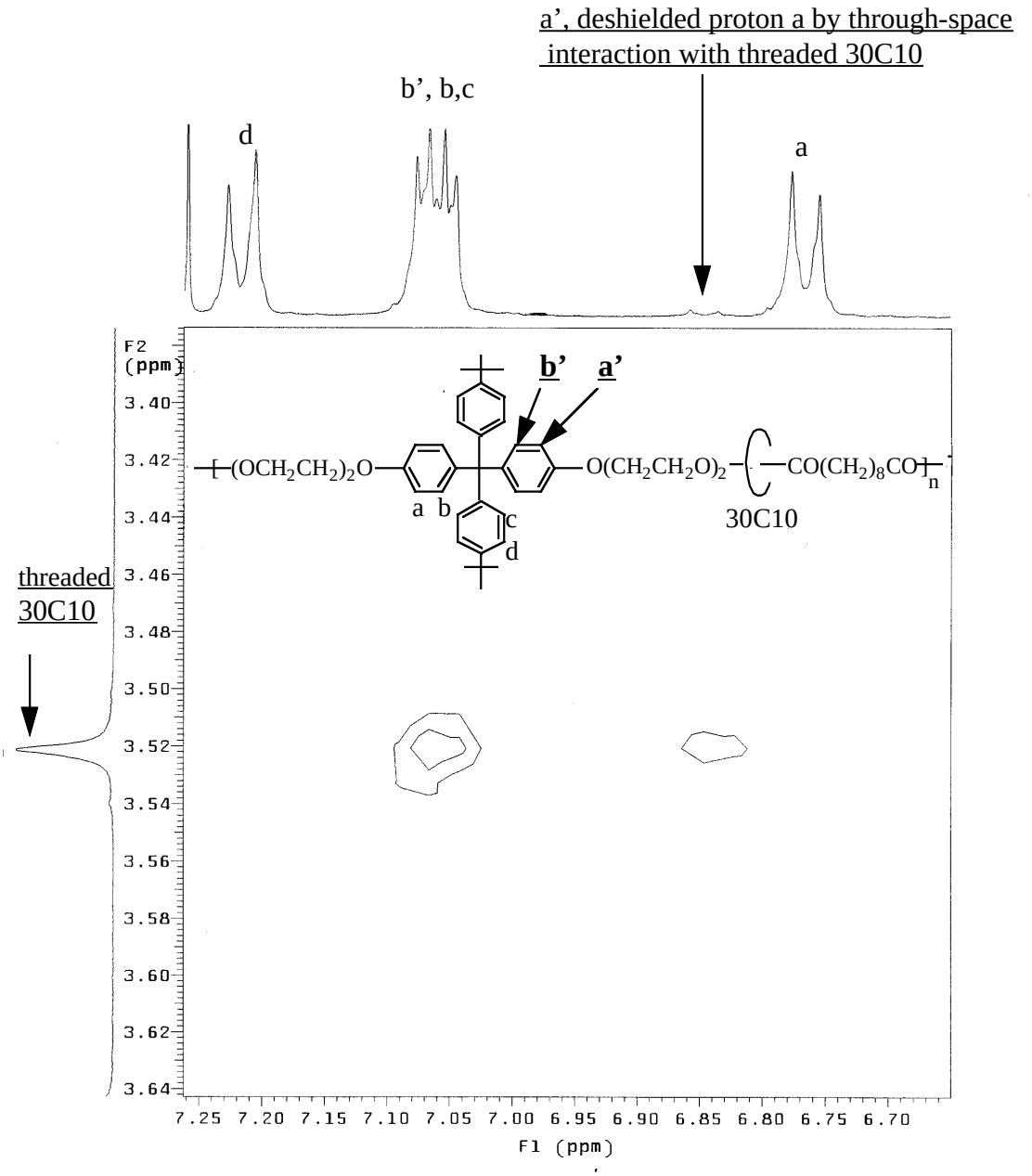
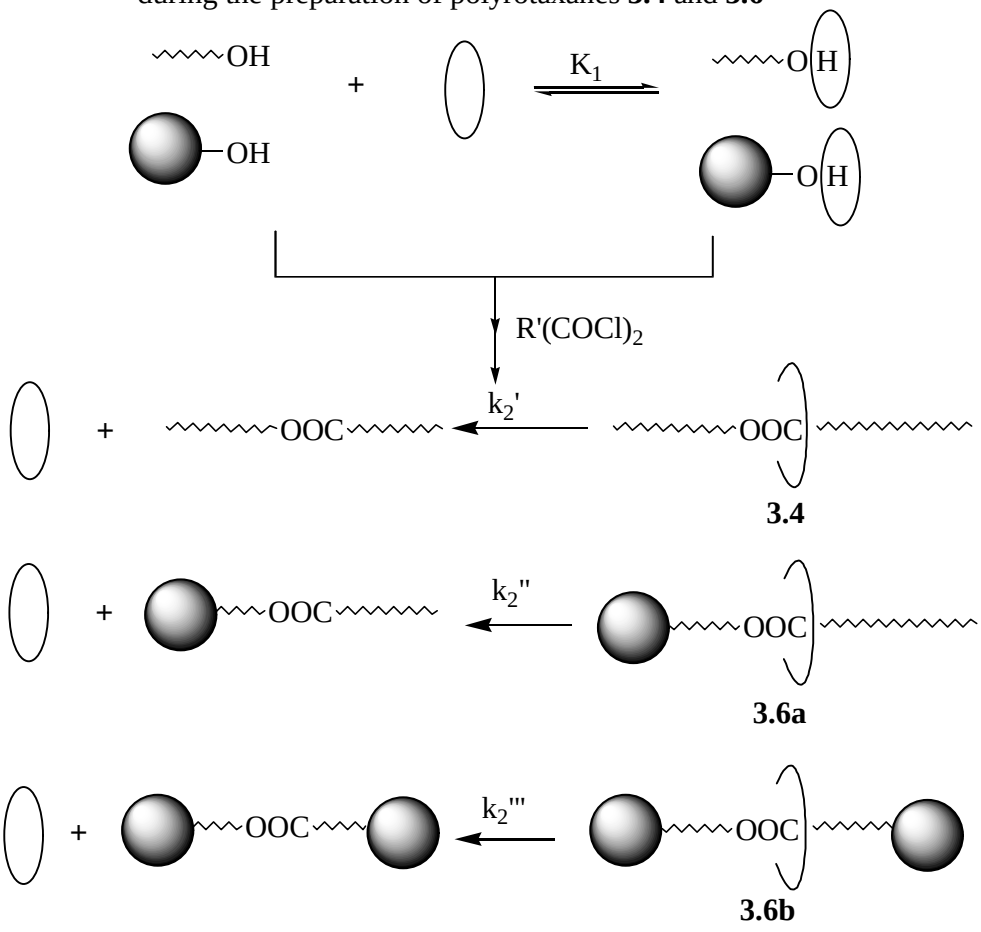


Figure 3.5 Correlated regions of 2D NOESY spectrum of polyrotaxane 3.8 in $CDCl_3$

3.2.3 Threading and dethreading

To study the constraining ability of diol BG **3.7**, the threading efficiency (m/n value) of polyrotaxane **3.8** was determined by the NMR integrals of the threaded 30C10 protons (δ3.52) and methylene protons of -OCH_2- (proton d, δ4.09) in the backbone. It was found that polyrotaxane **3.8** had an m/n value (0.061) five times as high as that of a polyrotaxane of type **3.4** without BG (m/n=0.012)[15] prepared from 1,10-decanediol, sebacoyl chloride and 30C10 under the same conditions. This result can be explained by threading and dethreading processes (Schemes 3.5-3.6).

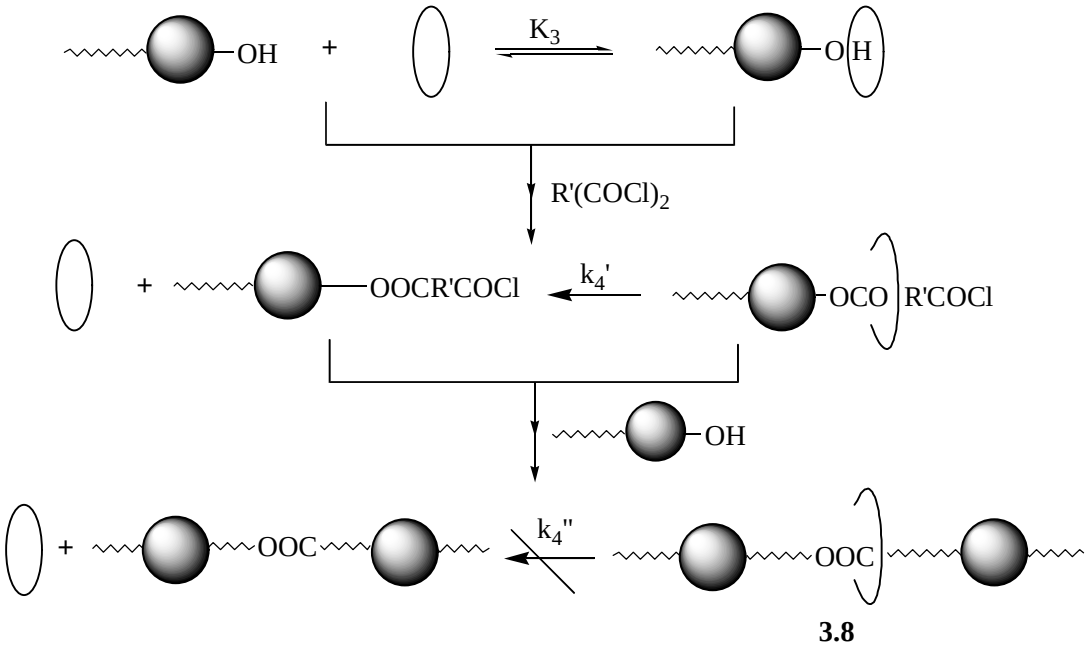
Scheme 3.5 Proposed threading and dethreading mechanisms during the preparation of polyrotaxanes **3.4** and **3.6**



[15] Gibson, H. W.; Liu, S. *Macromol. Symp.* **1996**, *102*, 55.

We believe that hydrogen bonding of -OH end groups with the crown ethers provides the driving force for the threading, formation of ester linkage taking place through the macrocyclic cavity in a proportion depending on ring size and other parameters. For polyrotaxane **3.4** (Scheme 3.5), there are not any stoppers to keep the cyclic molecules on the backbone. Since the ester groups presumably exert no attractive force on the threaded cyclic components, once the OH group has been converted to an ester moiety, the cyclic molecules can move along the polymer backbone and dethread during the polymerization period (k_2' > 0), especially while the polymer has a molecular weight lower than that of entanglement. Compared to **3.4**, polyrotaxane **3.6** with monofunctional BG can diminish the dethreading by the formation of **3.6a** and **3.6b** (k_2"' = 0 < k_2" <k_2'Scheme 3.5). However, dethreading still occurs during the preparation period because at any given time some macromolecules have only one end blocked (**3.6a**) and/or no ends blocked **3.4**.

Scheme 3.6 Proposed threading and dethreading mechanisms during the preparation of polyrotaxanes **3.8**



3.8

For polyrotaxane **3.8**, dethreading only happens during a very limited stage, whose extent will be minor compared to the cases for **3.4** and **3.6**. As shown in Scheme 3.6, as soon

as 30C10 is located in a BG-ester-ester-BG sequence (k_4' = 0), it will be restricted between the stoppers and thus can not slip off the backbone except when the chemical bonds of the backbone are broken. Using a diacid chloride BG together with **3.7** will eliminate all possible dethreading, once the ester bond is formed. The synthesis of this BG and its derived polyrotaxanes will be reported later in Chapter 5.[16]

3.2.4 Temperature and feed ratio dependence of threading efficiency

As shown in Scheme 3.6, hydrogen bonding between the crown ethers and the hydroxy groups of diol monomer is proposed to be driving force for threading. Thus the term for the enthalpy (ΔH^o) was expected to be negative in the free energy equation: $\Delta G^o = \Delta H^o - \Delta S^o$. Since the natural log of the equilibrium constant (K_3) in Scheme 3.6 for hydrogen bonding is a function of the reciprocal of temperature: $\ln K_3 = -(\Delta H^o)/RT + \Delta S^o/R$, the temperature dependence of threading efficiency was expected.

Table 3.1. Feed compositions[a] and m/n values for polyrotaxane **3.8** at different polymerization temperatures

3.7 (mmol)	feed ratio[b]	temp.[c] (K)	m/n[d]	M_w[e] (kg/mol)	M_n[e] (kg/mol)
0.6235	2.0	336	0.061	28.8	16.5
0.6325	2.0	359	0.046	20.1	10.8
0.6325	2.0	400	0.031	15.6	9.02
0.6325	2.0	426	0.020	11.3	6.90

a) mmol of acid chloride equal to that of **3.7.**
b) 30C10 vs. diol BG **3.7**.
c) ± 2 °C.
d) measured by proton NMR.
e) measured by GPC with PS standards in chloroform.

Indeed, polyrotaxanes **3.8** prepared at different polymerization temperatures had different m/n values; the lower the temperature was, the higher m/n was (Table 3.1 and

[16] Gong, C., Ji, Q., Glass, T. E., Gibson, H. W. *Macromolecules* **1997**, *30*, 4807 and Chapter 5.

Figure 3.6). This agrees with the expectation based on hydrogen bonding theory; since ΔH^o is negative, K_3 increases with lower temperature and thus more -OH groups form hydrogen bond with crown ethers; this finally gives higher threading efficiency. Thus the observation of temperature dependence consolidated the hydrogen bond hypothesis. However, why was m/n independent of temperature in the preparation of polyrotaxanes of type **3.4**?[6,7] As shown in Scheme 3.5, largest dethreading was involved in the preparation of **3.4** among three types of polyrotaxanes. Under the same condition, m/n of **3.4** was only 1/4.4 of **3.8**. Thus, the lack of temperature dependence for **3.4** is probably due to the heavy interference of the dethreading during the polymerization.

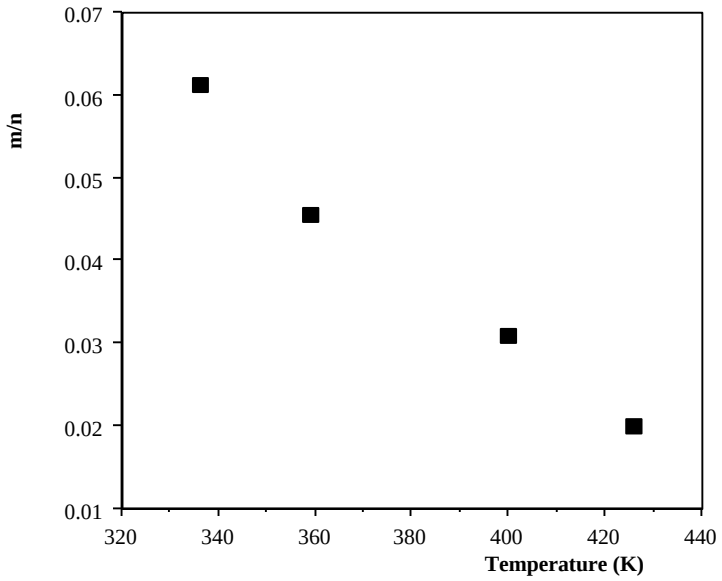


Figure 3.6 The relationship of threading efficiency of polyrotaxanes 3.8 vs. polymerization temperature

Since the equilibrium constant for hydrogen bonding is the same at a given temperature, the fraction of hydroxy groups associated with crown ethers also depends on the feed ratios of the cyclics vs. diol monomer. Therefore, polyrotaxanes **3.8** were prepared at different ratios at a constant temperature. Indeed, the higher the ratio was, the higher m/n

was, as shown in Table 3.2 and Figure 3.7. Thus, the feed ratio studies also agreed with hydrogen bonding mechanism.

Table 3.2. Feed compositions[a] and m/n values for polyrotaxanes **3.8** at the different feed ratios[b]

3.7 (mmol)	feed ratio[c]	m/n[d]	M_w[e] (kg/mol)	M_n[e] (kg/mol)
0.6235	1.0	0.036	28.6	12.2
0.6325	2.0	0.061	28.8	16.5
0.6325	3.0	0.082	28.9	16.0
0.6325	4.0	0.092	22.1	12.0

a) mmol of acid chloride equals to that of **3.7.**
b) 30C10 vs. diol BG **3.7**.
c) 63 ± 2 °C.
d) measured by proton NMR.

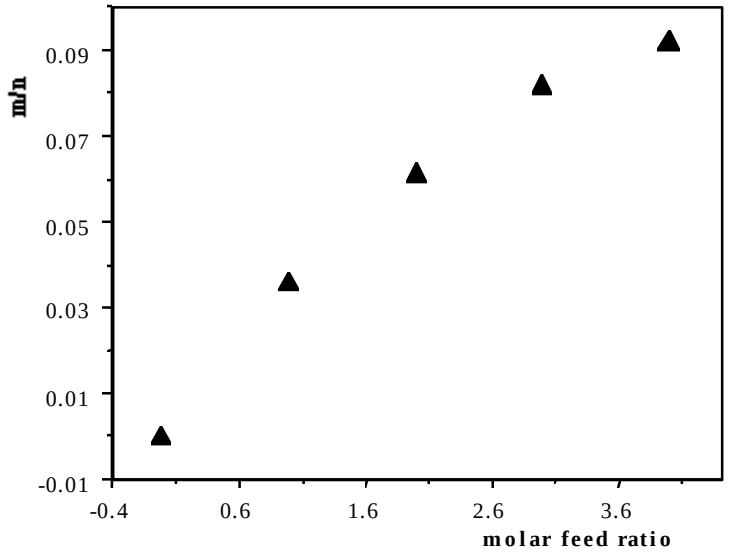
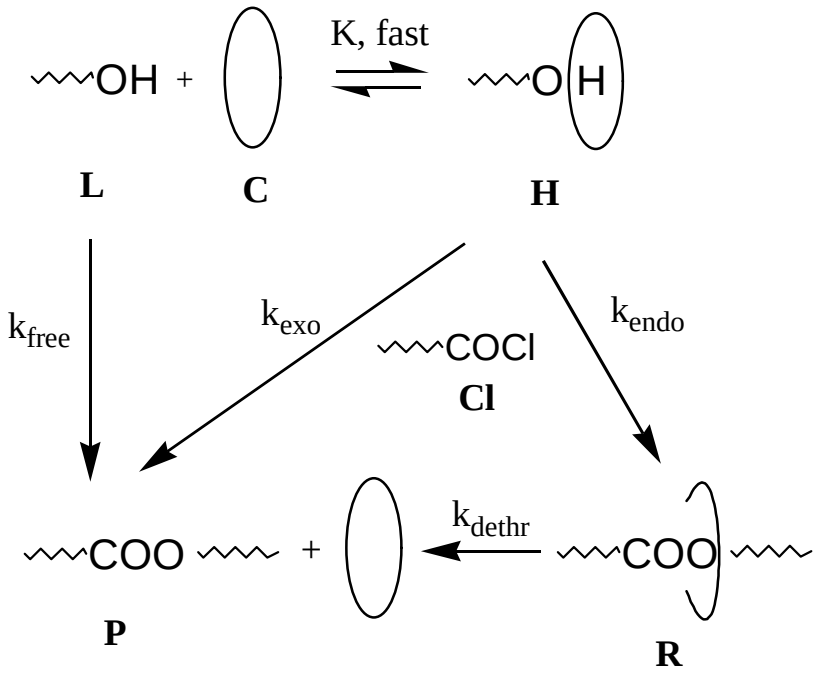


Figure 3.7 The relationship of threading efficiency of polyrotaxanes **3.8** vs. feed ratio of 30C10 vs. **3.7**

3.2.5 The relationship of H-bonding vs. m/n

Since hydrogen bonding is the driving force for threading, enthalpy and entropy changes determine the equilibrium and thus the m/n values. Their relationship is explored as follows.

Scheme 3.7



As soon as diol monomer is mixed with 30C10, the hydroxy group immediately H-bonds with the cyclic to achieve an equilibrium (Scheme 3.7).[17,18] Relative to the equilibrium process, the esterification is believed to be much slower and thus the rates of products **R** and **P** are determined by the rate constants of k_{endo}, k_{exo} and k_{free}.

If dethreading rate is k_{dethr}, $d[R]/dt = k_{endo}[H][Cl] - k_{dethr}[R]$ <1>

$d[P]/dt = k_{free}[L][Cl] + k_{exo}[H][Cl] + k_{dethr}[R]$ <2>

[17] R. M. Izatt, J. S. Bradshaw, K. Pawlak, R. L. Bruening, B. J. Tarbet, *Chem. Rev.* **1992**, *92*, 1261.
[18] Yakshin, V. V.; Abashkin, V. M.; Laskprin, B. N. *Dokl. Chem. Proc. Acad. Sci. USSR (Engl. Trans.)* **1979**, *224*, 27.

where [R], [H], [Cl], [P] and [L] are the instantaneous concentrations of rotaxane structure (**R**), the hydroxy group H-bonded with crown ether (**H**), acid chloride group (**Cl**), normal ester linkage (**P**), and the hydroxy group not H-bonded with crown ether (**L**).

Assuming that a constant fraction of **R** formed dethreads = 1-γ; fraction retained = γ and because [H] = K[L][C]: $d[R]/dt = \gamma k_{endo}K[L][C][Cl]$ <3>

$d[P]/dt = k_{free}[L][Cl] + k_{exo}K[L][C][Cl] + k_{endo}(1-\gamma)K[L][C][Cl]$ <4>

Thus <3>/<4> gives:

$d[R]/d[P] = \{\gamma k_{endo}K[C]\}/\{k_{free} + k_{exo}K[C] + k_{endo}(1-\gamma)K[C]\}$ <5>

Because m/n is very low and H-bonding is weak, [C] can be treated as a constant, the feed concentration ($[C]_o$). No other variables except R and P exist in equation <5>. Its integration affords: $[R]/[P] = \{\gamma k_{endo}K[C]_o\}/\{k_{free} + k_{exo}K[C]_o + k_{endo}(1-\gamma)K[C]_o\}$ <6>

$m/n = 2[R]/\{[P] + [R]\} = \{2\gamma k_{endo}K[C]_o\}/\{k_{free} + k_{exo}K[C]_o + k_{endo}K[C]_o\}$ <7>

Equation <7> shows that m/n will increase with higher concentration of crown ether, larger K value, agreeing with the obtained results; polyrotaxanes prepared with higher feed ratio of 30C10 to diol monomer and/or at lower temperature had higher m/n values. In addition, as demonstrated in Chapter 4 and Chapter 5, the use of diol BG effectively reduce dethreading (higher γ) and thus increased m/n. This again agrees with equation <7>. Apparently, without the kinetic data the relationship between K and m/n can not precisely be defined. However, assuming that $k_{free} = k_{exo} = k_{endo,}$ equation <7> can be further simplified as

$m/n = (2\gamma K[C]_o)/(1 + 2K[C]_o)$ or $K = (m/n)/\{2[C]_o(\gamma - m/n)\}$ <8>

γ mainly determined by the strength of the interaction between the backbone and 30C10 and steric effects, can be assumed to be constant (one or less) for a given system. For **3.8**, γ is 0.6 or less because it was found that about 40 % of threaded crown ether slipped off the backbone relative to that for a polyrotaxane without dethreading (γ=1.0).[16]

K at different assumed values of γ (Table 3.3) were calculated using equation <8> based on $[C]_o$, and experimental m/n values (Table 3.2). Because these polyrotaxanes **3.8** were prepared at the same temperature, K should be same. Thus γ with the least scatter is the most probable true value. As Table 3.3 shows, for γ lower than 0.30, the relative scatter is

significantly higher than others; indicating γ is indeed 0.40 or greater[16] and K is 0.12 M^{-1} or lower at 63 °C; this agrees with measured value for **3.8**.[16]

Table 3.3 K values for H-bonding of diol **7** and 30C10 calculated from observed m/n at 63 °C[a] at different assumed values of γ

γ	K (M^{-1}) (b=1)	K (M^{-1}) (b=2)	K (M^{-1}) (b=3)	K (M^{-1}) (b=4)	Average K (M^{-1})	STD[b]	Relative Scatter[c] (%)
0.01	-0.94?	-0.54?	-0.42?	-0.37?	-0.57?	0.26	45
0.03	-4.1?	-0.89?	-0.59?	-0.50?	-1.5?	1.7	110
0.05	1.7	-2.5?	-0.96?	-0.74?	-0.61?	1.8	290
0.07	0.72	3.1	-2.5?	-1.4?	-0.044?	2.5	560
0.09	0.45	0.95	3.8	-15?	-2.6?	8.7	341
0.10	0.38	0.70	1.7	3.9	1.7	1.6	94
0.20	0.15	0.20	0.26	0.29	0.22	0.061	27
0.30	0.093	0.11	0.14	0.15	0.12	0.025	20
0.40	0.067	0.081	0.096	0.10	0.086	0.015	17
0.50	0.053	0.063	0.073	0.076	0.066	0.010	16
0.60	0.044	0.051	0.059	0.061	0.054	0.0079	15

a) $[C] = [C]_0$ = 0.733, 1.11, 1.34 and 1.49 M corresponding to b = 1, 2, 3 and 4, respectively (Table 3.2).

b) standard deviation.

c) relative scatter: (STD/ave.K)(100) (%).

To estimate enthalpy and entropy changes, the m/n values at different temperatures (Table 3.1) were converted into K values (Table 3.4), too. LnK was then plotted against 1/T to afford the van't Hoff plots (Figure 3.8). ΔH as -Slope.R and ΔS as Intercept.R were obtained (Table 3.5). When γ is less than 0.05, invalid negative K values were obtained. Except for γ lower than 0.20, ΔH and ΔS are almost constant at about -15 to -16 kJ/mol and -

64 to -70 J/mol.K, respectively. The ΔH value is close to those reported for the H-bonding of 15-crown-5, 18-crown-6, dibenzo-18-crown-6 and dibenzo-24-crown-8 with methanol in CCl_4 at 25 ^{o}C (-15.1, -14.6, -10.5 and -14.2 kj/mol, respectively, but no ΔS values were reported);[17,18] this consolidates the obtained results. These values are important to understand and design polyrotaxanes because one can predict m/n. The negative ΔH term confirmed the existence of a strong interaction between the diol **3.7** and the crown ether, here, hydrogen bonding. The negative ΔS term is easy to understand since H-bonding restricts the motions of both diol monomer and the crown ether.

Table 3.4. K values for hydrogen bonding of diol **3.7** and 30C10 calculated from measured m/n values at different temperatures[a] at different assumed values of γ

γ	K (M^{-1}) (153 ^{0}C)	K (M^{-1}) (127 ^{o}C)	K (M^{-1}) (86 ^{0}C)	K (M^{-1}) (63 ^{0}C)	lnK (153 ^{0}C)	lnK (127 ^{o}C)	lnK (86 ^{0}C)	lnK (63 ^{0}C)
0.01	-0.54?	-0.58?	-0.66?	-0.90?	--	--	--	--
0.03	-0.89?	-1.3?	-14?	0.90	--	--	--	-0.10
0.05	-2.5?	5.2	0.73	0.30	--	1.6	-0.31	-1.2
0.07	3.0	0.86	0.36	0.18	1.1	-0.15	-1.0	-1.7
0.09	0.95	0.47	0.24	0.13	-0.054	-0.75	-1.4	-2.1
0.10	0.70	0.38	0.20	0.11	-0.35	-0.96	-1.6	-2.2
0.20	0.20	0.13	0.080	0.050	-1.6	-2.0	-2.5	-3.0
0.30	0.11	0.082	0.052	0.032	-2.2	-2.5	-3.0	-3.4
0.40	0.081	0.059	0.038	0.024	-2.5	-2.8	-3.3	-3.7
0.50	0.063	0.046	0.030	0.019	-2.8	-3.1	-3.5	-4.0
0.60	0.051	0.037	0.024	0.016	-3.0	-3.3	-3.7	-4.2

a) $[C]_0$ is 1.11 M corresponding to b = 2.

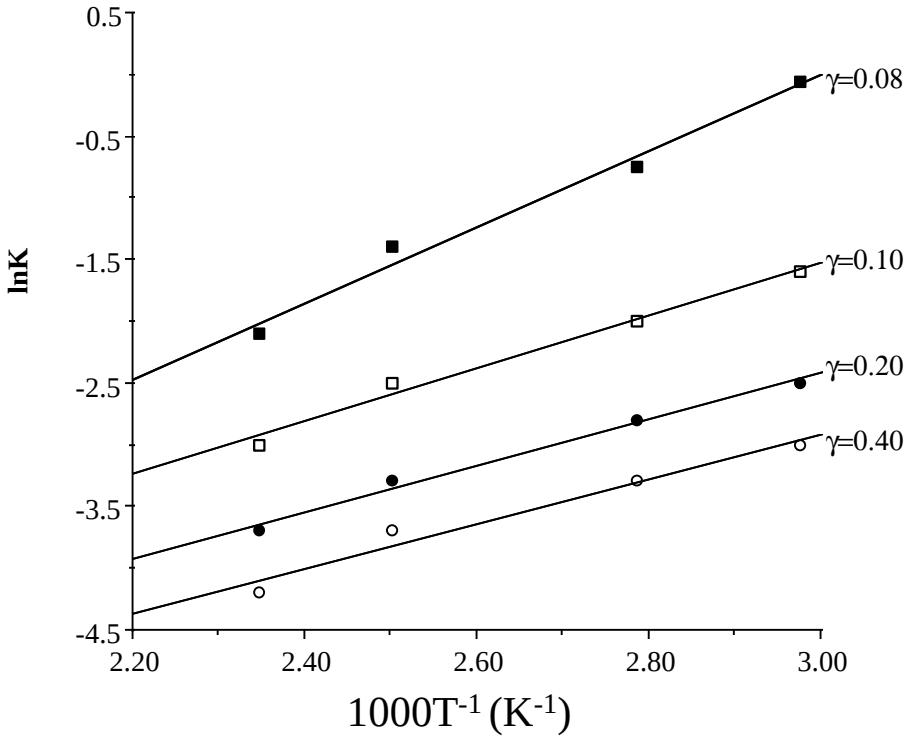


Figure 3.8 The van't Hoff plots at different assumed values of γ

Table 3.5. The ΔH and ΔS values based on van't Hoff plots at different γ values

γ	Intercept	Slope x 10^{-3} (K)	R^2	-ΔS (J/mol.K)	-ΔH (kJ/mol)
0.01	--	--	--	--	--
0.03	--	--	--	--	--
0.05	--	--	--	--	--
0.07	-12	4.2	0.97	100	35
0.09	-9.2	3.1	0.98	77	26
0.10	-8.8	2.8	0.99	73	23
0.20	-7.9	2.1	0.99	66	17
0.30	-7.7	1.9	0.99	64	16
0.40	-8.0	1.9	0.99	67	16
0.50	-8.1	1.8	0.97	67	15
0.60	-8.4	1.8	0.97	70	15

Because i) γ is probably not independent of temperature, ii) [C] is truly not constant and iii) k_{free}, k_{endo} and k_{exo}, may not equal to one another, the above calculated results are clearly not exact. However, they indicate a general trend and afford approximate values for the important variables involved in threading process.

3.3 Conclusions

A new difunctional blocking group (diol BG **3.7**) was prepared by a five step approach. Its derived polyester rotaxane **3.8** had a much higher m/n value than a corresponding system without BG. Because threaded 30C10 was restricted between stoppers and had a chemical environment different from the unthreaded species, new spectral evidence for the formation of the polyrotaxane was demonstrated. In addition, the threading efficiency of **3.8** was dependent on the polymerization temperature and the feed ratio of the cyclics vs. diol monomer; the lower the temperature was and the higher the feed ratio was, the higher m/n the polyrotaxane had. The m/n values were converted into corresponding K values by assuming various values for γ. ΔH and ΔS are estimated to be about -15 to -16 kJ/mol and -64 to -70 J/mol.K, respectively. Thus the enthalpy term favors threading while the entropy term does not.

3.4 Experimental

Chemical Reagents and Measurements

All chemicals were reagent grade and used directly as received from Aldrich unless otherwise specified. All solvents were HPLC or GC grade. 30C10 was prepared by a well-established procedure.[19] Melting points were taken in capillary tubes and have been corrected. Proton and carbon NMR spectra, reported in ppm, were obtained on a 400 MHz Varian spectrometer using chloroform-*d* solutions with tetramethylsilane as an internal standard. The NOESY study was performed at room temperature while mixing time was one second and relaxation time two seconds. The following abbreviations have been used in

[19] Bheda, M. C.; Merola, J. S.; Woodward, W. A.; Vasudevan, V. J.; Gibson, H. W. *J. Org. Chem.* **1994**, *59*, 1684.

describing NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet); coupling constants (J) are in Hertz. Elemental analyses were performed by Atlantic Microlab of Norcross, GA. GPC analyses were done with a Waters 150CALC/GPC system with polystyrene-divinylbenzene columns, using polystyrene standards. The instrument was fitted with a refractive index detector. The glass transition and melting temperatures of polymers were measured with a Perkin-Elmer thermal analysis system at a rate of 10 ^{o}C/min for both heating and cooling; all reported values were the centers of transitions from 2nd heating. TGA data were obtained using a DuPont TGA 951 instrument at a scan rate of 40 ^{o}C/min.

Ethyl 4-Benzyloxybenzoate (3.10)

After benzyl bromide (86.00 g, 502.8 mmol) and ethyl 4-hydroxybenzoate (56.00 g, 337.0 mmol) had been dissolved in 500 ml of DMF, 75.00 g (584.6 mmol) of potassium carbonate were added. The reaction ran for 18 hrs at 50-60 ^{o}C under the protection of nitrogen. After the system had been cooled down, the product was dissolved in toluene (300 mL) and washed with water (4x120 mL). A yellow solid was obtained after the solvent in the organic phase had been removed. The crude product was recrystallized in a mixture of hexane and ethyl acetate (250 mL, 1:6) to afford a white solid (68.0 g, 79%), mp 43.3-44.3 ^{o}C (lit.[18] 45.5 ^{o}C). ^{1}H NMR: 1.37 (t, J= 7.0; 3H); 4.33 (q, J=7.0, 2H); 5.12 (s, 2H); 6.99 (d, J=8.4, 2H); 7.34-7.44 (m, 5H); 7.98 (d, J=8.4; 2H).

Bis(*p*-*tert*-butylphenyl)(*p*-benzyloxylphenyl)methanol (3.11)

After 14.5 g (597 mmol) of magnesium turnings had been loaded into a 500 ml flask containing THF (100 ml, Na dried), 4-*tert*-butylbromobenzene (120.6 g, 565.9 mmol) in THF (100 mL) was added to the system dropwise under the protection of nitrogen over half an hour. The reaction was initiated by gently heating the mixture. After refluxing for one hour, the reaction ran for two more hours at room temperature. Then **3.10** (62.8 g, 245 mmol) in THF (150 mL, Na dried) was added to the system slowly and it was refluxed overnight. After the system had been cooled down, the mixture was neutralized with HCl (10%, 500 mL).

The product was extracted with toluene (2x250 mL). The combined organic phase was washed with water (3x500 mL). After the solvent in the organic phase had been removed, the crude product was recrystallized in a mixture of acetone and methanol (400 ml, 1:1). 73.0 g (62%) of white product, mp 63.0-64.0 ^{o}C, was obtained. ^{1}H NMR: 1.29 (s, 18H); 3.04 (s, 1H); 5.03 (s, 2H); 6.90 (d, J=6, 2H); 7.25-7.43 (m, 15H). ^{13}C NMR: 31.34; 34.37; 51.91; 69.95; 113.74; 124.51;127.53; 127.92; 128.24; 128.54; 130.15; 136.80; 137.06; 141.20; 149.34; 157.57 (16 peaks as required). Anal. Calcd for $C_{34}H_{38}O_2$: C, 85.31; H, 8.01. Found: C, 85.35; H, 8.05.

Bis(*p*-*tert*-butylphenyl)bis(*p*-hydroxyphenyl)methane (3.13) and bis(*p*-*tert*-butylphenyl)(*p*-hydroxyphenyl)(p-benzyloxyphenyl)methane (3.12)

3.11 (63.00 g, 131.6 mmol) was dissolved in phenol (260.0 g, 2.763 mol) by heating in a 1 L flask. As soon as four drops of 12 M HCl had been added as catalyst, the solution turned deep red immediately. The mixture was refluxed for 24 hours. After it had been cooled down, the mixture was dissolved in 800 ml of CH_2Cl_2 and was washed with water (8x250 mL). After the solvent in the organic phase was removed, the resulting oily residue was boiled in a mixture of hexane and toluene (1L, 1:1). A slightly yellow solid precipitated from the solution and was further purified by silica gel chromatography with methylene chloride as eluting solvent to afford two fractions. Second fraction (**3.13**): 17.0 g (28%), mp 270.7-273.0 ^{o}C. ^{1}H NMR: 1.29 (s, 18H); 4.85 (s, 2H); 6.79 (d, J=8.8, 4H); 7.02-7.08 (m, 8H); 7.24 (d, J=8.8, 4H). ^{13}C NMR: 31.34; 34.27; 70.44; 113.99; 124.08; 130.59; 132.31; 139.78; 144.12; 148.37; 153.31 (11 peaks as required). Anal. Calcd. for $C_{33}H_{36}O_2$: C, 85.30; H, 7.81. Found: C, 85.36; H, 7.88. First fraction (**3.12**): 25.2 g (34%). ^{1}H NMR: 4.70 (s, 1H); 5.02 (s, 2H); 6.70 (d, J=8.8, 2H); 6.85 (d, J=8.8, 2H); 7.10-7.03 (m, 8H); 7.22-7.25 (d, J=8.8, 4H); 7.32-7.44 (m, 5H). ^{13}C NMR: 31.34; 34.27; 69.94; 113.33; 113.97; 124.08; 127.54; 127.91; 128.54; 130.59; 132.13; 132.35; 139.84; 144.12; 148.35; 153.27 (16 peaks, theory: 20). **3.12** was converted to **3.13** as follows: 16.00 g (28.84 mmol) of compound **12** were dissolved in THF (200 ml) and 1 g of palladium on carbon (10%) was added as catalyst. The mixture was loaded into a 500 ml high pressure flask and subjected to deprotection at 60

psi of H_2 for 5 days. After the reaction had been finished, the catalyst was removed by filtration and solvent was evaporated to afford a white solid. The product was recrystallized in toluene (150 mL), 12 g (90 %).

Bis(*p*-*tert*-butylphenyl)bis[*p*-2-(2'-hydroxyethoxy)ethoxyphenyl]methane (3.7)

After **3.13** (15.0 g, 32.3 mmol) and 2-(2'-chloroethoxy)ethanol (85.0 g, 682 mmol) had been dissolved in DMF (500 mL), K_2CO_3 (15.0 g, 117 mmol) was added. The reaction ran for 5 days at 70-80 ^oC under the protection of nitrogen. After the system had been cooled down, salt was removed by filtration. Upon removal of DMF, the product was dissolved in CH_2Cl_2 (300 ml) and washed with water (2x250 ml). After the solvent in the organic phase had been removed, the resulting solid was purified by silica gel chromatography with ethyl acetate as eluting solvent. Yield: 13 g (63%); mp 164.7-165.6 ^oC. ^1H NMR (Figure 3.1): 1.30 (s, 18H); 2.20 (t, J=6, 2H); 3.67 (t, J=4.4, 4H); 3.74-3.78 (m, 4H); 3.89 (t, J=4.4, 4H); 4.12 (t, J=4.4, 4H); 6.79 (d, J=8.8, 4H); 7.05-7.09 (m, 8H); 7.22 (d, J=8.8, 4H). ^{13}C NMR: 31.34; 34.27; 61.69; 67.21; 69.71; 72.51; 113.11; 124.09; 130.58; 132.14; 139.97; 144.09; 148.35; 156.41 (14 peaks, theory: 15). Anal. Calcd. for $C_{41}H_{52}O_6$: C, 76.84; H, 8.18. Found: C, 76.86; H, 8.23.

General procedure for polyrotaxanes 3.8.

Diol BG **3.7** (399.6 mg, 0.6235 mmol) was dissolved in 30C10 (547.0 mg, 1.242 mmol) at 63 ^oC. The homogeneous solution was stirred for half hour under the protection of nitrogen to achieve a hydrogen bonding equilibrium between 30C10 and the hydroxyl groups of BG. Then sebacoyl chloride (150.1 mg, 0.6277 mmol) was added to the system. After polymerization had proceeded for two days, the product was dissolved in 3 mL of THF and precipitated into water (200 mL) 3 times, 0.47g (recovery: 93 %). ^1H NMR (Figure 3.2, top): 1.29 (s, 26H); 1.57 (s, broad, $\underline{H_2}O$ plus 4H of -$OCOCH_2C\underline{H_2}$-); 2.31 (t, J=7.6, 4H); 3.52 (s, variable); 3.75 (t, J=4.8, 4H); 3.83 (t, J=4.8, 4H); 4.09 (t, J=4.8, 4H); 4.24 (t, J=4.8, 4H); 6.77 (major peak) and 6.85 (minor peak) (d, J=8.8, total 4H); 7.04-7.08 (m, 8H); 7.22 (d, J=8.8, 4H); m/n: 1st ppt 0.061; 2nd ppt 0.060 and 3rd ppt 0.061 (3.4 mass% 30C10), based on the

integrals of H_d (δ4.09) and 30C10 protons (δ3.52). DSC results: T_g=15.2 ^oC but no T_m! TGA data: 294 ^oC ; 5% weight loss temperature in air.

A same procedure was also applied for the preparation of polyrotaxanes **3.8** at different temperatures and different feed ratios of 30C10 vs. diol BG **3.7**; the detailed conditions and starting feed materials were specified in Table 3.1 and Table 3.2, respectively.

Model Polymer 3.9.

Model polymer **3.9** is the backbone of polyrotaxane **3.8**. It was prepared by the same procedure as that for **3.8** except that THF was used as solvent instead of 30C10. ^1H NMR (Figure 3.2, bottom): 1.29 (s, 26H); 1.57 (s, broad, $\underline{H_2}O$ plus 4H of -$OCOCH_2C\underline{H_2}$-); 2.31 (t, J=7.6, 4H); 3.75 (t, J=4.8, 4H); 3.83 (t, J=4.8, 4H); 4.09 (t, J=4.8, 4H); 4.24 (t, J=4.8, 4H); 6.77 (d, J=8.8, 4H); 7.04-7.08 (m, 8H); 7.22 (d, J=8.8, 4H). GPC measurements: M_n=18.7 kg/mol and M_w=46.1 kg/mol (PS standards). DSC results: T_g=14.5 ^oC and T_m=39.8 ^oC. TGA data: 444 ^oC; 5% weight loss temperature in air.

Hydrolysis of Polyrotaxane 3.8.

390 mg of polyrotaxane **3.8** (m/n=0.061) were dissolved in THF (4 mL). After 3 ml of aqueous potassium hydroxide solution (10 mol/l) had been added, the mixture was refluxed for 24 hrs. Upon the removal of all solvent under reduced pressure, the hydrolysis product was extracted with $CHCl_3$ (3x50 ml); $CHCl_3$ was evaporated. It was found that both 30C10 and diol BG **7** were recovered; ^1H NMR: Figure 3.3, middle. Pure 30C10 (10 mg, 75%) was separated by further extraction using hexane (3x50 mL); ^1H NMR: Figure 3.3, top.

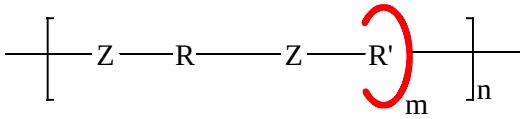
Chapter 4

Dethreading During the Rreparation of Poly(ester/crown ether rotaxane)s

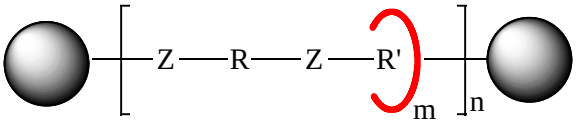
4.1 Introduction

A rotaxane is formed by threading a cyclic molecule onto a linear molecule without a covalent bond between these two components.[1,2,3] Depending on the molecular weight, rotaxanes can be classified as monorotaxanes,[1,2] in which the cyclic molecule is threaded onto a small molecule, or polyrotaxanes,[3,4] in which cyclic molecules are threaded onto a polymeric backbone.

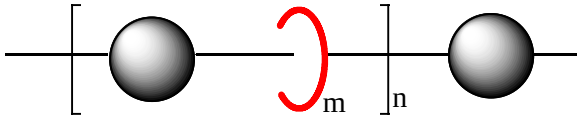
Scheme 4.1



4.1



4.2



4.3

Where X + Y = Z, e.g., X = COCl, Y = OH and Z = COO;

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[1] a) Schill, G. *Catenanes, Rotaxanes and Knots*, Academic Press: New York, 1971 b) Schill, G.; Logemann, E.; Littke, W. *Chem. Unserer Zeit* **1984**, *18*, 129.

[2] a) Harrison, I. T.; Harrison, S. *J. Am. Chem. Soc.* **1967**, *89*, 5723. b) Harrison, I. T. *J. Chem. Soc., Chem. Commun.* **1977**, *89*, 384.

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[4] Gibson, H. W.; Marand, H. *Adv. Mater*. **1993**, *5*, 11.

Using crown ethers as solvents, different polypseudorotaxanes **4.1** (i.e., those without blocking groups or stoppers to prevent dethreading) were prepared by polycondensation, including polyurethane rotaxanes[5,6] and polyester rotaxanes[7,8,9] with 30C10, 42-crown-14 and 60-crown-20 as macrocycles (Scheme 4.1). Since the threading efficiency of a polyrotaxane is directly related to its properties, controlling and increasing the m/n value became one of our research goals. However, ester groups presumably exert no attractive force on threaded crown ethers, so crown ethers can slip off the backbone during the reaction period and thus threading efficiency is depressed. The result reported by Harrison, that tris(*p-tert*-butylphenyl)methanol could constrain macrocycles comprised of up to 42 methylene groups[2a-c], introduced a solution to this problem. Encouraged by his result, different blocking groups with the same constraining ability were synthesized, including monofunctional BG[10] and difunctional BGs[11,12,13], and these BGs were successfully used for the syntheses of polyrotaxanes, **4.2** and **4.3**, respectively, (Schemes 4.1).[7,9,13] It was found that BGs can indeed decrease dethreading and diol BG **4.4**-based polyester rotaxane of type **4.3** had an m/n value (0.061) five times as high as that (0.012) of polyrotaxane of type **4.1** without BG under the same condition.[13]

In this chapter, I will discuss the syntheses and characterization of diol BG **4.4**-based copolyester 30C10 rotaxanes **4.8**, **4.9** and **4.10** by incorporating different amounts of 1,10-decanediol. In addition, the relationship of threading efficiency vs. the feed percentage of diol BG **4.4** in total diol is revealed.

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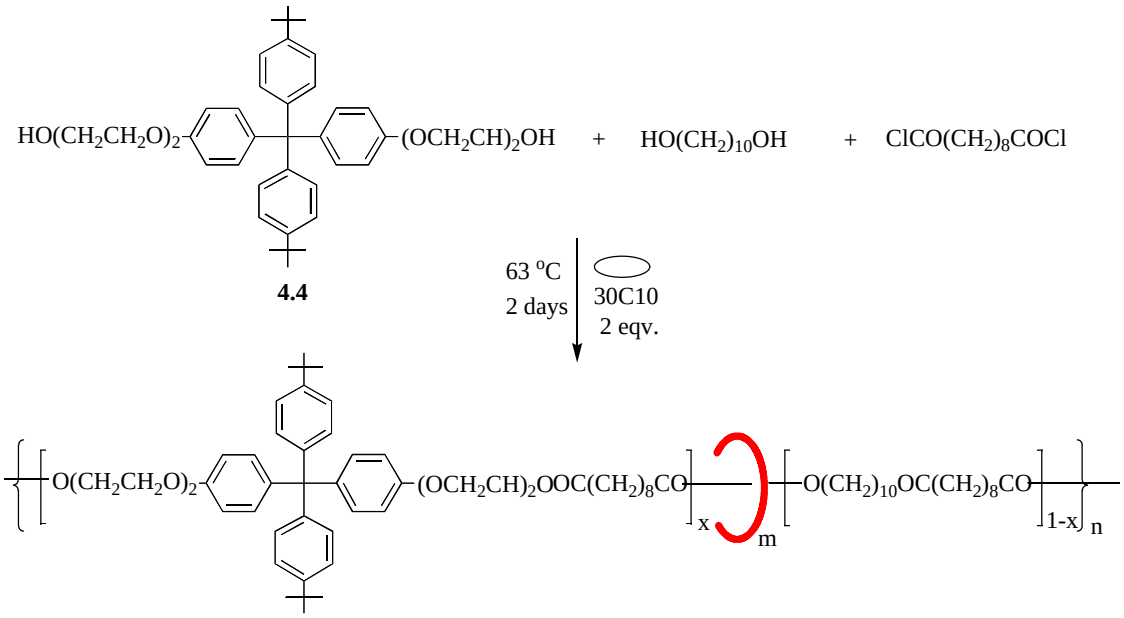
[5] Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.* **1994**, *116*, 537
[6] Marand, E.; Hu, Q.; Gibson, H. W.; Veytsman, B. *Macromolecules* **1996**, *29*, 2555.
[7] Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc*. **1995**, *117*, 852.
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[12] Liu, S.; Shen, Y. X.; Gibson, H. W. *J. Org. Chem.* 1995, *60*, 3155.
[13] a) Chapter 1. b) Gong, C.; Gibson, H. W. *Macromolecules* **1996**, *29*, 7029.

4.2 Results and discussion

4.2.1 Synthesis of diol BG-based copolyester 30C10 rotaxanes 4.8, 4.9 and 4.10

By variation of the ratio of diol BG **4.4** vs. 1,10-decanediol in the polycondensation with sebacoyl chloride in the presence of 30C10 as solvent (Scheme 4.2), copolyester 30C10 rotaxanes **4.8**, **4.9** and **4.10** were prepared. Unthreaded 30C10 was removed by three precipitations into methanol. The same procedure was applied for the preparation of model copolyester **4.7** except that THF was used instead of 30C10 as solvent.

Scheme 4.2



4.5: x = 0, m/n = 0.012
4.6: x = 1.00, m/n = 0.061
4.7: x = 0.400, m/n = 0
4.8: x = 0.100, m/n = 0.021
4.9: x = 0.400, m/n = 0.035
4.10: x = 0.700, m/n = 0.050

4.2.2 NMR Spectroscopy

Interestingly, compared to that of model copolyester **4.7** (Figure 4.1c), the proton NMR spectrum of BG-based copolyester 30C10 rotaxane **4.9** (Figure 4.1b) had many new signals in the region of δ3.52-3.65. Compared to that of BG-based homopolyester rotaxane **4.6** (Figure 4.1a),[13] the spectrum of polyrotaxane **4.9** had the same signal (δ3.52) and

additional signals between δ3.53-3.65. However, the chemical shift of free 30C10 in a mixture of free 30C10 and model copolyester **4.7** remained at 3.67 ppm. Are all of new signals in polyrotaxanes **4.9** from threaded 30C10? In order to answer to this question, we carefully characterized these polyrotaxanes as follows.

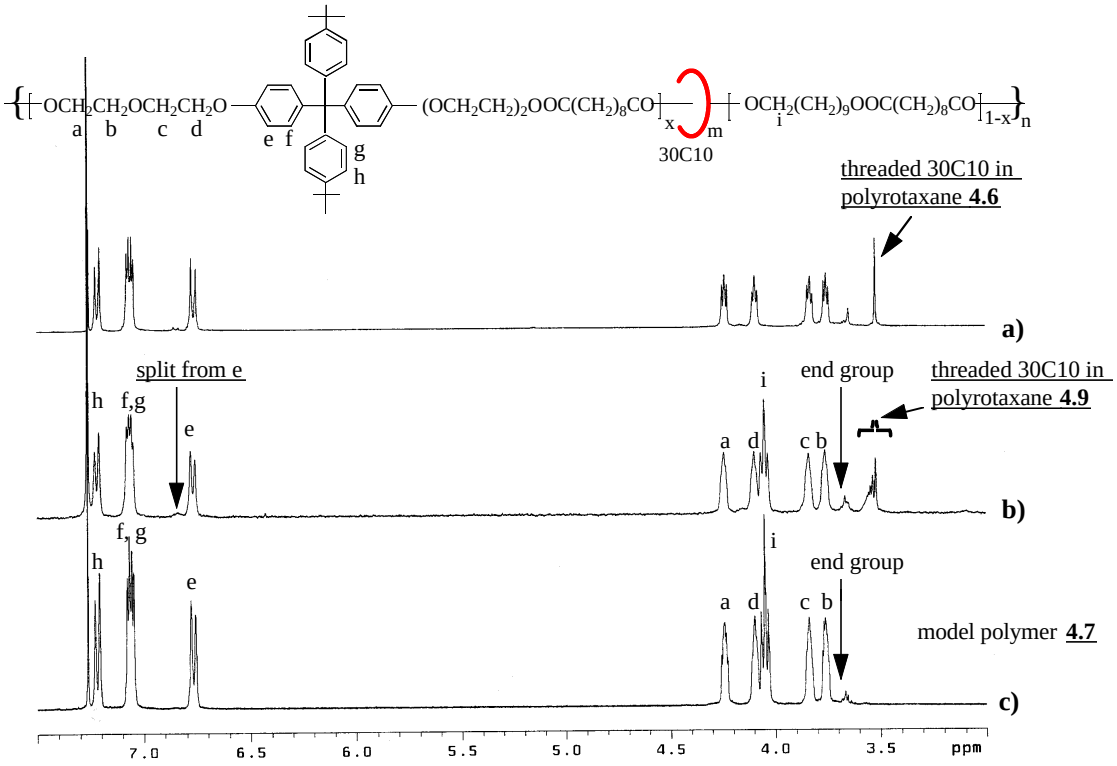


Figure 4.1 400 MHz proton NMR spectra of a) polyrotaxane 4.6, b) copolyester rotaxane 4.9 and c) model copolyester 4.7 in $CDCl_3$

i. Hydrolysis of copolyester 30C10 rotaxane 4.9

As proved by the proton NMR spectroscopy (Figure 4.2), all new signals in the copolyester rotaxane disappeared upon hydrolysis and the δ3.67 signal of free 30C10 returned (Figure 4.2b). By extraction of the hydrolytic products with cold hexane, pure 30C10 was recovered (Figure 4.2c); this directly proved that these new signals are from the protons of threaded 30C10.

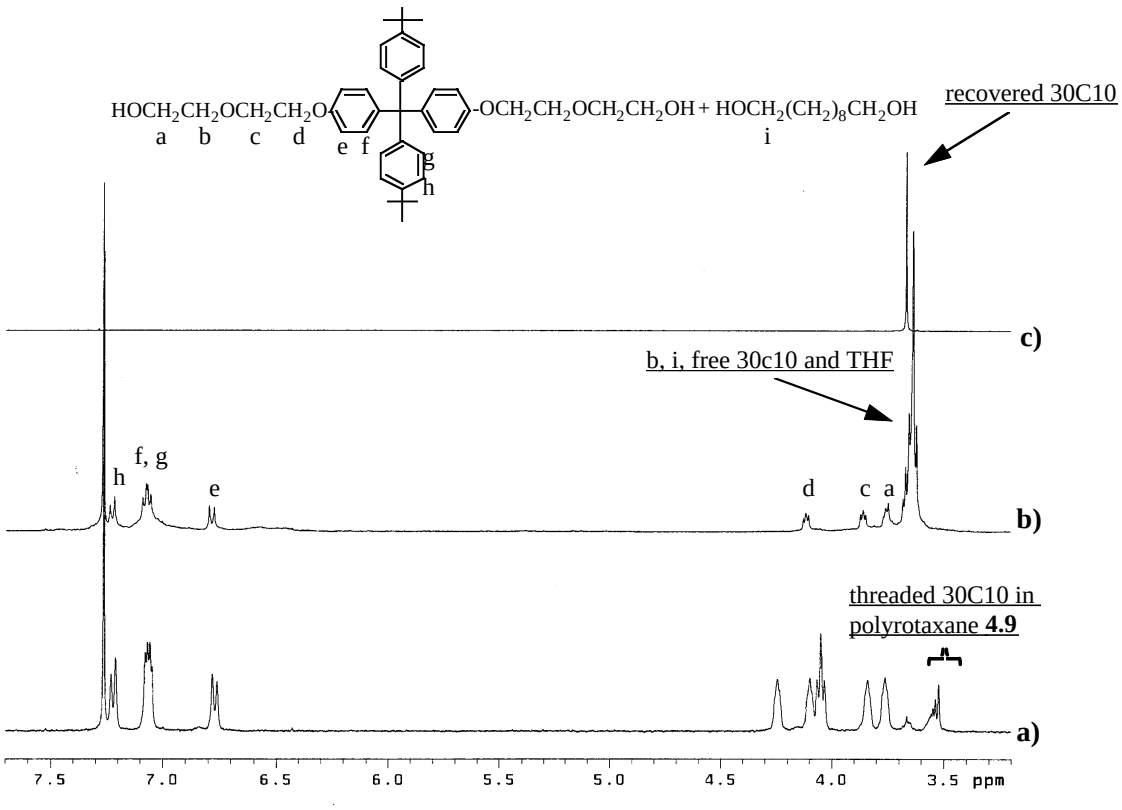


Figure 4.2 The 400 MHz proton NMR spectra of a) polyrotaxane 4.9, b) the hydrolytic neutral products from 4.9 and c) recovered 30C10 in $CDCl_3$

ii. 2D COSY and NOESY measurements

How can we explain all these different chemical shifts for the same molecule, threaded 30C10? According to the 2D COSY study, none of these signals are coupled with any peaks of polymer backbone (Figure 4.3); this eliminated the possibility that these signals are from protons chemically bonded to the backbone. Thus the only possible cause for the change of chemical shift is some through-space interaction.[13]

The NOESY spectrum (Figure 4.4) did show that all these signals correlated with the aromatic region, signals a' and b'. In polyrotaxane **4.5** with no aromatic units, the chemical shift of threaded 30C10 was 3.65 ppm. For diol BG-based homopolyester rotaxane **4.6**, the threaded 30C10 interacts with the aromatic BG unit through space, shielding by pi electrons via a ring current effect and thus shifted upfield to δ3.52.[13]

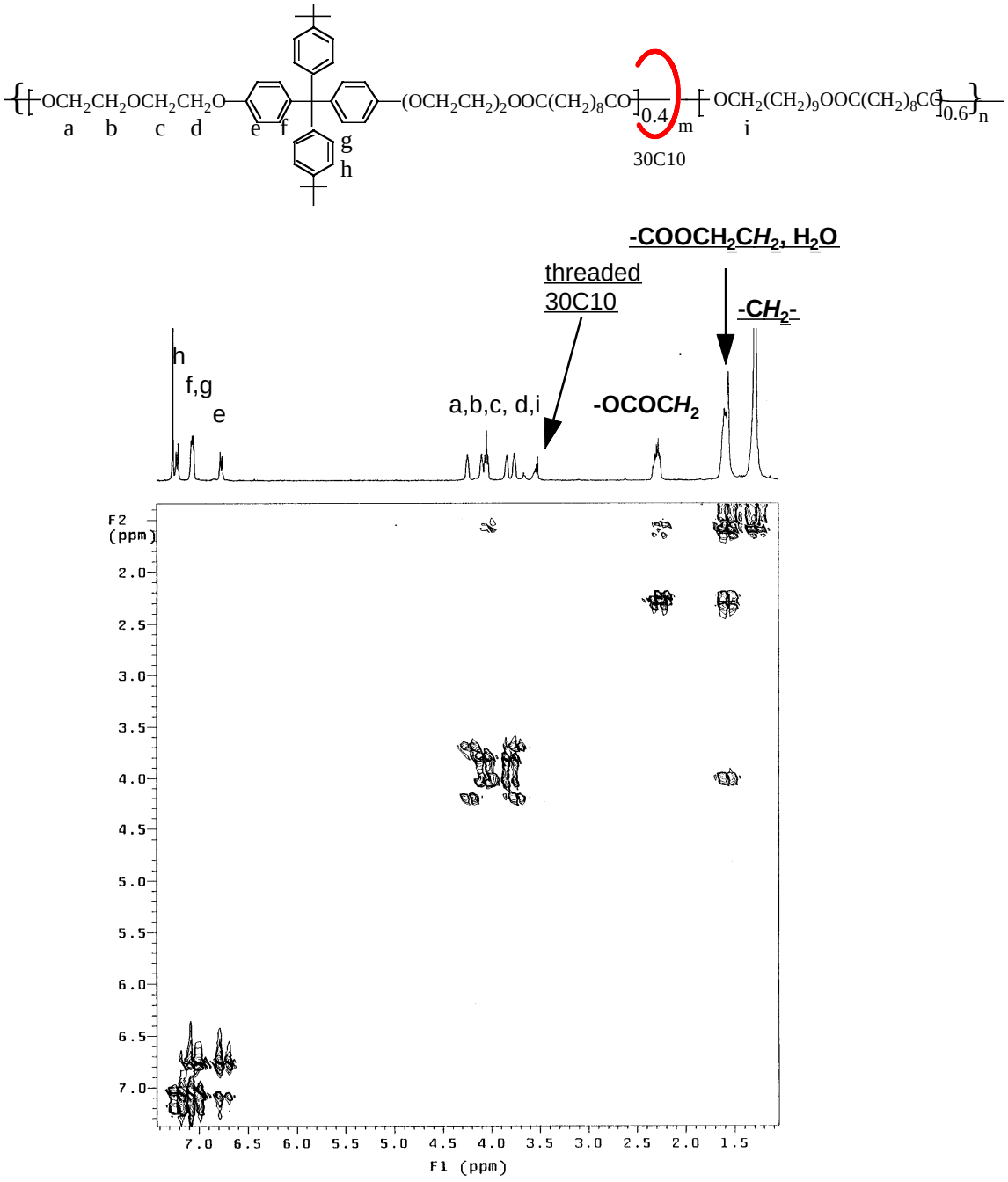


Figure 4.3 400 MHz proton 2D COSY spectrum of polyrotaxane 3.9 in $CDCl_3$

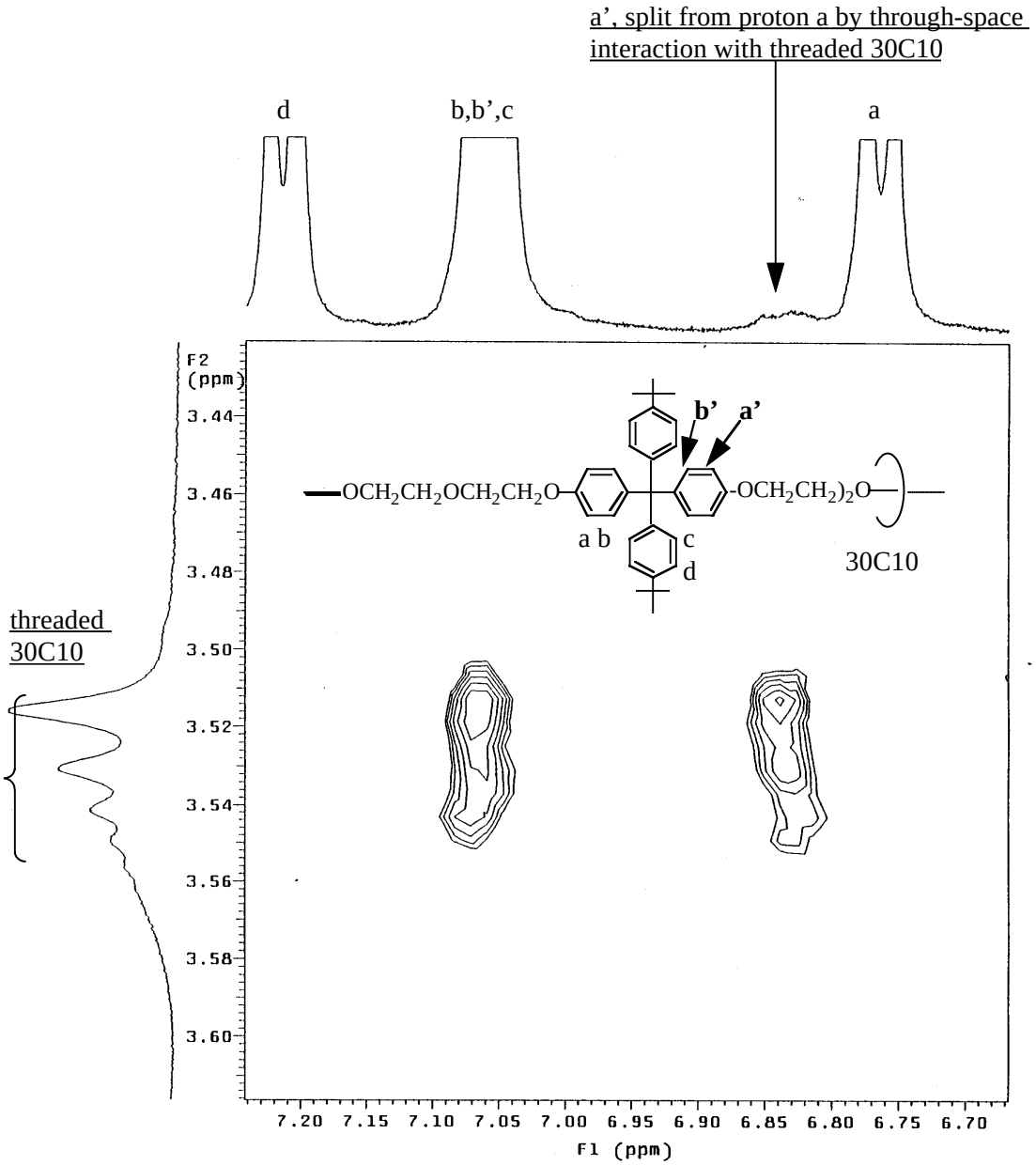


Figure 4.4 The correlated regions of 2D NOESY spectrum of polyrotaxane 4.9 in $CDCl_3$

By incorporating 1,10-decanediol, copolyester rotaxanes **4.8**, **4.9** and **4.10** will have different sequence structures, decided by both the relative reactivity of 1,10-decanediol vs. diol BG **4.4** and their relative feed ratios (Figure 4.5). Thus, 30C10 can be located in different sequences with different numbers of decamethylene sebacate moieties (C_{10} units) between BG units in the backbone. Threaded 30C10 molecules located in different sequences experience

different strengths of through-space interaction, shielding by pi electron via a ring current effect, as they move along the backbone and thus have different chemical shifts. It is worth noting that all the copolyester rotaxanes have exactly the same signals but in different proportions (Figure 4.5). The δ3.52 signal is the same as that of threaded 30C10 in homopolyester rotaxane **4.6**.[13] This observation is understandable because all the copolyester rotaxanes have a certain number of BG/BG sequence units (denoted as "0" in Figure 4.5), the same as that for **4.6**. Also others signals are presumably from those of 30C10 located in sequences labeled 1, 2, 3 and so on, respectively. By increasing the amount of BG in total diol, the number of signals for threaded 30C10 became fewer and fewer and the relative integral of each signal continuously changed (Figure 4.5). For example, the relative integral of the δ3.52 signal increased with the percentage of diol BG, which is consistent with prediction since the number of "0" sequence units increased.

Assuming that diol BG **4.4** and 1,10-decanedol have the same reactivity, the probabilities for the formation of different sequences can be calculated.[14] The theoretical ratios of sequences "0", "1" and "2" are 1.0:0.81:0.66 for **4.8**, 1.0:0.36:0.13 for **4.9**, and 1.0:0.090:0.0080 for **4.10**.[14] The ratios were also estimated by the integrals of the corresponding 30C10 signals in proton NMR spectra (Figure 4.5) to be 1.0:0.85:0.81 for **4.8**, 1.0:0.66:0.46 for **4.9**, and 1.0:0.36:0.14 for **4.10** provided that 30C10 is threaded onto each sequence in equal probability. Relative to sequence "0", the experimental values for both "1" and "2" are greater than the calculated; this can be attributed to threading process. With H-bonding as driving force each esterification contributes threading. Therefore, sequences "1"

[14] Assuming the instantaneous concentrations of the -OH of diol BG, the -OH of 1,10-decanediol and the -COCl of sebacoyl chloride are [BG], [C_{10}] and [Cl], respectively, -d[BG]/dt = k_{BG}[BG][Cl] and -d[C_{10}]/dt = k_{C10}[C_{10}][Cl], where k_{BG} and k_{C10} are the esterification rate constants of diol BG and 1,10-decanediol, respectively. If k_{BG} = k_{C10}, d[BG]/d[C_{10}] = [BG]/[C_{10}]. [BG]/[C_{10}] = $[BG]_0/[C_{10}]_0$ = feed ratio (r) where $[BG]_0$ and $[C_{10}]_0$ are the feed concentrations. The probability for the esterification of the OH of diol BG with COCl, P_{BG}, is d[BG]/{d[BG]+d[C_{10}] = {k_{BG}[BG][Cl]}/{k_{BG}[BG][Cl]+k_{C10}[][C_{10}Cl]} = {[BG]/[C_{10}]}/{1+([BG]/[C_{10}])} = r/(1+r). The probability for the esterification of the -OH of 1,10-decanediol with -COCl, P_{C10}, is 1-P_{BG}. Therefore, the probabilities for the sequences "0", "1" and "2" are P_{BG}^2, $P_{BG}^2(1-P_{BG})^2$ and $P_{BG}^2(1-P_{BG})^4$, for example, 0.01, 0.0081 and 0.0066 for **4.8**. The relative product ratios of sequences "0", "1" and "2" are 1:0.81:0.66, 1:0.36:0.13 and 1:0.09:0.08 for **4.8**, **4.9** and **4.10**, respectively.

and “2”, the products of 4- and 7-step of esterification, respectively, will thread more 30C10 molecules per sequence than “0”, the product of 2-step esterification; the experimental value overestimated the amounts of “1” and “2” relative to “0”. In addition, possible different reactivities of two diol monomers and different degree of dethreading further complicate the issue. However, the calculated and measured values indeed have similar trends. Thus this finding may still imply a novel method to define copolymer sequence structures by the syntheses of polyrotaxanes.

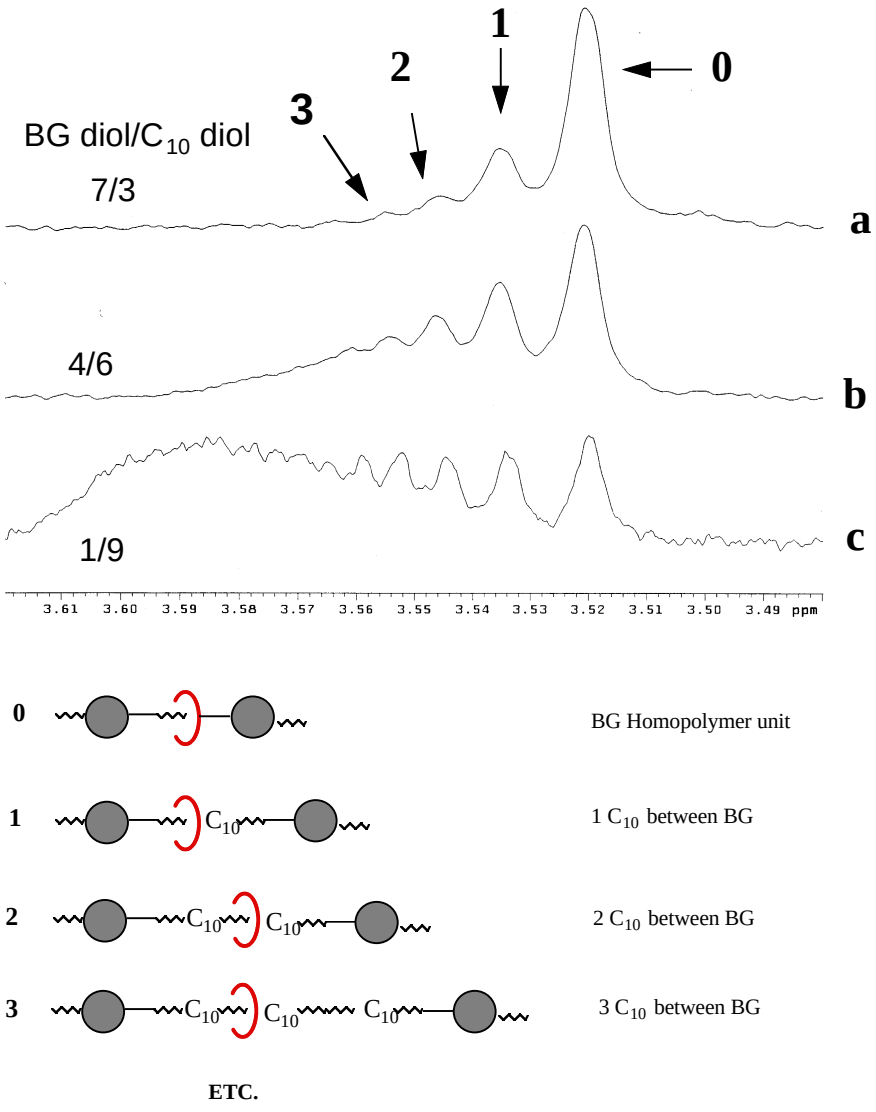


Figure 4.5 Expanded region for threaded 30C10 in 400 MHz proton NMR spectra of a) 4.10, b) 4.9 and c) 4.8 in $CDCl_3$

4.2.3 Threading and dethreading

After the formation of polyrotaxanes had been proved, m/n values of these copolyester 30C10 rotaxanes were measured by proton NMR spectroscopy. As the results in Figure 4.6 and Table 4.1 show, by incorporating diol BG **4.4**, the m/n values are always higher than that of polyrotaxane **4.5** without BG[8] and lower than that of polyrotaxane **4.6** with only diol BG **4.4** as the diol monomer, all made under the same conditions.[13] In addition, the threading efficiencies of the copolyester rotaxanes increased with the percentage of diol BG in the total diol. The linear relationship of m/n value vs. the proportion of diol BG **4.4** in the copolymers is shown in Figure 4.6.

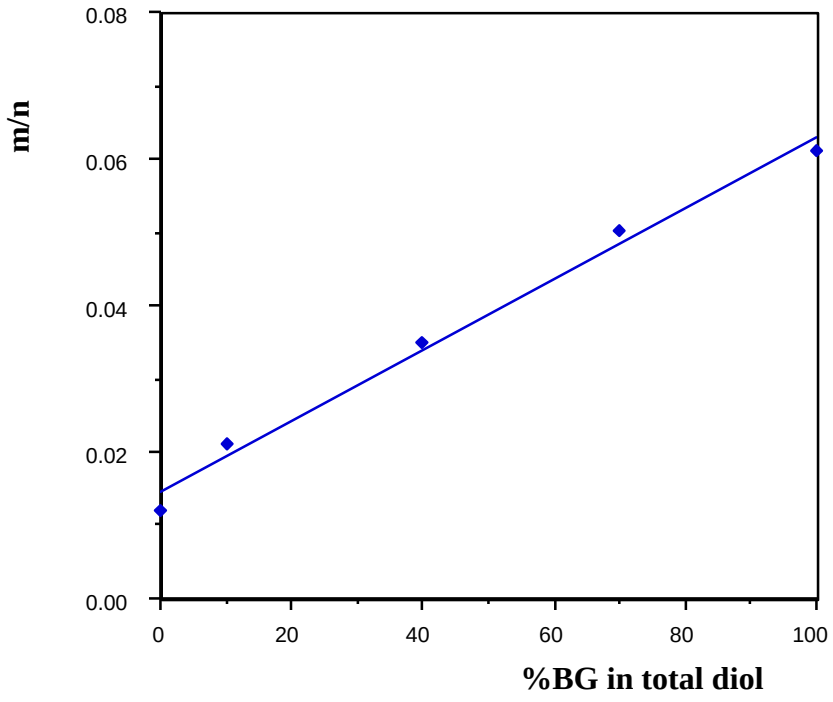


Figure 4.6 The relationship of threading efficiency of copolyrotaxanes vs. the feed percentage of diol BG 4.4 in total diol

Table 4.1: Threading efficiencies of copolyester rotaxanes with different feed ratios of BG **4.4** vs. total diol

polyrotaxane	% diol BG in total diol	1st ppt m/n[a]	2nd ppt m/n[a]	3rd ppt m/n[a]
4.5[8]	0			0.012
4.8	10	0.020	0.022	0.021
4.9	40	0.035	0.034	0.035
4.10	70	0.049	0.050	0.050
4.6[13]	100	0.061	0.060	0.061

a) estimated experimental error 5% relative.

All these results can be explained by proposed threading and dethreading processes during polymerization (Scheme 4.3). Once the polymer has formed dethreading is extremely slow as we have shown previously[9] and by the precipitation results of Table 4.1. After diol and 30C10 are mixed together, we believe that they form hydrogen bonds, a driving force for threading; some fraction of the esterification between -COCl and -OH takes place through the cavity of the crown ether. The possibility of esterification through the macrocyclic cavity depends on the ring size and other parameters. However, the resulting ester linkage presumably provides no attractive force to retain the threaded crown ether and thus dethreading can happen (Scheme 4.3). For copolyester rotaxanes, three types of structures, **4.11**, **4.12** and **4.13**, can be formed during the chain growth. For structure **4.12** derived from decanediol only, no end is blocked and threaded 30C10 can slip off in both directions. For structure **4.11** derived from BG diol, only one end is stoppered and dethreading can still occur but only in one direction. As soon as it is confined in structure **4.13** by reaction of **4.11** with a second BG diol, 30C10 can not dethread at all. Polymerization of decanediol with sebacoyl chloride can only produce structure **4.12** and thus polyrotaxane **4.5** has the largest dethreading degree. Polymerization of BG diol **4.4** and sebacoyl chloride only yields structures **4.11** and **4.13** and dethreading only happens in the time period before structure **4.13** is formed and thus polyrotaxane **4.6** has the lowest dethreading degree. However, during the syntheses of copolyester rotaxanes **4.8**, **4.9** and **4.10**, all three structures exist. When more BG is applied,

there is more structure **4.13** and less structure **4.12** and thus less dethreading and higher m/n values. Since polyrotaxane **4.6** has a maximum m/n value in the present study, the degree of dethreading during the polymerization period for the copolymeric polyrotaxanes can be determined as follows:

$$\text{Degree of Dethreading (\%)} = \left[\frac{(m/n)_{max} - (m/n)_{co}}{(m/n)_{max}}\right] x100\ \%$$

$(m/n)_{max}$: threading efficiency of diol BG-based homopolyester 30C10 rotaxane **4.6**

$(m/n)_{co}$: threading efficiency of diol BG-based copolyester 30C10 rotaxanes (**4.8**-**4.10**).

Scheme 4.3: The proposed threading and dethreading mechanisms for polyester 30C10 rotaxanes

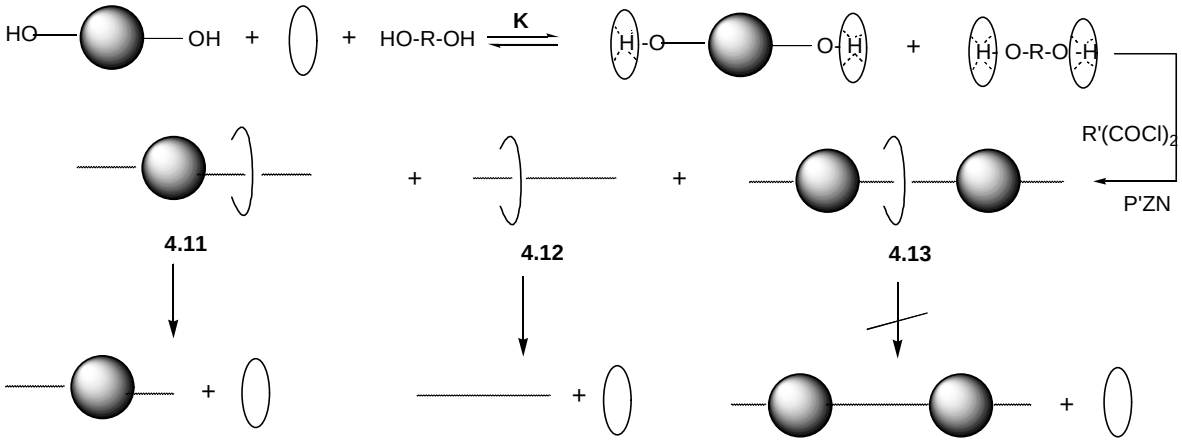


Table 4.2: Extent of dethreading in the preparation of copolyester 30C10 rotaxanes relative to polyrotaxane **4.6**

Polyrotaxane	**4.5**	**4.8**	**4.9**	**4.10**	**4.6**
% Diol BG in Total Diol	0	10	40	70	100
Dethreading Degree (%)	80	67	43	19	0

Based on the results in Table 4.1, the degree of dethreading was calculated (Table 4.2). Interestingly, the extent of dethreading vs. the amount of BG in copolymer is a very good linear relationship (Figure 4.7); the more BG, the less dethreading.

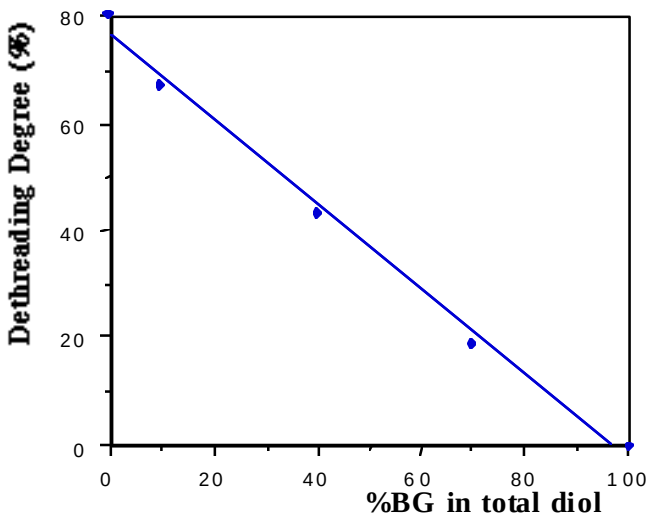


Figure 4.7 The relationship of dethreading degree vs. the feed percentage of diol BG 4.4 in total diol

4.3 Conclusions

Diol BG-based copolyester rotaxanes were synthesized. The polyrotaxanes were characterized by proton and carbon NMR spectroscopy, hydrolytic recovery of 30C10 and 2D NOESY studies. Threaded 30C10 exhibits a range of chemical shifts, reflecting the range of sequence structures in which it is located. In addition, the threading efficiency increases with diol BG content and a linear relationship of degree of dethreading vs. the percentage of diol BG was found.

4.4 Experimental

Chemical Reagents and Measurements

All chemicals were reagent grade and used directly as received from Aldrich unless otherwise specified. All solvents were HPLC or GC grade. 30C10 was prepared by a well-established procedure.[11] Diol BG **4.4** was synthesized by a reported method.[9] Proton NMR spectra, reported in ppm, were obtained on a 400 MHz Varian Unity spectrometer using chloroform-*d* solutions with tetramethylsilane as an internal standard. The NOESY study

was performed at room temperature with a mixing time of one second and a relaxation delay of two seconds. The following abbreviations have been used in describing NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet); coupling constants (J) are in Hertz. The m/n values of polyrotaxanes were measured by proton NMR spectroscopy and calculated from the integrals of threaded 30C10 vs. the methylene protons a, b, c and d of BG units in the backbone (Figure 4.1b). GPC analyses were done with a 150C ALC/GPC chromatograph equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel. The mobile phase was $CHCl_3$ and data were recorded at 35^oC at a flow rate of 1.0 ml/min. Molecular weights were calculated using the universal calibration and thus are absolute values.

Diol BG-based model copolyester 4.7

Diol BG **4.4** (259.6 mg, 0.4050 mmol) and 1,10-decanediol (105.8 mg, 0.6070 mmol) were dissolved in THF (3 mL, Na dried). After sebacoyl chloride (242.2 mg, 1.012 mmol) had been added, polymerization was run for 2 days under the protection of nitrogen at 63 ^oC. After it had been cooled down, the resulting polymer was purified by precipitation into methanol (200 mL). A dry rubbery material (503 mg, 94%) was obtained. GPC: M_n=8.6 kg/mol and PDI=1.8. ^1H NMR in $CDCl_3$ (Figure 4.1c): 7.22 (d, J=8.8, 1.6H), 7.06 (m, 3.2H), 6.77 (d, J=8.8, 1.6H), 4.24 (m, 1.6H), 4.10 (s, broad, 1.6H), 4.05 (t, J=6.8, 2.4H), 3.84 (s, broad, 1.6H), 3.76 (m, 1.6H), 2.29 (m, 4H), 1.59 (m, $\underline{H_2}O$ plus 6.4H), 1.29 (s, 22.4H); ^{13}C NMR in $CDCl_3$: 173.94, 173.79, 156.50, 148.35, 144.16, 139.87, 132.23, 130.61, 124.10, 113.11, 69.71, 69.38, 67.23, 64.39, 63.34, 62.78, 34.36, 34.29, 34.16, 31.38, 29.46, 29.24, 29.11, 28.66, 25.92, 24.97, 24.85.

Diol BG-based copolyester 30C10 rotaxanes 4.8, 4.9 and 4.10

Diol BG **4.4** and 1,10-decanediol (total 1 eqv.) were dissolved in 30C10 (2 eqv.) at 63 ^oC and then the solution was stirred for 30 minutes to achieve equilibrium. After sebacoyl chloride (1 eqv.) had been added, polymerization was run for 2 days at the same temperature. After the system had been cooled down, the product was precipitated from THF into water

(3x200 mL). The polyrotaxanes were proved to be free of the unthreaded 30C10 by the disappearance of the δ3.67 signal in ^{1}H NMR spectra. For different copolymer rotaxanes, starting feed ratios were as shown in Table 4.3.

Table 4.3 Starting feed ratios for copolyester rotaxanes

polyrotaxane	ratio (BG vs. decanediol)	diol BG **4.4** (mg/mmol)	decanediol (mg/mmol)	30C10 (mg/mmol)	acid chloride (mg/mmol)
4.8	1/9	32.0/0.050	78.4/0.450	440/1.00	120/0.500
4.9	4/6	128/0.200	52.2/0.30	440/1.00	120/0.500
4.10	7/3	224/0.350	26.1/0.150	440/1.00	120/0.500

The recovery for polyrotaxanes after three precipitations were from 92% to 94%. ^{1}H NMR in $CDCl_3$ for diol BG-based copolyester rotaxanes: a) polyrotaxane **4.8**, 7.22 (d, J=8.8, 0.4H), 7.06 (m, 0.8H), 6.77 (d, J=8.8, 0.4H), 4.24 (t, J=4.8, 0.4H), 4.10 (t, J=4.8, 0.4H), 4.04 (t, J=6.8, 3.6H), 3.83 (t, J=4.8, 0.4H), 3.76 (t, J=4.8, 0.4H), 3.65-3.52 (m, variable), 2.29 (m, 4H), 1.59 (m, 7.6H plus $\underline{H_2O}$), 1.29 (s, 20.6H); b) polyrotaxane **9** (Figure 4.1b), 7.22 (d, J=8.8, 1.6H), 7.06 (m, 3.2H), 6.84 (m, minor) and 6.77 (d, J=8.8, major) (total 1.6H), 4.24 (s, broad, 1.6H), 4.10 (s, broad, 1.6H), 4.04 (t, J=6.8, 2.4H), 3.83 (s, broad, 1.6H), 3.76 (s, broad, 1.6H), 3.58-3.52 (m, variable), 2.29 (m, 4H), 1.59 (m, 6.4H plus $\underline{H_2O}$), 1.29 (s, 22.4H); c) polyrotaxane **4.10**, 7.22 (d, J=8.8, 2.8H), 7.06 (m, 5.6H), 6.84 (m, minor) and 6.77 (d, J=8.8, major) (total 2.8H), 4.24 (m, 2.8H), 4.10 (s, broad, 2.8H), 4.05 (t, J=6.8, 1.2H), 3.84 (s, broad, 2.8H), 3.76 (m, 2.8H), 3.56-3.52 (m, variable), 2.29 (m, 4H), 1.59 (m, $\underline{H_2O}$ plus 5.2H), 1.29 (s, 24.2H); ^{13}C NMR in $CDCl_3$ of polyrotaxane **4.9**: 173.94, 173.79, 156.50, 148.35, 144.16, 139.87, 132.23, 130.61, 124.10, 113.11, 70.52-70.6, 69.71, 69.38, 67.23, 64.39, 63.34, 62.78, 34.36, 34.29, 34.16, 31.38, 29.46, 29.24, 29.11, 28.66, 25.92, 24.97, 24.85. GPC: M_n=17.2 kg/mol and PDI=1.8 for **4.8**; M_n=22.4 kg/mol and PDI=1.8 for **4.9**; M_n=17.2 kg/mol and PDI=1.9 for **4.10**.

Hydrolysis of diol BG-based copolyester 30C10 rotaxane 4.9

Diol BG-based copolyetser 30C10 rotaxane **4.9** (m/n=0.0214) (100 mg) was dissolved in THF (3 mL). Then potassium hydroxide (500 mg) in water (2 mL) was added to the THF solution. After refluxing for 24 hours, all solvents were removed by rotary evaporation under vacuum. The solid product was extracted with chloroform to afford neutral hydrolysis products. It was found that only decanediol, diol BG **4.4** and free 30C10 were present (Figure 4.2b). Pure 30C10 was recovered by the extraction of the neutral products with hexane, ^{1}H NMR: 3.67 (s) (Figure 4.2c).