THE SYNTHESIS AND CHARACTERISATION OF SOME POLYMERS OF NOVEL TOPOLOGY

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by

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ABSTRACT

This thesis deals with the synthesis and characterisation of some polymers of novel topology. It is split into two sections, Part one dealing with the synthesis of some polypseudorotaxanes and part two dealing with the synthesis of cyclic oligomers.

Part One

Polypseudorotaxanes have been synthesised using the Stoddart cyclophane **(1)** with aromatic polyether/esters. The polypseudorotaxanes where examined mainly using ^{1}H NMR spectroscopy which gives information on the structure of the polymer chain but also using UV spectroscopy and viscosity studies.

Part Two

Cyclic oligomers have been synthesised previously using a polymer-support, in some cases a mass increase was observed in the polymer-support after cyclisation. In the present case a degradable network was synthesised which was then used as the polymer-support to carry out cyclisation reactions. The mass of the polymer-support was carefully monitored and if a weight increase was observed the polymer-support was degraded and the soluble fragments were analysed for any evidence of released cyclic oligomers.

DECLARATION

This Thesis is Submitted to the faculty of Science for the degree of Doctor of Philosophy at the University of Manchester, England, UK. It represents the author's research work carried out in this university from October 1993 to October 1996.

All the data and spectra presented in this thesis are entirely aujthentic and original unless stated otherwise. No portion of this Thesis has been submitted in support of an application for any other degree or qualification of this or any other university or institute of learning.

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All the technicians at the University of Manchester for carrying out analysis.

THIS THESIS IS DEDICATED TO

CAROLINE

AND

TO MY PARENTS.

ABBREVIATIONS

1. General

DMF	N,N -Dimethylformamide
DP	Degree of Polymerisation
DVB	Divinylbenzene(s)
PEG	Poly(ethylene glycol)
THF	Tetrahydofuran
Ts	Toluene-*p*-sulphonyl chloride

2. Description of Nuclear Magnetic Resonance (NMR) Spectra.

br	broad
d	doublet
m	multiplet
q	quartet
s	singlet
t	triplet

3. Mass Spectra

MS	Mass Spectrometry
CI	Chemical Ionisation
EI	Electronic Ionisation
FAB	Fast Atom Bombardment
MALDI	Matrix Assisted Laser Desorption Ionisation
TOF	Time of Flight

CHAPTER 1

GENERAL INTRODUCTION

Polymers have been used by Nature since the beginning of time. For example, DNA, the building block of life is a polymer.[1] It may be surprising then that man did not start to characterise and synthesise polymers until early this century. The first polymer to be studied in depth was rubber.[2] Since then many polymers have been well documented. Linear polymers are well known, for example, poly(styrene) or poly(methyl methacrylate), and these have found uses in many areas.[3] Cross-linked polymers or polymer networks are also well known, for example, vulcanised rubber or many of today's thermosets and these also have found uses in many areas.[4] Much is now known about simple polymers like linears or networks but there are still many interesting areas open to us: one of these is in dealing with polymers of novel topology.

Topology is the study of connectivity. Polymers of novel topology are interesting because they may have interesting properties. Polymers of novel topology include, for example, ladders, stars, dendrimers, catenanes and cyclics. Cyclic polymers are included in the list of polymers with novel topology as even this simple shape may lead to some interesting properties. Although the shape of cyclic polymers is a simple one the synthetic methods required for their production and their characterisation are not straightforward. The present projects are involved with the synthesis of polymers of novel topology, in particular cyclic oligomers and polypseudorotaxanes.

Some examples of polymers of novel topology will be discussed briefly in the following sections.

1.1 LADDER POLYMERS

One of the first types of polymer of novel topology to be synthesised were the ladder polymers.[5] These polymers, as their name suggests, are formed in the general shape of a ladder, see Figure 1 . Overberger and Moore have defined a ladder polymer as ' a polymer constructed of an uninterrupted series of rings connected by sterically restrictive links around which rotation cannot occur without bond rupture.' [5]

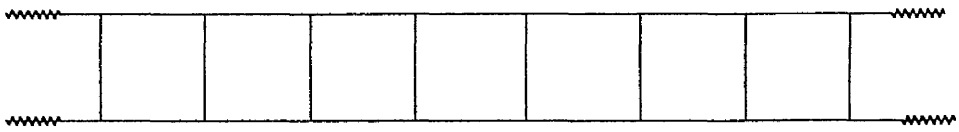


Figure 1

One of the main reasons for the interest in ladder polymers is their potentially high thermal stability. This enhanced thermal stability is derived from the fact that in order to destroy the properties of a polymer, the chain must be broken, that is, the molecular weight of the polymer must be reduced. The reduction in the molecular weight of a linear polymer may be achieved by the cleavage of just one bond and this can be any bond along the polymer chain. To effect a reduction in molecular weight of a ladder polymer, it is necessary to cleave a least two bonds in any one ring. This is very unlikely in a polymer where all the bonds are of comparable strength, as the cleavage of bonds is a random process. The stability of the ladder polymers is further enhanced by the fact that when a bond is broken,

the two free ends are held in close proximity to one another and hence, recombination may occur.

One example of a ladder polymer was the product formed from the cyclisation of poly(3,4-isoprene), see Figure 2.[6,7,8] The resulting ladder polymer had an initial modulus of 2.5 - 3.5 x 10^5 psi a tensile strength of 2,300 - 4,700 psi and an elongation of only 1 - 2% whereas the initial linear polymer had an initial modulus and tensile strength of less than 500 psi and an elongation of 435%. The Tg increased from -20 °C to +90 °C, the inherent viscosity from 0.3 - 0.5 to 0.8 - 1.2 and the molecular weight Mn: 33,000 to 44,000 and Mw: 85,000 to 120,000. This increase in the molecular weight suggests that some intermolecular reactions have taken place during the cyclisation.[5]

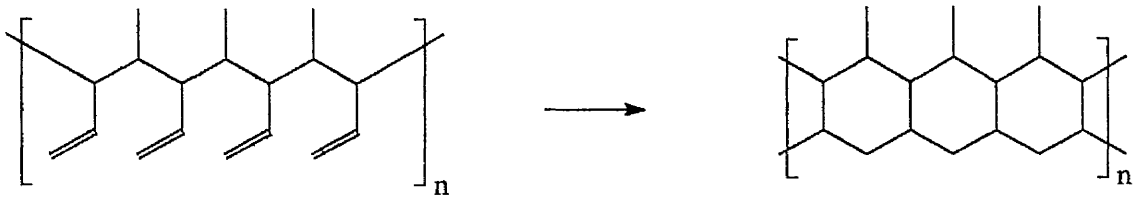


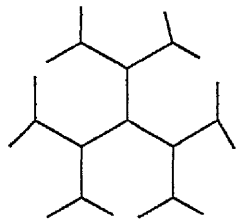
Figure 2

By synthesising a ladder polymer consisting of aromatic moieties, the thermal stability of the resulting polymer is increased still further due to the high strength of the aromatic components.

Ladder polymers are often very insoluble and hence, they may be difficult to synthesise. There are many examples of ladder polymers and much work has been done in this area.

1.2 STARS AND DENDRIMERS.

The word dendrimer is derived from the Greek word "dendron" meaning tree.[9] A dendrimer is a molecule which starts at a focal point and extends outwards with many branches (like a tree).



There are two main approaches to the synthesis of dendritic polymers. One is the "Divergent" approach i.e. starting at the focal point and working outwards. The other is the "Convergent" approach i.e. starting at the outside and working towards the focal point.

The divergent approach is in principle the simplest method of synthesising dendrimers. Many dendrimers have been prepared by the divergent approach, for example, Tomalia *et al* have produced dendrimers using ammonia as the core, see Figure 3.[10] Unfortunately, in practice the divergent approach may produce dendrimers with many deletions. This is due to the fact that if a reaction does not go to completion, then a branch may be missing and this imperfection would continue along the structure. The imperfect structure would be very difficult to separate from the perfect structure, probably the only method available is column chromatography. Even this method, however, does not always permit full

purification. Moreover it is a very slow process and thus to build up a dendrimer of reasonable size would take a long time.

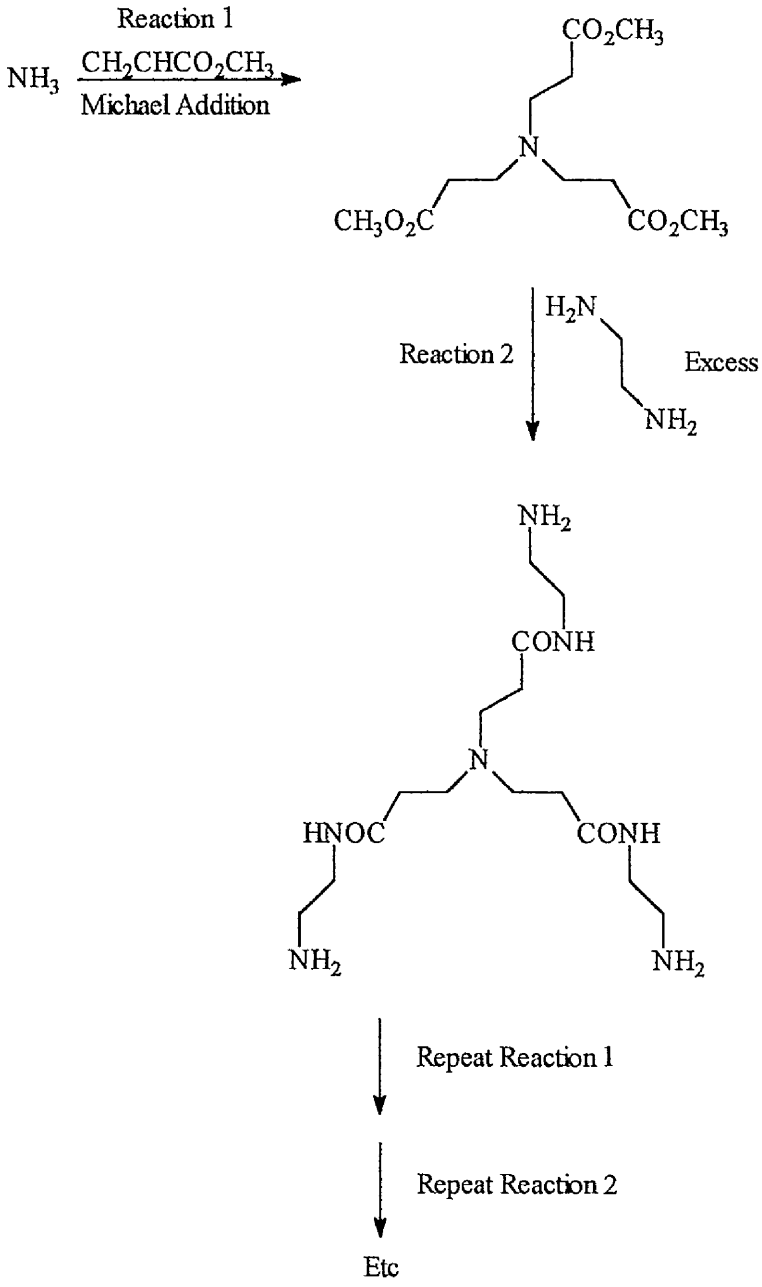


Figure 3

The convergent approach for the synthesis of dendrimers is more complicated. Frechet *et al* have produced dendrimers using the convergent approach.[11] The strategy of such a synthesis is outlined in Figure 4. The dendron monomers or 'wedges' are produced initially. These may then be purified before being attached to the core. Care must be taken when preparing dendrimers in this way, as, if the wedges produced are too large then the addition of these wedges to the central core may not be possible due to steric hinderance.

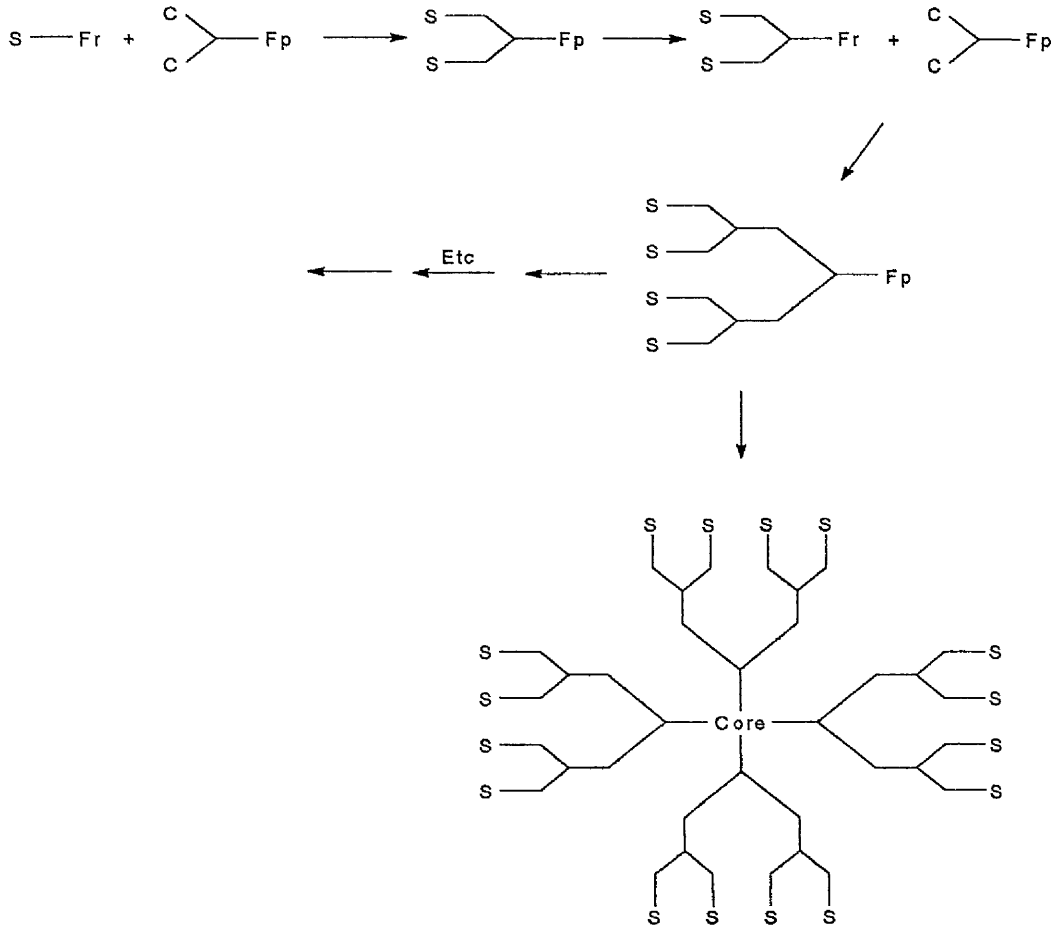


Figure 4

Dendrimers have an approximately spherical shape and may, if the outer shell is hydrophilic, have properties similar to those of micelles.[12] Dendritic micelles are more stable than their monomeric counterparts because they cannot dissociate. Dendrimers also have unexpectedly high solubilities and low viscosities due to their topology.

The examples of polymers of novel topology discussed above illustrate how novel structures can confer novel properties to the system and this explains our interest in this area of polymer chemistry.

The work described in this thesis has been split into two parts, one dealing with the synthesis of cyclic oligomers and polymers and the second dealing with the synthesis of polyrotaxanes. We will begin by reviewing previous work on each of these topics before discussing the results gained during the course of the present research.

1.3 MOLECULAR MODELLING

Molecular modelling was found to be a useful tool to aid in the structure elucidation of the polypseudorotaxanes. Although the structures determined may not be accurate they do appear to filt well with X-ray crystal structure data acquired by Stoddart and with the ^{1}H NMR spectra obtained.

The molecular modelling was carried out on Silicon Graphics workstations using the Macromodel program.

PART 1

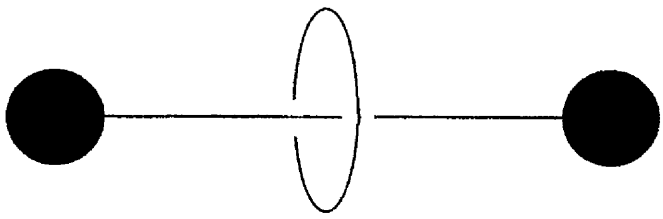
POLYMERIC ROTAXANES

CHAPTER 2

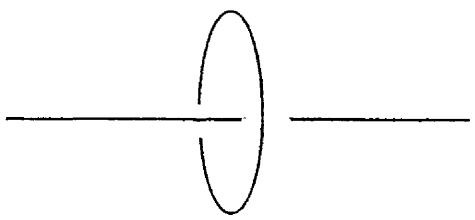
INTRODUCTION FOR ROTAXANES

2.1 WHAT IS A ROTAXANE?

The word rotaxane is derived from the Latin words "rota" meaning wheel and "axis" meaning axle.[13] A rotaxane is, therefore, defined as a cyclic compound through which passes a linear thread. A rotaxane classically has large "stoppers" at either end of the linear thread to prevent the cyclic component from falling off the ends.[14] If these large stoppers are absent, then the resulting species is defined as a pseudorotaxane, see Figure 5. If the thread used is polymeric then the prefix 'poly' is used to denote the polymeric nature of the rotaxane or pseudorotaxane.



A ROTAXANE



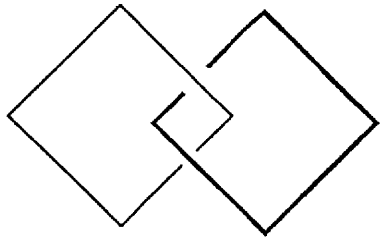
A PSEUDOROTAXANE

Figure 5

2.1.1 RELATED SYSTEMS - CATENANES

Catenanes are included here as often - especially where recognition techniques are used for the synthesis of rotaxanes - the same general methods can be used for catenane synthesis as for the synthesis of rotaxanes.

The word catenane is derived from the Latin word "catena" meaning chain.[15] Catenanes are defined as " a molecule which contains two or more interlocked rings, which are inseparable without the breaking of a covalent bond".[16,17] This is shown schematically in Figure 6.



A Catenane

Figure 6

2.2 HOW CAN ROTAXANES AND PSEUDOROTAXANES BE SYNTHESISED?

There are two different approaches to rotaxane synthesis.

2.2.1 ROTAXANES FORMED BY STATISTICAL METHODS.

In general cyclic molecules which have at least 22 ring atoms, mixed with any linear chain, should give some degree of threading.[18,19,20] The cyclic molecule must have at least 22 ring atoms in order to give a large enough ring cavity through which a simple linear hydrocarbon chain may thread. The chance of a cyclic molecule initially threading onto a linear one is purely statistical. This cyclic molecule may then remain threaded, or it may leave the linear chain. The amount of threading expected in this case would be small, as often the entopy of the system would be decreased by forming a rotaxane due to the restricted movement of the threaded cyclic.[21]

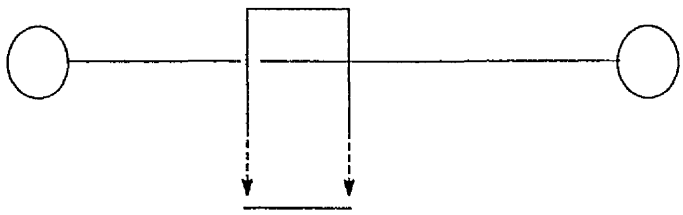
2.2.2 ROTAXANE FORMATION ASSISTED BY MOLECULAR RECOGNITION.

In order to increase the amount of threaded cyclics present in a rotaxane system and also the yield of rotaxane formation, a favourable interaction between the cyclic and linear molecules is desirable.[22-24] This positive interaction will increase the enthalpy of the system. If this increase in enthalpy is greater than the decrease in entropy then any threaded cyclics should remain on the chain. This system will give better yields of rotaxane but both the linear and cyclic molecules must be carefully designed in order to observe molecular recognition.

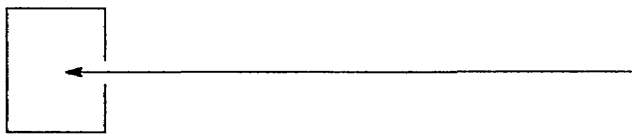
There are three ways in which to produce rotaxanes. These are shown in Figure 7. All these methods are useful for different reasons and they are all used to synthesise

different rotaxane systems.

"CLIPPING"



"THREADING"



"SLIPPING"

Figure 7

2.2.2.1 "Clipping" [25]

This is a very useful method if the cyclic component that is to be used is either insoluble in the required solvent system : some cyclic components are insoluble if formed as a single entity but are very soluble when incorporated into a rotaxane system

eg cyclic amides, see Section 2.4.1.2, or when the synthesis of the cyclic component as a free entity is very difficult : in some systems the cyclic component may be strained and unstable when formed as a single entity but may be stable when formed as part of a rotaxane system. An example of this, is the electron poor cyclophane **(1)** synthesised by Stoddart, see Section 2.5. In the case of "Clipping" purification is often quite difficult due to the presence of many different reaction products as follows.

1) A mixture of many sizes of cyclic and linear material may be formed during the cyclisation reaction.

2) Linear Component. This should be pure as long as no de-composition has occurred during cyclisation.

3) Rotaxane formed from an interaction between the linear and cyclic components. There may be many different rotaxanes due to the large amount of linear and cyclic materials.

2.2.2.2 "Threading" [26]

This is often an easier method for the synthesis of pseudorotaxanes if the cyclic and linear components are easily obtained as pure free entities. In this case purification is often much easier than the purification of rotaxanes made by "Clipping" as there will only be three compounds present as follows.

1) Pure cyclic component

2) Pure linear component

3) Rotaxane

2.2.2.3 "Slipping"[27]

This method is very similar to the "Threading" method, in this case though, bulky end groups may be needed at each end of the thread to prevent the loss of the cyclic component. It is sometimes possible to "squeeze" the cyclic component over the bulky end groups by a high energy process, once this energy is removed, no de-threading will occur. This system is again usually relatively easy to purify for the same reasons as for the "Threading" method.

The only way to produce a catenane is to use the "Clipping" method as it is not possible to thread one cyclic molecule onto another. As we have two cyclic molecules it is possible to close either one of them to form the catenane.

2.3 SOME EXAMPLES OF PSEUDOROTAXANES AND POLYPSEUDOROTAXANES

2.3.1 EARLY ATTEMPTS AT ROTAXANE SYNTHESIS.

Harrison and Harrison synthesised the first rotaxane in 1967, see Figure 8 [28]. This was formed by the statistical method and hence the yield was low. To counteract this the reaction was carried out using a polymer-supported ring. This facilitated the repetition

of the threading process seventy times. The product was then cleaved from the support. Overall the rotaxane was formed in 6% yield. This is clearly not a very practical synthesis due to the large amount of repetition and the low yield but it did prove that the synthesis of rotaxanes was possible.

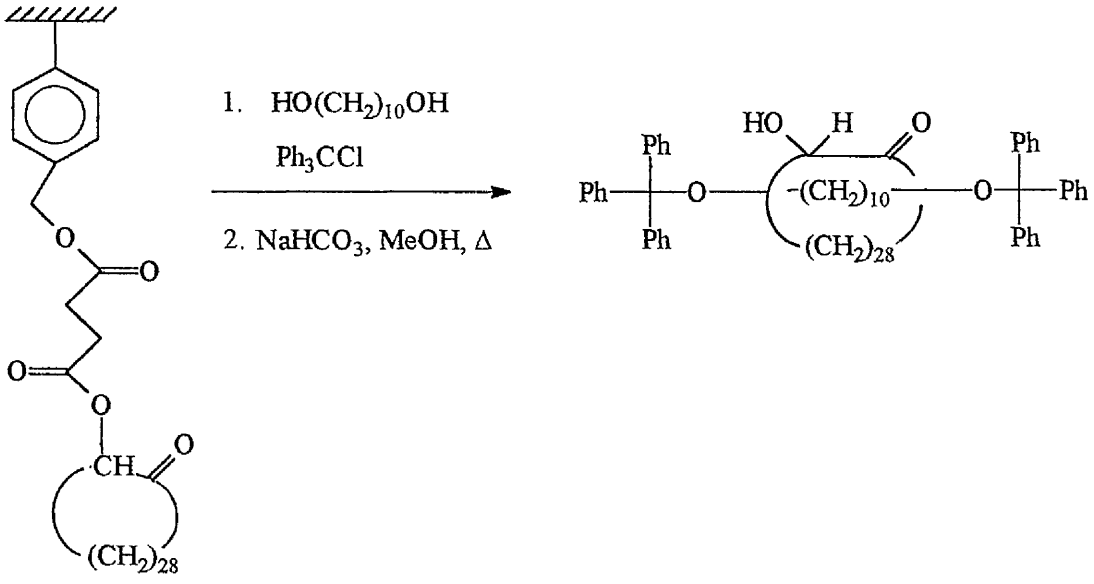


Figure 8

The same rotaxane as shown in Figure 8 was synthesised by I.T.Harrison using the "Clipping" method, see Figure 9.[29] The synthesis was also carried out with different sizes of ring. The length of the chain in the cyclic was varied from 27 - 39 CH_2 units. It was found that a ring containing 29 CH_2 units did not de-thread at ambient temperature whereas rings containing 33 or more CH_2 units where found to de-thread quite rapidly. Thus, the trityl groups only act as stoppers for rings containing less than

33 CH_2 units. Although the maximum yield achieved using this method was only 1.6%, it is nevertheless an improvement on the first synthesis as the reaction was only carried out once.

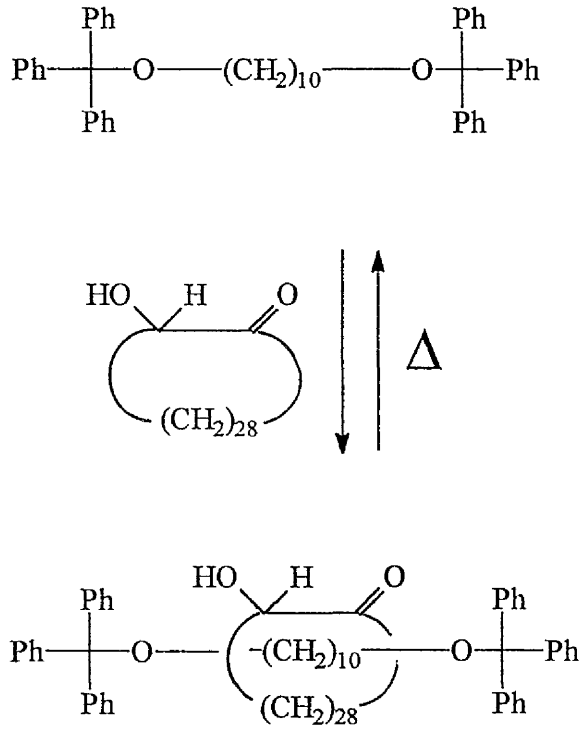


Figure 9

2.3.2 ROTAXANES FORMED FROM CROWN ETHERS

Higher yields of rotaxane were achieved by Zilkha and Agam in 1976.[30,31] They used polyethyleneglycols as the linear component and dibenzocrown ethers as the cyclic component. These components were allowed to mix before adding naphthalene-1,5-diisocyanate to form a polyurethane rotaxane. The yield of the rotaxane, i.e. the

percentage of the crown present in the product, was ca. 15%, see Figure 10. Other rotaxanes using crown ethers have been produced by H.W.Gibson *et al*, in this case many different threads were used showing the variety allowable using the statistical threading method.[32-35]

Gibson demonstrated the formation of rotaxanes using a combination of techniques.[33]

1) After completion of the reaction selective precipitation was used to collect any crown that was not threaded. This procedure was repeated several times. The mass of crown recovered was then compared to the original mass used. This showed a loss of mass which was then attributed to threaded material.

2) After all free cyclics have been removed, NMR spectral analysis showed signals due to the presence of the crown ether in the final polymer.

3) GPC analysis of the final product showed just one peak. A mixture of polymer and crown ether showed two peaks.

By these techniques it was possible to show that crown ethers had been incorporated into the polymer structure.

Gibson has shown that by using the crown ethers as the solvent the yield of rotaxane is increased significantly.[35] The crown ethers are very good solvents due to their polar nature.

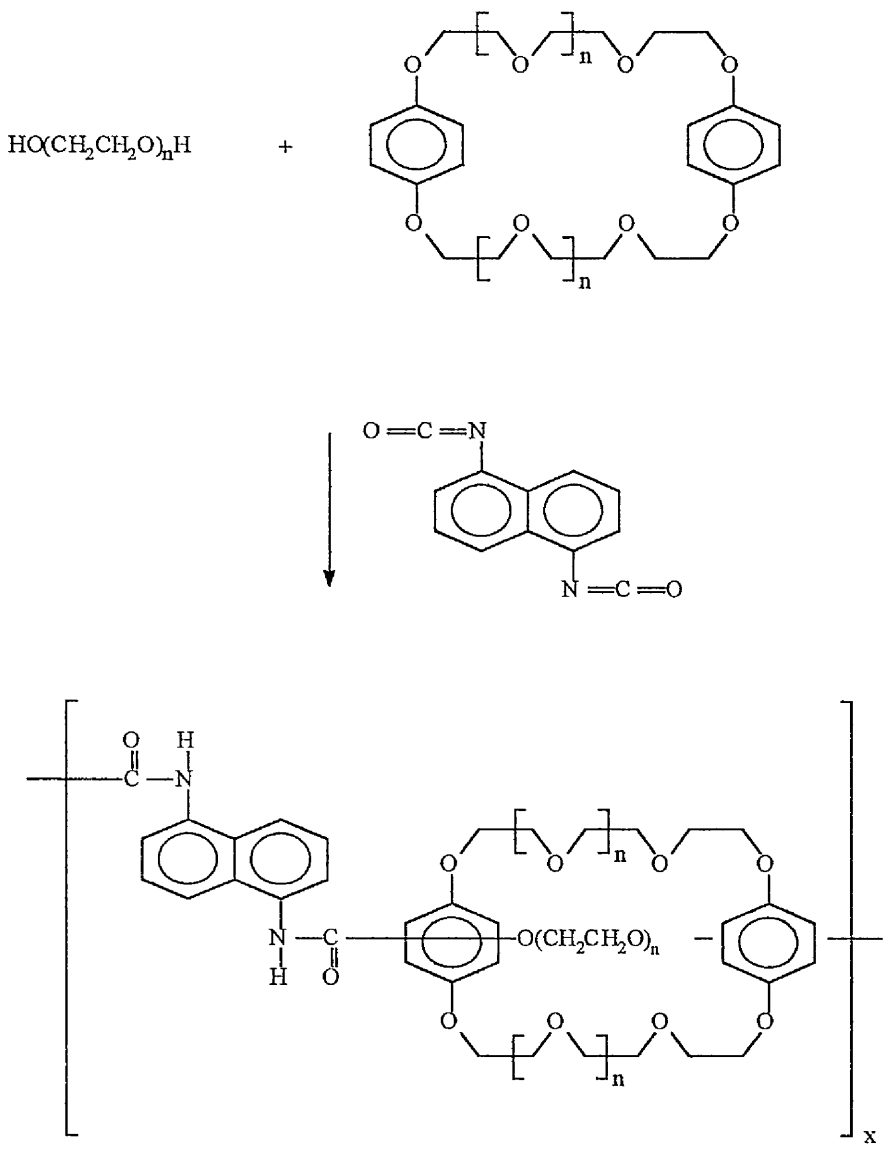


Figure 10

Another interesting property of the crown ether rotaxanes is their solubility. Gibson has shown how the very soluble crown ethers help to solubilise the less soluble threads. For example, a polyurethane that is insoluble in solvents such as water, dichloromethane and acetone, when used to form a rotaxane containing crown ethers, gives products which are soluble in both dichloromethane and acetone.[36] This shows

that one possible use for rotaxanes is in the processing of polymers.

Results taken from both Harrison's and Gibson's work show that the amount of threaded cyclics obtained for any given reaction is dependant on a number of factors as discussed below.[33,36]

1) The Ratio of Cyclics : Linears

The higher this ratio then the larger the amount of threaded cyclics obtained.

2) The Size of the Cyclics Used

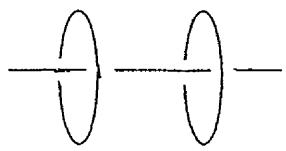
A cyclic must have a large enough cavity to enable the threading of the linear chain. Above this minimum ring size, the larger the cyclics that are used then the higher the amounts that are threaded.

3) The Length of the Threads

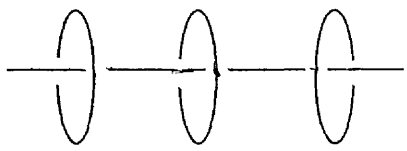
The longer the thread used then the higher the amount of threaded cyclics. It should be noted that it is more difficult to cause the de-threading of cyclics when a longer chain is used for the thread. This is due to two reasons.

a) A longer chain existing as a random coil may in effect tie itself in a knot thus preventing the de-threading of any cyclics trapped in the region of the chain that is knotted.

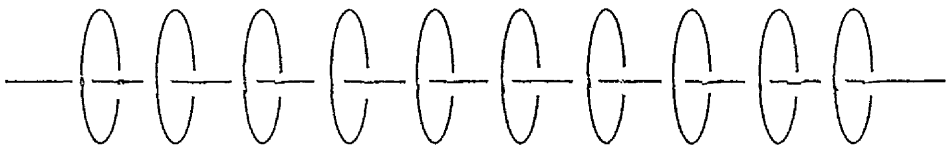
b) There is a "queuing" effect present for long chain threads.[37] A cyclic in the middle of the chain cannot become free until the cyclics at the ends of the chain are free, see Figure 11.



Both cyclics are able to escape from the chain



2 out of 3 of the cyclics are able to escape from the chain



In the case of a long chain the majority of the cyclics are trapped on the chain by neighboring cyclic molecules, hence the "queuing effect"

Figure 11

4) The Concentration of the Reaction

The higher the concentration of the reactants, i.e. the linear thread and the cyclics, then the more likely it is for the cyclic and linear molecules to meet and therefore possibly thread, hence the higher the amount of threaded cyclics present.

2.4 ROTAXANES FORMED USING MOLECULAR RECOGNITION TECHNIQUES.

In order to increase the yield of rotaxane formation to practically useful levels it is necessary to introduce some form of favourable interaction to force the reaction

equilibrium between cyclic and linear towards rotaxane formation, see Figure 12. Recently there have been many studies of such systems and the following sections will examine some of these.[38]

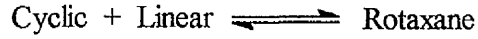


Figure 12

2.4.1 ROTAXANES USING HYDROGEN-BONDING TO AID COMPLEXATION

2.4.1.1 Rotaxanes Formed Using Cyclodextrins as Cyclics.

Luttringhaus and co-workers reported the first attempted catenane synthesis in 1958.[15] They chose to use the readily available α-cyclodextrin as one cyclic component, see Figure 13.[39,40] Luttringhaus attempted the synthesis of a catenane using α–cyclodextrin as shown in Figure 14. Although this synthesis may have failed the precursor to this is in fact a pseudorotaxane.

Ogino and co-workers in 1981 published the synthesis of [2]rotaxanes containing α–cyclodextrins using the α,ω–diaminoalkane thread shown in Figure 15.[41] The yield of [2]rotaxane was between 2 and 19%.

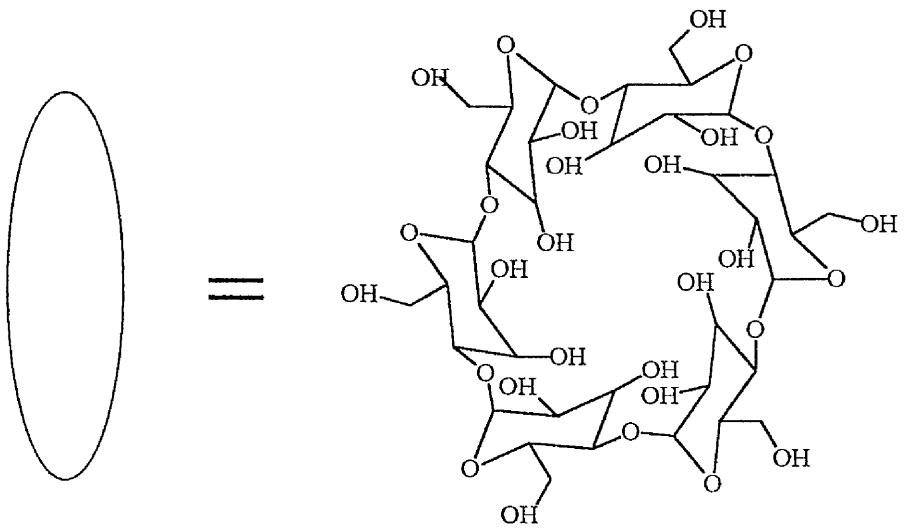
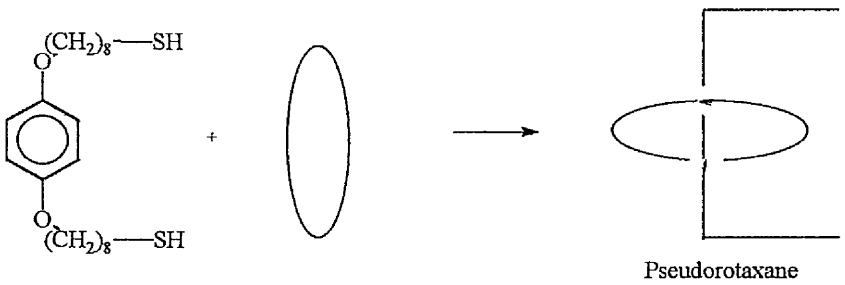


Figure 13



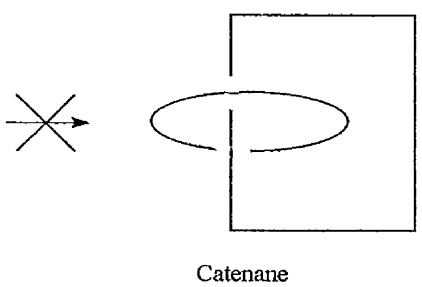


Figure 14

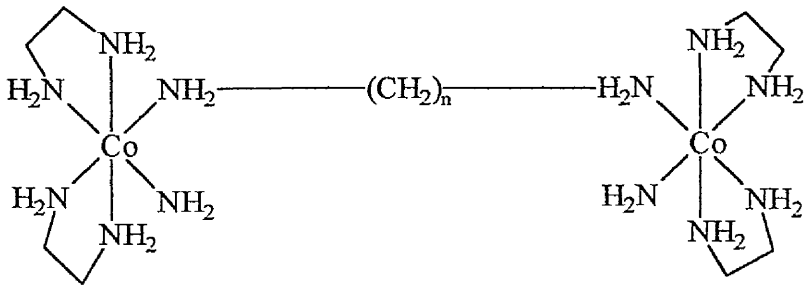


Figure 15

Lawrence and co-workers published the synthesis of a similar [2]rotaxane in 1990 using α–cyclodextrin and the thread shown in Figure 16.[42] This [2]rotaxane was synthesised in a much more respectable yield of 71% probably because of a stronger complex formed between the α–cyclodextrin and this thread compared to the one shown in Figure 15.

Figure 16

Ogata and co-workers in 1976 published the synthesis of a poly(pseudorotaxane) containing many α–cyclodextrins as the cyclics, and they showed that these poly(pseudorotaxanes) -many of which were formed from polyamides- had a marked

increase in solubility when complexed with the cyclodextrins.[43]

Some novel tubular polymers have recently been synthesised using polyrotaxanes as precursors, see Figure 17.[44] The α–cyclodextrin rings threaded onto the polymer chain are linked together by reaction of the pendant alcohols in the α–cyclodextrin with epichlorohydrin. Removal of the stoppers at either end of the chain then allows de-threading to take place leaving a polymer tubule. The latter was obtained in 92% yield. This is clearly a very complex structure whose synthesis has been made possible by the use of a polyrotaxane.

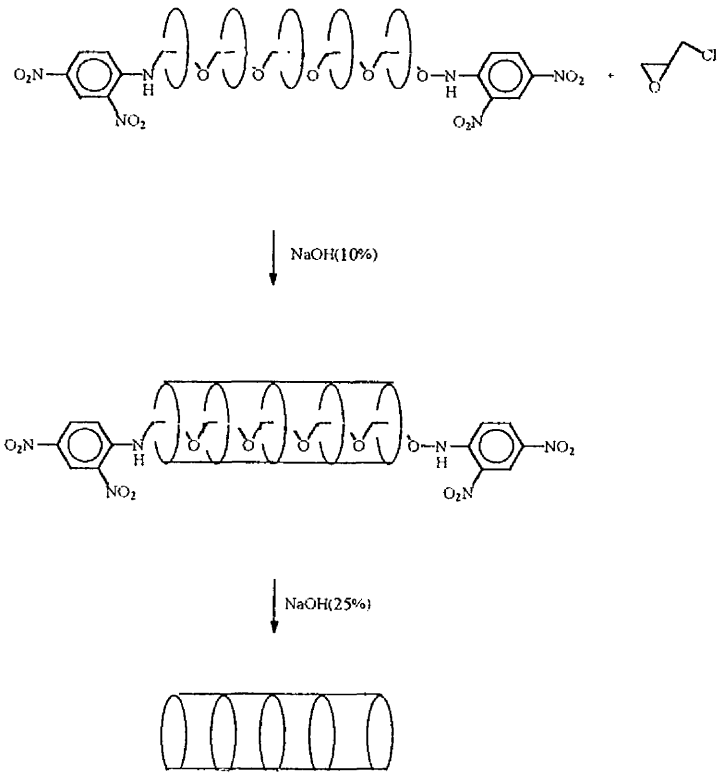


Figure 17

2.4.1.2 Template Directed Synthesis Using Amides As Hydrogen Bonding Moieties

Polyamides have long been known to act as hydrogen bonding acceptor-donors.[45] Polyamides are notoriously insoluble due to hydrogen bonding interactions in the crystal structure resulting in, in effect a network like structure. It is not surprising then that amides can be used to aid the formation of rotaxanes.

Hunter and co-workers published the synthesis of the first amide containing catenane in 1992.[46] The synthesis of this catenane was reportedly found by accident. The research group had synthesised the macrocycle shown in Figure 18 and were attempting to increase the yield. In order to increase the yield of the reaction a precursor to the cyclic was synthesised. This precursor was formed by reacting two moles of diamine with one mole of diacid chloride. This was then cyclised by reacting with one equivalent of the diacid chloride. Mass spectral analysis of the resulting compound showed a mass twice that expected for the required macrocycle. What had actually been synthesised was a catenane formed by the interaction of two of these macrocycles, and this had been formed in 34% yield, see Figure 19.

In 1995 Leigh and co-workers published the synthesis of a similar amide containing catenane.[47] The Leigh catenane was formed from a 2+2+2+2 cycloaddition using readily available p-xylylene diamine and isophthaloyl dichloride. In this case the catenane was formed in 20% yield. The single macrocycle that was also formed in the reaction was found to be insoluble in chloroform whereas the catenane is soluble in the

same solvent. This again shows how the use of rotaxanes and catenanes may aid with the processability of polymers.

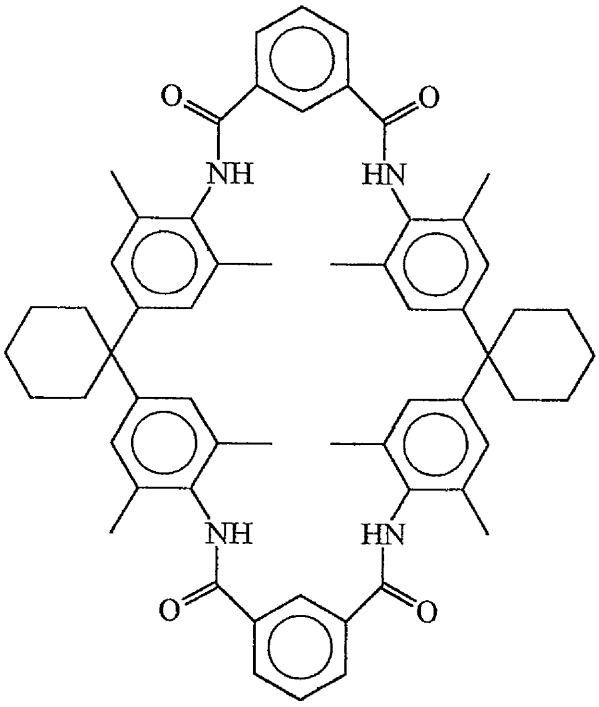


Figure 18

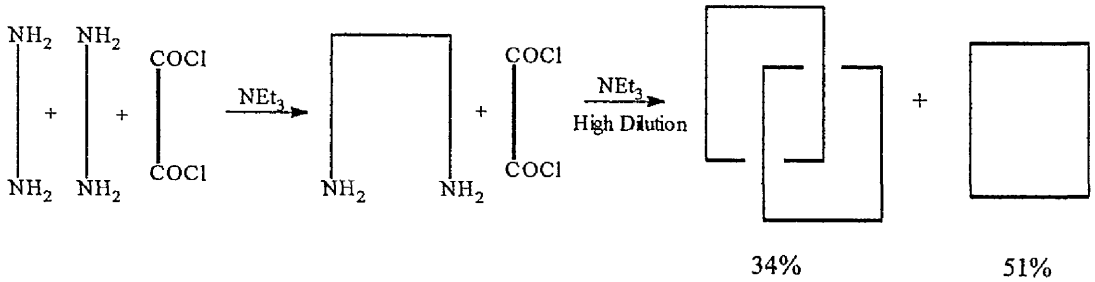


Figure 19

2.4.1.3 Template Directed Synthesis Using Metal Ions As Binding Moieties

Sauvage and co-workers have published the synthesis of many novel topological structures using metal ions as templates.[48,49] Copper(I) was chosen due to the tetrahedral shape of many of its complexes.[50] Although many novel structures have been formed using this approach the basic structure, shown in Figure 20, remains the same. The phenolic groups that terminate the above structure allow many possible reactions to take place. A few examples of this are discussed below.

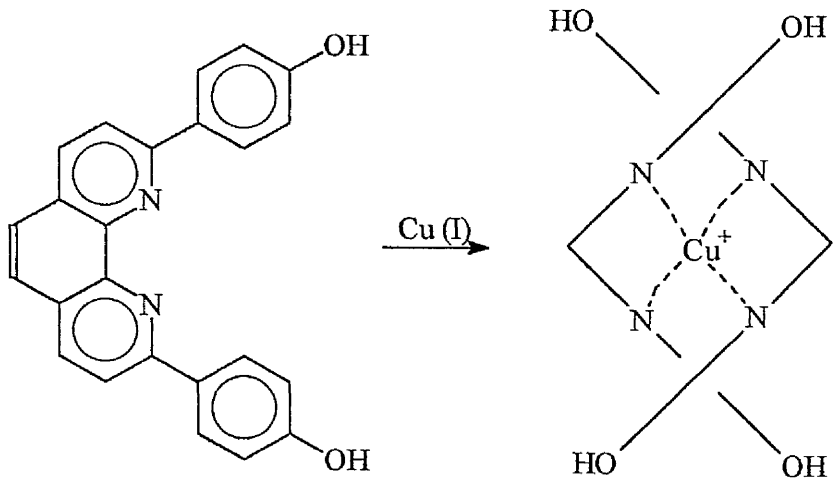
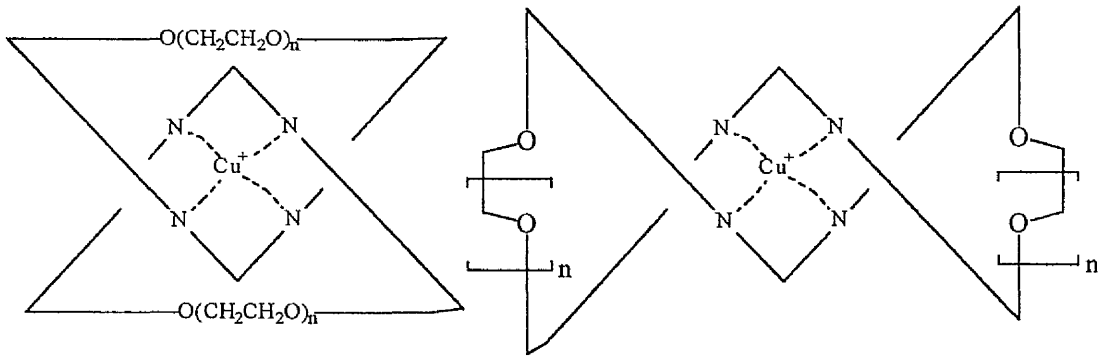


Figure 20

a) The phenolic groups can be linked together using pentaethyleneglycol diiodide or tetraethyleneglycol diiodide to give two possible structures, see Figure 21.[51] The catenane shown in Figure 21 was synthesised in 42% yield using a pentaethyleneglycol spacer and 3.3% yield using tetraethyleneglycol. This reduction in yield for the smaller

spacer length is due to the large increase in rigidity of the catenane formed using the shorter spacer compared to that produced using the larger one. The other isomer of the catenane shown was not detected. This is probably due to the specific geometry adopted by the starting "clipped" species.



Catenane Catenane Isomer

Figure 21

It is possible to effect the de-metalation using cyanide ions giving rise to the structure shown in Figure 22.[52] Although the demetalation of the catenane can be affected using either cyanide ions or electrochemically, these catenane structures are much more stable towards de-metalation than their "clipped" starting materials shown in Figure 20. This work was carried out by Sauvage and co-workers in 1993-94.[53,54]

b) The phenolic groups on one of the species can be reacted with bulky end groups in order to produce a linear terminally blocked thread.[55-58] The phenolic groups of the

second species can be linked together as in the synthesis of a catenane. This will then produce a [2]rotaxane, see Figure 23.

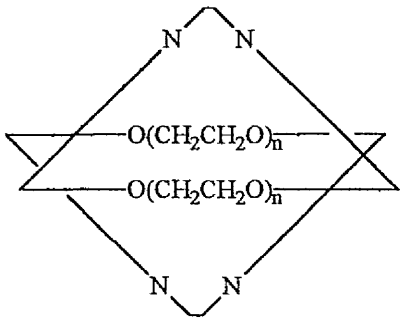


Figure 22

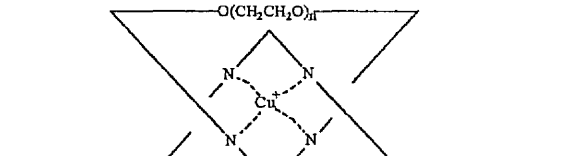


Figure 23

The synthesis of a [2]rotaxane similar to that shown in Figure 23 was carried out in 1991 by Gibson and co-workers.[59] Gibson used triarylmethyl as the bulky end groups, and the resulting [2]rotaxane was synthesised in 42% yield. Another similar [2]rotaxane was synthesised by Sauvage and co-workers in 1992, in this case porphyrins were used as the bulky end groups.[60] When the porphyrins are used as stoppers, some linking reactions

take place resulting in higher rotaxanes. Using this method a [2]rotaxane was synthesised in 25% yield and a [3]rotaxane in 32% yield.

c) It is possible to form a pseudorotaxane by joining the ends of one of the two species together. If the free ends of the resulting pseudorotaxane are linked under high dilution conditions then higher order catenanes may be produced, see Figure 24.
This work was carried out by Sauvage and co-workers in 1986.[61] The [3]catenane was synthesised in upto 58% yield, the [4]catenane in upto 22% yield, the [5]catenane has also been detected by mass spectroscopy.

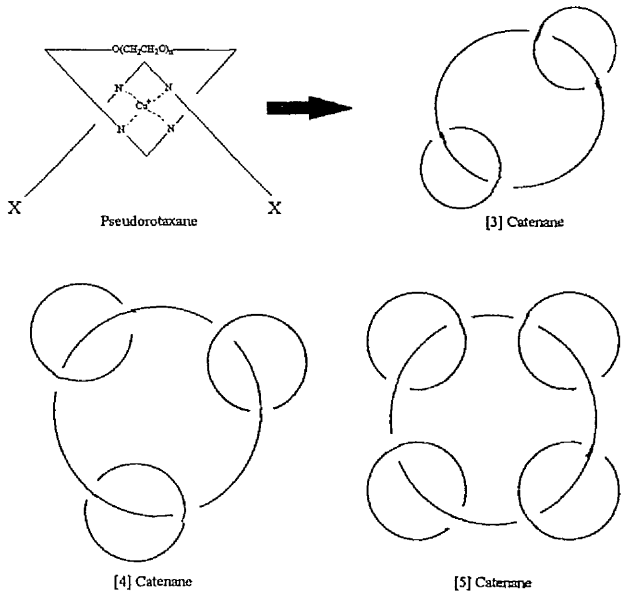


Figure 24

2.4.1.4 Template Directed Synthesis Using π-Electron Donors and π–Electron Acceptors.

Stoddart has published extensively on the use of π-electron donors and π-electron acceptors as molecular recognition moieties.[38] This work came about when Stoddart and co-workers discovered that the 2,2'-bipyridyl complex $[Pt(bipy)(NH_3)_2][PF_6]_2$ complexed with dibenzocrown ethers, see Figure 25.[62] Stoddart also found that diquat and paraquat, shown in Figure 26, complexed in a similar manner to the 2,2-bipyridyl complex.[63,64]

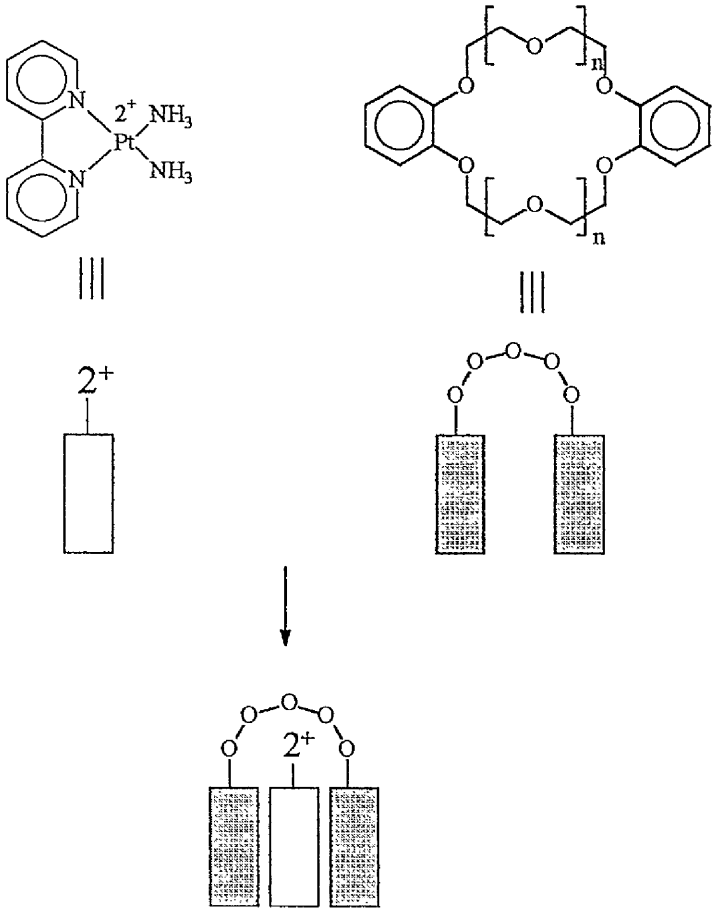
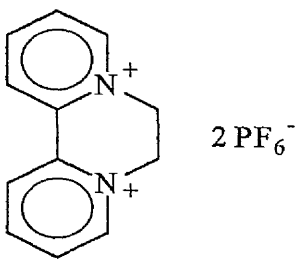
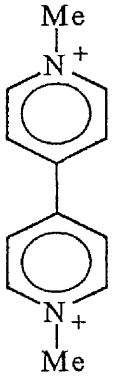


Figure 25

Stoddart attempted the synthesis of a complex between paraquat and a dinaphthalene crown ether.[65] Whilst investigating this complex using x-ray crystallography he found that a novel structure had been produced, see Figure 27. This "Stack" was produced due to each paraquat complexing with two of the dinaphthalene rings. This result then prompted Stoddart to produce an electron-poor cyclophane that could be used in a similar way to the electron-poor paraquat. In order to produce this electron-poor cyclophane, cyclophane **(1)** , Stoddart took 4,4'-bipyridine as a starting block and reacted this with 1,4-bis(bromomethyl)benzene using a template in order to aid the formation of cyclophane **(1)** over linear polymer.[66] Once Stoddart had achieved the synthesis of this electron-poor cyclophane he was able to produce many novel catenanes and rotaxanes. Stoddart's work uses easily produced benzylic ethers with the electron-poor cyclophane to produce very strong complexes and it was therefore decided to use this methodology to attempt the synthesis of some polypseudorotaxanes. The work of Stoddart is discussed briefly in the following sections.

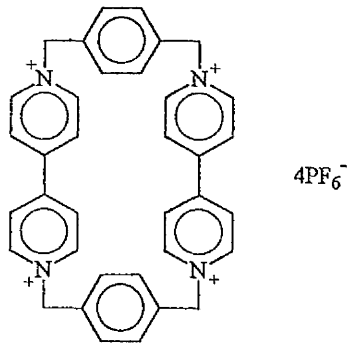


Diquat [$2PF_6^-$]



Paraquat [$2PF_6^-$]

Figure 26



Cyclophane (1)

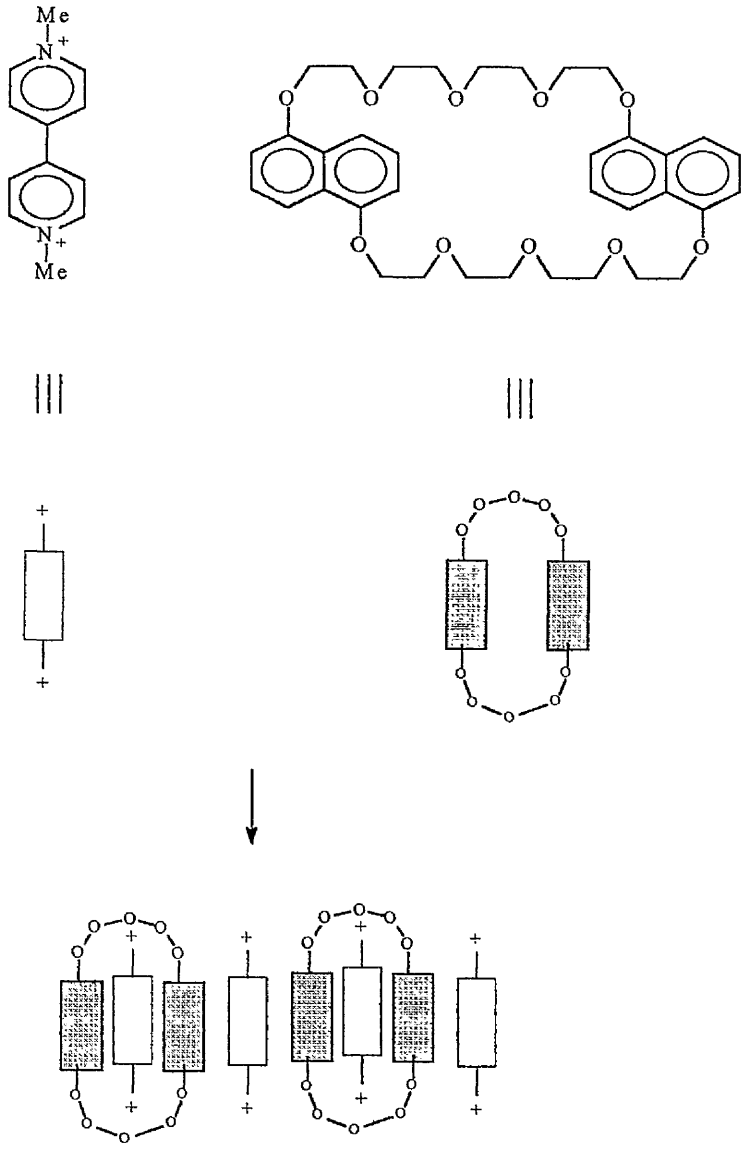


Figure 27

2.4.1.4.1 Catenane Synthesis using the Stoddart Cyclophane.

Following on from the above work Stoddart synthesised the catenane shown in Figure 28.[67] All the catenanes produced by Stoddart are synthesised using the "Clipping" method, i.e. taking the preformed dibenzocrown ether and forming the electron-poor cyclophane around this. The catenane shown in Figure 28 was also synthesised using 1,5-dihydroxynaphthalene instead of the 1,4-dihydroxybenzene shown.[68] In both cases large shifts in the ^1H NMR spectra were observed for the signals due to the aromatic component. This is because, in the complex both the electron rich aromatic units and the electron poor cyclophane units are in each other's ring currents. The ^1H NMR shifts observed for the two catenanes are shown in Table 1.

Table 1 : ^1H NMR Shifts for Catenanes formed from Cyclophane (1) and 1,5-Dihydroxynaphthalene or Hydroquinone

Free Crown Ether Ring				Complexed Catenane			
1,4-Dihydroxybenzene	1,5-Dihydroxynaphthalene			1,4-Dihydroxybenzene	1,5-Dihydroxynaphthalene		
	H 2/6	H 3/7	H 4/8		H 2/6	H 3/7	H 4/8
				Inside	Inside	Inside	Inside
6.8ppm	7.18ppm	6.73ppm	6.33ppm	3.46ppm	6.14	5.99	2.43
				Between	Between	Between	Between
				6.16ppm	7.11	7.01	6.33

"Inside" and "Between" refer to the position of the aromatic ring in relation to the electron-poor cyclophane, see Figure 29.

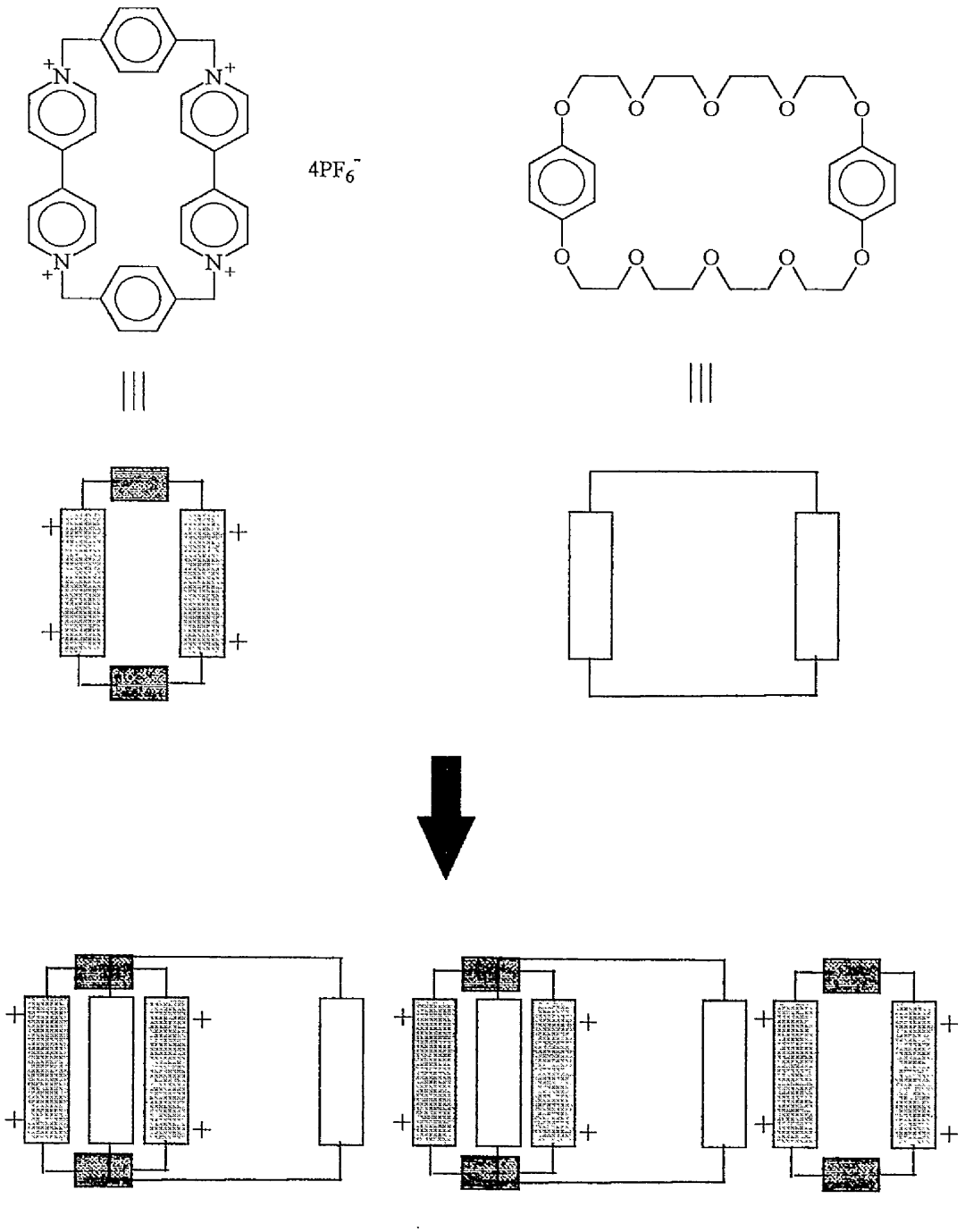


Figure 28

The two interlocked rings are in constant motion and it is possible to monitor the speed at which these two rings move using variable temperature ^{1}H NMR spectroscopy. In this technique, at an appropriate temperature, a coalescence between the signals due to the "Inside" and "Between" environments can be seen. This can be used to gain information on the speed at which these two rings are moving. The data obtained is summarised in Table 2.

Table 2 : Variable Temperature ^{1}H NMR results for Hydroquinone and 1,5-Dihydroxynaphthalene Containing Catenanes

	Benzene Catenane	Naphthalene Catenane
Tc	81°C	86°C
ΔG	14 kcal / mol	17.2 kcal / mol
Kc	$1500s^{-1}$	$240s^{-1}$

Tc is the temperature at which coalescence occurs
ΔG is the free energy of activation for this motion
Kc is the number of jumps that the rings are making at the coalescence temperature

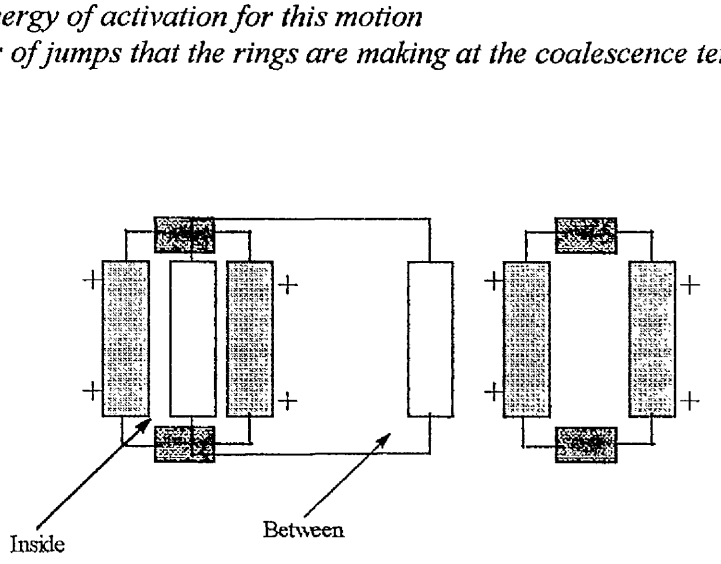


Figure 29

The above results suggest that the complex formed between the electron-poor cyclophane and a naphthalene-containing crown ether is stronger than the complex formed with a benzene-containing crown ether. In order to confirm this Stoddart synthesised a crown ether that contained one naphthalene unit and one benzene unit.[69] When a catenane was produced from this species Stoddart was able to measure the relative amounts of complexation with each aromatic unit in the ring using ^{1}H NMR spectroscopy. The results showed that 65% of the naphthalene units where present in the "Inside" environment whilst only 35% of the benzene units where present in the "Inside" environment. This confirms the fact that naphthalene is a better π-electron donor than benzene.

In order to monitor the movement of the rings Stoddart synthesised a crown ether containing four hydroquinone moieties which he then used to form a catenane, see Figure 30.[70] Stoddart called this system his "Train Set", the four benzene units being the "Stations" and the electron-poor cyclophane being the "Train". Stoddart was able to produce a [2]catenane and a [3]catenane. Both catenanes were synthesised using the "Clipping" method. The conditions used differed in each case. In order to produce the [2]catenane the reaction was carried out under atmospheric pressure producing the catenane in 12% yield; in order to produce the [3]catenane the reaction was carried out at a pressure of 10 kbars producing the catenane in 11% yield. The motion of the rings was then monitored for both the [2]catenane and the [3]catenane. This gave free energies of activation of 14.1kcal/mole and 13.7 kcal/mole respectively.

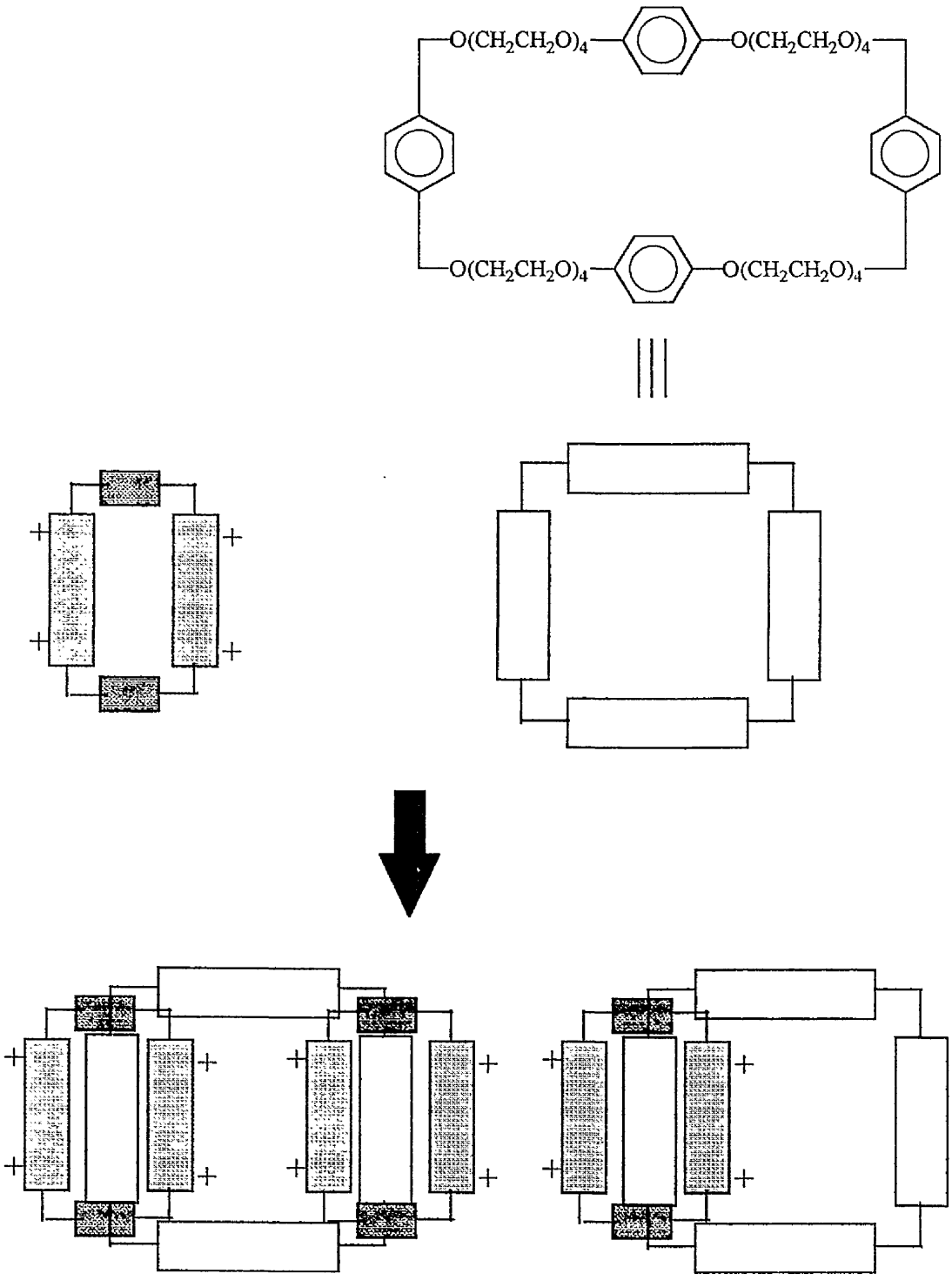


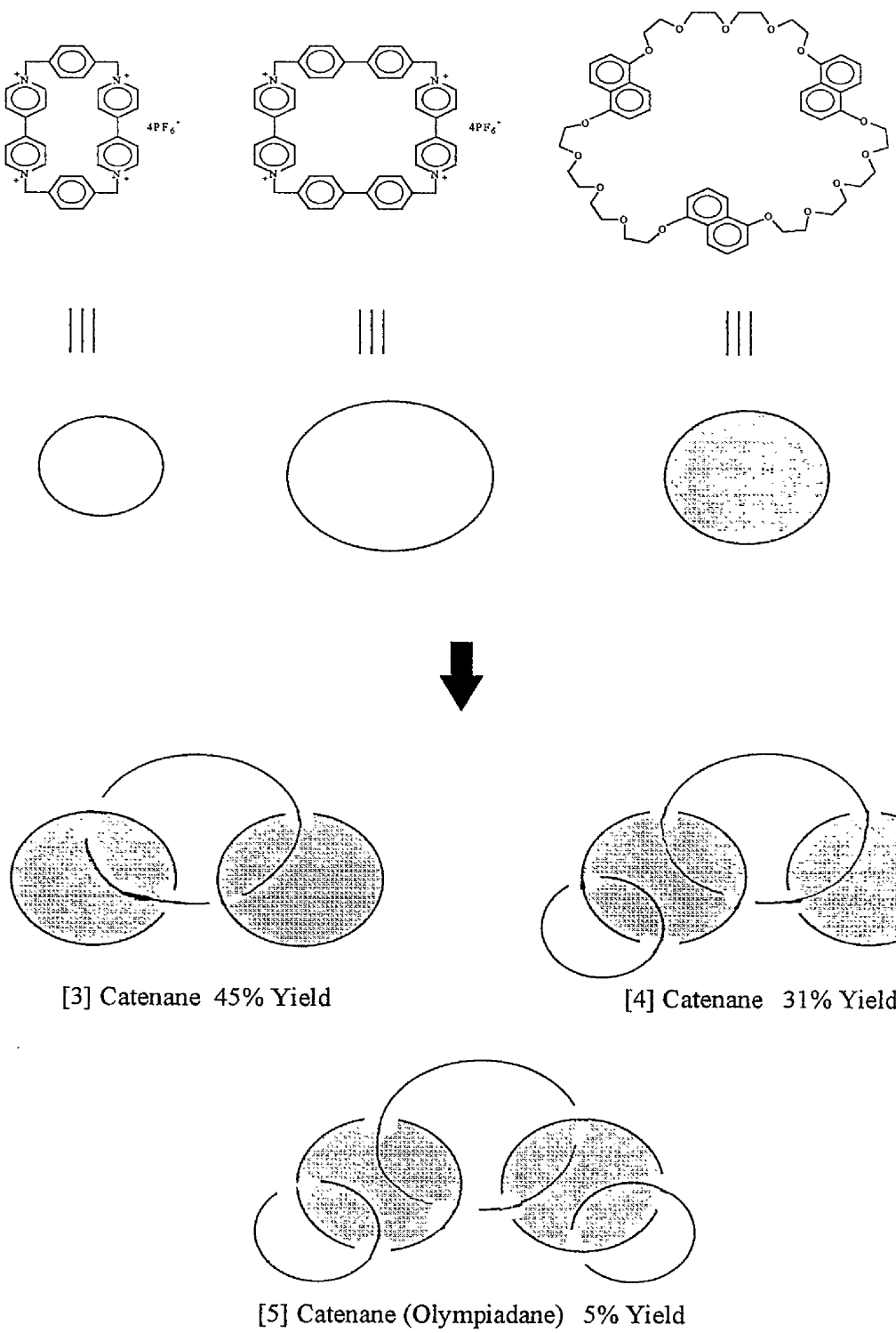
Figure 30

It is obviously more difficult to cause the rings to move when a greater number of rings are present as some of the possible free sites normally available for complexation will be blocked. In the case of the Stoddart "Train Set" two electron-poor cyclophanes cannot exist on neighbouring benzene units due to repulsion between the positive charges on the cyclophanes. Thus, these cyclophanes - which must exist on alternate hydroquinone moieties - must move together. This is a higher energy process. This fact must be taken into account when synthesising polypseudorotaxanes, as in this case there may be a large number of electron-poor cyclophanes on the polymer chain and hence only a small number of free sites.

One of the more interesting structures synthesised by Stoddart was a [5]catenane which he named "Olympiadane" due to the similarity of its shape to the olympic symbol, see Figure 31.[71,72] The reaction used to produce the [5]catenane also produced side products, these products were some remaining [3]catenane (45% yield), a [4]catenane (31% yield), and the [5]catenane (5% yield). Stoddart was still able to observe the movement of the rings in this system and was able to calculate the values shown in Table 3.

Table 3 : Variable Temperature ^{1}H NMR Studies for a [5]Catenane

Tc	37°C
ΔG	14.5 kcal / mole
Kc	370 s^{-1}



[3] Catenane 45% Yield

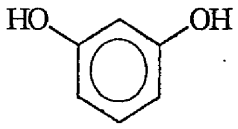
[4] Catenane 31% Yield

[5] Catenane (Olympiadane) 5% Yield

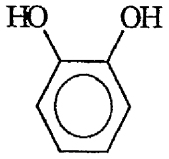
Figure 31

Many other catenanes have been synthesised by Stoddart using different electron-poor cyclophanes and different electron-rich cyclics.[38] Some of these alternative systems are shown below with a brief explanation of what they may be used for.

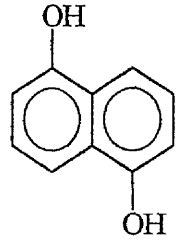
Hydroquinone



Resorcinol

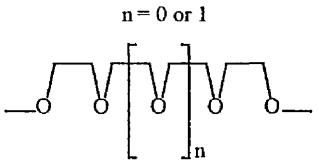


Catechol

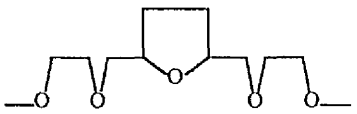


1,5-Dihydroxynaphthalene

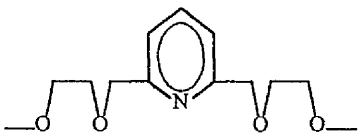
Each of the above electron-rich units have been used in the synthesis of catenanes showing the variety allowable. The strength of the complexation of the electron-poor cyclophane with each of the electron-rich units decreases by proceeding from 1,5-dihydroxynaphthalene to 1,4-dihydroxybenzene to 1,3-dihydroxybenzene to 1,2-dihydroxybenzene.



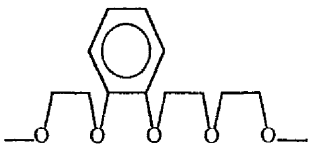
Spacer 1



Spacer 2



Spacer 3



Spacer 4

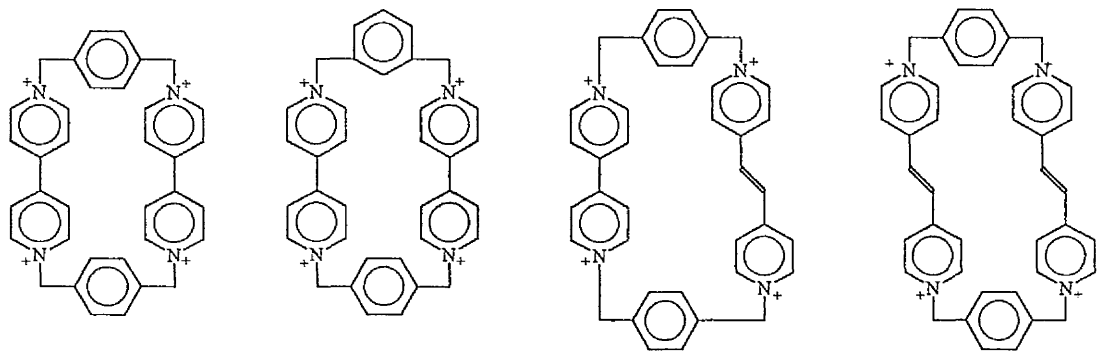
Each of the above spacers have been used in the crown ethers which form part of the catenanes, again this shows the variety available.[73] Stoddart has produced crown ethers containing two spacers - like spacer 1 - these may be different sizes from each other. The results below, see Table 4, show the percentage yield of catenane formed using these different length spacers.

Table 4 : Percentage Yield for the Synthesis of Catenanes using Hydroquinone Linked by Ethyleneoxy units of Various Length

n_1	n_2	Yield (%)
0	0	10
1	0	70
2	0	55
2	1	54
3	1	40
3	2	49

The percentage yield of catenane formation is greatest when the two spacers are of similar length, and when the length of the spacer is around four ethyleneoxy units.

Spacer 4 has been used by Stoddart to hinder the movement of the electron-poor cyclophane around the crown ether.[74] The benzene group in the ethyleneoxy chain provides steric hinderance when the nearest aromatic ring is complexed but there is no steric hinderance when the other aromatic ring is complexed.



Each of the electron-poor cyclophanes shown above have been used by Stoddart in the synthesis of catenanes.[75] This shows that much variation is possible in the electron-poor cyclophane as well as in the electron-rich crown ether. The electron-poor cyclophanes containing the double bonds could be used to form catenanes, thus changing the solubility of the crown ether used. The double bond contained in these cyclophanes may then be degraded to effect the removal of this cyclophane thus changing the solubilty back to that of the original crown ether.

It has been shown that there are many catenanes that may be synthesised using the complexation between π–electron donors and π–electron acceptors. The same systems

can also be used for the synthesis of rotaxanes, in this case a linear aromatic ether is used instead of the cyclic aromatic crown ether.

2.4.1.4.2 Rotaxane Synthesis Using the Stoddart Cyclophane.

Stoddart has synthesised rotaxanes from his electron-poor cyclophane and a linear thread containing hydroquinone units with ethyleneglycol spacers.[76] The rotaxane shown in Figure 32 is obviously similar to the catenane synthesised from the electron-poor cyclophane and a dibenzocrown ether. It is therefore possible to compare the ^{1}H NMR shifts and the motion of the electron-poor cyclophane in the rotaxane and catenane. The data acquired by Stoddart is shown in Table 5. Figure 33 shows the position of the "Bound", "Between" and "Alongside" environments.

Table 5 : ^{1}H NMR Shift Positions and Variable Temperature Results for Rotaxanes and Catenanes formed using Hydroquinone residues

		Rotaxane		Catenane	
^{1}H NMR Spectroscopy	Alongside	Between	Bound	Between	Bound
	6.38ppm	6.16ppm	3.40ppm	6.16ppm	3.46ppm
Motion of cyclophane					
ΔG	13.2 k cal/mole			14 kcal/mole	
Kc		2360 s^{-1}		1500 s^{-1}	
Tc		34°C		81°C	

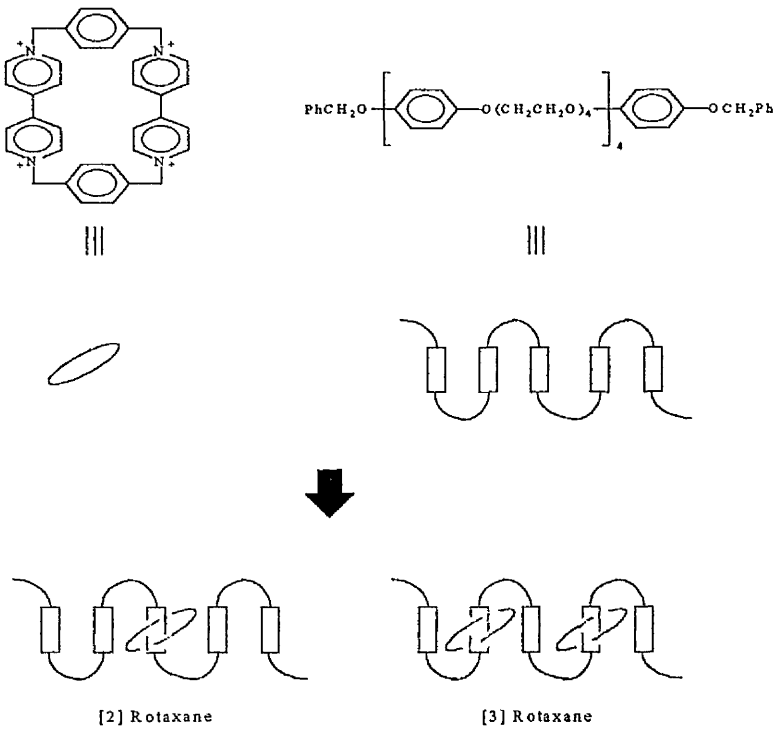


Figure 32

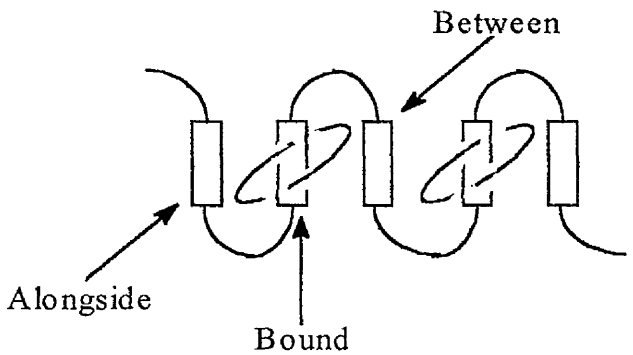


Figure 33

One of the suggested possible uses for these rotaxanes is in the synthesis of a molecular switch. Stoddart has shown how this may be possible by synthesising a "Chemically and Electrochemically Switchable Molecular Shuttle", shown in Figure

34.[77] The electron-poor cyclophane has been shown to sit preferentially over the benzidine ring. When this ring is protonated the electron-poor cyclophane moves to a position where it now sits over the biphenol ring. This is due to repulsion between the positive charges on the electron-poor cyclophane and the protonated benzidine ring. Figure 34 shows how Stoddart has achieved this switching using various methods. At the present time the speed at which this switching takes place is far slower than the speed at which electron transfer takes place and so conventional switching cannot at this time be replaced using rotaxanes.

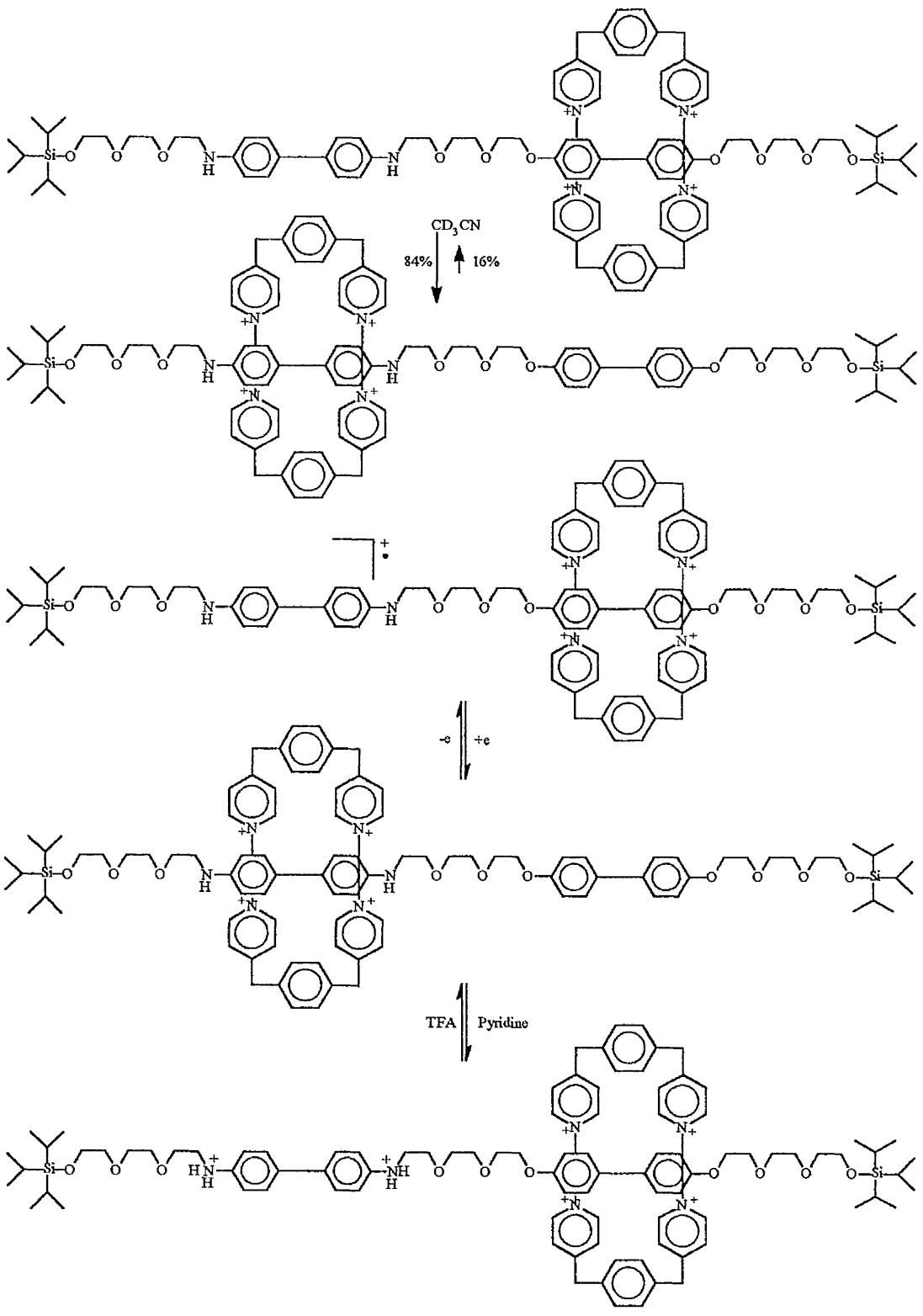


Figure 34

CHAPTER 3

RESULTS AND DISCUSSION FOR ROTAXANES

This chapter will deal with the synthesis and characterisation of polypseudorotaxanes based on the Stoddart systems discussed earlier (see Section 2.4.1.4). In order to synthesise these pseudorotaxanes a number of points needed to be addressed. These were as follows.

a) The synthesis of polymers containing molecular recognition moieties capable of binding with cyclophane (1). Stoddart has shown how π–electron-rich aromatic diols linked through ethyleneglycol spacers are good building blocks for the synthesis of threads to be used for rotaxane formation with cyclophane **(1)**.[38] Thus, in the present work polyethers and polyesters incorporating these features were synthesised and characterised. Since Stoddart has shown that low molecular weight building blocks self-assemble,[78] the polymers first investigated lacked "Stoppers".

b) The synthesis of pseudorotaxanes using the "Clipping" method. Considering the methods available for the synthesis of pseudorotaxanes, it was decided that the "Clipping" method may be the best in the present case. Thus, this method was initially investigated for the synthesis of pseudorotaxanes.

c) The synthesis of cyclophane (1). In order to be able to produce pseudorotaxanes using the "Threading" method it was first necessary to synthesise cyclophane **(1)** in useful quantities.

d) The synthesis of pseudorotaxanes using the "Threading" method. Once cyclophane **(1)** had been synthesised it was possible to attempt the synthesis of pseudorotaxanes using the "Threading" method.

e) The analysis of pseudorotaxanes. Once the synthesis of pseudorotaxanes had been achieved, they were characterised using ^{1}H NMR spectroscopy, UV spectroscopy and inherent viscosity studies.

3.1 SYNTHESIS AND CHARACTERISATION OF POLYMERS

3.1.1 POLYETHERS

It was decided to attempt to synthesise polypseudorotaxanes using molecular recognition and to use the Stoddart system combining a π–electron-poor cyclophane with a π–electron-rich thread. It has been shown that threads containing an aromatic ether component linked by tetraethyleneglycol spacers give strong complexes with cyclophane **(1)**.[79] Accordingly attempts were made to synthesise polymers containing these functionalities.

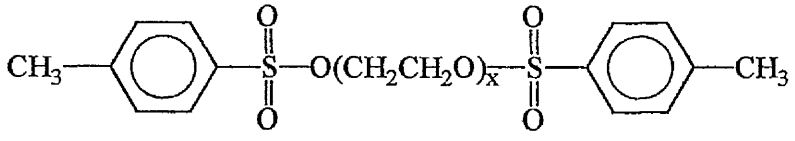
The synthetic approach adopted was to react tetra- or tri-ethyleneglycol bistosylates, bistosylates **(2)** and **(3)** respectively, with the selected dihydroxybenzenes under basic phase-transfer conditions. The results are summarised in Table 6.

Table 6 : Synthesis and Characterisation of Polyethers [Polymers (6-11)]

Entry	Starting Materials			Yield	Molecular Weights			Solubility
	Polymeric Product	Aromatic Diol	Bistosylate		Mn [a]	Mw [a]	DP [b]	
1	polymer (6)	Hydroquinone	Bistosylate (2)	36%	3455	4660	14	Acetonitrile
2	Polymer (7)	Hydroquinone	Bistosylate (3)	83%	11291	19110	92.5	DMF (partial)
3	Polymer (8)	Hydroquinone	Bistosylate (4)	78%	N/A	N/A	N/A	Hot DMF (partial)
4	Polymer (9)	Di-t-butyl-hydroquinone	Bistosylate (3)	61%	6595	13193	33.6	DMF
5	Polymer (10)	Resorcinol	Bistosylate (3)	53%	7822	12589	74.3	Acetonitrile
6	Polymer (11)	1,5-Dihydroxy naphthalene	Bistosylate (3)	77%	7490	15600	28.2	Hot DMF

[a] *Determined by GPC using polystyrene standards*

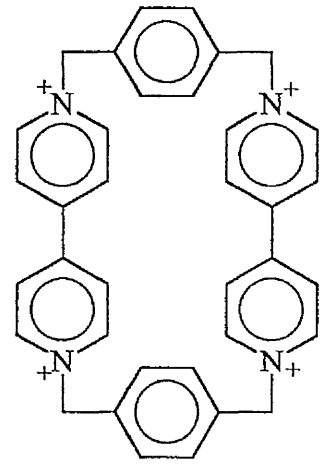
[b] *The average number of aromatic units per chain calculated from the M_{peak} values*



x = 4 : Bistosylate **(2)**
x = 3 : Bistosylate **(3)**
x = 2 : Bistosylate **(4)**
x = 5 : Bistosylate **(5)**

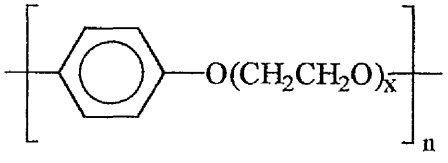
Treatment of triethyleneglycol or diethyleneglycol with p-toluenesulphonyl chloride, in pyridine afforded bistosylates **(3)** and **(4)** respectively in high yield. These compounds were crystalline and easily purified by recrystallisation.

The analogous reactions starting from tetraethyleneglycol or pentaethyleneglycol were attempted but the syntheses were not successful. Bistosylates **(2)** and **(5)** were therefore

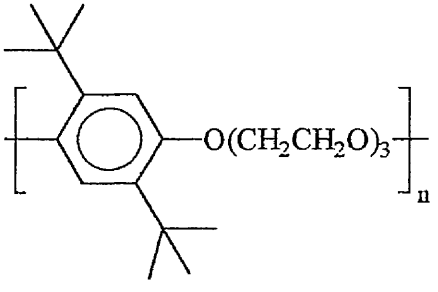


$4PF_6^-$

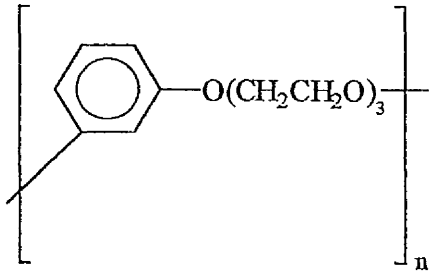
Cyclophane **(1)**



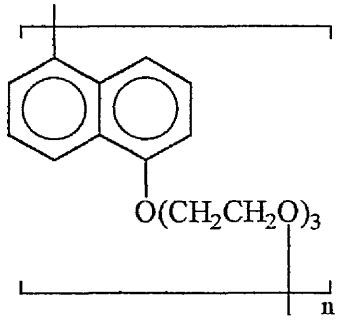
x = 4 : Polymer **(6)**
x = 3 : Polymer **(7)**
x = 2 : Polymer **(8)**



Polymer **(9)**



Polymer **(10)**



Polymer **(11)**

purchased from Aldrich. They were obtained as viscous oils with a claimed purity > 95%. All attempts to crystallise these oils failed. Distillation was also attempted but the volatility of the products, even under vacuum, was too low to allow this method of purification to be used.

Reaction of bistosylates **(2)-(4)** in 1,2-dichlorobenzene with hydroquinone in aqueous tetra-n-butylammonium hydroxide at 100°C for 5 days afforded polymers of the desired structures in good yield. The products had satisfactory ^{1}H NMR spectra and by GPC they had, relative to polystyrene standards, molecular weights as shown in Table 6. The polymer **(6)** obtained from the reaction with bistosylate **(2)** had relatively low molecular weight which corresponded to a DP of only ca.14. The synthesis was repeated several times without improvement. It was concluded that perhaps the oily bistosylate **(2)** was not of sufficiently high purity for the synthesis of polymers with DP's much greater than ca. 14. Being oily the bistosylate **(2)** was not easily purified. The polymer **(7)** obtained from the reaction with bistosylate **(3)** was soluble in chloroform and it had a reasonably high molecular weight, which corres ponded to a DP of ca. 93. The polymer **(8)** obtained from the reaction with bistosylate **(4)** was insoluble in all solvents tried, although it was partially soluble in hot DMF. For this reason no further work was carried out using this polymer.

The reaction between bistosylate **(5)** and hydroquinone failed to produce a polymer. It was concluded that this was due to the bistosylate **(5)** not being of sufficiently high purity to produce polymer of sufficiently high molecular weight to allow easy separation from unreacted starting materials.

Similar reactions between either 2,5-di^{t}butylhydroquinone or resorcinol and bistosylate **(3)** were carried out. The products, polymers **(9)** and **(10)** respectively, had satisfactory ^{1}H NMR spectra and GPC data relative to polystyrene standards. The results are summarised in Table 6.

Attempts to synthesise a polymer using 1,5-dihydroxynaphthalene and bistosylate **(3)** under phase-transfer conditions failed due to the poor solubility of the product. The synthesis was, however, achieved successfully by reacting the diol with sodium hydride and bistosylate **(3)** in DMF at 100°C. Due to the poor solubility of the polymer **(11)** the molecular weight was determined by GPC in hot DMF. This measurement was made by the EPSRC service at RAPRA.[80] The results are summarised in Table 6.

It was clearly important for pseudorotaxane formation, that cyclophane **(1)**, the polymer being studied, and the pseudorotaxane product were all soluble in the same solvent. Cyclophane **(1)** is soluble in solvents such as acetonitrile and DMF. For ^{1}H NMR studies the preferred solvents based on cost were d^3-acetonitrile then d^6-DMF. Accordingly the solubilities of the polymers in one or more of these solvents were tested. These results are also shown in Table 6.

As indicated in Table 6, polymer **(6)** was soluble in acetonitrile and DMF and so was a good candidate for the synthesis of pseudorotaxanes. Polymer **(7)** was only partially soluble in DMF and so in this case it was anticipated that solubility might be a problem when attempting to produce pseudorotaxanes. Polymers **(2)** and **(10)** were soluble in

DMF and acetonitrile respectively and they had significantly higher molecular weights than the other polymers. These were therefore expected to be the better candidates for the synthesis of pseudorotaxanes. Polymers **(8)** and **(11)** were, however only soluble in hot DMF and even though their molecular weights were probably sufficiently high [that of polymer **(8)** was not determined] it was expected that they would not be suitable candidates for the synthesis of pseudorotaxanes.

3.1.2 POLYESTERS

As noted in the Introduction it is of interest to make polyesters which can not only be used to prepare pseudorotaxanes using cyclophane **(1)** but can also be used to prepare cyclics, so opening up the way to a synthetic route to catenanes.[81] In this preliminary study of polyesters it was decided to prepare them from α,ω--diacids and α,ω–diols, because, such symmetrical monomers are more readily available than, for example, ω–hydroxyacids.

A diester monomer containing a hydroquinone ether moiety is diester **(12)** . This was prepared in good yield by reacting hydroquinone in ethanolic potassium carbonate with ethyl chloroacetate. Polymers **(14)** and **(15)** were prepared by reacting diester **(12)** with diethyleneglycol and triethyleneglycol respectively in the presence of a catalytic amount of titanium isopropoxide whilst distilling out the ethanol. These polymers had satisfactory

^{1}H NMR spectra and good molecular weights as determined by GPC relative to poly(ethyleneglycol) standards. Table 7 summarises the results.

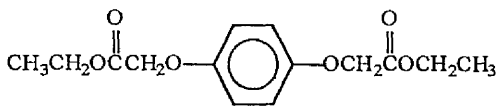
Table 7: Synthesis and Characterisation of Polyesters [Polymers (14-16)]

Entry	Polymeric Product	Starting Materials: Aromatic Component	Starting Materials: Spacer Unit	Yield	Molecular Weights: Mn [a]	Molecular Weights: Mw [a]	Molecular Weights: DP [b]	Solubility
1	Polymer (14)	Diester (12)	Diethyleneglycol	89%	18600	23400	91.1	Acetonitrile
2	Polymer (15)	Diester (12)	Triethyleneglycol	92%	20500	24900	101.5	Acetonitrile
3	Polymer (16)	Diol (13)	Dimethyloxalate	47%	7100	10300	38.2	Acetonitrile

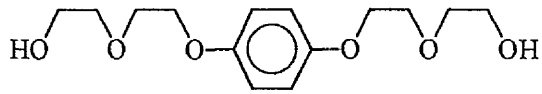
[a] *Determined by GPC in DMA using poly(ethyleneglycol) standards*

[b] *The average number of aromatic units per chain calculated from the M_{peak} values*

A diol monomer containing a hydroquinone moiety is diol **(13)**. This was prepared in good yield by reacting hydroquinone in ethanolic potassium carbonate with 2-(2-chloroethoxy)ethanol. Polymer **(16)** was prepared by reacting diol **(13)** with dimethyl oxalate in the presence of titanium isopropoxide as catalyst whilst distilling out the ethanol. This polymer had a satisfactory ^{1}H NMR spectrum and a satisfactory molecular weight as determined by GPC relative to poly(ethyleneglycol) standards. Table 7 summarises the results.

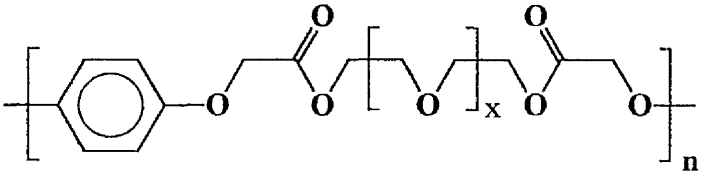


Diester (12)

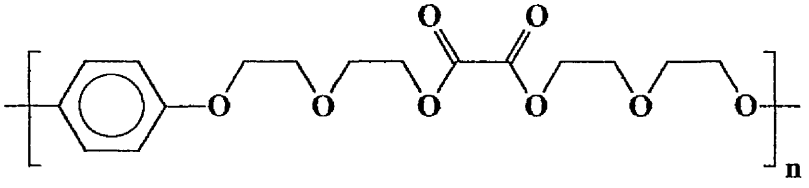


Diol (13)

All these polyesters prepared were soluble in acetonitrile and were, therefore, expected to be good candidates for the synthesis of pseudorotaxanes. It is worth noting that the polyesters were generally more soluble than the corresponding polyethers and that they could also be prepared with higher molecular weights.



x = 1 : Polymer **(14)**
x = 2 : Polymer **(15)**



Polymer **(16)**

3.2 CYCLO-DEPOLYMERISATION OF POLYESTERS

The cyclo-depolymerisation of polyesters to give cyclics has been investigated in this group by Dr Ruddick. Dibutoxydibutyltin has been shown to be an excellent catalyst when the starting materials are polyesters.[82] In the present work dilute solutions of polymers **(14)** and **(15)** in 1,2-dichlorobenzene were treated with 0.2mole% of dibutoxydibutyltin at 170°C for 2 days. Analysis of the GPC traces for the initial polyester and for the products obtained by heating with the tin catalyst showed that de-polymerisation had occurred. Results by other members of the group have shown high cyclic contents in the de-polymerisation mixtures but this has yet to be confirmed in the present case.[83] MALDI-TOF mass spectroscopy is usually used to analyse the de-polymerisation mixture in order to demonstrate the presence of cyclic oligomers.[84] In the present case it was expected that the polyesters would form complexes with cyclophane **(1)** and that this could be used to separate the cyclic and linear fragments. Thus, complexation of the linear chains would change their solubility and make it dramatically different to the solubility of the cyclics. In order to do this it must first be determined whether or not the polymers form strong complexes with cyclophane **(1)**.

3.3 SYNTHESIS OF POLYPSEUDOROTAXANES

Having synthesised several polymers which could be expected to form pseudorotaxanes, attention was next paid to the possible methods which could be used to produce the pseudorotaxanes from these polymers. As described earlier (see Section 2.2), there are a

number of ways of producing rotaxanes: these are "Clipping", "Threading" and "Slipping". Which of the above methods is the best for synthesising polypseudorotaxanes in the present cases?

It was expected that "Threading" by polymers would be a very slow process as the concentration of end groups would be very low. Thus, the probability of cyclophane **(1)** finding a polymer chain end and "Threading" onto the chain would be low. Another factor that may slow down the "Threading" process could be that one or both of the end groups could be buried within the random coil conformation of the polymer in solution.

Synthesising polypseudorotaxanes using the "Clipping" method does not involve the end groups at all and so the synthesis of polypseudorotaxanes should proceed at a rate similar to that of the synthesis of their monomeric analogues. It was, therefore, decided to initially try the "Clipping" method to synthesise the polypseudorotaxanes

3.3.1 SYNTHESIS BY "CLIPPING"

In the present context the "Clipping" reaction is that shown in Figure 35. The required "semicircle" **(17)** was prepared as described by Stoddart, i.e. by treating 4,4'-bipyridine with 1,4-bis(bromomethyl)benzene in acetonitrile at 80°C.[85] This gave "semi-circle" **(17)** in 66% yield. Attempts were made to prepare pseudorotaxanes by heating "semi-circle" **(17)** with 1,4-bis(bromomethyl)benzene in DMF in the presence of polymer **(7)**. It was hoped the product would be a polypseudorotaxane.

Stoddart showed that a characteristic colour change could be observed during the formation of a rotaxane.[86] He showed that whilst the two starting materials were white solids the produced rotaxane was a red solid. In the present work this expected colour change was observed for the attempted synthesis of a polypseudorotaxane. It was expected that this method would not give a pure polypseudorotaxane, but that the following species may also be present.

i) Unreacted 1,4-bis(bromomethyl)benzene

ii) Uncomplexed polymer

iii) Uncomplexed cyclophane **(1)**, plus possibly other larger cyclophanes.

iv) Linear polymers produced from the reaction with semi-circle **(17)** and 1,4-bis(bromomethyl)benzene

In order to produce a pure polypseudorotaxane it was necessary to remove these various side products. Simple solubility tests showed that the 1,4-bis(bromomethyl)benzene was the only one of the side-products to be soluble in benzene. It was also shown that the uncomplexed polymer was the only one of the side-products to be soluble in chloroform. It should, therefore, be possible to remove these impurities by washing the crude product with the relevant solvents. Unfortunately, linear and cyclic products obtained from the reaction between 1,4-bis(bromomethyl)benzene and "semi-circle" **(17)** are only soluble in solvents such as acetone, acetonitrile and DMF along with the desired polypseudorotaxane product. It was not, therefore, possible to remove these impurities from the reaction mixture. The results gained from this washing procedure are discussed in the following sections. In each case the mass percentage of product removed and the ^{1}H NMR spectra of that product are given.

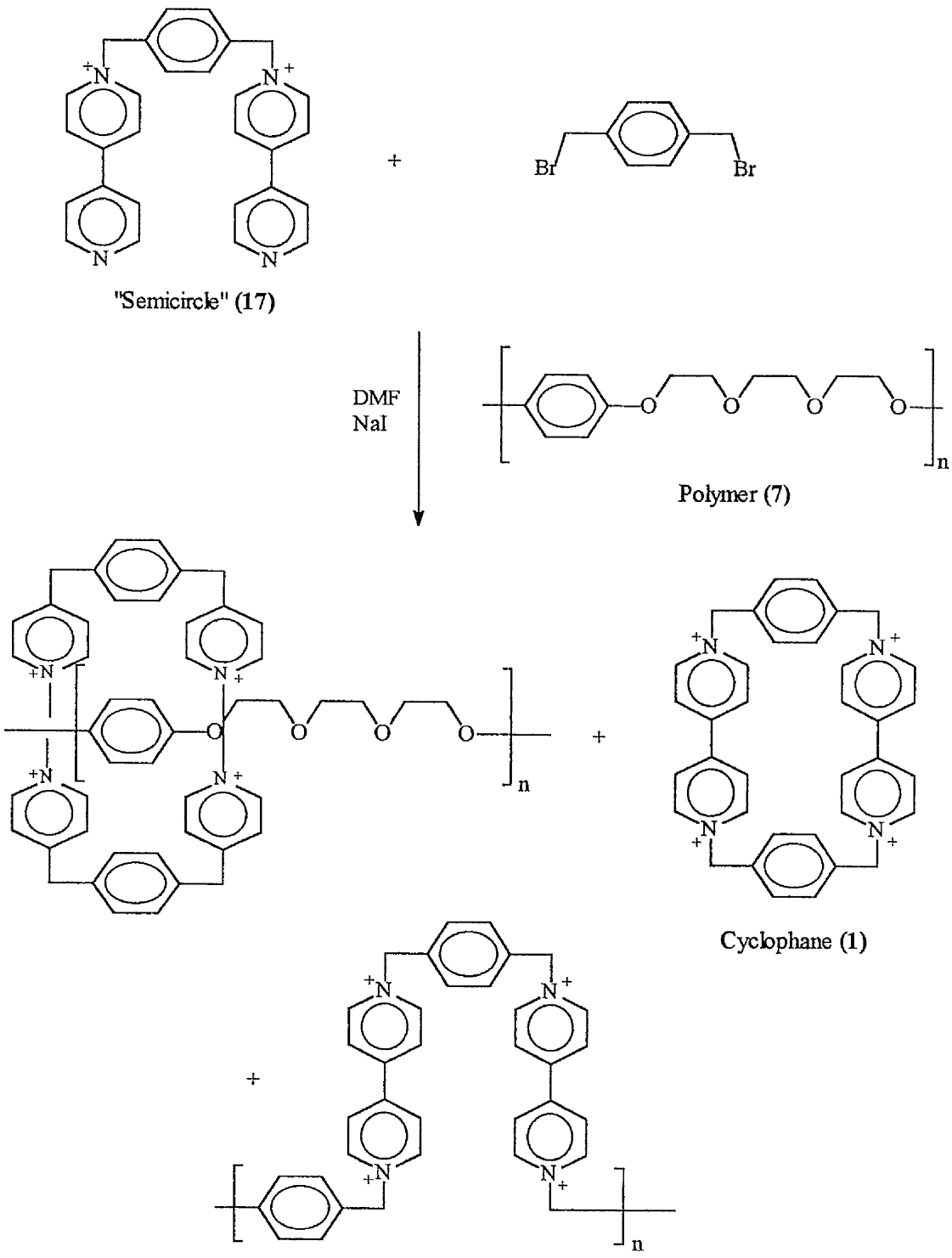


Figure 35

3.3.1.1 Benzene-Soluble Fraction.

It can be seen by examining Figure 36 that the small amount of benzene-soluble material recovered (<1%) was pure 1,4-bis(bromomethyl)benzene starting material. The mass of this extract was very small indicating that most of this starting material had been used in the reaction. The question was, has the 1,4-bis(bromomethyl)benzene been used to produce cyclophane **(1)** that was complexed with the polymer in some manner?

3.3.1.2 Chloroform-Soluble Fraction

It can be seen by examining Figure 36 that the chloroform-soluble fraction was pure polymer **(7)**, i.e. starting polymer. Only 37% of the initially used polymer was recovered at this stage. This suggests that the remaining mass of polyether had been changed in some way, i.e. a reaction had occurred. The question was, is the new polymer produced a polypseudorotaxane? The remaining red solid, equivalent to a yield of ca. 60mole%, was soluble in DMSO, and was analysed by ^{1}H NMR spectroscopy. The spectrum is shown in Figure 37. It can be seen that there is no signal at 6.8ppm, the position at which the hydroquinone component appears in the starting polymer. According to Stoddart this is indicative of the presence of rotaxane.[87] Analysis of the remainder of the spectrum is very difficult due to the presence of multiple signals. This result suggests, however, that a polypseudorotaxane was synthesised, but that despite the solvent washings it was impure. The impurity was probably oligomeric cyclic and linear π–electron-poor components that may or may not be complexed with polymer **(7)**. In all other reported cases of rotaxane synthesis of the Stoddart type, the purification of the rotaxane was achieved using column

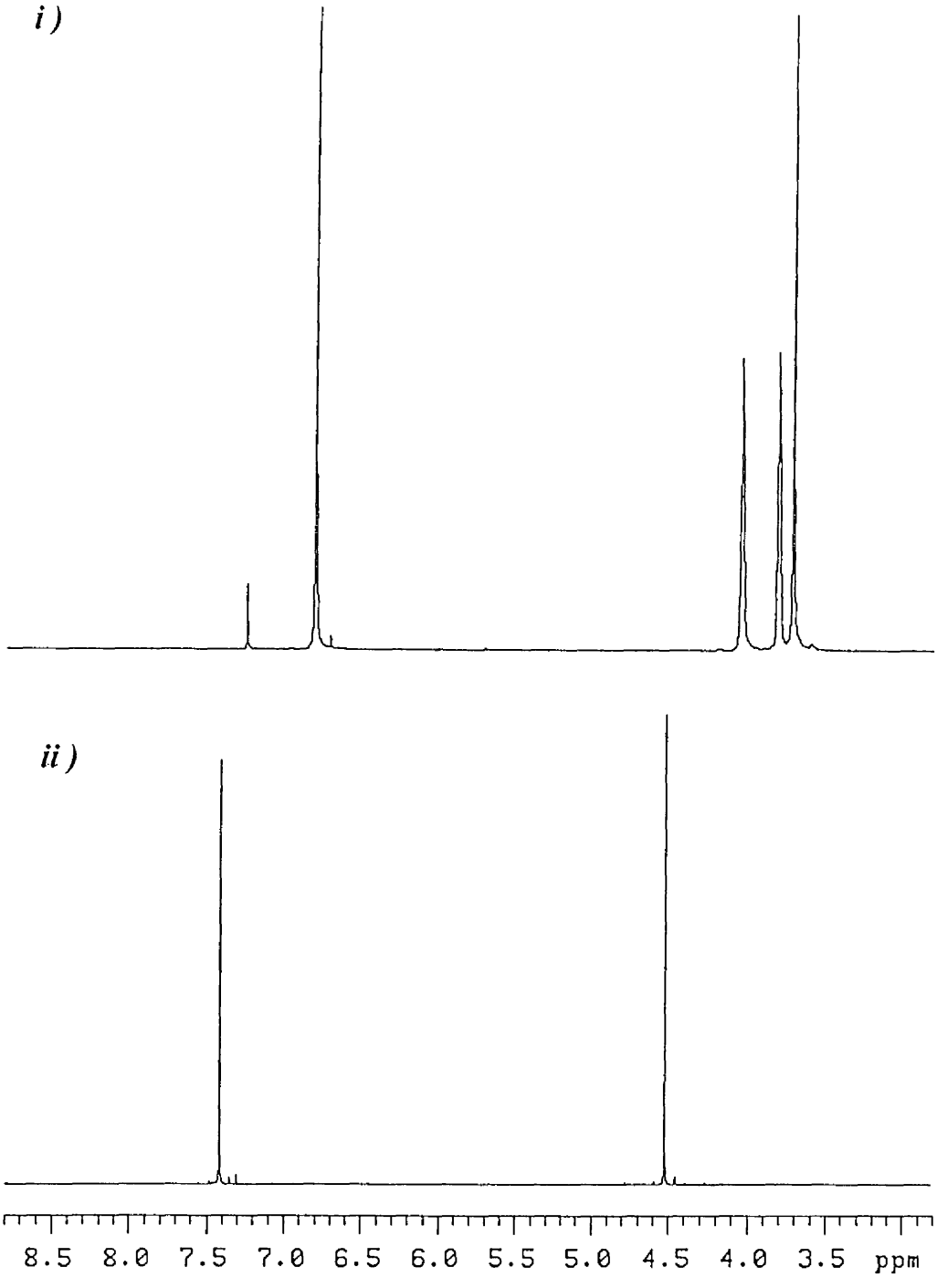


Figure 36

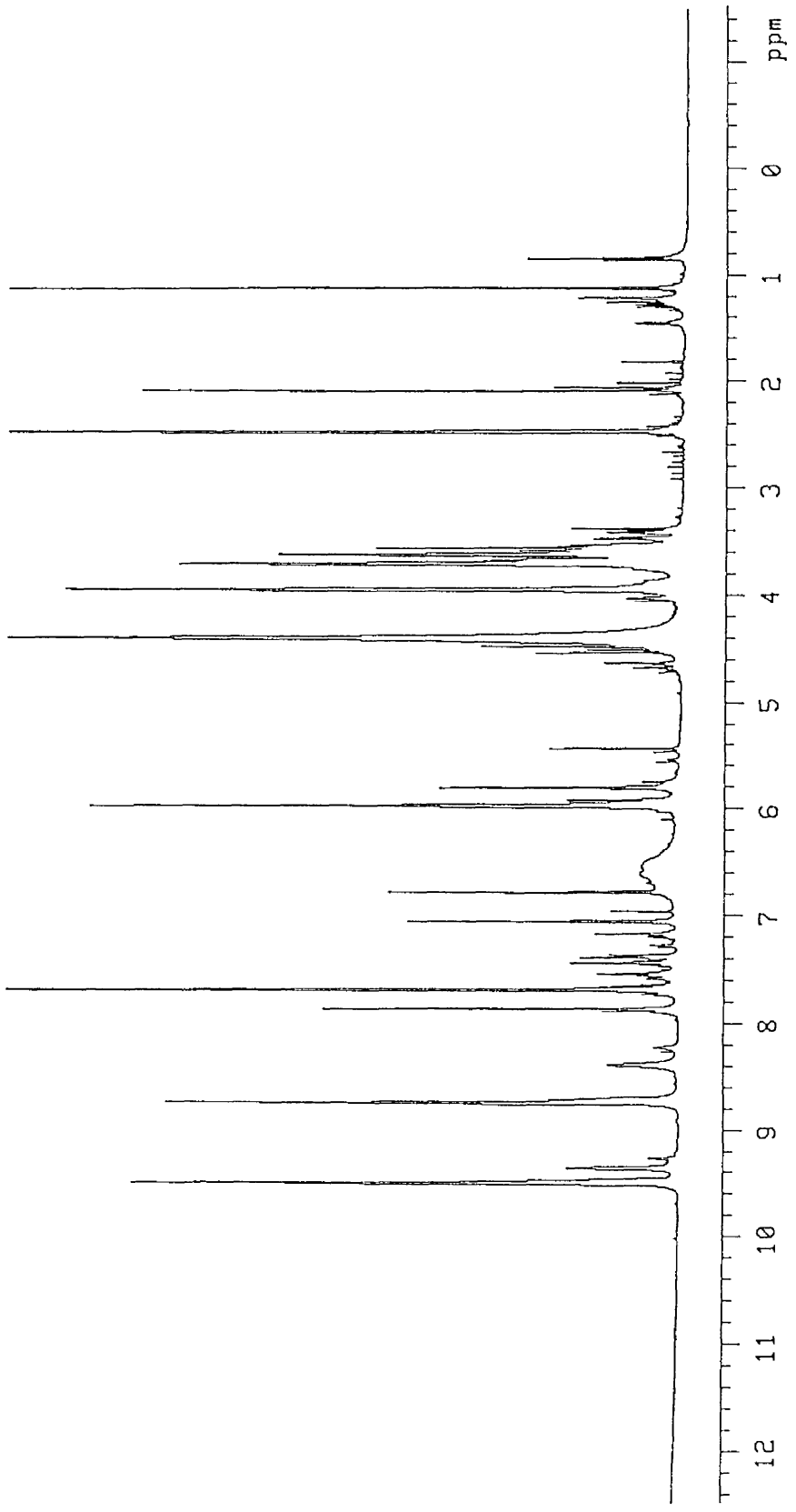


Figure 37

chromatography. This was clearly impossible in the present case due to the oligomeric or polymeric nature of several of the products. For this reason the synthesis of polypseudorotaxanes by "Clipping" was abandoned. Syntheses were then attempted using the "Threading" approach.

3.3.2 SYNTHESIS BY "THREADING"

After the partial success in synthesising polypseudorotaxanes using the "Clipping" method, it was decided to attempt the synthesis using the "Threading" method, despite the initial reservations. This first required the synthesis of cyclophane **(1)**.

3.3.2.1 Synthesis of Cyclophane (1)

Cyclophane **(1)** was produced as described by Stoddart, i.e. by treating "semi-circle" **(17)** with 1,4-bis(bromomethyl)benzene in the presence of diol **(13)** as a template.[88] This produced cyclophane **(1)** in 37% yield. Diol **(13)** was used as a template to encourage the synthesis of cyclophane **(1)** over the synthesis of other linear and cyclic products.

3.3.2.2 Synthesis of Polypseudorotaxanes

As a trial, cyclophane **(1)** (25mole%) was mixed initially with polymer **(6)** in acetonitrile. Surprisingly a red colour developed instantly suggesting that a rotaxane had been formed, and moreover, formed rapidly. This is clearly a much cleaner way of synthesising

polypseudorotaxanes as no side-reactions can occur and therefore only the following may be produced.

i) Pure cyclophane **(1)**

ii) Pure polymer **(6)**

iii) Polypseudorotaxane

Also using the method of "Threading" it is possible to accurately control the number of cyclophanes available per polymer repeat unit and thus to monitor the properties of the polymer at these different "Feeds".

"Threading" was successfully attempted using all the polymers **(6)**, **(7)**, **(9)** and **(10)**. The products were studied most extensively by ^{1}H NMR spectroscopy, but also by UV spectroscopy. The next sections, therefore, discuss the results gained using these techniques.

3.4 POLYETHERS CONTAINING HYDROQUINONE

3.4.1 ^{1}H NMR STUDIES

Stoddart has shown that, compared to those observed in the pure polymer, there are very large shifts in the ^{1}H NMR spectra of the aromatic ether unit in the thread when it is complexed to cyclophane **(1)**.[89] This is due to the large ring current of cyclophane **(1)** which has a shielding effect on the hydroquinone complexed with it.[90]

Figure 38 shows schematically cyclophane **(1)** threaded onto a segment of the polymer chain. The aromatic ether component experiences a substantial shielding effect, as it sits in the middle of cyclophane **(1)**. Figure 38 also shows that the ethyleneglycol spacer assists with the stabilisation of cyclophane **(1)** by interacting with the positive charges on cyclophane **(1)**, just as a crown ether stabilises a cation placed in its centre.[91] As a consequence the protons in the ethyleneglycol units will also have shifts in the ^{1}H NMR spectrum different from those in the pure polymer. The shift values obtained by Stoddart for the [3] rotaxane [Stoddart Thread **(19)**] are shown in Table 8.[89] Stoddart decided that this rotaxane had the π–stacked structure shown in Figure 39.

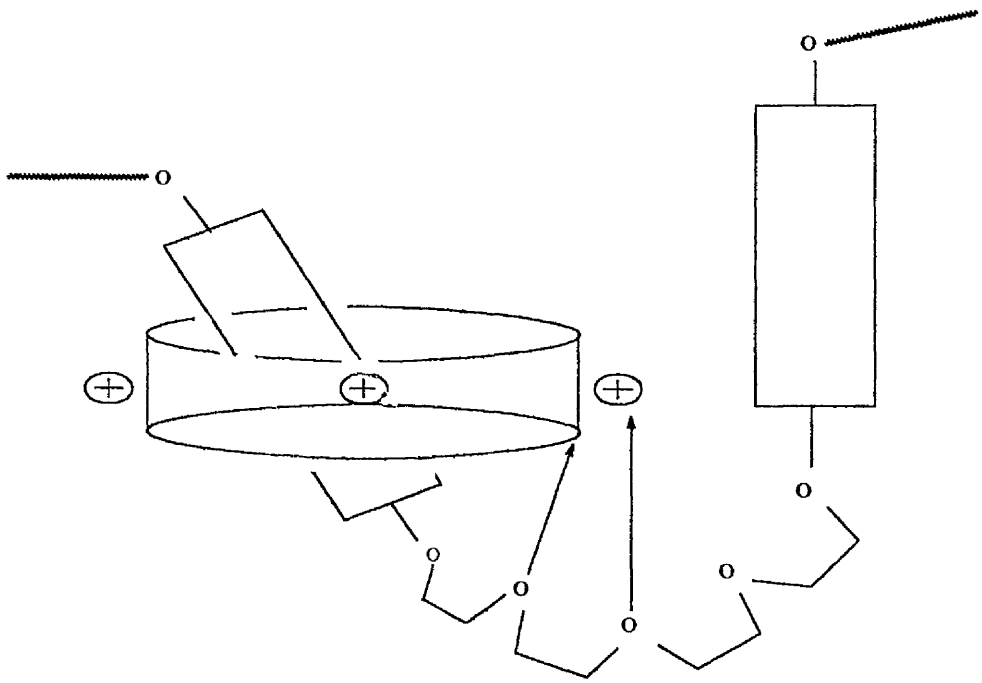
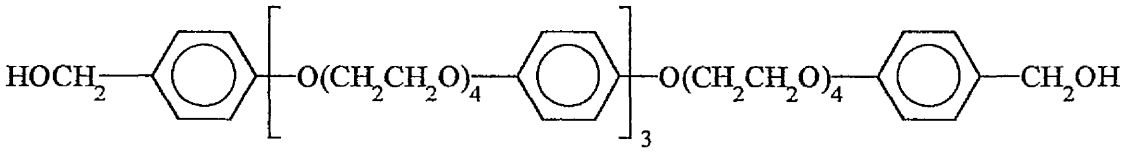


Figure 38

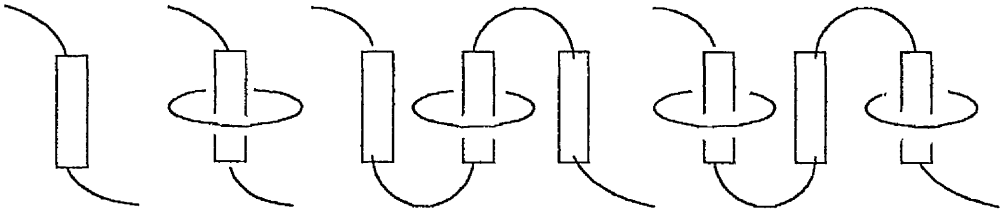


Stoddart Thread **(19)**

Table 8: ^{1}H NMR Shift Positions for the Rotaxane formed from Stoddart Thread (19)

Compound		Cyclophane Component		
	α-CH	β–CH	C_6H_4	CH_2N^+
Stoddart Thread **(19)**	N/A	N/A	N/A	N/A
Cyclophane **(1)**	8.9ppm	8.2ppm	7.5ppm	5.7ppm
Rotaxane	8.8ppm	7.5ppm	7.7ppm	5.6ppm

		Polymer Component				
ArH (Free)	ArH (Alongside)	ArH (Between)	ArH (Bound)	α–OCH_2	β–OCH_2	γ–OCH_2
6.8ppm	N/A	N/A	N/A	4.0ppm	3.7ppm	3.6ppm
N/A	N/A	N/A	N/A	N/A	N/A	N/A
6.8ppm	6.5 and 6.3ppm	6.2ppm	3.4ppm	(Signals have broadened 3.2 - 4.0ppm)		



F*ree* **T***hreaded* **A***longside* **B***etween*

Figure 39

Given the above information it was possible to analyse the spectra of the polypseudorotaxanes.

3.4.2 ANALYSIS OF THE ^{1}H NMR SPECTRA OF THE PSEUDOROTAXANES FORMED FROM POLYMER (6).

Initially the complex formed between cyclophane **(1)** and polymer **(6)** was studied. This was a good starting point due to the similar solubilities of cyclophane **(1)** and polymer **(6)**. A low feed of 5 mole% of cyclophane **(1)** per polymer repeat unit was used in order to produce the simplest ^{1}H NMR spectra. The loading refers to the mole% of cyclophane **(1)** incorporated onto the polymer chain per polymer repeat unit.

Figure 40 shows the ^{1}H NMR spectra obtained for:

i) Pure cyclophane **(1)**,

ii) Pure polymer **(6)**, and

iii) A mixture of the cyclophane and the polymer

The spectra were all acquired at -40°C in acetonitrile. This temperature was chosen in order to eliminate any exchange on the NMR time scale that may occur.[92]

It is immediately obvious that the third spectrum is not a simple addition of the other two. Indeed, it does not appear to contain any signals due to free cyclophane **(1)** although signals were observed at 6.8ppm, the position at which signals are normally observed for the aromatic protons in pure polymer **(6)**. These could be due to pure polymer being present or indeed, due to "Free" aromatic residues in the polypseudorotaxane.

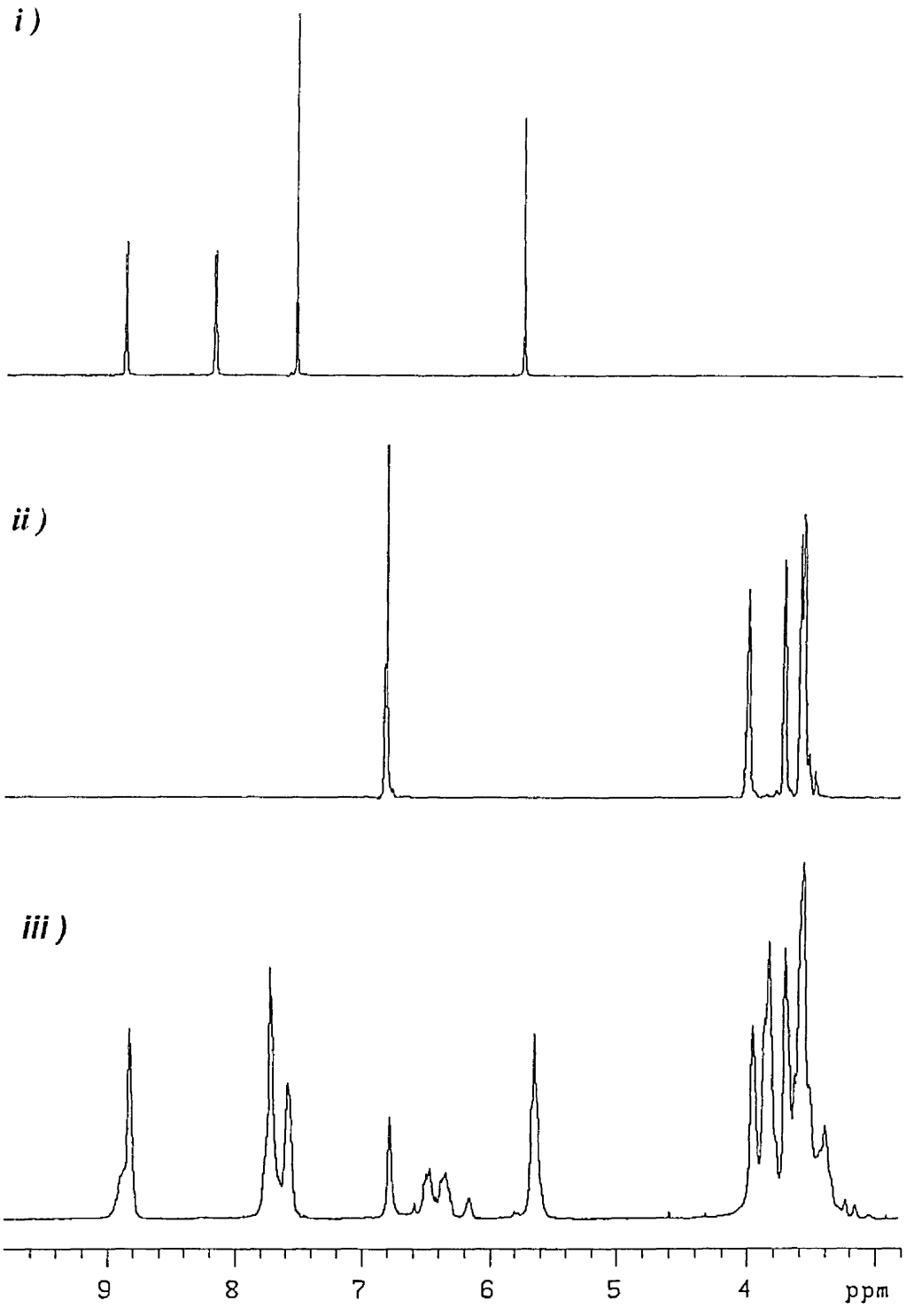


Figure 40

In order to determine whether or not a polypseudorotaxane had been synthesised, it was necessary to determine the shift position of the hydroquinone in the ^{1}H NMR spectrum. It is known that hydroquinone in polymer **(6)** has a shift position of 6.8ppm and that in a rotaxane, taken from results by Stoddart, it has a shift position of 3.4 - 4.0ppm.[93] It can be seen by examining spectrum (ii) that the ethyleneglycol signals occur in this same region. By examining spectrum (iii) it can also be seen that the signals in the region in the ^{1}H NMR spectrum between 3.4 and 4.0ppm have broadened. This may be due to shifts in the signals due to the ethyleneglycol moieties that may be complexed with cyclophane **(1)** and also any hydroquinone that may be complexed to cyclophane **(1)**. For this reason accurate integrals of individual signals in this region cannot be determined easily and therefore, an alternative method must be found to determine the intensity of any hydroquinone signals that may be shifted into this upfield position. In order to do this the ratio of the signals due to hydroquinone compared to all those due to the ethyleneglycol moieties in the ^{1}H NMR spectrum of the pure polymer needed to be determined. This ratio cannot change and hence any difference between this ratio in the pure polymer and that in the polypseudorotaxane, must be due to complexed hydroquinone. Equation1 can be derived in order to calculate the intensity of any complexed hydroquinone that may be shifted to the up-field position.

$$\mathbf{EG - X = Y(Ar + X)}$$

$$\mathbf{EG - X = YAr + XY}$$

$$\mathbf{XY + X = EG - YAr}$$

Equation1

X is the intensity of the signals due to the complexed hydroquinone

Y is the ratio of the signals due to hydroquinone compared to those due to the ethyleneglycol moieties in the pure polymer

EG is the total intensity of the signals in the ethyleneglycol region of the spectrum (3.4 - 4.0ppm)

Ar is the total intensity of the signals in the aromatic region

New signals appeared at 6.5 - 6.3ppm. Stoddart suggested in his work, that these signals were due to the aromatic component of the polymer being present in a third environment, (neither totally "Free" nor "Threaded").[93] To check that these new signals were due to the aromatic component in the polymer two calculations were carried out using Equation 1. The intention was to calculate the loading first on the assumption that the signals at 6.5-6.3ppm were due to residues other than hydroquinone, and secondly on the assumption that these signals were due to hydroquinone residues.

Calculation 1

Let **Ar** be the intensity of the signal at 6.8ppm (totally free). In this case the following values were obtained:-

Y = 4.24, EG = 136.33, and Ar = 28.05.

Hence, X = 3.32 and the amount of bound aromatics (i.e. the loading) was calculated as being 13 mole%

Calculation 2

Let **Ar** be the intensity of the signals between 6.8 and 6.3ppm. In this case the following values were obtained:-

Y = 4.42, EG = 136.33, and Ar = 29.83

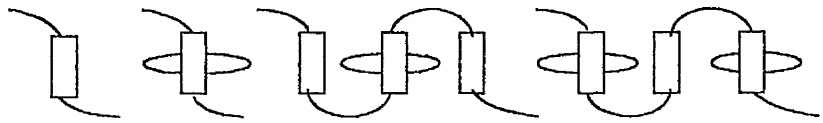
Hence, X = 1.88 and the amount of bound aromatic (i.e. the loading) was calculated as being 6 mole%

The masses of cyclophane **(1)** and polymer **(6)** were accurately measured in order to achieve a loading of 5 mole%. Calculation 2 gave the value closest to this and hence it appears that the signals at 6.5 and 6.3ppm are indeed due to the aromatic component of the polymer. In order to prove this more fully these calculations were repeated for polymers of different loadings. In every case calculation 2 gave the value closest to that expected.

At loadings greater than ca. 10%, a signal appears at 6.2ppm. This also had to be included as being due to the aromatic component in polymer **(6)** in order to get an accurate value for the loading. This signal is, therefore, due to hydroquinone residues in yet another environment.

In summary, it has been shown that the aromatic component of the polymer can exist in four distinct environments. This result agrees with those of Stoddart referred to earlier. These four environments are shown in Figure 41.

An important question is why the aromatic residues in the "Alongside" environment appear as a distorted A_2B_2 system? It has been suggested, that this distortion may be due to end group effects. However, for the polypseudorotaxane loaded to 5% the two signals are of equal intensity. If an end group effect was causing two signals to be produced then the relative intensity of these two signals would change as the loading was changed. Thus, aromatic components in the middle of the chain would not be affected by the end groups whereas those at the ends would be affected. This was found not to be the case. Indeed, the two signals at 6.5 and 6.3ppm are always found to be of equal intensity. This suggests that these two signals are from the same hydroquinone ring. This is further supported by 2D-COSY experiments which show coupling between these two signals, see Figure 42. To rationalise these observations consider the environment of the "Alongside" aromatic residues. The ethyleneglycol spacer that separates the adjacent π–electron-rich aromatic components in the polymer folds round to allow both the adjacent aromatics to interact with cyclophane **(1)**. This is illustrated by data acquired from molecular modelling, see Figure 43. Stoddart has shown by X-ray crystallography that cyclophane **(1)** sits at an angle over the aromatic ether component in the thread.[85] This means that two hydrogen atoms of the adjacent aromatic ether component are nearer to the cyclophane than the other two and hence, are closer to the shielding field of cyclophane **(1)**. This gives rise to different shifts for each of these hydrogen atoms and thus the A_2B_2 system, see Figure 44. The distortion from a simple A_2B_2 system comes from the fact that the angle at which cyclophane **(1)** sits over the aromatic component may not always be exactly the same, also adjacent aromatic components in the polymer may be twisted to different extents in relation to one another.



	Free	Threaded	Alongside	Between
^{1}H NMR SHIFTS *	Singlet 6.78ppm	Singlet 3.40ppm	Distorted A_2B_2 6.30 & 6.48ppm	Singlet 6.16ppm

* For solutions in acetonitrile at -40°C

Figure 41

Only one singlet arises from aromatics in the "Between" environment. This means that these aromatics must be in a symmetrical arrangement. For this to be the case, cyclophane **(1)** must sit at approximately the same angle over each of the aromatics along the polymer chain i.e. they must be arranged as shown in Figure 45a and not as in Figure 45b.

It is known that there are interactions between the ethyleneglycol spacers and cyclophane **(1)**, see Figure 38. This requires the cyclophane **(1)** ring and in particular the charges to be near the spacer unit. It is probably for this reason that cyclophane **(1)** does indeed sit at approximately the same angle over each of the aromatic ether components in the polymer.

Having identified all the signals due to the polymer components in the rotaxane it was now necessary to identify those due to the cyclophane **(1)** components of the rotaxane. The 2D-COSY spectra, see Figure 42 obtained for the 25% loaded pseudorotaxane of polymer **(6)** indicated that, there was coupling between the signals at 8.8ppm and those at 7.5ppm. These signals must therefore be due to the α-CH and C_6H_4 components of cyclophane **(1)**

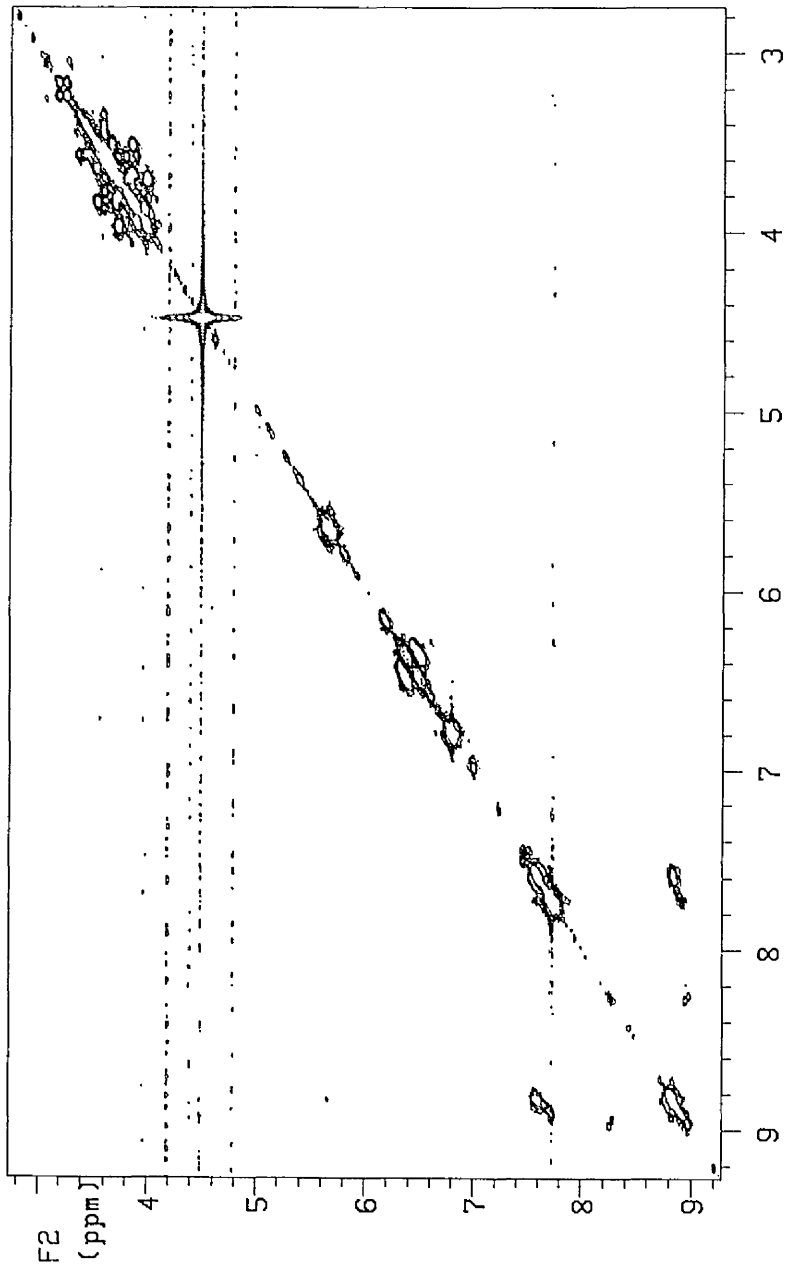


Figure 42

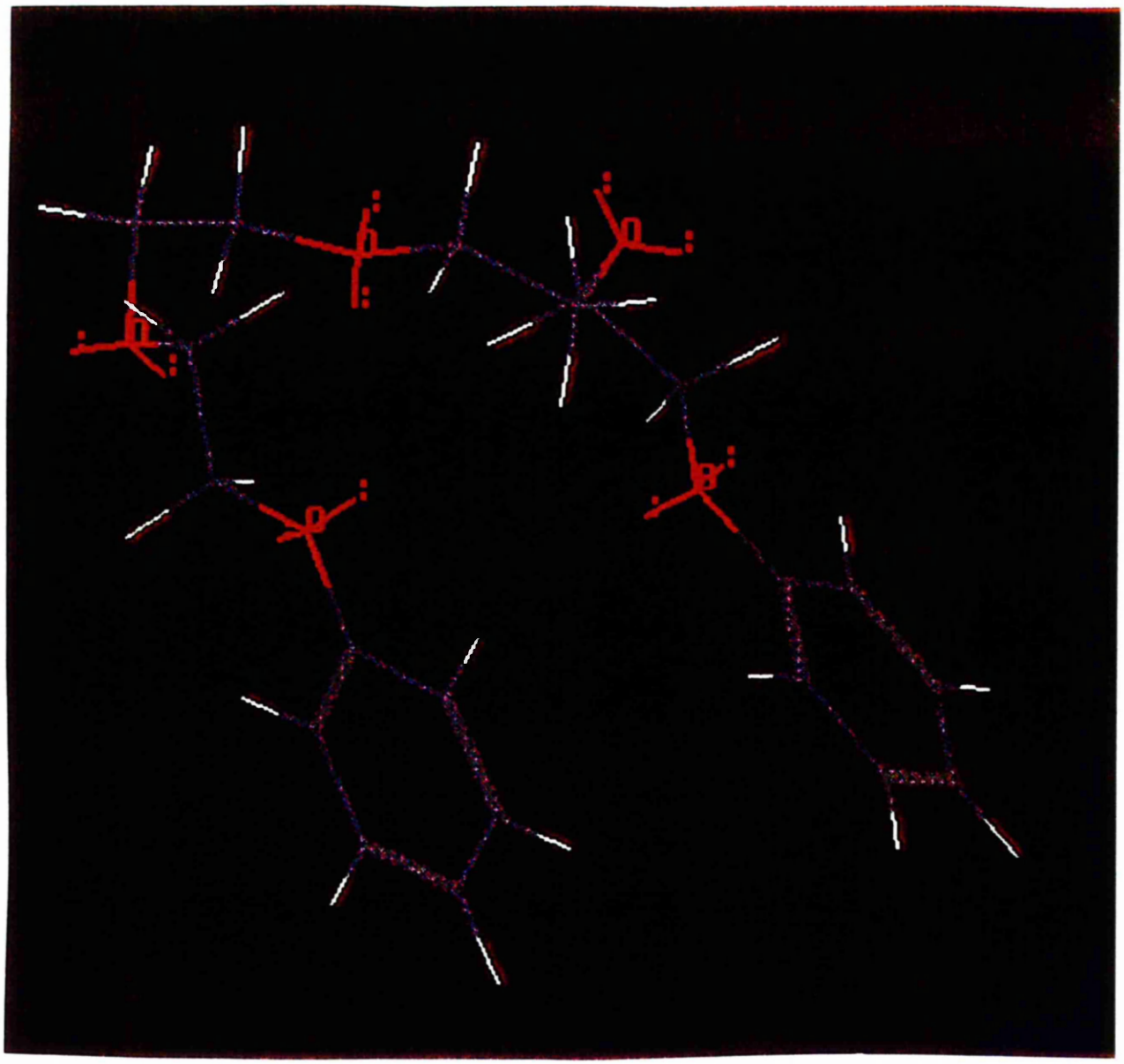


Figure 43

respectively, see Figure 46. This allows the signals at 7.7ppm to be assigned to the β-CH component of cyclophane **(1)** and the signals at 5.6ppm to the CH_2N^+ component of cyclophane **(1)**. At loadings above 30% signals are observed at 8.2ppm which is the same position as for pure cyclophane **(1)**: these must therefore be due to "Free" cyclophane **(1)**. It is possible to obtain accurate integrals for the signal at 8.2ppm and hence this was used to calculate the percentages of bound cyclophane. The ^1H NMR shift positions for each component in each of the pure polymer **(6)**, the pure cyclophane **(1)** and the corresponding polypseudorotaxane are shown in Table 9.

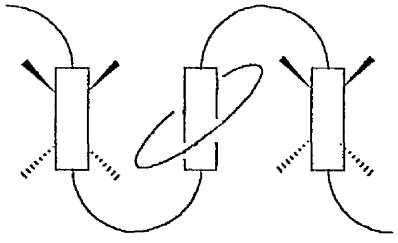


Figure 44

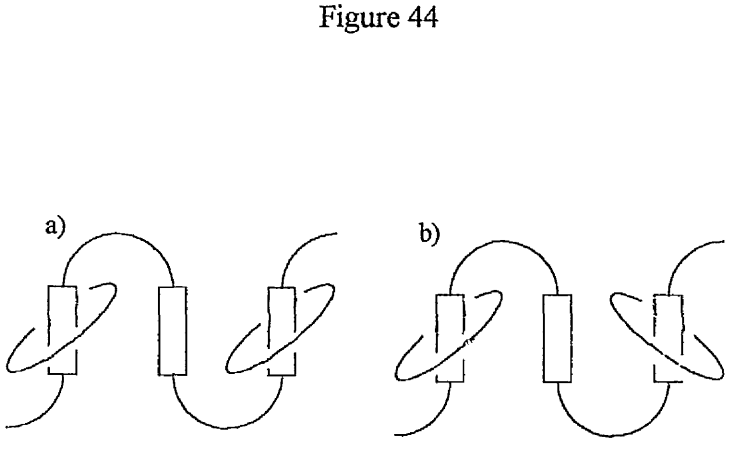


Figure 45

Table 9 : ^{1}H NMR Shift Data Determined for Pseudorotaxanes of Polymer (6).

Compound		Cyclophane Component		
	a-CH	b-CH	C_6H_4	CH_2N^+
Polymer (1)	N/A	N/A	N/A	N/A
Cyclophane (1)	8.9ppm	8.2ppm	7.5ppm	5.7ppm
Poly(pseudorotaxane)	8.8ppm	7.5ppm	7.7ppm	5.6ppm
Shifts due to formation of poly(pseudorotaxane)	-0.1	-0.7	0.2	-0.1

		Polymer Component				
ArH (Free)	ArH (Alongside)	ArH (Between)	ArH (Bound)	a-OCH_2	b-OCH_2	g-OCH_2
6.8ppm	N/A	N/A	N/A	4.0ppm	3.7ppm	3.6ppm
N/A	N/A	N/A	N/A	N/A	N/A	N/A
6.8ppm	6.5 and 6.3ppm	6.2ppm	3.4ppm	(Signals have broadened 3.2 - 4.0ppm)		
0	-0.3 and -0.5	-0.6	-3.4			

3.4.2.1 The Relative Proportions of Hydroquinone Ether Units of Pseudorotaxanes of Polymer (6) Present in the Various Environments.

It was now possible to determine the relative amounts of each environment present in the pseudorotaxanes formed from polymer **(6)** and cyclophane **(1)** as the feed of cyclophane **(1)** was changed. Table 10 shows the data acquired. The ^{1}H NMR spectra were all obtained from a 10mg solution of polymer **(6)** in 1ml of deuterated-acetonitrile with the appropriate amount of cyclophane **(1)** being added. The ^{1}H NMR spectra were obtained at -40°C in

order to eliminate any exchange processes on the NMR time scale. Above this temperature broadening of the spectra occurs and this prevents accurate analysis. The results are plotted out in Figure 47.

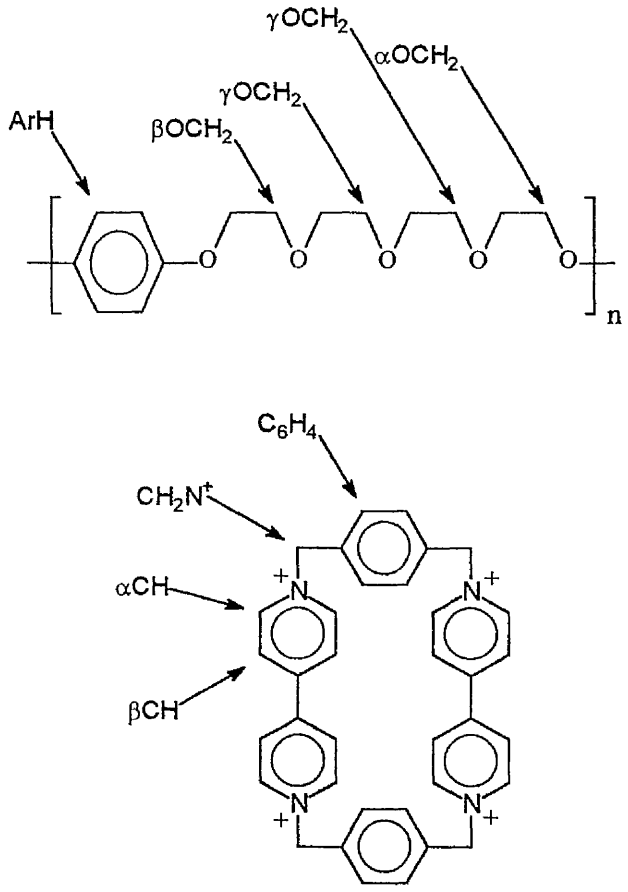


Figure 46

Several points are evident from Table 10. These points are discussed below.

a) At feeds up to ca. 30%, all cyclophane **(1)** that is added becomes threaded.

b) At feeds, and in view of (a), loadings of up to ca. 10%, the amount of aromatics present in the "Alongside" environment is close to being twice that of those that are "Bound". At feeds greater than ca. 10% signals appear which are due to the "Between" environment. The amount of aromatics present in the "Alongside" environment then begins to decrease as those in the "Between" environment begin to increase.

c) As the feed increases above ca. 70% the amount of aromatics present in the "Between" environment begins to fall and those that are "Bound" continue to rise to a plateau of ca. 70% loading.

Table 10 : The Relative Proportions of the Hydroquinone Ether Units in Pseudorotaxanes of Polymer (6) Present in the Various Environments.

Feed (%)	Free (%)	Alongside (%)	Between (%)	Bound (%)	Free Collar (%)	Max. loading (%)
5	84	11	0	5	0	5
11	69	22	0	9	0	11
29	23	42	6	29	0	29
35	15	41	13	30	2.4	35
43	12	24	21	43	1.8	43
50	8	18	24	49	3.7	50
58	5	15	28	53	5.2	58
67	6	14	28	52	16.4	67
99	4	10	22	63	36.3	99
153	5	8	15	72	51	100
259	4	10	19	67	73	100

The first point suggests that a reasonably strong complex is formed between cyclophane **(1)** and polymer **(6)**.

The second point is as expected from Stoddart's work. Thus, initially when hydroquinone ether units are relatively plentiful, each "Threaded" hydroquinone ether unit is flanked on either side by "Alongside" units. Each cyclophane interacts with these hydroquinone ether units. The general arrangement is shown in Figure 48a. This is clearly π–stacking. As the hydroquinone ether units become less plentiful "Free" units begin to be shared between "Threaded" units, i.e. the arrangement shown in Figure 48b, involving five hydroquinone rings, become important. After about 40% feed the percentage of "Alongside" units is less than twice the number of "Between" units and major arrangements must be ones similar to that shown in Figure 48c.

The third point noted above, indicates that some adjacent hydroquinone ether units on the chain were "Threaded", see for example Figure 48d. This phenomenon has not been noted previously and was an unexpected result. Thus, it was expected that the repulsions between the cyclophanes, each of which contains four ionic bonds, would not allow such a close approach. It is important to note that the arrangement is never entirely as shown in Figures 48b - 48c. As an example it is evident that, even when loading on adjacent rings occurs there are still some "Free" hydroquinone units.

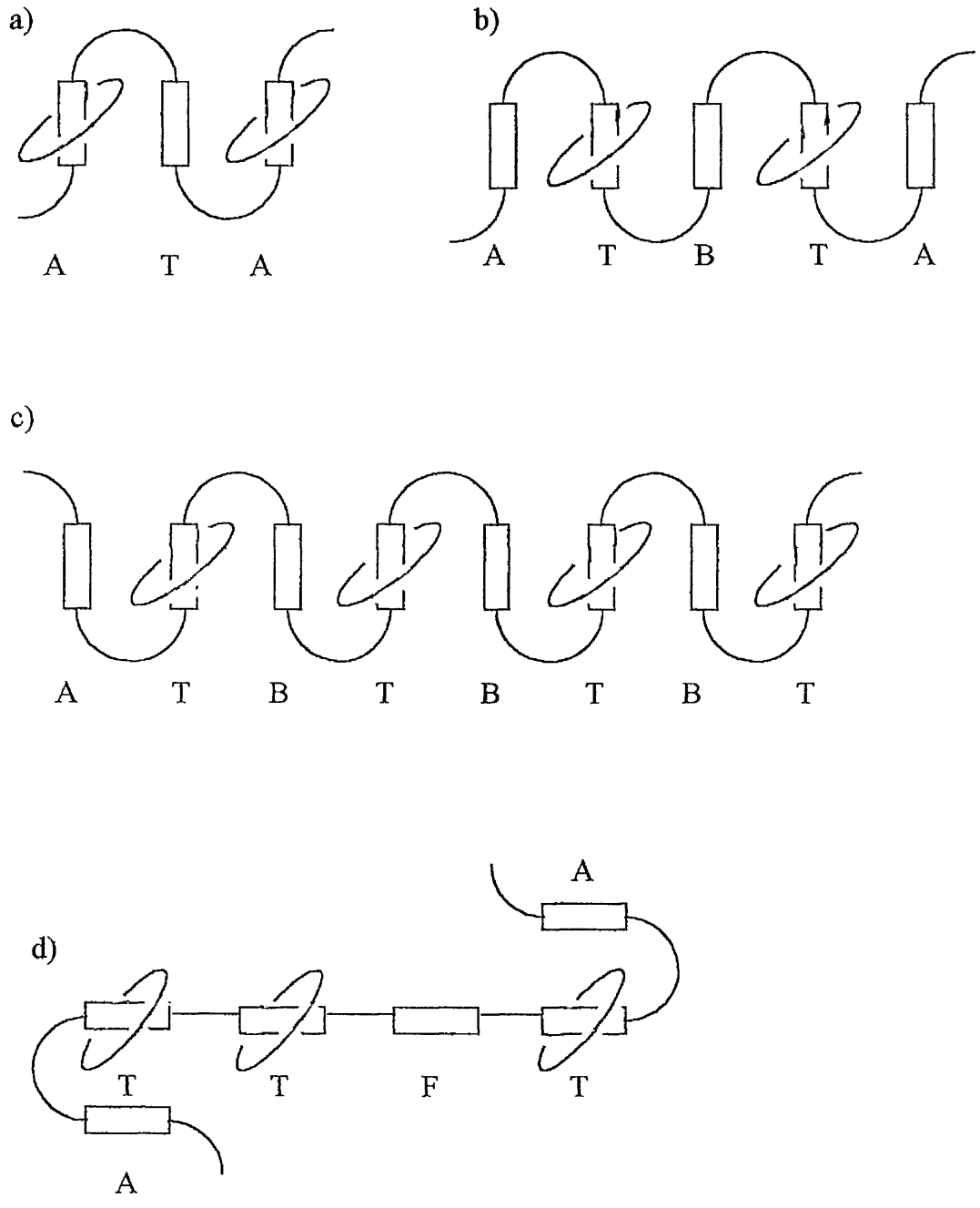


Figure 48

Another example comes from examining the data for the 50% loaded rotaxane. If a loading of 50% is actually achieved i.e. the amount of aromatics present in the "Bound" environment is 50% (as it is in this case) then the amount of aromatics present in the

"Alongside" environment should be zero and those in the "Between" environment should be 50%. In fact the amount of aromatics present in the "Alongside" environment is 18% and those in the "Between" environment is 24%. This means that the polymer does not adopt a completely folded structure and there must be some segments that adopt an extended structure.

The first point means that the binding of cyclophane **(1)** must be very strong in order to push the equilibrium towards pseudorotaxane formation. Beyond a loading of 50% it obviously becomes more difficult to add further cyclophane **(1)** onto the polymer chain as it is becoming very crowded and movement along the chain is therefore difficult.

3.4.2.2 Variable Temperature ^{1}H NMR Analysis of Pseudorotaxanes of Polymer (6)

Initially a pseudorotaxane of polymer **(6)** with a loading of 30% was studied. The cyclophanes in the pseudorotaxane are able to move along the polymer chain by "Jumping" from one aromatic ether unit to a "Free" adjacent one. By examining the ^{1}H NMR spectrum of the pseudorotaxane as a function of temperature it is possible to calculate the speed at which these jumps occur by using Equation 2.

The Relative Proportions of Hydroquinone Ether Units in a Pseudorotaxane of Polymer **(6)** in the Various Environments

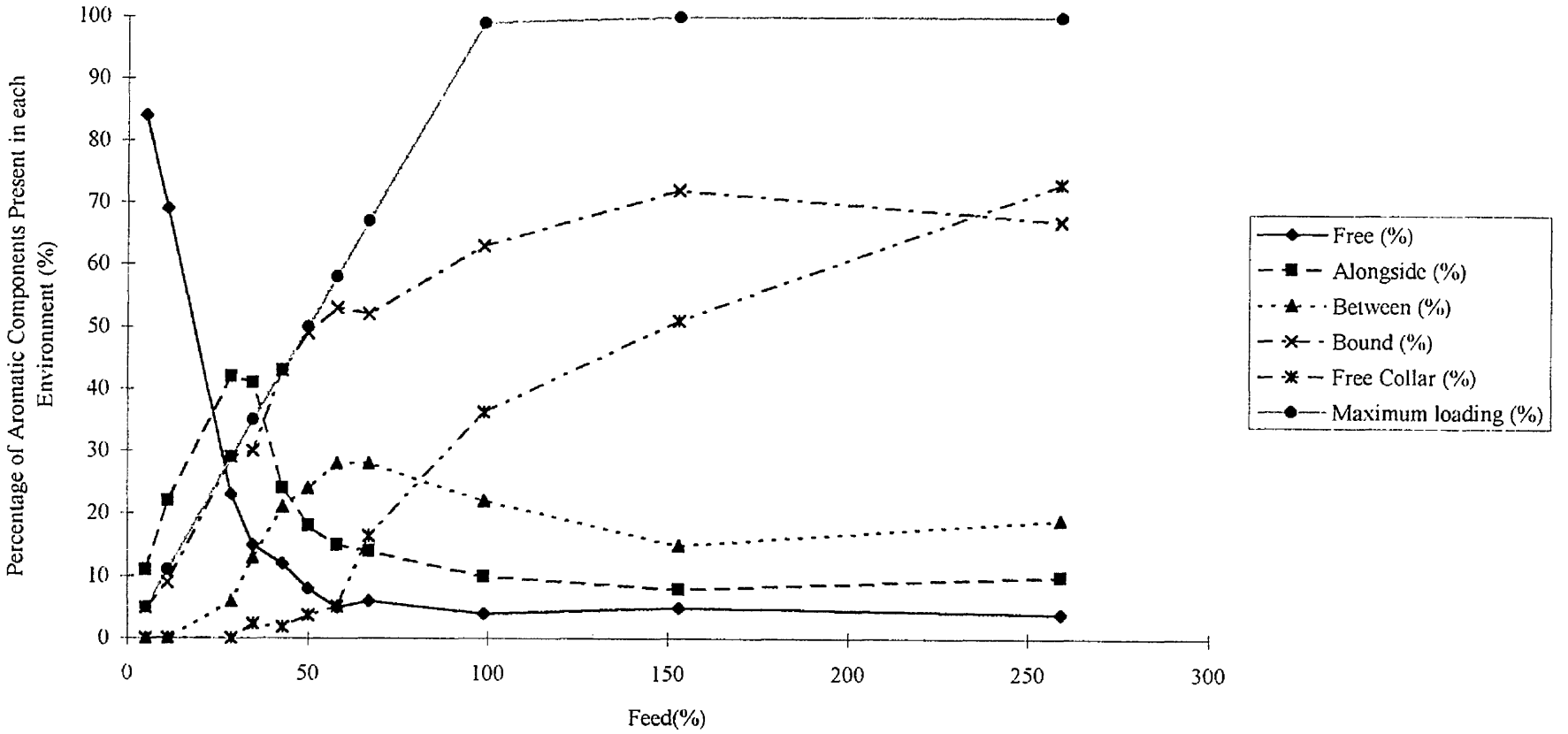


Figure 47

$$K_c = \frac{\pi(\Delta\nu)}{\sqrt{2}}$$

Equation 2

K_c is the rate at which the cyclophanes are moving along the polymer chain

$\Delta\nu$ is the width of the signal of interest at coalescence

Two points of coalescence can be observed by examining the ^{1}H NMR spectrum as a function of temperature.[94] The possible processes that give rise to these points of coalescence are discussed below.

a) Coalescence can be observed between signals due to "Free" and "Threaded" aromatic ether protons, that is the signals at 6.8 and 3.4ppm respectively. Figure 49a shows the process involved in causing the coalescence of these signals.

In the present system it is very difficult to determine the exact temperature at which coalescence occurs as the coalescing signals occur 3.4ppm, i.e. 1700Hz apart when the 500 Mhz NMR machine is used. This means that at coalescence the signal is extremely broad and hence, identifying the temperature at which this is at it's maximum broadening is very difficult. The coalescence temperature was determined to be 318K within 5K. Using Equation 2 it is possible to calculate the speed at which the cyclophanes **(1)** are moving at this temperature. This gives a value of 3776s^{-1} for K_c at a temperature of 318K (+/- 5K).

b) Coalescence can be observed for signals due to aromatics in the "Alongside" and "Between" environments, that is signals at 6.5 and 6.3ppm and at 6.2ppm respectively. Figure 49b shows the possible processes involved in causing the coalescence of these signals.

In Figure 49a, a "Between" signal is replaced by an "Alongside" signal by a "Jumping" process. The same change is achieved by "Reordering" as shown in Figure 49b.

The temperature at which this coalescence occurs was determined to be 278K. Using Equation 2 gives a value of $333s^{-1}$ for K_c at a temperature of 278K.

Stoddart calculated a value of $2360s^{-1}$ for K_c at a temperature of 307K for a monomeric rotaxane of the same general type as the polypseudorotaxane investigated here.[95] Bearing in mind the temperature differences, this result is comparable to the values of K_c calculated in this work. Hence, it appears that the speed at which the cyclophane **(1)** moves maybe independent of the chain length of the polymer.

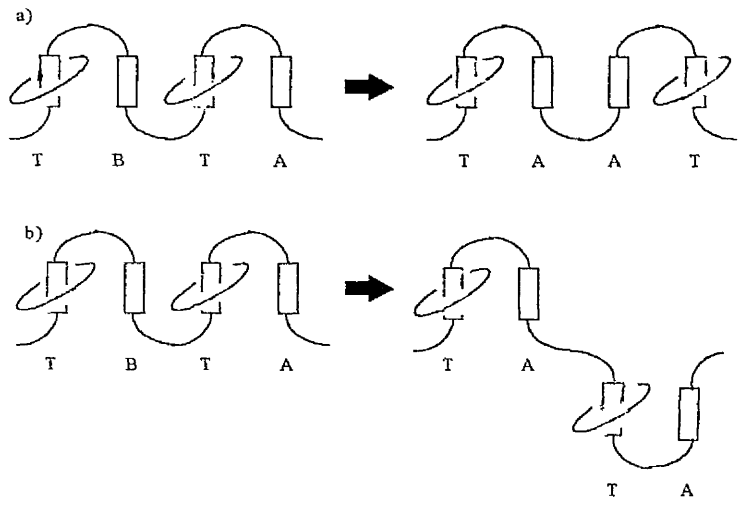


Figure 49

Identical results were found for all loadings of polypseudorotaxane from 5% to 70%. This means one of the following interpretations is the case.

a) The rate at which cyclophane **(1)** moves along the polymer chain is not affected by the number of cyclophanes **(1)** occupying that chain. This seems very unlikely as cyclophanes **(1)** in a highly loaded polypseudorotaxane would be unable to move until a neighbouring aromatic site became "Free". This would therefore slow down the rate at which the cyclophanes **(1)** could move.

b) As the temperature of coalescence is substantially higher than -40°C, a substantial amount of de-threading of the polypseudorotaxane occured. This means that "Bound" cyclophanes **(1)** had more available "Free" aromatic sites and hence, the rate at which they can move may not be affected by the number of cyclophanes **(1)** available for binding with the polymer chain. This is particularly likely to be true if the total number of threaded sites is >50%.

It was not possible to measure the percentage of "Bound" aromatic sites as the temperature is increased due to the occurrence of severe broadening, therefore, an alternative method had to be found to enable the monitoring of the percentage of "Bound" aromatic sites as a function of temperature. UV spectral analysis was investigated for this.

3.4.3 UV SPECTRAL STUDIES

When cyclophane **(1)** complexes with the π–electron-rich aromatic component of a thread such as with polymer **(6)** a bright red colour is observed. This colour is not present for a solution of either pure cyclophane **(1)** or pure polymer **(6)** and it is due to the formation of a charge-transfer complex.[96] This makes it possible to monitor the complexation in a polypseudorotaxane. Using this technique in principle it should be possible to collect data regarding two phenomenon:-

a) Any de-threading that may occur as the temperature of the system is increased.

b) The rate at which cyclophane **(1)** initially threads onto the polymer chain.

In order to do this, it is necessary to assume that the position and extinction coefficient of the charge-transfer band are independant of the pseudorotaxanes detailed environment. It is also neccessary to know the amount of threaded cyclophane **(1)** under standard conditions, so that the extinction coefficient can be determined. Unfortunately, it was not possible to achieve the latter as the ^{1}H NMR was recorded at -40°C and it was not possible to measure the UV spectra below ca. -10°C. Nevertheless, UV spectra were recorded for a known amount of polymer **(6)** in acetonitrile having cyclophane **(1)** added in portions, each time calculating the feed used. The temperature at which the spectra were taken was accurately controlled and noted. The results for the change in the absorbance due a change in temperature are shown in Figure 50. The results for the change in the absorbance due a change in Feed are shown in figure 51.

It is evident that the UV spectral absorbance increased as the feed of cyclophane **(1)** was increased. Not surprisingly, in view of the ^{1}H NMR spectra results, it did not increase linearly, but tended towards a plateau.

The UV absorbance of a polypseudorotaxane resulting from a 30 mole% feed of cyclophane **(1)** was monitored as the temperature of the system was increased. Figure 51 shows that the absorbance decreased linearly as the temperature was increased. This is almost certainly the result of the de-threading of cyclophane **(1)**. The plot suggests that raising the temperature from 0°C to ca. 50°C approximately halves the loading that exists at 0°C. If the plot remains roughly linear to -40°C, at which temperature it is known from the ^{1}H NMR spectra studies that the mole% of rotaxane at this feed is 30%, then it can be deduced that at 0°C it has become ca. 21% and that by 50°C it has become ca. 10%. These figures are clearly approximate as they assume that the plot remains linear in the extrapolated region and they ignore concentration differences between the ^{1}H NMR spectral data and the UV spectral data. Even so the figures give a rough estimate of the extent of de-threading.

It is also possible to monitor the speed at which cyclophane **(1)** threads onto the polymer chain by monitoring the appearance of the UV absorbance at 466.5 nm due to the charge-transfer complex. It is possible to acquire spectra every 30 seconds and by doing this it was shown that after the first acquisition no further change in the UV spectral absorbance is observed. This means that equilibrium has been reached within 30 seconds at -10°C.

UV Spectral Data for a 30% loaded Pseudorotaxane of Polymer (7) as a Function of temperature.

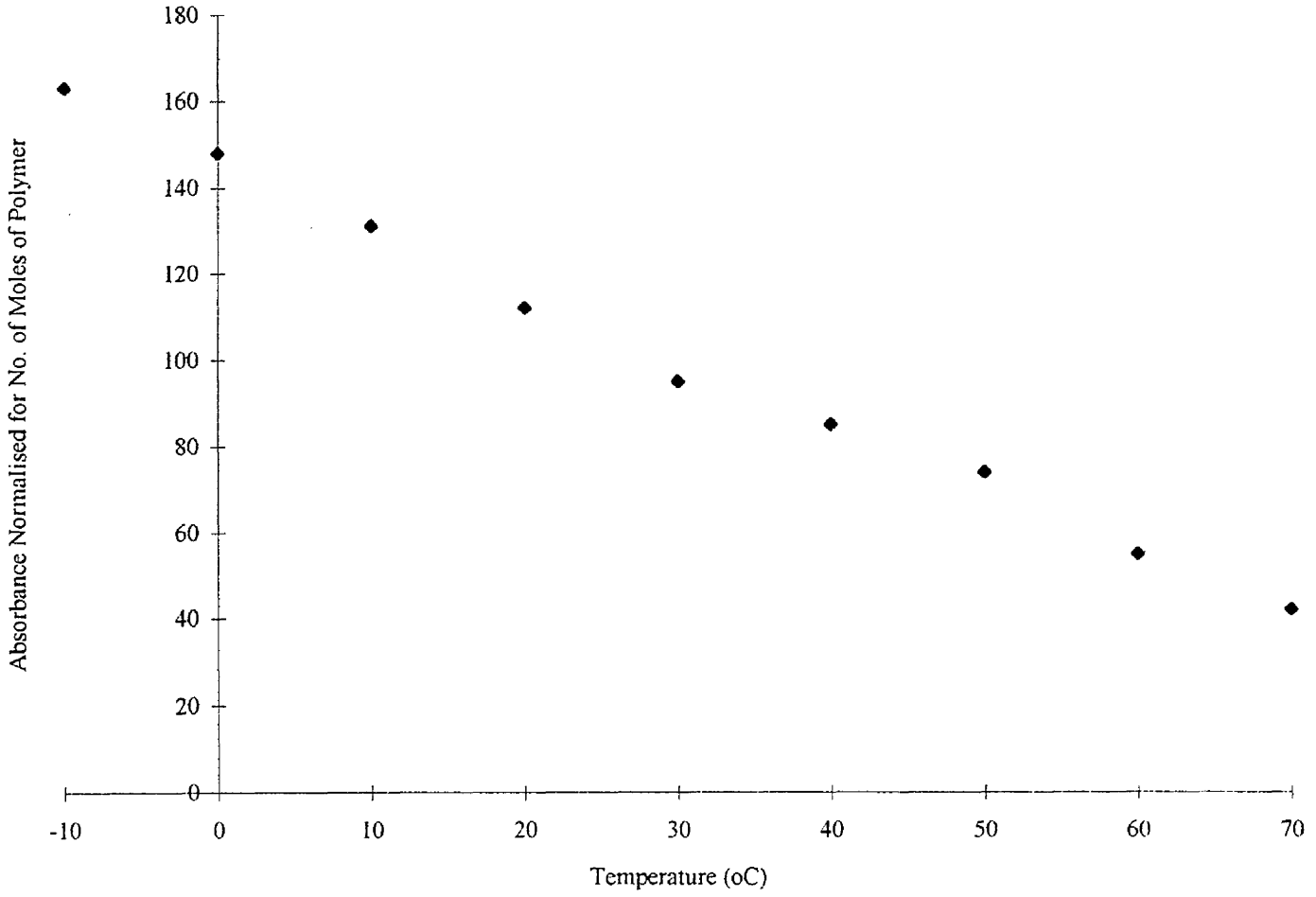


Figure 50

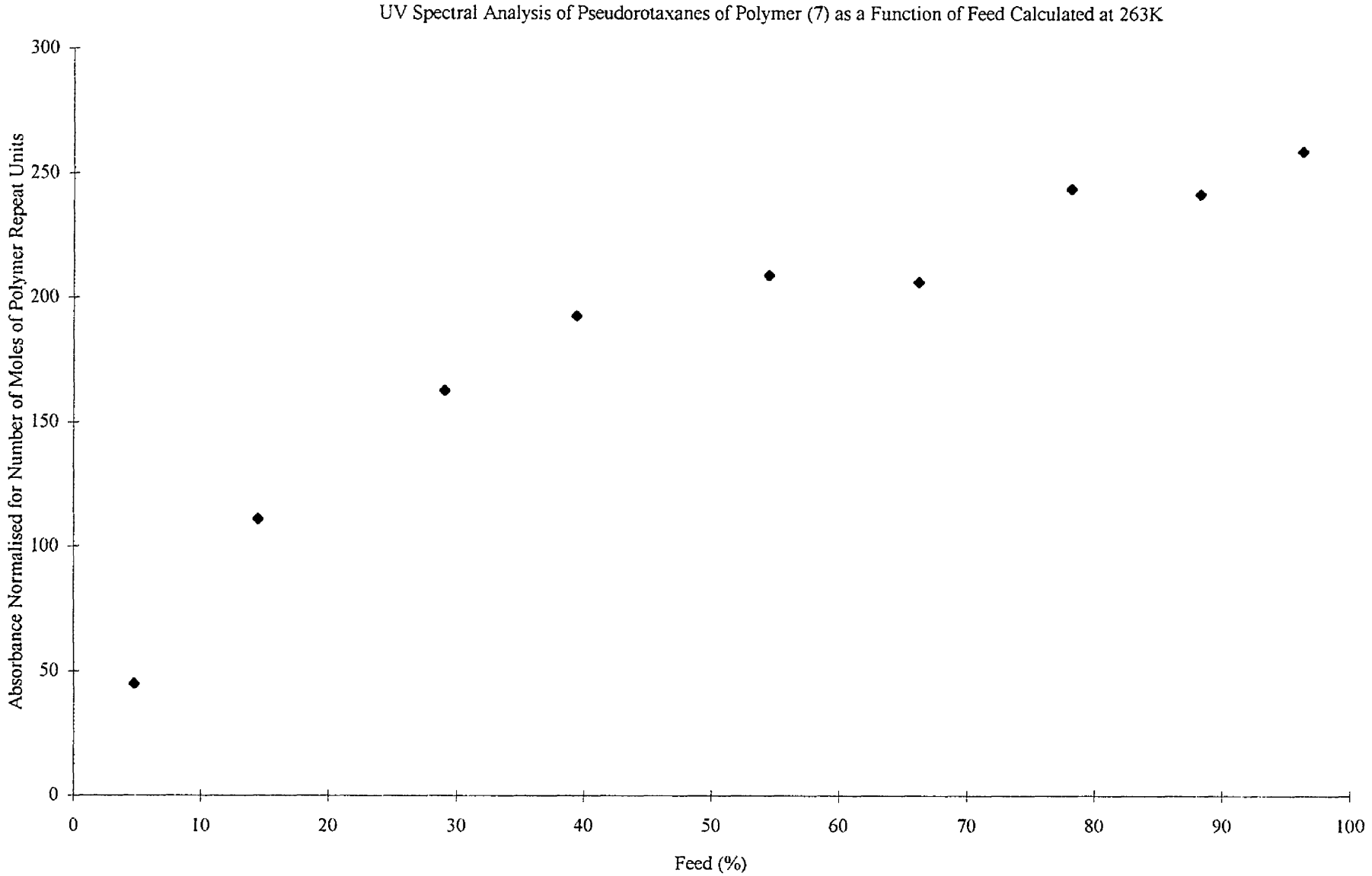

UV Spectral Analysis of Pseudorotaxanes of Polymer (7) as a Function of Feed Calculated at 263K
Absorbance Normalised for Number of Moles of Polymer Repeat Units
300
250
200
150
100
50
0
0
10
20
30
40
50
60
70
80
90
100
Feed (%)

Figure 51

3.5 THE SYNTHESIS OF PSEUDOROTAXANES USING POLYMER (7)

The same experiments were carried out on the pseudorotaxanes formed from polymer (7) as they were for those formed from polymer **(6)**. Again these pseudorotaxanes were characterised mainly using ^{1}H NMR spectroscopy, but also by using inherent viscosity studies. The results gained from this work, together with a comparison with the results gained from the work on pseudorotaxanes formed from polymer **(6)**, are presented in the following sections.

3.5.1 ^{1}H NMR SPECTRAL STUDIES

By examining Figure 52, which shows the ^{1}H NMR spectra of the pseudorotaxanes formed from polymer **(7)** and from polymer **(6)**, it can be seen that they are very similar. The only difference between the two spectra is the shift position of the "Alongside" environment. Table 11 shows the shift positions for this environment in each of the pseudorotaxanes.

Table 11 : Shift Positions of the "Alongside" Environments in Pseudorotaxanes Formed from Polymer (6) and from Polymer (7).

Polymer Used	Alongside
Polymer (6)	6.35 and 6.50ppm
Polymer (7)	6.40 and 6.45ppm

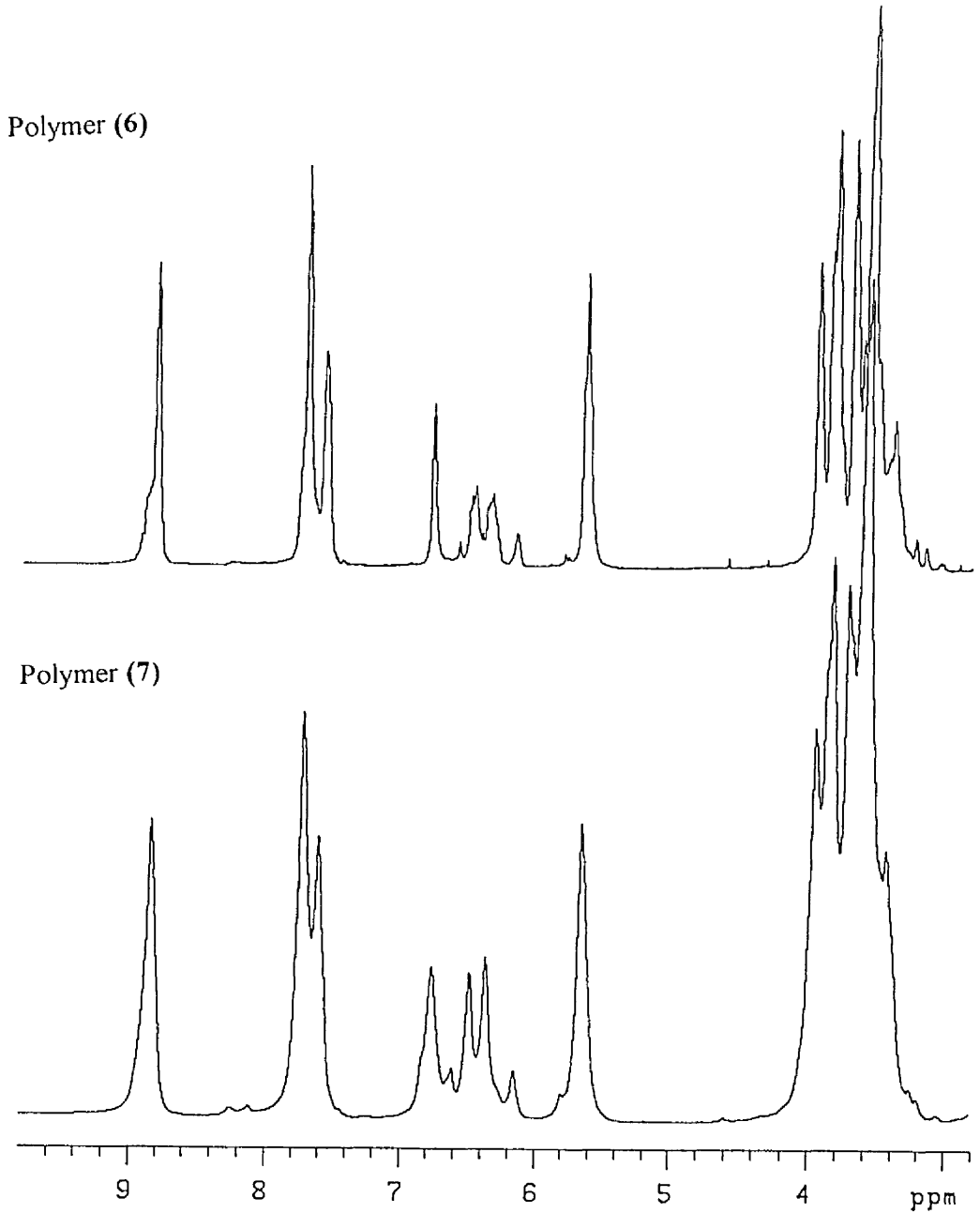


Figure 52

By examining molecular modelling data, see Figure 53, it can be seen that for polymer **(7)**, the triethyleneglycol spacer is not long enough to allow the same degree of folding as is present in polymer **(6)**, which has a tetraethyleneglycol spacer. This therefore means that the shielding effect experienced by a "Free" aromatic ether unit adjacent to one which is "Threaded", will be different in the two polymers. Figure 54 shows schematically some possible positions of adjacent aromatic ether units in polymers **(7)** and **(6)**. Whatever the detailed explanation, it is clear that the position of cyclophane **(1)** in relation to an adjacent aromatic ether unit changes as the spacer length changes, and that this causes a difference in the ^{1}H NMR shifts of the "Alongside" environment. By examining Figure 54a, it can be seen that for an E4 spacer cyclophane **(1)** associated with a "Threaded" aromatic interacts towards the top of an adjacent "Free" aromatic. Hence, the protons at the top of this aromatic will be more shielded than those at the bottom. For an E3 spacer (see Figure 54b), cyclophane **(1)** associated with a "Threaded" aromatic seemingly interacts more strongly with the less shielded protons and less strongly with the more shielded protons due to the proximity of the cyclophane to these protons. Hence, the shift positions of these two sets of protons will be brought closer together.

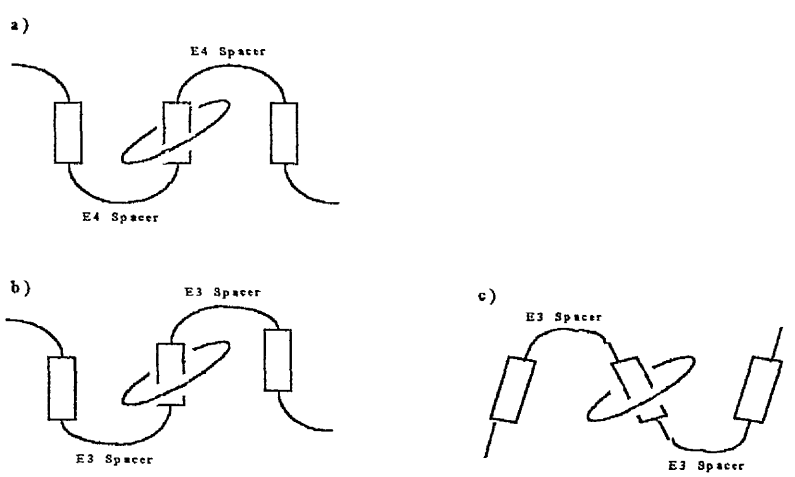


Figure 54

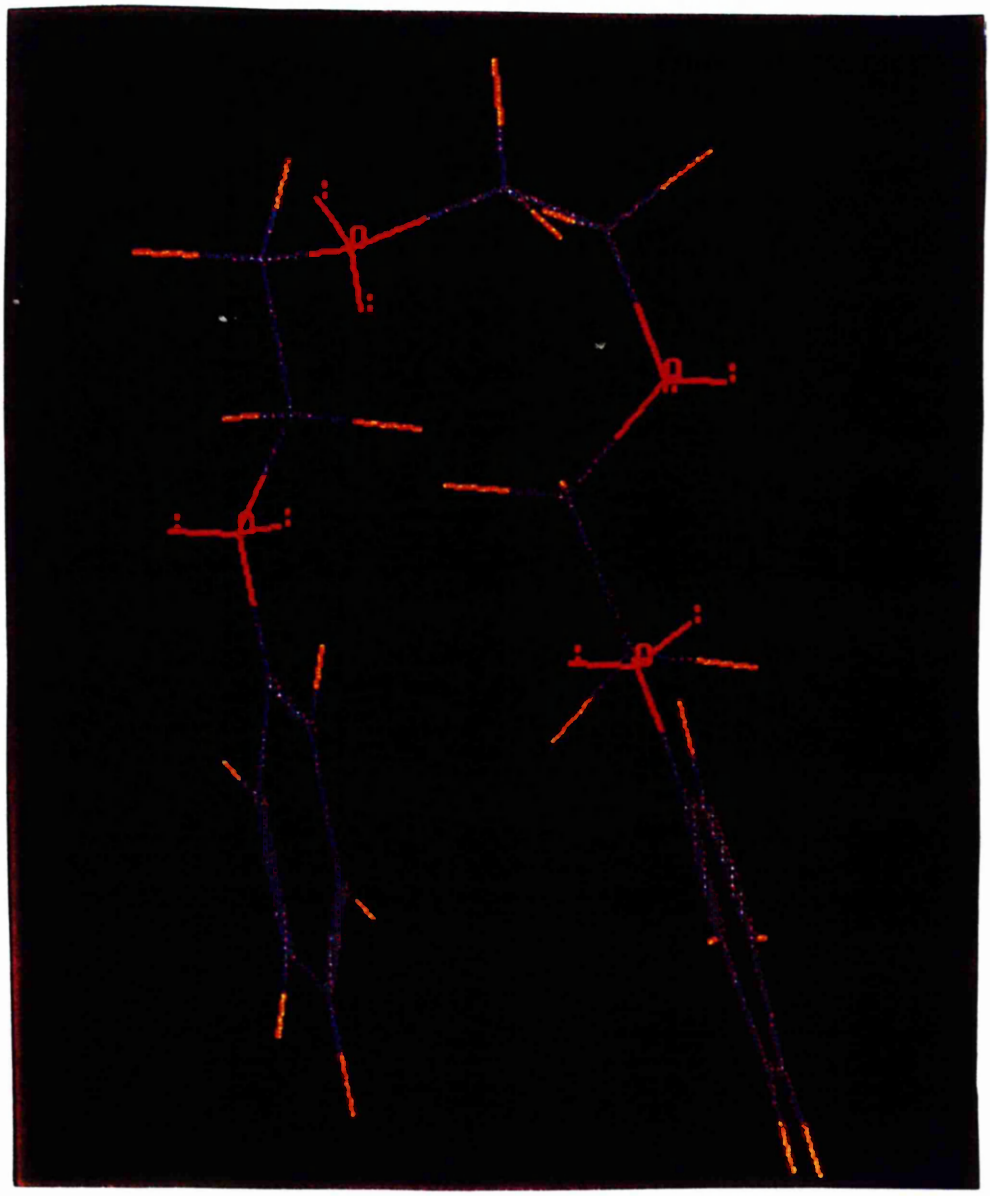


Figure 53

It is now possible to calculate the percentage of aromatics present in each environment for the pseudorotaxanes formed from polymer **(7)**, as it was for the pseudorotaxanes formed from polymer **(6)**. The results for this are shown in Figure 55. The results are very similar to the ones acquired for the pseudorotaxanes formed from polymer **(6)**, but there are two major differences between these types of pseudorotaxanes. These are as follows.

a) For the pseudorotaxanes formed from polymer **(7)**, the percentage of "Threaded" aromatics deviates rapidly from the maximum possible loading at feeds over ca. 40%, whereas for the pseudorotaxanes formed from polymer **(6)**, it stays close to this line until a loading of 50% is achieved. Hence, it is more difficult to achieve high loadings for the pseudorotaxanes formed from polymer **(7)**.

b) The maximum percentage of "Threaded" aromatics for pseudorotaxanes of polymer **(7)** only reaches 50%, whereas for pseudorotaxanes of polymer **(6)** it reaches 70%.

As the percentage of "Threaded" aromatics reaches 50% we can again monitor the percentage of "Alongside" and "Between" aromatics in order to gain information on the chain structure. Table 12 shows these values for the two pseudorotaxanes.

Table 12 : The Percentage of Aromatic Ether units Present in the "Alongside" and "Between" Environments at a Loading of 50%

Polymer Used	"Alongside"	"Between"
Polymer (6)	13%	32%
Polymer (7)	18%	24%

The Relative Proportions of Hydroquinone Ether Units of a Pseudorotaxane of polymer (7) present in the Various Environments

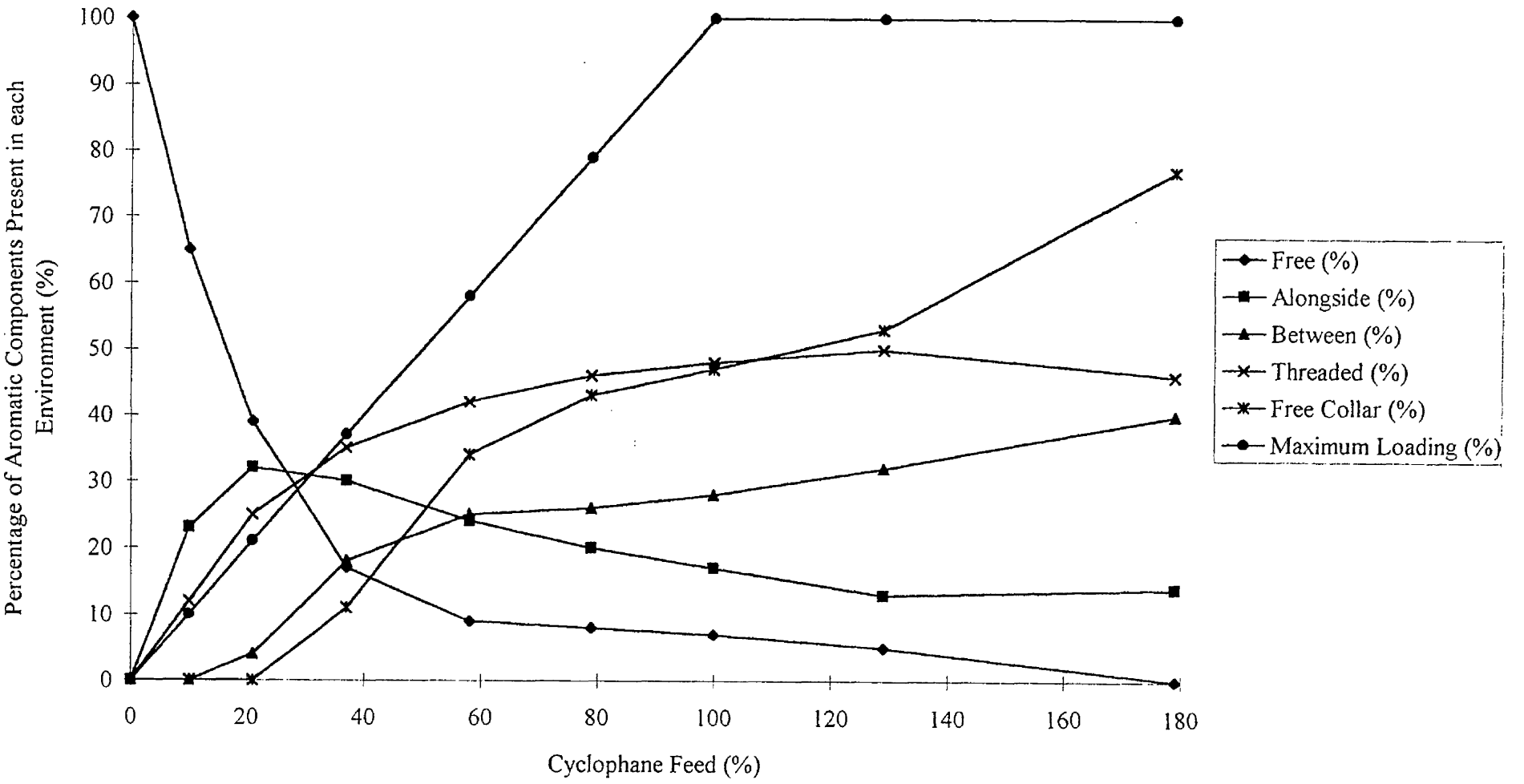


Figure 55

It can again be seen that the polymer chain does not exist entirely as a folded structure, but that some segments of the chain exist in an extended structure. In the case of the pseudorotaxanes formed from polymer **(6)** this allowed loadings of greater than 50% to be achieved, but for the pseudorotaxanes formed from polymer **(7)** the loading never increased above 50%. This shows that the triethyleneglycol spacer is too short, so it is unfavourable for the charged cyclophanes **(1)** to exist on adjacent aromatic components, even if an extended conformation is adopted. It should be noted, however, that whilst it discourages such close packing it does not prevent it. Thus even at 50% loading there is still some 8-10% of the hydroquinone ether units that are "Free". This must clearly be compensated by the presence of some "Adjacent" rotaxane units. Overall the major arrangement for the most highly loaded polypseudorotaxanes is a π-stacked one.

3.5.1.1 Variable Temperature ^{1}H NMR Studies

The results obtained by studying the variable temperature ^{1}H NMR spectra of the pseudorotaxanes formed from polymer **(7)** were essentially the same as those of the pseudorotaxanes formed from polymer **(6)**. For both families of pseudorotaxanes the rate at which the cyclophane moves from one aromatic component to an adjacent one is $3776s^{-1}$ at 45°C (+/- 5°C) . This is not unexpected for a strong complex where cyclophane **(1)** would spend most of the time residing over one of the aromatic ether units in the polymer chain. The speed at which cyclophane **(1)** moves from one aromatic to the next could be very quick and so the speed at which we see the movement would be dominated by the time it resides over one aromatic.

3.5.2 INHERENT VISCOSITY STUDIES

Polymer **(7)** is a reasonably high molecular weight polymer and it is therefore possible to carry out significant inherent viscosity studies on pseudorotaxanes of this polymer. It was not useful to carry out such studies on the pseudorotaxanes formed from polymer **(6)** due to the very low molecular weight of the starting polymer.

The inherent viscosities are obtained using 1% solutions of the polymer and/or cyclophane **(1)** in DMF at 25°C. The inherent viscosities were obtained for the pseudorotaxanes formed with feeds from 10-150%. Figure 57 shows how the viscosity of the pseudorotaxanes changes as the feed of cyclophane **(1)** is increased. It can be seen that the viscosity of this polymer decreases as the feed is increased. In general, charged polymers have higher viscosities than their neutral counterparts as the charges repel each other causing the volume of the polymer to increase, thus, increasing the radius of gyration and the viscosity.[97] Therefore, it would be expected that the viscosity of a polymer would rise as the number of charges that it carries increased. As the loading of a pseudorotaxane of the present type is increased, then the number of charges it contains dramatically increases as for every cyclophane **(1)** added, four ionic bonds are introduced. In practice, as is evident from Figure 57, the viscosity decreased. This is possibly because with the present case, as the polymer chain becomes more heavily loaded, it becomes increasingly π-stacked as shown in Figure 58 and hence the radius of gyration and the inherent viscosity decreases.

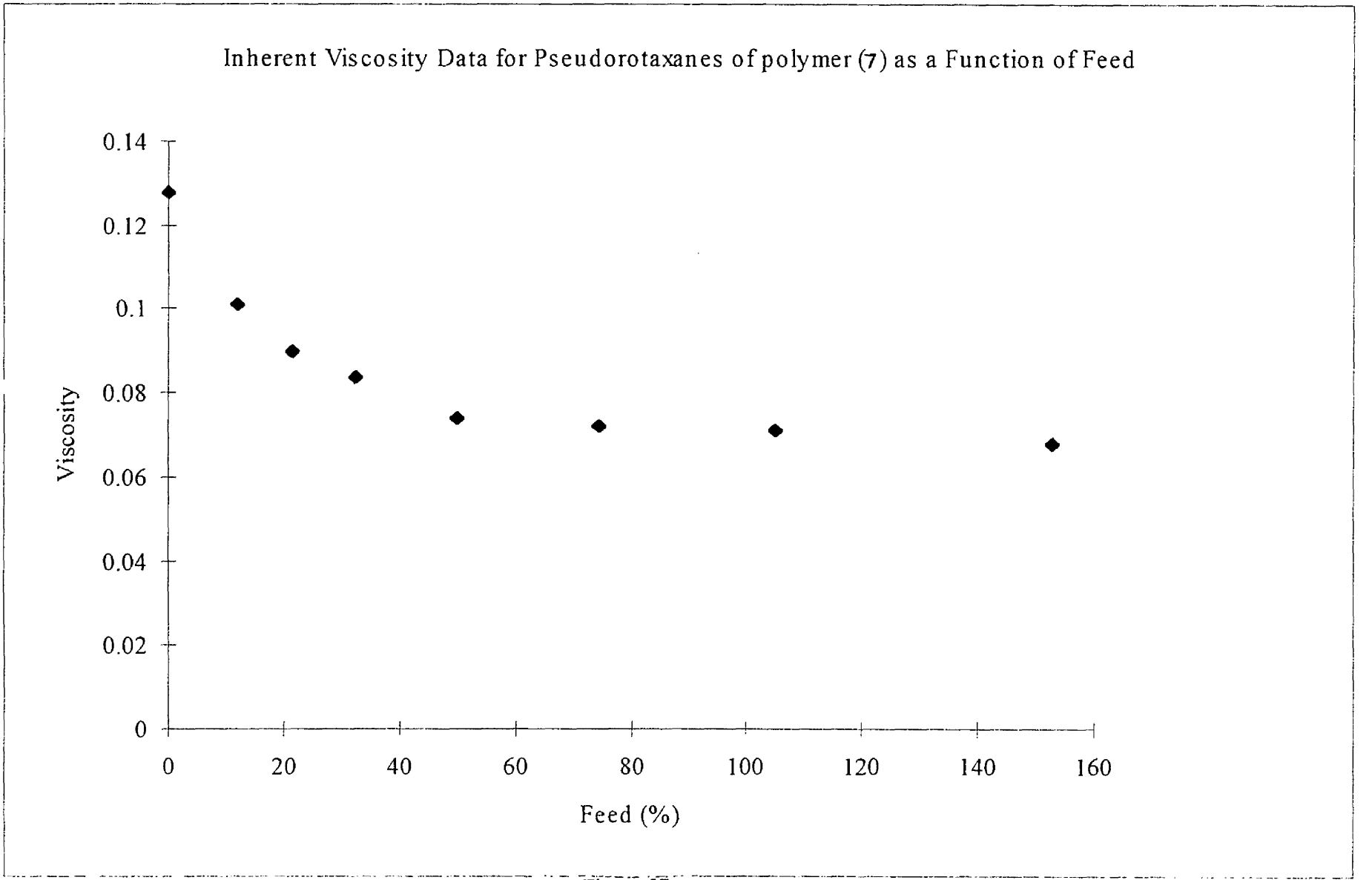

Inherent Viscosity Data for Pseudorotaxanes of polymer (7) as a Function of Feed
Viscosity
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
20
40
60
80
100
120
140
160
Feed (%)

Figure 57

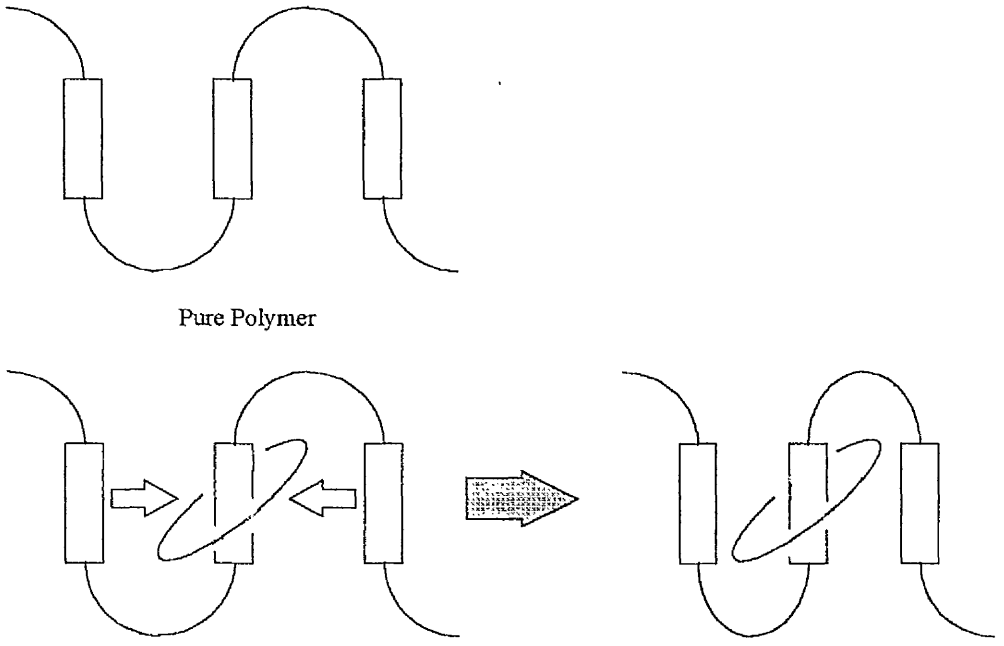


Figure 58

3.6 THE FORMATION OF POLYPSEUDOROTAXANES) USING POLYMER (9)

With polymers it is very difficult to efficiently add bulky groups to the end of the polymer chain, i.e. in the present context to convert a polymer suitable for polypseudorotaxane formation into one suitable for polyrotaxane formation. One solution to this problem is to place bulky groups along the polymer chain. In order to test the feasibility of this a polymer was synthesised containing 100% of 2,5-di-^{t}butyl hydroquinone as the bulky group and an attempt was made to produce a rotaxane from this polymer.

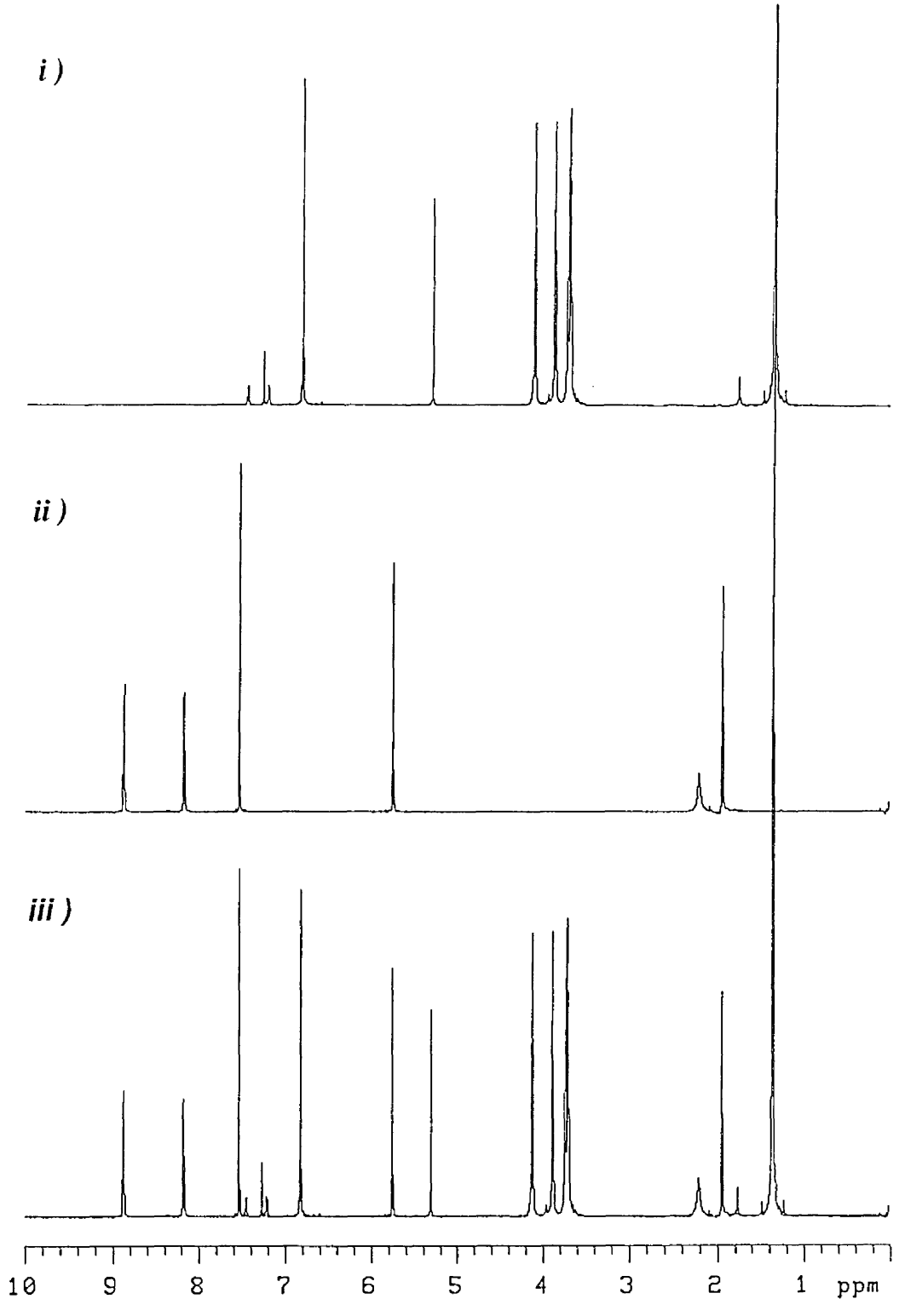


Figure 59

Figure 59 shows the ^{1}H NMR spectra of the following, each spectra being acquired from a solution of the relevant sample in acetonitrile at -40°C.

i) Polymer **(9)**

ii) Cyclophane **(1)**

iii) The mixture of i) and ii)

It can be seen that spectrum iii) is a simple addition of spectra i) and ii) and it is therefore obvious that there is no complexation between polymer **(9)** and cyclophane **(1)**. This shows that the di-^{t}butyl-hydroquinone is an efficient stopper unit for cyclophane **(1)**. As noted previously, it was initially expected that the polypseudorotaxanes would be prepared by "Clipping". In this event a polymer would have been prepared with, say, 95% hydroquinone ether units and 5% di^{t}butylhydroquinone ether units. The cyclophanes "Clipped" around hydroquinone's would then be trapped. However, the failure of the "Clipping" method meant that this was not possible, but, this system was studied to ensure that the di^{t}butylhydroquinone unit is large enough to be used as a stopper for possible future work on the "Clipping" method.

3.7 THE FORMATION OF POLYPSEUDOROTAXANES) USING POLYESTERS

As discussed earlier, it is possible to synthesise cyclic oligomers from polyesters in dilute solution using dibutoxydibutyltin as a transesterification catalyst. It may also be possible to synthesise pseudorotaxanes from linear polyesters. It may then be possible to synthesise polycatenanes from these polypseudorotaxanes. In order to do this efficiently the following criteria must be met:-

a) The chemical equilibrium shown below must lie strongly to the right, i.e. the percentage of free cyclophane **(1)** at low loadings (ca. 30%) must be little or none. If free cyclophane **(1)** were present in the reaction mixture then this would make purification of the desired product more difficult.

Polymer + Cyclophane $\rightleftharpoons$ Poly(pseudorotaxane)

b) The strength of the complex between cyclophane **(1)** and the polymer must be strong enough to effectively prevent de-threading during cyclisation.

A strong complex must be produced in order to fulfil (b), but (b) will not necessarily be fulfilled just because a strong complex is formed. If the spacer length is too short then charge-charge repulsion effects will push the equilibrium to the left producing free cyclophane **(1)**.

3.8 THE FORMATION OF POLYPSEUDOROTAXANES USING POLYMER (14) AND POLYMER (15)

3.8.1 SYNTHESIS OF POLYMERS (14) AND (15)

As discussed before, polymers **(14)** and **(15)** were synthesised by reacting diester **(12)** with diethyleneglycol or triethyleneglycol respectively. The products had satisfactory molecular weights and were both soluble in acetonitrile making them good candidates for the synthesis of pseudorotaxanes.

Polypseudorotaxanes prepared from polyesters were prepared in the same way as for those prepared from polyethers and were studied using ^{1}H NMR spectroscopy.

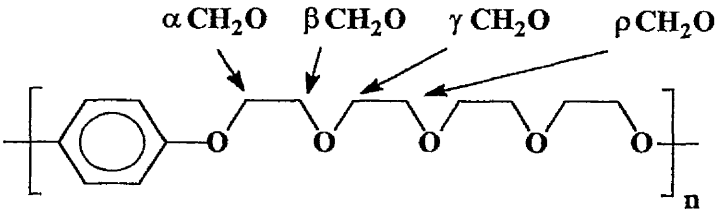
3.8.2 ^{1}H NMR STUDIES

It is instructive to compare the ^{1}H NMR spectra obtained from the pseudorotaxanes formed from polyethers eg polymer **(6)** with those of the pseudorotaxanes formed from polyesters eg, polymer **(14)** or polymer **(15)** which have spacers of similar length between the hydroquinone units. It is evident from Figure 60, that although there are many similarities between the polyether pseudorotaxanes and the polyester pseudorotaxanes there are also some differences. For example, it can be seen that the ethyleneglycol region of the spectrum is much better resolved for the polyester pseudorotaxanes than for the polyether pseudorotaxanes. For the pure polymers it can be seen that the ethyleneglycol region of the polyester spectrum is spread over a wider region than that for the polyether

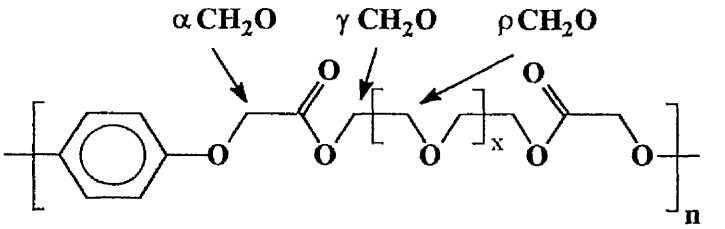
spectrum. This is due to the chemical shifts caused by the carbonyl groups in the chain and also the loss of signals where a methylene group has been replaced by a carbonyl group. Table 13 compares the shifts for the ethyleneglycol components in the polymers.

Table 13 : Shift Positions of the Ethyleneglycol Signals in a Polyester and a Polyether

Polymer used	α–CH_2O	β–CH_2O	γ–CH_2O	ρ–CH_2O
Polymer (6)	4.00ppm	3.70ppm	3.60ppm	3.55ppm
Polymer (14)	4.60ppm	N/A	4.35ppm	3.70ppm
Polymer (15)	4.60ppm	N/A	4.35ppm	3.70ppm



Polymer (6)



x = 1 : Polymer (14)
x = 2 : Polymer (15)

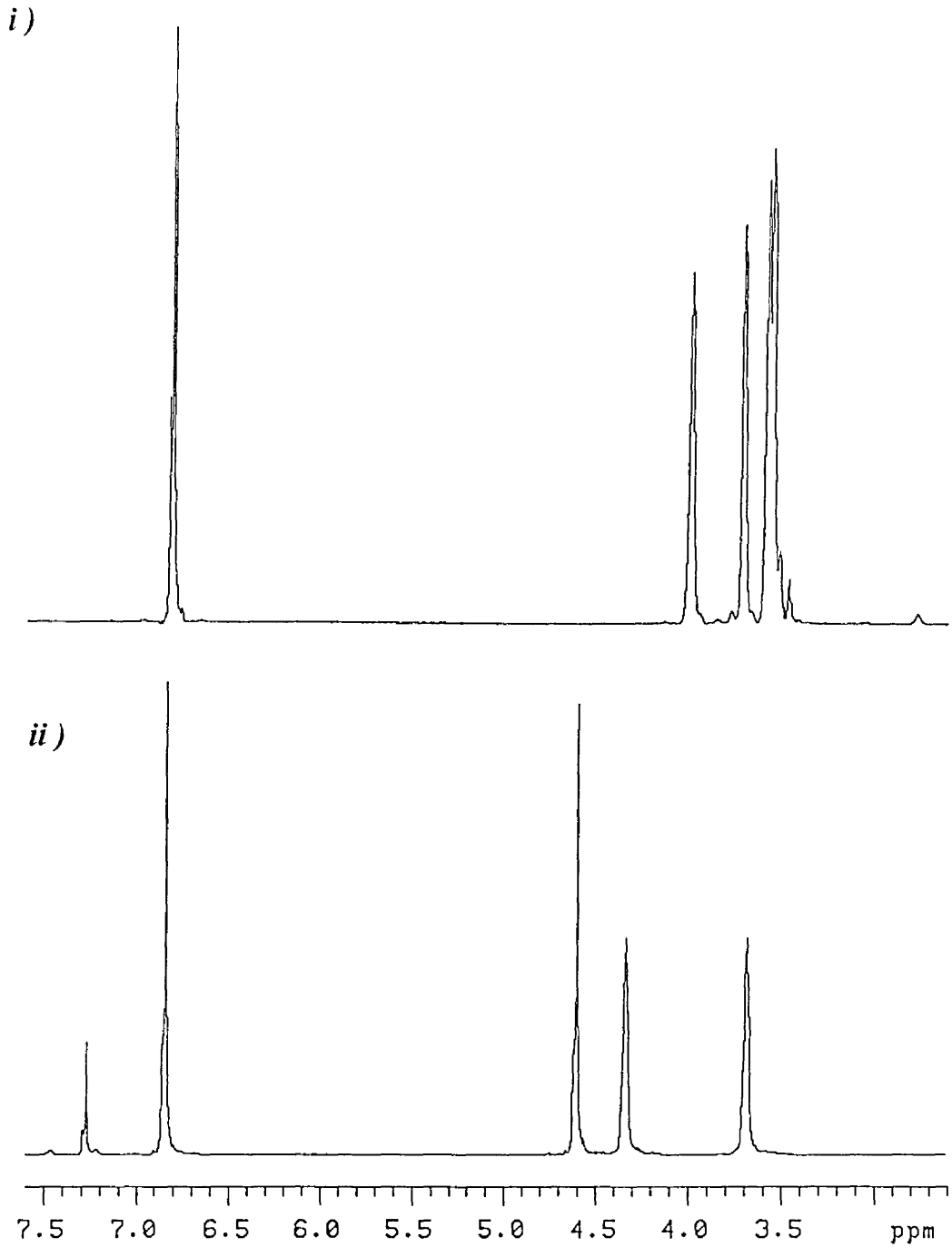


Figure 60

A very important and surprising difference between the spectra, is the absence in the spectra of pseudorotaxanes formed from the polyesters of any signals due to "Alongside" or "Between" environments. Molecular modelling studies show that the introduction of a carbonyl group into the ethyleneglycol spacer of these polymers discourages the folding of the polymer chain, see Figure 61 and hence any π–stacking. This arises from the fact that the preferred conformation of the ester linkage is trans, see Figure 62 and this tends to straighten the chain.

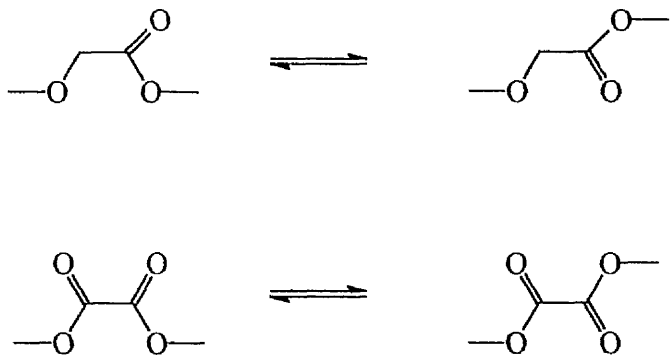


Figure 62

The extents of loading achieved with the polyesters as a function of the amount of cyclophane **(1)** feed were determined by ^{1}H NMR spectroscopy for solutions in deuterated acetonitrile at -40°C. The ^{1}H NMR spectral results are summarised in Figure 63 together with those of the previous work with polymer **(6)** and polymer **(7)**. It is clear from there that the ease with which cyclophane **(1)** is threaded onto the polymer chain is lower for the polyesters than for the polyethers.

By examining Figure 63, it can be seen that for pseudorotaxanes of polymers **(14)** and **(15)** the experimental results are different from the theoretical ones even at very low loadings, ca. 5%. This cannot be due to the steric reasons observed at higher loadings for pseudorotaxanes of polymers **(6)** and **(7)** and must therefore be due to a lower strength of complexation. There are three possible reasons for the lower strength of complexation for pseudorotaxanes of polymers **(14)** and **(15)** compared to that experienced by pseudorotaxanes of polymers **(6)** and **(7)**.

a) The carbonyl group of the ester may be able to withdraw a small amount of electron density from the aromatic ring.

b) Molecular modelling, see Figure 64 shows that the ethyleneglycol spacer in polymer **(14)** does not fold around the aromatic ring as it does in polymer **(6)** and therefore, any interactions between the "Threaded" cyclophane **(1)** and the ethyleneglycol chain are not possible in this polymer. It was shown earlier that these interactions helped to stabilise the cyclophane **(1)** and thus, there absence would lead to a reduced strength for the complex formed.

c) The interaction of a "Threaded" cyclophane **(1)** with adjacent aromatic components in the polymer chain is absent for pseudorotaxanes of polymers **(7)** and **(8)**. These interactions may help to stabilise the threaded cyclophane **(1)** and therefore, their absence will reduce the overall strength of complexation.

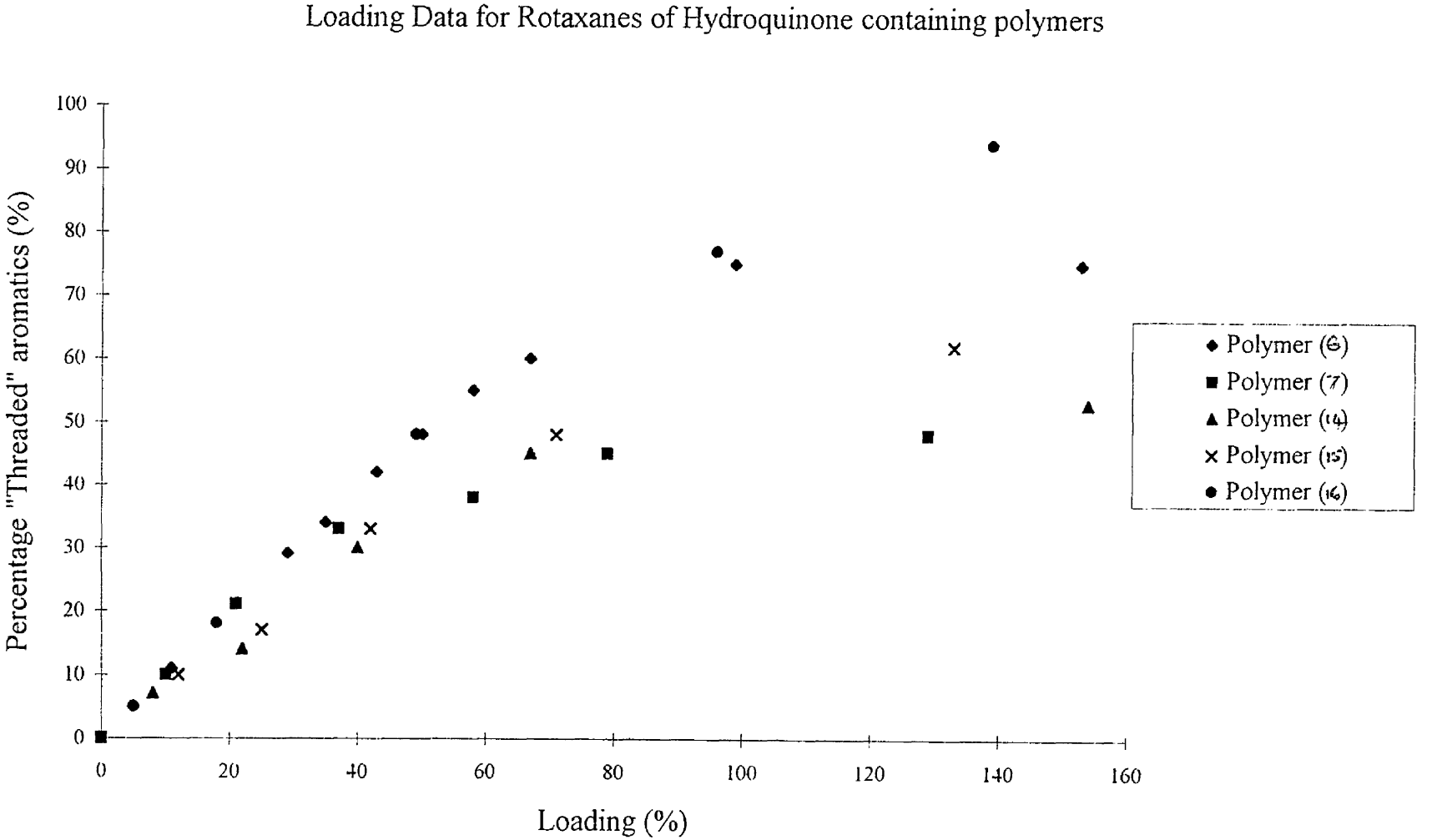

Loading Data for Rotaxanes of Hydroquinone containing polymers
Percentage "Threaded" aromatics (%)
Loading (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
Polymer (6)
Polymer (7)
Polymer (14)
Polymer (15)
Polymer (16)

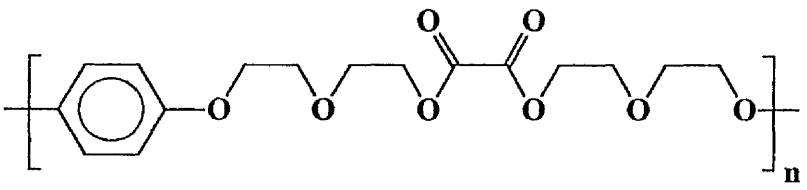
Figure 63

In fact all of the above reasons may contribute to the reduced strength of complexation, in order to investigate this the pseudorotaxanes formed from polymer **(16)** were examined.

3.9 THE FORMATION OF POLYPSEUDOROTAXANES USING POLYMER (16)

3.9.1 SYNTHESIS OF POLYMER (16)

As discussed before, polymer **(16)** was synthesised by reacting diol **(13)** with dimethyloxalate. The product had satisfactory molecular weight and was soluble in acetonitrile, making it a good candidate for the synthesis of pseudorotaxanes.



Polymer (16)

Polymer **(16)** has the carbonyl groups placed in the middle of the ethyleneglycol spacer and therefore, this is too far removed from the aromatic ring to have any effect on its electron density. Molecular modelling studies, see Figure 65, show that the ethyleneglycol spacer in this polymer does fold around to some extent and will therefore enable complexation between the ethyleneglycol chain and "Threaded" cyclophane **(1)**.

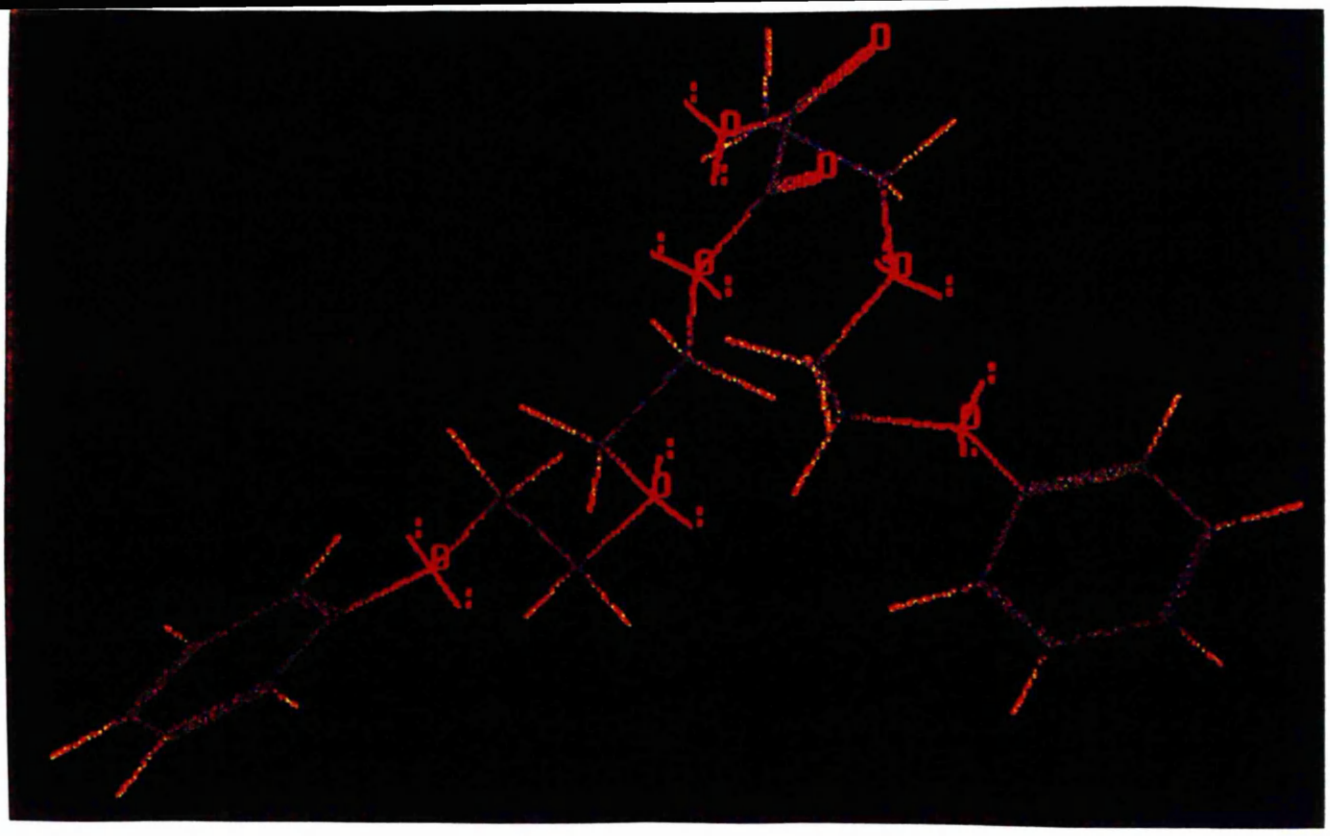


Figure 64

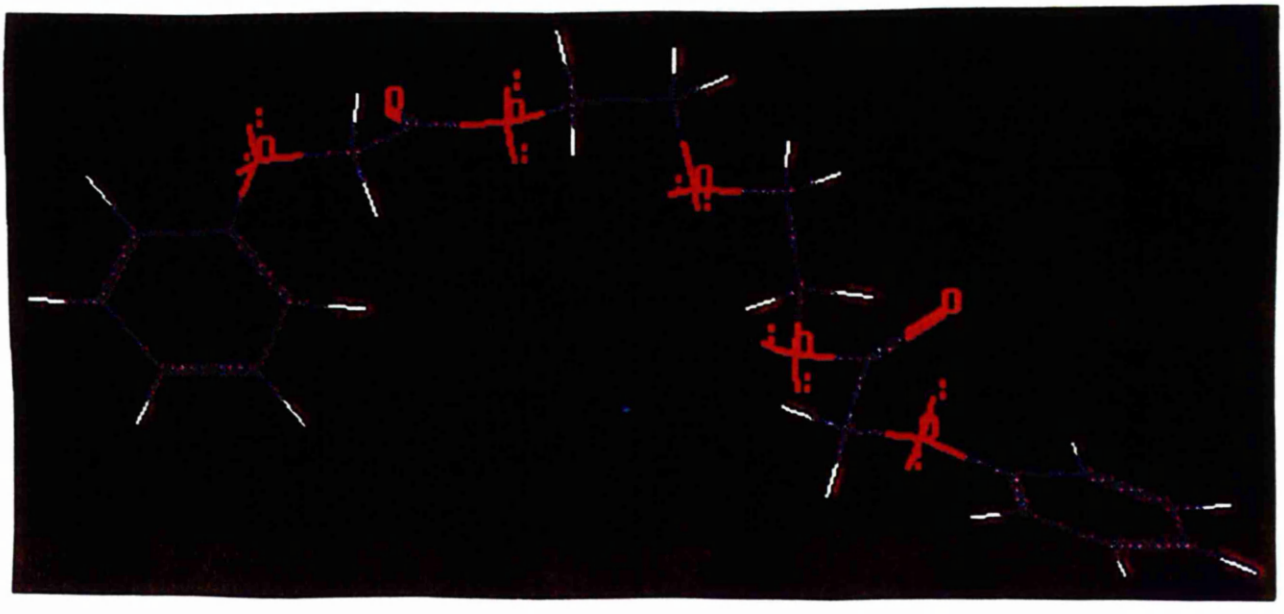


Figure 65

The extent of folding does not allow π–π stacking and indeed the ^{1}H NMR spectra of pseudorotaxanes of polymer **(16)** shows that there are no "Alongside" or "Between" environments present. This suggests that it is the stabilisation of cyclophane **(1)** by the ethyleneglycol spacer that is the main factor that determines the difference in complexation strength between the polyethers and the polyesters and not the interaction between a "Threaded" cyclophane **(1)** and an adjacent "Free" aromatic ether unit.

By examining Figure 63 it can be seen that for the pseudorotaxanes of polymer **(16)** the experimental results closely follow the theoretical ones until the maximum experimental loading is approached (94% for polymer **(16)**). This means that a polymer has now been synthesised in which a similar strength of complexation can be achieved as for the polyether pseudorotaxanes.

3.10 THE FORMATION OF POLYPSEUDOROTAXANES USING POLYMER (10)

Earlier in this thesis, it has been shown that pseudorotaxanes can be formed from cyclophane **(1)** and polymers containing hydroquinone units linked by ethyleneglycol moieties as spacers. The present section is concerned with the preparation of analogous pseudorotaxanes containing resorcinol units in place of the hydroquinone units. With these systems the characterisation has been achieved using ^{1}H NMR spectroscopy.

3.10.1 SYNTHESIS OF POLYMER (10)

As discussed before, polymer **(10)** was synthesised in 53% yield by reacting bistosylate **(3)** with resorcinol under basic phase-transfer conditions. This product had a satisfactory ^{1}H NMR spectrum and a reasonably high molecular weight. It was also soluble in acetonitrile and hence, a very good candidate for the synthesis of pseudorotaxanes.

3.10.2 ^{1}H NMR STUDIES

Figure 66 shows the ^{1}H NMR of :-

i) Polymer **(10)**

ii) Cyclophane **(1)**

iii) A 1:1 mixture of (i) and (ii)

Spectra (i) and (ii) were acquired for solutions in deuterated acetonitrile at room temperature. Spectrum (iii) was acquired as a solution of 10mg of polymer **(10)** with 49mg of cyclophane **(1)** in 1ml of d_3-acetonitrile at -40°C .

It is clear from Figure 66 that spectrum (iii) is not simply an addition of spectra (i) and (ii). There are significant shifts of the aromatic protons from polymer **(10)** and the protons from cyclophane **(1)** as expected for the production of a pseudorotaxane. In this case, however, there is the added complication that cyclophane **(1)** might complex externally to the polymer chain, as shown in Figure 67.

In order to determine whether or not threading had occurred two model compounds, resorcinol model **(20)** and resorcinol model **(21),** were synthesised as follows.

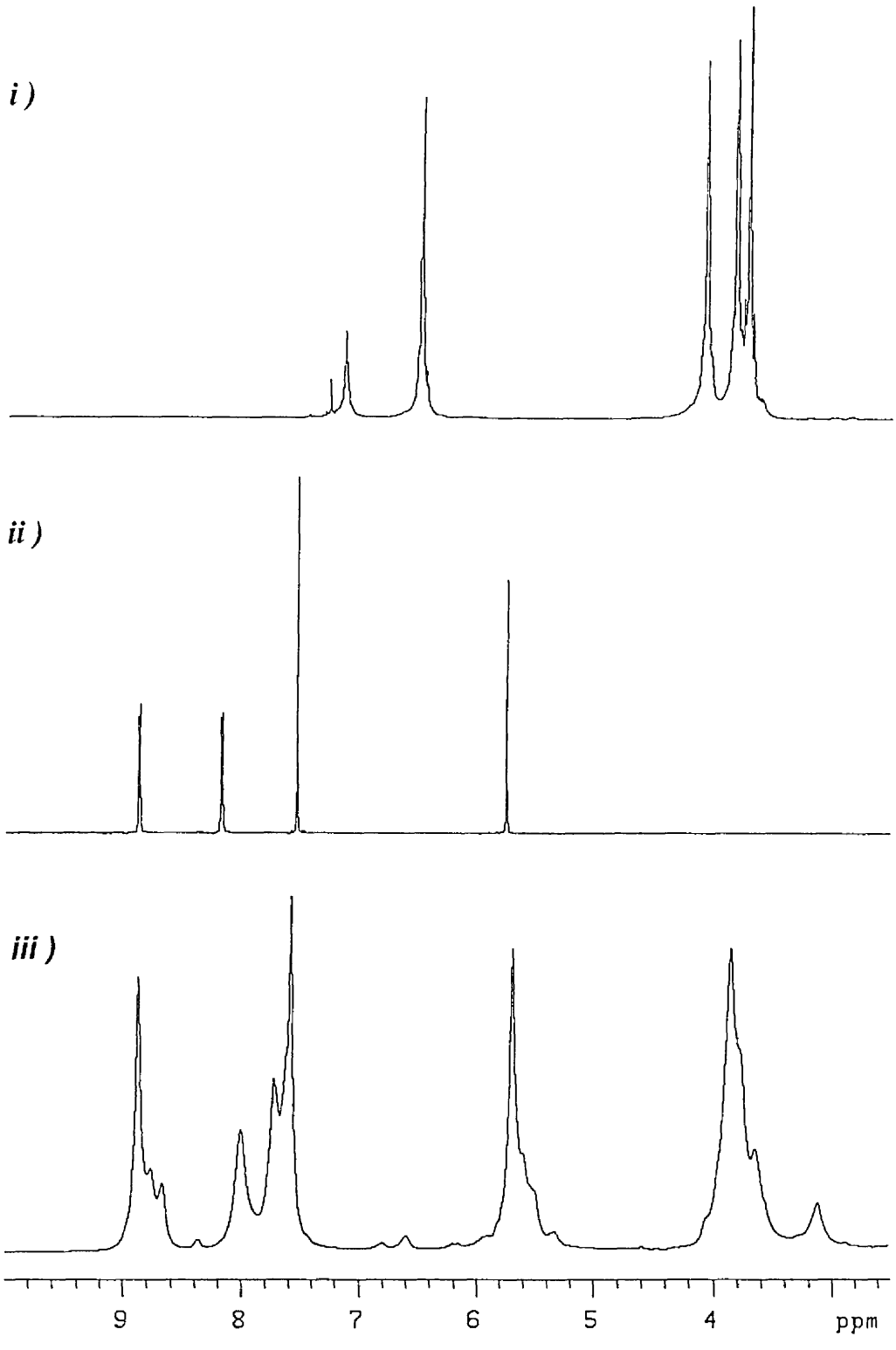


Figure 66

RESORCINOL-CONTAINING POLYMERS

a)

Two Possible Conformations :-

Complexed but Not Threaded

Complexed and Threaded

HYDROQUINONE CONTAINING POLYMERS

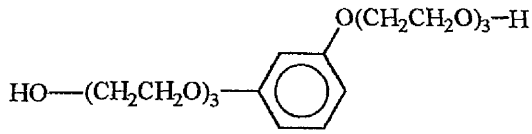
b)

Only One Conformation :- Complexed and Threaded

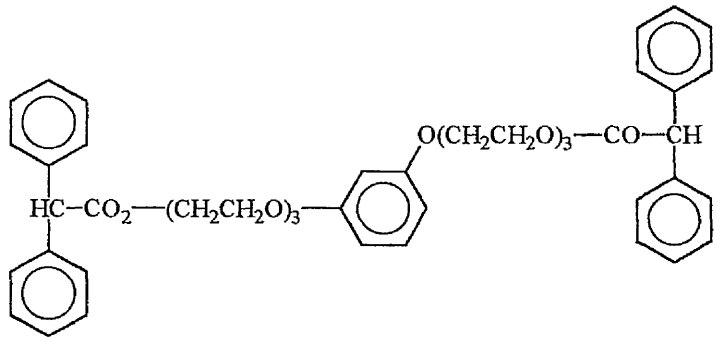
Figure 67

a) Resorcinol model **(20)** was produced in 60% yield by reacting resorcinol with 2-(2-chloroethoxy)ethanol in ethanolic potassium carbonate at 85°C for 3 days. This product had satisfactory ^{1}H NMR and mass spectra.

b) Resorcinol model **(21)** was produced in 60% yield by reacting resorcinol model **(20)** and diphenylacetyl chloride in pyridine / dichloromethane at room temperature for 24 hours. This product had satisfactory ^{1}H NMR and mass spectra.



Resorcinol Model (20)



Resorcinol Model (21)

Using molecular modelling studies, it can be seen that the diphenylacetyl stoppers are large enough to prevent threading of the cyclophane, but are not too large so as to stop the cyclophane **(1)** from complexing externally with the resorcinol chain. It is now possible, therefore, to determine whether complexation without threading is possible using resorcinol as the electron-rich aromatic ether unit. Figure 68 shows the ^{1}H NMR spectra of :-

i) Resorcinol model **(20)**

ii) Resorcinol model **(20)** plus cyclophane **(1)**

iii) Cyclophane **(1)**

iv) Resorcinol model **(21)**

v) Resorcinol model **(21)** plus cyclophane **(1)**

Spectra (i), (iii) and (iv) are obtained from a solution of the relevant compound in acetonitrile at room temperature. Spectra (ii) and (v) are obtained from a solution of 10mg of the corresponding model with 1 mole equivalent of cyclophane **(1)** in 1ml of acetonitrile at -40°C.

It can be seen from Figure 68, that spectrum (v) is a simple addition of the two components showing that there are no interactions between these two components. Spectrum (ii), however, is not a simple mixture and significant shifts are present. Moreover, these shifts are very similar to the ones observed in the spectrum of the pseudorotaxane formed from polymer **(10)** and also those with the spectrum of the pseudorotaxane formed from polymer **(6)** discussed earlier. This suggests that the complex observed between cyclophane **(1)** and polymer **(10)** is due to cyclophane **(1)** being threaded. There are some interesting differences between the pseudorotaxanes formed with polymer **(10)** and those formed with polymer **(6)**. The major difference is that whilst there are signals due to the "Alongside" environments there are none due to the "Between" environments Molecular modelling, see Figure 69, suggests that the reason for this is the substitution of the aromatic components, meaning that "Threaded" cyclophanes **(1)** are only able to interact with one neighbouring aromatic component.

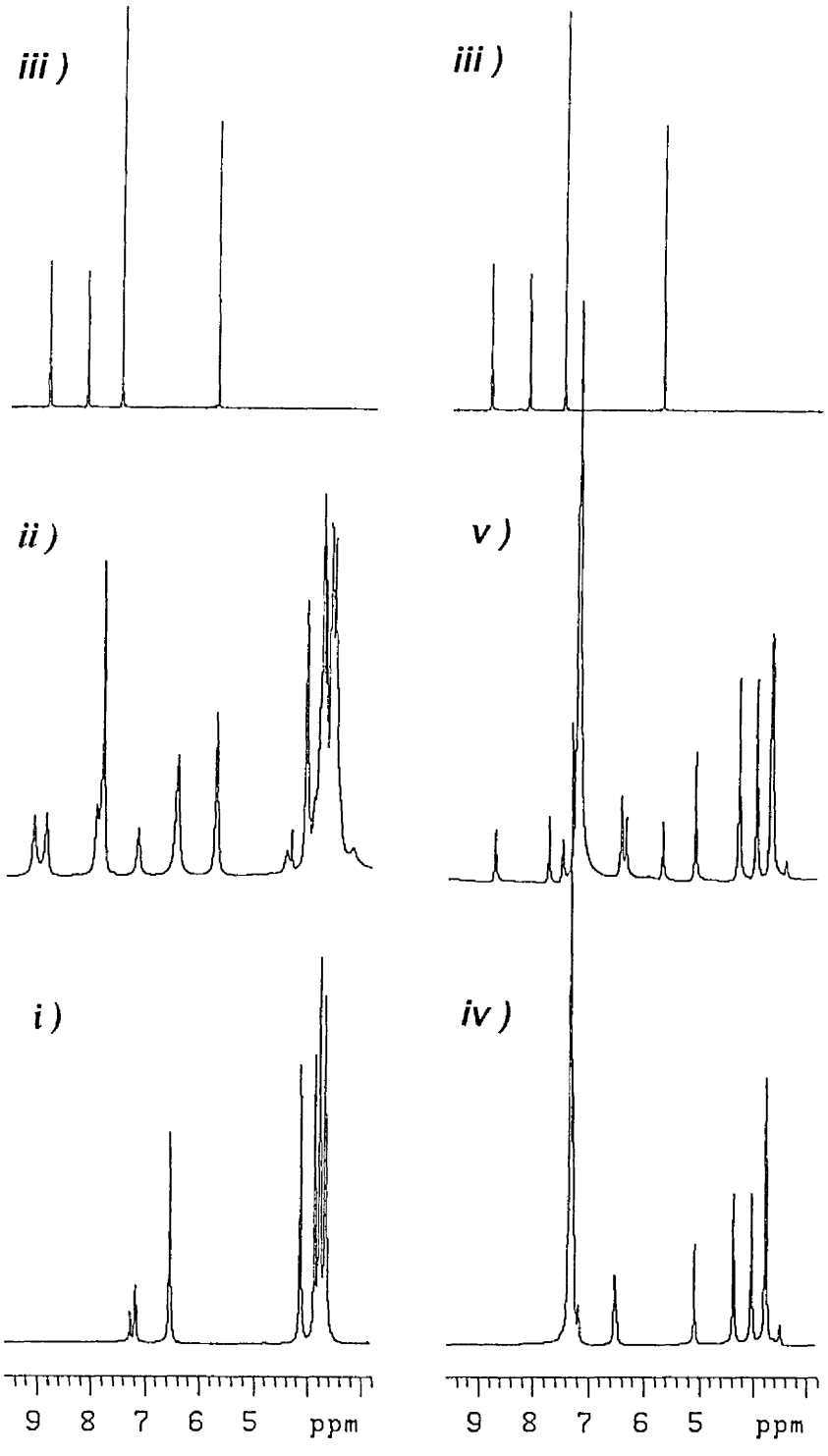


Figure 68

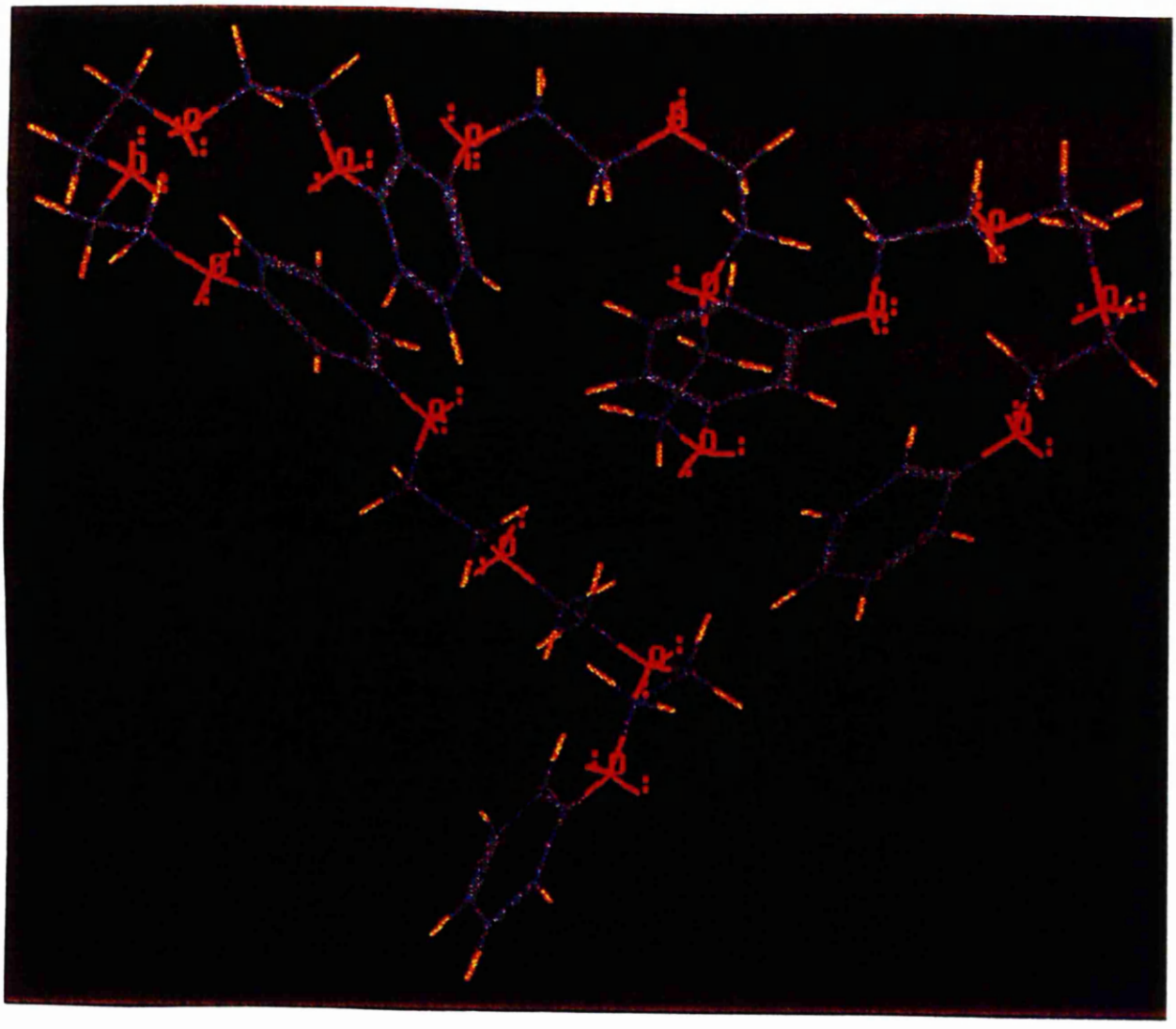


Figure 69

The relative Proportions of Resorcinol Ether Units of Pseudorotaxanes of Polymer (10) in the Various Environments

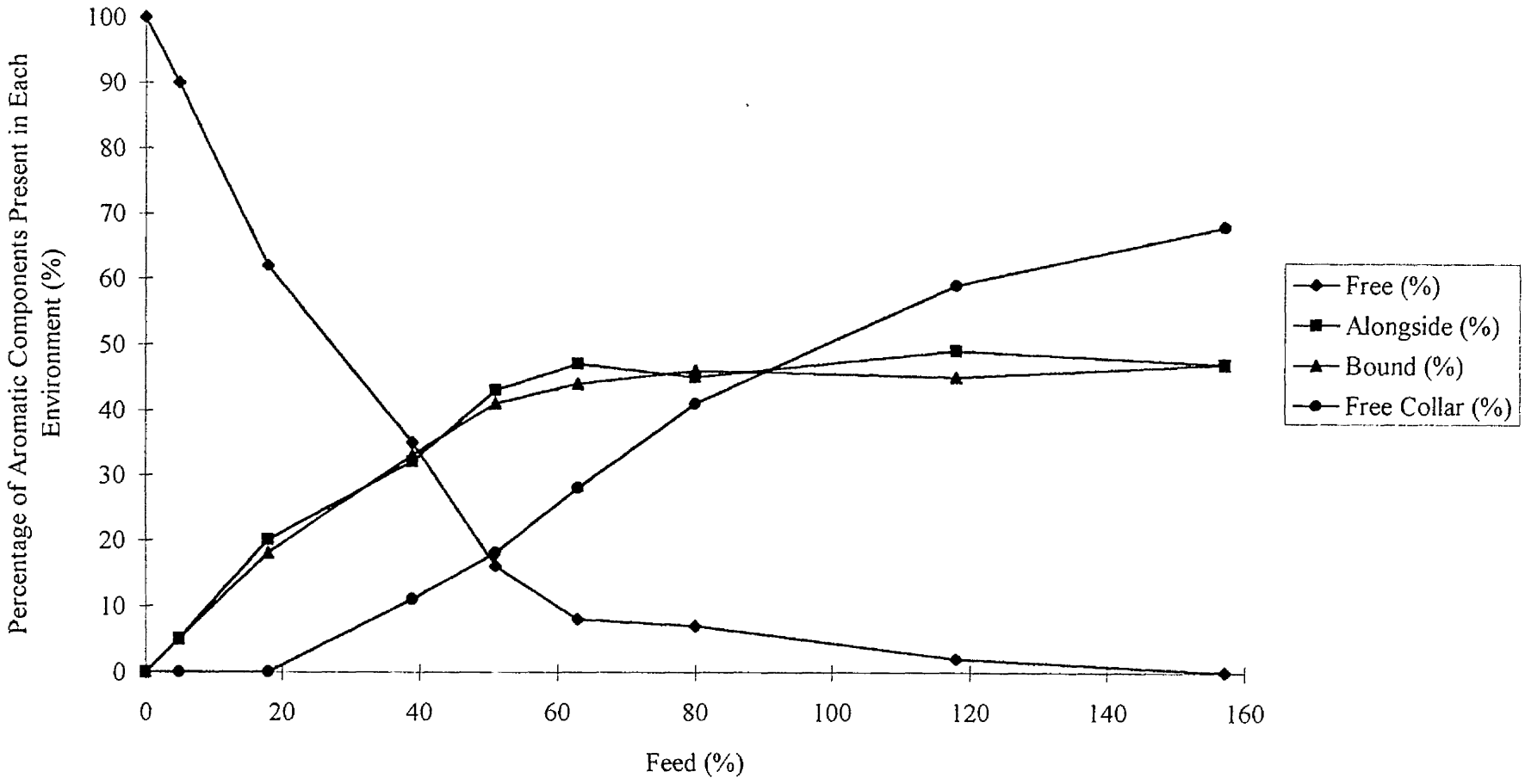


Figure 70

It is now possible to analyse the ^{1}H NMR spectra of pseudorotaxanes of polymer **(10)** as has previously been done for other pseudorotaxanes. Figure 70 shows the percentage of each environment present at different feeds of cyclophane **(1)**. The percentage of aromatics present in the "Alongside" environment is equal to the percentage present in the "Threaded" environment. This shows that "Threaded" cyclophanes only interact with one adjacent aromatic unit giving further evidence for the absence of aromatics in the "Between" environment.

The maximum loading observed for pseudorotaxanes of polymer **(10)** is 50% as for pseudorotaxanes of polymer **(7)** this is again due to the spacer length preventing two cyclophanes existing on adjacent aromatics.

3.11 THE SYNTHESIS OF POLYPSEUDOROTAXANES) USING POLYMER (11)

Stoddart has shown how the use of naphthalene as the aromatic ether unit produces rotaxanes that contain very strong charge-transfer complexes.[98] This is due to the fact that naphthalene diols have more π–electron-density than hydroquinone or resorcinol. For this reason the attempted synthesis of pseudorotaxanes using polymer **(11)** was attempted. The analysis of these pseudorotaxanes was undertaken using ^{1}H NMR spectroscopy and the results gained from this work are presented below.

3.11.1 SYNTHESIS OF POLYMER (11)

As discussed earlier, polymer **(11)** was synthesised in 77% yield by reacting bistosylate **(3)** with 1,5-dihydroxynaphthalene and sodium hydride in dry DMF. This product had a satisfactory ^{1}H NMR spectrum and reasonably high molecular weight (Mn= 7490, Mw=15,600, DP=28.2).

3.11.2 ^{1}H NMR SPECTRAL STUDIES

Polymer **(11)** unfortunately has at best a poor solubility in all the solvents available to us. To solubilise this polymer DMF or DMSO at temperatures of 100°C had to be used. This solubility problem remains on addition of cyclophane **(1)** although the temperature at which polymer **(11)** became soluble was reduced as the amount of cyclophane **(1)** was increased. Unfortunately a loading of >70% must be reached before cooling the polymer down to -40°C to allow the ^{1}H NMR analysis also yields soluble material. Once such a high loading is reached the spectra become very complex and analysis therefore becomes very difficult. Figure 71 shows the ^{1}H NMR spectra of a 70% loaded polypseudorotaxane, formed from polymer **(11)** and cyclophane **(1)**, it can be seen that there are many broad signals and this prevents accurate analysis. It is obvious though that different shifts are present in the ^{1}H NMR spectra of the mixture of polymer **(11)** and cyclophane **(1)** compared to those observed for pure polymer **(11)** Many of these shifts are very similar to those observed for pseudorotaxanes of hydroquinone containing polymers (polymers **(6)** and **(7)**). The presence of these large differences in the ^{1}H NMR spectra indicate that in all probability a pseudorotaxane has been produced.

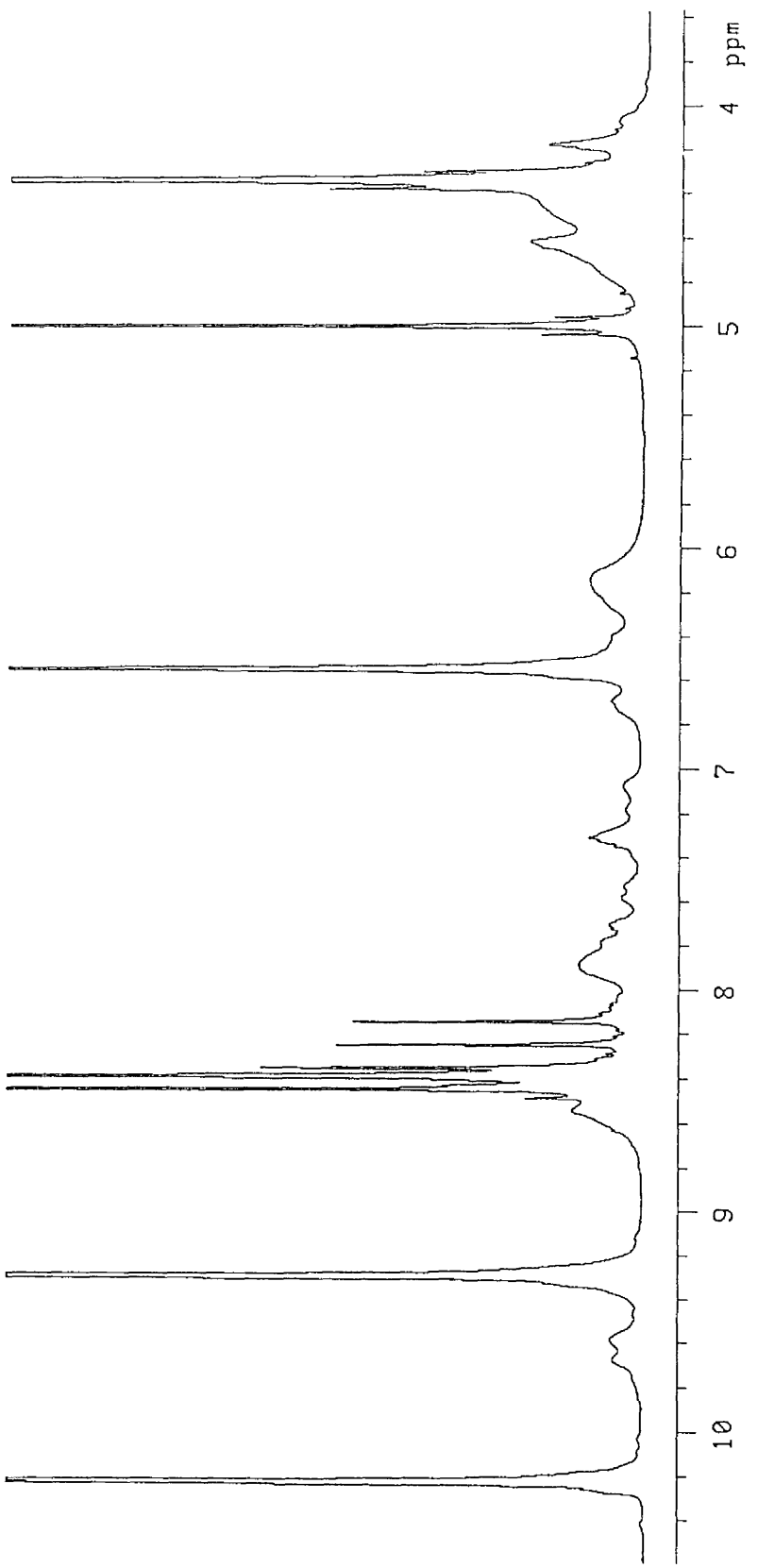


Figure 71

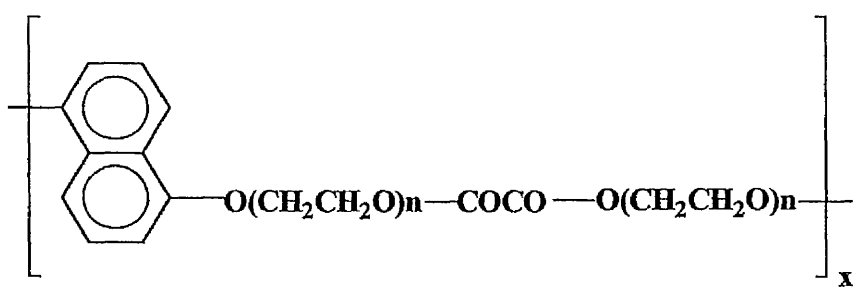
3.12 FUTURE WORK.

Pseudorotaxanes of polymers containing many different electron-rich moieties have been synthesised and characterised. The pseudorotaxanes that have been synthesised contain ether or ester type spacers. The polymers containing ester type spacers can almost certainly be converted into cyclic oligomers by cyclo-de-polymerisation using dibutoxydibutyltin as transesterification catalyst. The polyesters are also more soluble than their polyether counterparts.

This work may be continued in many possible ways as shown below.

3.12.1 THE SYNTHESIS OF A SOLUBLE NAPHTHALENE CONTAINING POLYMER.

The polyether containing naphthalene was shown to be insoluble in all solvents other than DMSO or DMF at elevated temperature. It may however, be possible to produce a soluble naphthalene-containing polymer by introducing esters into the ethyleneglycol spacer eg polymer **(22)**.



Polymer **(22)**

By increasing the length of the ethyleneglycol spacer it is possible to increase the solubility of the polymer in polar solvents such as acetonitrile. Therefore, it should be possible to produce a polymer that contains naphthalene as the electron-rich moeity and which is soluble in polar solvents such as acetonitrile. It may also be possible to synthesise polymers containing naphthalene with different substitution eg using 2,6-dihydroxynaphthalene rather than 1,5-dihydroxynaphthalene.

3.12.2 CYCLISATION OF POLYESTERS TO GIVE NOVEL PRODUCTS.

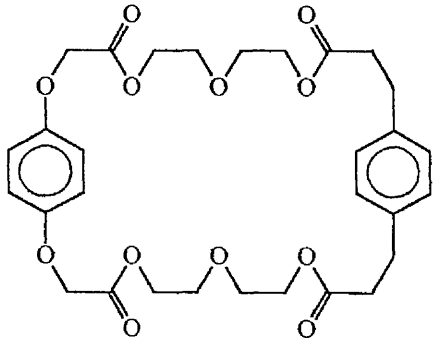
It has been shown by other members of the group that it is possible to cyclo-de-polymerise linear polyesters in order to produce cyclic oligomers. It may be possible to use the complexation of cyclophane **(1)** with the electron-rich moieties of these polymers to produce two novel products.

1) It may be possible to use cyclophane **(1)** as a method of purifying the cyclic-linear mixture produced upon de-polymerisation of the linear polyester. It is known that the starting polymers are soluble in non-polar solvents such as chloroform but that pseudorotaxanes produced upon complexation with the cyclophane **(1)** are only soluble in polar solvents such as acetonitrile. As it is obviously impossible to thread cyclophane **(1)** onto cyclic oligomers, then on addition of cyclophane **(1)** only the linear polymers will thread producing pseudorotaxane. It should then be possible to extract any remaining cyclic oligomers from the mixture with chloroform.

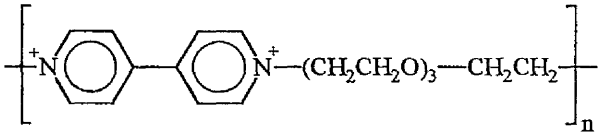
2) It may be possible to carry out the de-polymerisation of the polyester in the presence of cyclophane **(1)** hence turning the polypseudorotaxane into a polycatenane. In order to do this it must first be ensured that cyclophane **(1)** is stable under the de-polymerisation conditions, and that the amount of de-threading due to the elevated temperature is kept to a minimum.

3.12.3 REVERSAL OF CYCLOPHANE AND THREAD FOR ROTAXANE SYNTHESIS

It should be possible to reverse the cyclophane and the thread used in the above methods for the synthesis of polypseudorotaxanes using, for example, cyclophane **(23)** and polymer **(24)** .



Cyclophane (23)



Polymer (24)

As described earlier it is possible to produce the above cyclic using the

cyclo-de-polymerisation of the linear polyesters used in the previous sections. It should be possible to combine the synthesis of this alternative pseudorotaxane with a combinatorial approach to finding the best pairing of electron-rich cyclics and electron-poor polymer. It should be possible to produce a large variation of electron-rich cyclics by changing the electron-rich moeity and also by changing the spacer length and the position of the ester group along this spacer. Many different sizes of cyclics will be produced using the cyclo-de-polymerisation technique. By taking a mixture of these different cyclics along with some of the electron-poor polymer it should be possible to determine which of these cyclics are good donors in order to produce strong complexes, thus, finding the best system for pseudorotaxane synthesis.

CHAPTER 4

EXPERIMENTAL FOR ROTAXANES

Since most of the reactions carried out were examples of a few types only, a general example of each type is given in detail. Details of the other reactions are summarised in tabular form.

All products were dried under vacuum using a two-stage oil pump at 60^{o}C unless stated otherwise.

The DMF used was dried over activated 4A molecular sieves and azeotroped with toluene before use.

The THF used was dried by distillation over sodium wire.

4.1 INSTRUMENTATION DETAILS

4.1.1 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

NMR instruments

Varian Gemini 200 MHz NMR spectrometer.

Varian Unity 500 MHz NMR spectrometer.

Conditions for recording spectra

The solvent used was d-chloroform unless otherwise indicated. Each spectrum was recorded at 25 °C unless otherwise indicated. The 200MHz spectrometer was used for

most measurements but the 500 MHz spectrometer was used for measuring the spectra for the polypseudorotaxanes and for all variable temperature analysis.

4.1.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR spectrometers

ATI Mattson Genesis Series FTIR spectrometer equipped with a computer software package with a resolution of $>4cm^{-1}$

Sample Preparation

Liquid samples were run as a film between two NaCl plates

Soluble solid samples were run as evaporated films

Insoluble solid samples were run as KBr disks

4.1.3 MASS SPECTROSCOPY

Mass Spectra Instruments

Fast Atom Bombardment Mass Spectrometer (FAB) : A Kratos Concept 1S spectrometer was used for mass spectroscopic measurements of high molecular weight compounds (Mw 600 - 2000). The ionisation method was achieved by the bombardment of the sample matrix suspended in *m*-nitrobenzyl alcohol with xenon atoms and was calibrated to 2000 Da (m/z).

Electronic / Chemical ionisation (EI / CI) mass spectroscopy : A VG Trio 2000 spectrometer was used for mass spectroscopic measurements of low molecular weight compounds (Mw up to 600). The electronic ionisation method was achieved by the bombardment of the sample matrix suspended in *m*-nitrobenzyl alcohol with xenon atoms The chemical ionisation method was achieved by bombardment of the sample with ammonium ions. The machine was calibrated to 600 Da (m/z).

4.1.4 GEL PERMEATION CHROMATOGRAPHY (GPC)

The GPC appartus were assembled in house by Dr C Booth from commercial components.

GPC Apparatus A (GPC-A)

Solvent: DMA.

Column: Plgel 30cm-2 x mixed B, 1 x 10μ 500A.

Temperature: 74 °C.

Detector: Knauer HT Differential Refractometer.

Detector Temperature: 60 °C.

Detector Sensitivity: x4.

Injection Volume: 100μl.

Pump: Waters 501

Flow Rate: 1 cm^3 / min

Chart Speed: 1 cm / min

Reference Marker: H_2O

The GPC-A was calibrated with a range of polyethyleneglycol standards of up to a molecular weight of 1.8×10^6. Average molecular weights were calculated from calibration charts by classical methods the retention times being corrected.

GPC Apparatus B (GPC-B)

Solvent: THF.

Column: PLgel 30 cm 10μ-2 x mixed B + 1, 500A.

Temperature: Ambient.

Detector: Waters 401 Differential Refractometer.

Detector Temperature: 35 °C.

Detector Sensitivity: 32, scale factor 10.

Injection Volume: 100 μl.

Pump: Knauer 64.

Flow Rate: $1cm^3$ / min.

Chart Speed: 1cm / min.

Reference Marker: n-octane; retention time 27.97 min.

Sample Concentration: 0.2%

GPC-B was calibrated with a range of polystyrene standards with molecular weights up to 2.0×10^6. The RI output was collected and processed by a computer fixed with a Waters GPC 6000 system.

GPC Apparatus C (GPC-C)

Solvent: Chloroform.

Column: Plgel 30cm x 4; mixed E, 3μ - 500A.

Temperature: Ambient.

Detector: Polymer Laboratories, GPC LC 1240 RI Detector

Detector Temperature: 35 °C

Detector Sensitivity: 2 x 10^{-5} RIU / FS

Injection Volume: 100μl

Pump: Gilson 307

Flow Rate: 0.3cm^3 / min

Chart Speed: 1cm / min

Reference Marker 1: Polystyrene Mw = 1.7 x 10^5, Mw / Mn = 1.04, retention time = 72.05 minutes at a pressure of 8.5Mpa.

Reference Marker 2: Solvent, retention time = 125.0 minutes at a pressure of 8.5Mpa.

4.1.5 OTHER TECHNIQUES

Thin Layer Chromatography (TLC)

Plates: POLYGRAM SIL G/UV_{254} plates (10 x 50mm), precoated with 0.25mm silica gel containing fluorescent indicator UV_{254}.

Mobile Phase: As indicated in the text.

Visualisation was achieved using a 254Nm UV lamp unless indicated otherwise

Melting points

All melting points were measured using Gallenkamp Melting Points apparatus and are uncorrected.

Elemental Analysis

C, H, N, and S elemental analysis were obtained in house using a Carlo Erba 1108 elemental analyser.

Fluorine analyses were done in house by a colorimetric method with a Cecil Instruments UV / VIS Spectrophotometer.

Chlorine and bromine analyses were carried out in house using potentiometric titration with a Metrohm Autotitration System.

4.2 RECRYSTALLISATION OF MONOMERS

All monomers were recrystallised three times before use. Recrystallisations were carried out from the following solvents.

Triethyleneglycol di-*p*-tosylate	- Methanol
Hydroquinone	- Methanol
Resorcinol	- Methanol
1,5-Dihydroxynaphthalene	- Nitromethane
1,4-Bis(hydroxyethoxyethoxy)benzene	- Toluene
1,4-Bis(carboethoxymethyl)benzene	- Ethanol

4.3 SYNTHESIS OF MONOMERS AND MODEL COMPOUNDS

4.3.1 SYNTHESIS OF TRIETHYLENEGLYCOL DITOSYLATE [99]

4-Toluenesulphonyl chloride (133.5g, 700mmol) was added slowly over a period of 2 hours to a stirred solution of triethyleneglycol (50g, 333mmol) in pyridine (300ml) at 0°C. Stirring was continued for 6 hours after which time the pyridine solution was added to water (1500ml). Hydrochloric acid (300ml,10M solution) was added slowly to the resulting aqueous suspension until the solution was pH 6. The triethyleneglycol di-*p*-tosylate precipitate was collected by filtration, washed with water (1000ml) and dried before being recrystallised from methanol.

Yield:- 133g (87%) mp.:- 80-82 °C (lit mp - 81-82 °C) [100] Mass Spec:- 458 (M^+) (EI) ^{1}H NMR (δ/ppm):- 7.80 (4H, d, J=8Hz, aromatic protons), 7.35 (4H, d, J=8Hz, aromatic protons), 4.15 (4H, m, α–OCH_2), 3.65 (4H, m, β–OCH_2), 3.50 (4H, s, γ–OCH_2), 2.55 (6H, s, CH_3)

4.3.2 SYNTHESIS OF 1,4-BIS(HYDROXYETHOXYETHOXY)BENZENE 1,4-(BHEEB) [85]

Nitrogen gas was bubbled through a solution of hydroquinone (10g, 91mmol) in ethanol (150ml) in order to purge the system of any oxygen. Potassium carbonate (25.2g, 182mmol) was added and the resulting suspension was stirred at room temperature for 30 minutes. 2,(2-Chloroethoxy)ethanol (34g, 273mmol) was added and the resulting suspension was stirred at 85°C for 3 days. After this time the ethanol was removed by evaporation under reduced pressure, chloroform (100ml) was added and the resulting suspension was filtered to remove any salts. The chloroform solution was then washed with sodium hydroxide (3x100ml, 2M solution), hydrochloric acid (3x100ml, 1M solution) and finally water (3x100ml) before being evaporated to dryness under reduced pressure. The white solid residue was recrystallised from dichloromethane / petroleum ether.

Yield:- 19.8g (76%) mp. :- 76 - 77°C (lit. mp. 75 - 77°C) [85] Mass Spec:- 286 (M^+) (EI) ^{1}H NMR (δ/ppm):- 6.85 (4H, s, aromatic protons), 4.05 - 4.10 (4H, m,

CH_2OH), 3.80 - 3.90 (4H, m, α–OCH_2), 3.75 - 3.80 (4H, m, β–OCH_2), 3.65 - 3.70 (4H, m, γ-OCH_2)

4.3.3 SYNTHESIS OF 1,4-BIS(CARBOETHOXYMETHYL)BENZENE [101]

Nitrogen gas was bubbled through a solution of hydroquinone (10g, 91mmol) in DMF (150ml) in order to purge the system of any oxygen. Potassium carbonate (25.2g, 182mmol) was added and the resulting suspension was stirred at room temperature for 30 minutes. Ethyl chloroacetate (33.5g, 273mmol) was added and the resulting suspension was stirred at 110°C for 1 day. After this time the DMF suspension was precipitated into water (1500ml) and the required 1,4-bis(carboethoxymethyl)benzene was extracted using chloroform (3x100ml). The chloroform solution was then washed with sodium hydroxide (3x100ml of a 2M solution), hydrochloric acid (3x100ml of a 1M solution) and finally water (3x100ml) before being evaporated to dryness under reduced pressure to yield a white solid which was recrystallised from ethanol and dried. Yield:- 13.4g (52%) mp.:- 74°C (lit. mp. 72 °C) [101] Mass Spec:- 282 (M^+) (EI) IR: ν/cm^{-1}:- 1753 (Ethyl ester) Elemental Analysis - Found: C, 59.42, H, 6.50, O, 34.08% $C_{14}H_{18}O_6$ requires C,59.57, H, 6.43, O, 34.01% ^{1}H NMR (δ/ppm):- 6.80 (4H, s, aromatic protons), 4.60 (4H, s, α–OCH_2), 4.30 (4H, q, J=8Hz, $CO_2\underline{CH_2}CH_3$), 1.35 (6H, t, J=8Hz, $CO_2CH_2\underline{CH_3}$)

4.3.4 SYNTHESIS OF 1,3-BIS(HYDROXYETHOXYETHOXY)BENZENE 1,3-(BHEEB) [102]

The procedure used for the synthesis of 1,4(BHEEB) was repeated using resorcinol instead of hydroquinone. The reaction was worked up as follows.

The ethanol was removed by evaporation under reduced pressure, chloroform (100ml) was added and the resulting suspension was filtered to remove any salts. The chloroform solution was then washed with sodium hydroxide (3x100ml of a 2M solution), hydrochloric acid (3x100ml of a 1M solution) and finally water (3x100ml) before being evaporated to dryness under reduced pressure to yield an oil. The excess 2,(2-chloroethoxy)ethanol was removed by distillation at 100°C/5mmHg to yield a waxy solid which was dried under vacuum. This was then placed in diethyl ether (10ml) and crystallised at -5 °C

Yield:- 15.6g (60%) mp. :- 46-49 °C (lit. mp. 48-49 °C) [102] Mass spec:- 286 (M^+) (EI) ^{1}H NMR (δ/ppm):- 7.10 - 7.15 (1H, m, aromatic proton), 6.50 - 6.55 (3H, m, aromatic protons), 4.05 - 4.10 (4H, m, CH_2OH), 3.80 - 3.90 (4H, m, α-OCH_2), 3.75 - 3.80 (4H, m, β-OCH_2), 3.65 - 3.70 (4H, m, γ–OCH_2)

4.3.5 SYNTHESIS OF 1,3-BIS(DIPHENYLACETYLETHOXYETHOXY)BENZENE

1,3-Bis(hydroxyethoxyethoxy)benzene (1g, 3.5mmol), diphenylacetyl chloride

(5.6g, 8mmol) and triethylamine (1ml, 10mmol) in DCM (50ml) were stirred at room temperature for 24 hours. After this time the triethylamine salts where removed by filtration, the resulting DCM solution was then washed with hydrochloric acid (3x100ml of a 1M solution) and water (3x100ml) before being dried over magnesium sulphate. The solution was filtered and evaporated to dryness under reduced pressure to yield an oil which was purified by column chromatography using [1:1] ether:petrol (Rf = 0.2) and dried.

Yield:- 15.6g (60%) Mass Spec:- 675 (M^+) (EI) IR: ν/cm^{-1}:- 1737 (Ester)

Elemental Analysis - Found: C, 74.72, H, 6.26, O, 19.02 $C_{42}H_{42}O_8$ requires : C, 74.76, H, 6.27, O, 18.97 ^1H NMR (δ/ppm):- 7.15 - 7.35 (21H, m, aromatic protons), 6.50 - 6.55 (3H, m, aromatic protons), 5.10 (2H, s, CH), 3.30 - 4.40 (4H, m, α–OCH_2), 4.00 - 4.05 (4H, m, β–OCH_2), 3.75 - 3.80 (8H, m, γ–OCH_2)

4.4 POLYMERISATION OF AROMATIC DIOLS WITH ETHYLENEGLYCOLS

4.4.1 SYNTHESIS OF POLYMER (7) : TYPICAL REACTION FOR THE SYNTHESIS OF POLYETHERS 103

Hydroquinone (2.000g,18.2mmol), triethyleneglycol di-*p*-tosylate (8.337g,18.2mmol), 1,2-dichlorobenzene (75ml), and water (25ml) were vigorously stirred. Nitrogen gas was bubbled through this solution for 30 minutes in order to purge it of any oxygen.

After this time tetrabutylammonium hydroxide (23.566g, 36.4mmol as a 40wt% solution in water) was added whilst maintaining the nitrogen flow. The reaction vessel was then sealed under a positive pressure of nitrogen and stirred at 100°C for 5 days. The resulting polymer was precipitated into methanol and collected by filtration, reprecipitated from chloroform into methanol and dried.

Yield:- 3.42g (83%) GPC-B:- Mn - 11291 ; Mw - 19110 ; DP - 92.5 ^{1}H NMR (δ/ppm):- 6.80 (4H, s, aromatic protons), 3.95 - 4.00 (4H, br. s, α–OCH_2), 3.70 - 3.75 (4H, br , s, β–OCH_2), 3.55 - 3.60 (4H, br. s, γ–OCH_2)

Polymers of hydroquinone/tetraethyleneglycol, di-*tert*butylhydroquinone/triethyleneglycol and resorcinol/triethyleneglycol where synthesised in the same way as for polymer (7) using the required di-*p*-tosylate and benzenediol

.

4.4.1.1 Poly(hydroquinone/tetraethyleneglycol) (Polymer (6))

Yield:- 1.51g (36%) GPC-B:- Mn - 3455 ; Mw - 4660 ; DP - 14.0 ^{1}H NMR (δ/ppm):- 6.80 (4H, s, aromatic protons), 3.70 - 3.75 (4H, br , s, β–OCH_2), 3.55 - 3.60 (8H, br. s, γ–OCH_2), 3.95 - 4.00 (4H, br. s, α–OCH_2),

4.4.1.2 Poly(di-*tert*butylhydroquinone/triethyleneglycol) (Polymer (9))

Yield:- 2.50g (61%) GPC-B :- Mn - 6595 ; Mw - 13193 ; DP - 33.6 ^{1}H NMR (δ/ppm):- 6.80 (4H, s, aromatic protons), 4.10 - 4.15 (4H, br. s, α–OCH_2), 3.85 - 3.90 (4H, br. s, β–OCH_2), 3.65 - 3.75 (4H, br. s, γ–OCH_2), 1.35 (18H, s, CH_3)

4.4.1.3 Poly(resorcinol/triethyleneglycol) (Polymer (10))

Yield:- 2.18g (53%) GPC-B:- Mn - 7822 ; Mw - 12589 ; DP - 74.3 ^{1}H NMR (δ/ppm):- 7.10 - 7.15 (1H, br. s, aromatic protons), 6.50 - 6.55 (3H, br. s, aromatic protons), 3.95 - 4.00 (4H, br. s, α–OCH_2), 3.70 - 3.75 (4H, br , s, β–OCH_2), 3.55 - 3.60 (4H, br. s, γ–OCH_2)

4.4.2 SYNTHESIS OF POLYMER (11).

1,5-Dihydroxynaphthalene (2.403g, 15mmol), triethyleneglycol di-*p*-tosylate (6.879g,15mmol) and DMF (150ml) were stirred. Nitrogen gas was bubbled through this solution for 30 minutes in order to purge it of any oxygen. After this time sodium hydride (1.200g, 30mmol as a 60% dispersion in mineral oil) was added whilst maintaining the nitrogen flow. The reaction vessel was then sealed under a positive pressure of nitrogen and stirred at 100°C for 5 days. The resulting polymer (poly(1,5-dihydroxynaphthalene/triethyleneglycol)) (Polymer **(11)**) precipitated into methanol was collected by filtration reprecipitated from DMF into methanol and dried.

Yield:- 3.19g (77%) GPC-A:- Mn - 7490 ; Mw - 15600 ; DP - 28.2 ^{1}H NMR (δ/ppm):- 7.15 - 7.20 (2H, br. s, aromatic protons), 6.70 - 6.75 (2H, br. s, aromatic protons), 6.30 - 6.35 (2H, br. s, aromatic protons), 3.65 - 3.70 (4H, br. s, α–OCH_2), 3.30 - 3.35 (4H, br. s, β–OCH_2), 3.10 - 3.15 (4H, br. s, γ–OCH_2)

4.4.3 SYNTHESIS OF POLYMER (14): A TYPICAL EXAMPLE FOR THE SYNTHESIS OF POLYESTERS. [104]

1,4-Bis(carboethoxymethyl)benzene (2.000g, 7.1mmol) and diethyleneglycol (0.752g ,7.1mmol) were heated together without solvent at 100°C under a flow of nitrogen for 1 day. The apparatus was set up for distillation to remove the ethanol by-product as it was formed. It was then heated at 150°C under nitrogen for 1 day and finally at 150°C under vacuum (0.5mmHg) for 3 days. The resulting oil was allowed to cool, chloroform was added and the mixture was allowed to stand for 18 hours to allow it to dissolve fully. The polymer was precipitated into THF, collected by filtration and then dried under vacuum.

Yield:- 1.93g (89%) GPC-A:- Mn - 18600 ; Mw - 23400 ; DP - 91.1 IR: ν/cm^{-1} :- 1753 (Ester) ^{1}H NMR (δ/ppm):- 6.85 (4H, s, aromatic protons), 4.60 - 4.65 (4H, br. s, α–OCH_2), 4.30 - 4.35 (4H, br. s, β–OCH_2), 3.65 - 3.70 (4H, br. s, γ–OCH_2)

Polymers of 1,4-bis(carboethoxymethyl)benzene/triethyleneglycol, 1,4-bis(carboethoxymethyl)benzene/1,4-bis(hydroxyethoxyethoxy)benzene and

1,4-bis(hydroxyethoxyethoxy)benzene/dimethyloxalate where prepared in the same way as for the polymer of 1,4-bis(carboethoxymethyl)benzene/diethyleneglycol. In some cases an oil was obtained after precipitation and this was then collected by decanting off the chloroform/THF mixture.

4.4.3.1 Polymer of 1,4-bis(carboethoxymethyl)benzene/triethyleneglycol Polymer (15)

Yield:- 2.02g (92%) GPC-A:- Mn - 20500 ; Mw - 24900 ; DP - 101.5 IR: ν/cm^{-1} :- 1753 (Ester) ^1H NMR (δ/ppm):- 6.85 (4H, s, aromatic protons), 4.60 - 4.65 (4H, br. s, $CH_2C{=}O$), 4.35 - 4.40 (4H, br. s, α–OCH_2), 3.70 - 3.75 (4H, br. s, β–OCH_2), 3.60 - 3.65 (4H, br. s, γ–OCH_2)

4.4.3.2 Polymer of 1,4-Bis(hydroxyethoxyethoxy)benzene/dimethyloxalate Polymer (16)

Yield:- 1.13g (47%) GPC-A:- Mn - 7100 ; Mw - 10300 ; DP - 38.2 IR: ν/cm^{-1} :- 1743 and 1764 (Oxalate) ^1H NMR (δ/ppm):- 6.85 (4H, s, aromatic protons), 4.50 - 4.45 (4H, br. s, $CH_2OC{=}O$), 4.10 - 4.05 (4H, br. s, α–OCH_2), 3.80 - 3.70 (8H, br. s, β–OCH_2, γ–OCH_2)

4.5 SYNTHESIS OF A CYCLOPHANE CAPABLE OF MOLECULAR RECOGNITION

4.5.1 SYNTHESIS OF BIS(BIPYRIDINIUMXYLYLENE).2PF_6 [85]

1,4-Bis(bromomethyl)benzene (22.0g, 83.3mmol) was added slowly over a period of 8 hours to a stirred solution of 4-4' bipyridine (31.2g, 200mmol) in dry acetonitrile (300ml) at 80°C. The resulting solution was stirred at 80°C for 36 hours then cooled. The pale yellow precipitate which formed was collected by filtration and washed with acetonitrile (50ml) and diethyl ether (50ml), then dissolved in water (3 litres) and washed with ether (4 x 250ml). The aqueous solution was concentrated down to 300ml and on cooling bisbipyridiniumxylylene[2Br] crystallised. The resulting yellow solid was re-crystallised twice from water, then dissolved in hot water. A saturated solution of ammoniumhexafluorophosphate was added until no further precipitation occured. The resulting precipitate was collected by filtration and recrytallised from acetone - water to yield pure bisbipyridiniumxylylene[2PF_6]
Yield:- 39.40g (66%) mp. :- 141°C (dec) [lit mp. 145°C (dec)] Mass spec:- 561 $(M - PF_6)^+$ (FAB) ^1H NMR (δ/ppm):- 9.30 - 9.35 (4H, m, aromatic protons), 8.80 - 8.90 (4H, m, aromatic protons), 8.65 - 8.70 (4H, m, aromatic protons), 7.95 - 8.00 (4H, m, aromatic protons), 7.80 (4H, s, aromatic protons), 6.16 (4H, s, CH_2N^+)

4.5.2 SYNTHESIS OF BIS(BIPYRIDINIUMBISXYLYLENE).4PF_6 CYCLOPHANE (1) [85]

1,4-Bis(bromomethyl)benzene (2.64g, 10mmol) was added to a stirred solution of 1,4-bishydroxyethoxyethoxybenzene (8.58g, 30mmol), bisbipyridiniumbisxylylene.2PF_6 (7.06g, 10mmol) and sodium iodide (0.5g, 3.33mmol) in dry DMF at room temperature. The resulting solution was stirred for 5 days after which time a precipitate had formed. The DMF suspension was precipitated into THF to yield a red solid which was collected by filtration. This red solid product was dissolved in water (gentle heating at 60°C was used to aid solubility) and this was continually washed with DCM for 14 days to remove the 1,4-bis(hydroxyethoxyethoxy)benzene template. The resulting aqueous solution was taken and the water was removed under reduced pressure to yield crude bisbipyridiniumbisxylylene.4PF_6. This crude product was purified by column chromatography, a 6cm diameter column was used filled to a height of 15cm with silica. The crude product was absorbed onto silica from an aqueous solution and placed on top of the prepared column. Any impurity was removed by eluting with [9:1] methanol:saturated ammonium chloride solution (500ml), the pure product was then collected by eluting with [5:4:1] methanol:water:saturated ammonium chloride solution. The methanol:water:saturated ammonium chloride solution was evaporated to dryness under reduced pressure and replaced with water (100ml). Ammonium hexafluorophosphate (20g) was then added and the required product was extracted with nitromethane. The nitromethane was removed under reduced pressure and replaced by ammonium hexafluorophosphate (100ml of a 2M solution) to remove any

remaining chloride salts. The required product was collected by filtration recrystallised from acetone/water and dried at room temperature under vacuum.

Yield:- 4.12g (37%) mp:- >275°C Mass spec:- 955 ($M-PF_6^-$) (FAB) ^1H NMR (δ/ppm):- 8.85 - 8.90 (8H, m, aromatic protons), 8.15 - 8.20 (8H, m, aromatic protons), 7.50 (8H, s, aromatic protons), 5.75 (8H, s, CH_2N^+)

4.6 SYNTHESIS OF POLYPSEUDOROTAXANES

4.6.1 "CLIPPING" [25]

1,4-Bis(bromomethyl)benzene (1.2g, 4.5mmol) was added to a stirred solution of polymer **(7)** (1.0g, 4.5mmol of repeat units) and bisbipyridiniumbisxylylene.$4PF_6$ (3.2g, 4.5mmol) in DMF at 60°C. Stirring at 60°C was continued for 5 days and then the DMF was removed under reduced pressure. The resulting red solid was washed firstly with chloroform to remove any unreacted polymer **(7)** and then with benzene to remove any unreacted 1,4-bis(bromomethyl)benzene. The resulting polypseudorotaxane was collected and dried. Both the chloroform and the benzene soluble fractions where also collected by removing the solvent under reduced pressure and drying under high vacuum (0.5mmHg) at room temperature.

Spectroscopic data is discussed in chapter 4 results and discussion

4.6.2 THREADING [26]

Polymer **(7)** (10mg, 45μmol of repeat units) and bisbipyridiniumbisxylylene.$4PF_6$ (49.1mg, 45μmol) where stirred in DMF at 60°C for 30 minutes. The polypseudorotaxane that was produced was precipitated into THF and collected by filtration.

For the above polypseudorotaxane every polymer repeat unit has a bisbipyridiniumbisxylylene.$4PF_6$ collar available to it i.e. a 100% "Feed". Rotaxanes of different "Feeds" are synthesised in the same way but are collected by precipitation into different solvents. Rotaxanes loaded to lower than 50% are precipitated into Methanol and 50% and higher loadings are precipitated into THF. For loadings around 50% a mixture of THF and Methanol may be neccessary.

Rotaxanes synthesised from other polymers are synthesised in the same way as for the rotaxanes of polymer **(7)** except that different solvents and temperatures are used. These are as follows:-

Poly(hydroquinone/tetraethyleneglycol)	- Acetonitrile/room temperature
Poly(resorcinol/triethyleneglycol)	- Acetonitrile/45°C
Poly(1,5-dihydroxynaphthalene/triethyleneglycol)	- DMF/100°C
Poly(di-*tert*-butylhydroquinone/triethyleneglycol)	- Acetonitrile/45°C

Poly(1,4-bis(carboethoxymethyl)benzene/triethyleneglycol)	- Acetonitrile/room temperature
Poly(1,4-bis(carboethoxymethyl)benzene/triethyleneglycol)	- Acetonitrile/45°C
Poly(1,4-bishydroxyethoxyethoxybenzene/ dimethyloxalate)	- Acetonitrile/room temperature
Poly(1,4-bis(carboethoxymethyl)benzene/ 1,4-bishydroxyethoxyethoxybenzene)	- DMF/60°C

Spectroscopic data is discussed in chapter 4 results and discussion

PART 2

THE TOPOLOGICAL TRAPPING OF RINGS ON NETWORKS

CHAPTER 5

INTRODUCTION FOR RINGS TOPOLOGICALLY TRAPPED ON NETWORKS

5.1 WHY ARE CYCLIC POLYMERS OF INTEREST?

Cyclic polymers have many novel properties due to their shape or topology and there is therefore much interest in them as possible materials for industrial use.[105] In the following sections we will discuss some of the properties of cyclic polymers and some possible uses of them.

5.1.1 THEORETICAL STUDIES [106]

One of the major differences between cyclic polymers and their linear counterparts is the absence of end-groups in the cyclic polymers. This, for example, prevents the cyclics from diffusing using a simple reptation process. It also means that in general, cyclics cannot be chain extended like linear polymers, although it is possible to introduce reactive side chains to enable addition onto the periphery of the rings.

5.1.2 NOVEL PHYSICAL PROPERTIES

Cyclics do not pack as well as their linear analogues, they are, therefore, generally more soluble and have lower melting points. Cyclics have a smaller hydrodynamic volume than their linear analogues, in effect, because the end groups of the linear analogue are pulled together to form a ring so reducing the volume of the coil, and as a consequence, the viscosity.[107]

5.1.3 POTENTIAL RECOGNITION PROPERTIES [108]

Cyclic oligomers which contain co-ordinating groups - for example ethylene glycol units - can be expected to complex species where part of the recognition arises from the size of the ring cavity.

5.1.4 NOVEL STRUCTURES USING CYCLICS

The cyclic moieties might form the basis of polymeric rotaxanes and catenanes.[85] These structures are discussed in detail in the following chapter.

5.1.5 RING-OPENING POLYMERISATION

When the cyclics contain, for example, ester linkages, the ring may be opened to give linear polymers of high molecular weight.[109] The molecular weights achieved using this method can be very large if few end groups are introduced. This clearly allows the molecular weight of linear polymer produced to be controlled. The more end groups that are added to the system, then the lower the molecular weight of the linear polymer. It also allows control over the chemical nature of the end-groups present.

5.2 HOW CAN CYCLIC OLIGOMERS AND POLYMERS BE SYNTHESISED?

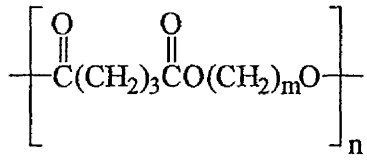
During a normal polymerisation reaction the formation of linear polymer far outweighs the formation of cyclic oligomers and cyclic polymers. It is, therefore, necessary to use special techniques in order to produce cyclic oligomers and polymers. Some of these methods are discussed below.

5.2.1 THE DILUTION EFFECT [110,111]

If a standard polymerisation is carried out at a high dilution then there is an increased chance of forming cyclics. Thus, at high dilution the probability of intermolecular reaction is decreased, whilst the probability of intramolecular reaction remains the same. Hence with dilution the probability of cyclic formation is increased. Although, as the proportion of cyclics in the product increases, the molecular weight of the linear material produced decreases.

5.2.2 BOND INTERCHANGE REACTIONS

Carothers and co-workers found that polyesters as in polymer **(24)**, thermally de-polymerise in the presence of tin dichloride to form cyclic oligomers.[112]



Polymer **(24)**

When m is 2 or 3 then dimers i.e. 16- or 18-membered rings are preferentially formed, but when m > 3 then cyclic monomers are preferentially formed. This is because the 8- or 9-membered cyclic monomers are strained "medium sized" rings.

5.2.3 REACTIONS USING POLYMER SUPPORTS

A research programme at Manchester University has developed methods for the synthesis of cyclic oligomers and polymers based on the following principles.[113]

a) If a step-growth polymer is derived from A - B type monomers, then all the linear polymers produced will have one "A" type end-group and one "B" type end-group.

b) Because of (a), if polymers are synthesised where, say, the "A" type end-groups are bound to a polymer support, then all the linears produced in the polymerisation will be polymer-supported and they can, therefore, be removed easily from the cyclic product by filtering off the polymer beads.

c) Since cyclic oligomers and polymers do not have end-groups, such molecules produced in a polymer-supported polymerisation will, in contrast to the linears, become free of the polymer-support and can therefore be washed away.

d) In order for the processes to produce oligomers, the polymer support needs to allow extensive site-site interactions.

The process described above is shown diagrammatically in Figure 72.

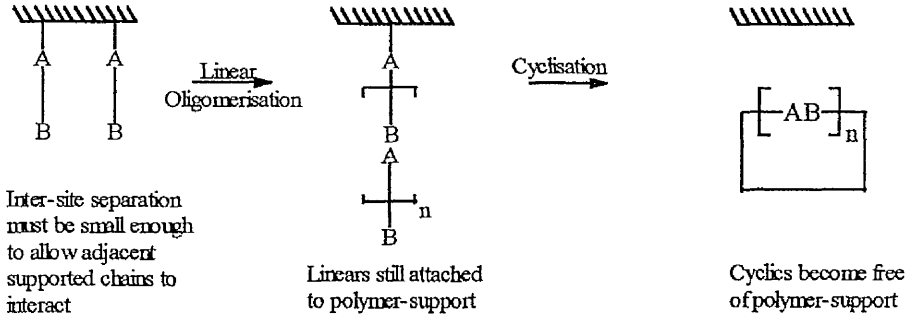


Figure 72

Two main types of synthesis utilising these principles have been investigated at Manchester: one involves the synthesis of amides and the other the synthesis of esters. These two synthetic routes are considered below.

5.2.3.1 Amide Synthesis [114]

The amide synthesis involves the attachment of amino acids to polymer supports via active ester linkages. An example is shown in Figure 73. Here the monomer is covalently bound through an activated phenyl ester linkage.

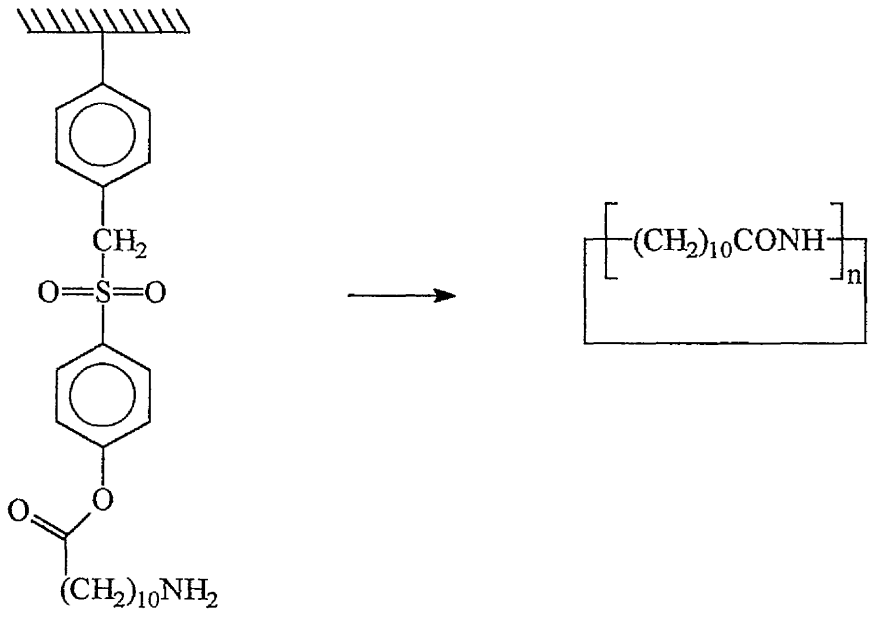


Figure 73

Aminolysis of the ester link affords, at least in principle, linear oligo- and poly-amides bound to the polymer-support and cyclic oligoamides in solution. In practice cyclic amides were obtained with values of n from 2 to 6 but the yields of these were only 20-30%. This was a consequence of poor solubility of the higher cyclic oligoamides which results from the extensive hydrogen-bonding interactions. This prompted

analogous syntheses of ester-amides, shown in Figure 74, which will have fewer hydrogen-bonds. As expected these ester-amides were obtained in higher yields, 40-60% with values of n upto 10.

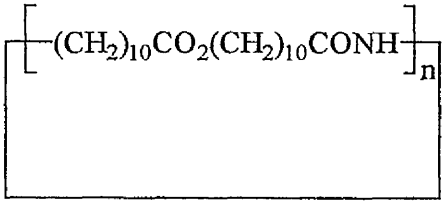


Figure 74

5.2.3.2 Ester Synthesis [115]

The ester syntheses are superficially similar to the amide syntheses described above. The syntheses of cyclic esters are based on the less-common method of ester synthesis shown in Figure 75.

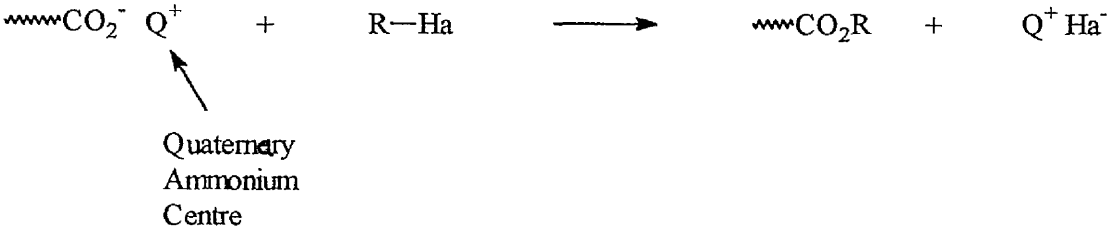


Figure 75

By using ω–bromoalkanoic acids as the monomers and replacing Q^+ with the commercially available anion-exchange resin Amberlsyt A-26 shown in Figure 76, polymer-supported polymerisations were carried out.

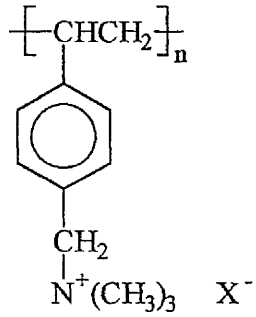
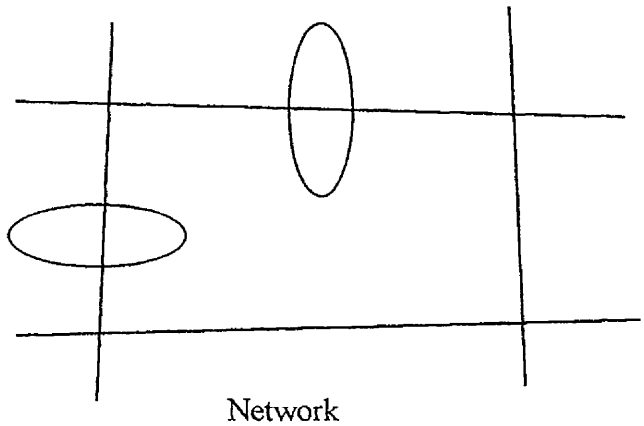


Figure 76

It was already known that ester linkages could be prepared using Amberlyst A-26 from the work of Cannelli and co-workers who prepared a wide range of simple esters.[116] In practice the polymer-supported synthesis starting with 11-bromoundecanoic acid gave soluble products in yields of ca. 50% with ca. 70% of the molecules produced being cyclic.[115]

It was noted in these syntheses, especially the amide syntheses, that the polymer support recovered at the end of the reaction weighed heavier than expected.[114] It seemed very likely that this was due to cyclic oligomers being physically trapped in the supports. This is shown schematically in Figure 77.

Cyclic Molecules



Network

Figure 77

In support of this claim it should be noted that Semlyen and co-workers have synthesised cyclic oligomers and then synthesised networks in the presence of these cyclics.[117-120] It was found that a significant fraction of the cyclics became trapped. In the work discussed here it is suggested that trapping occurs during the synthesis of the cyclics rather than after.

To prove that trapping had indeed occurred, it was proposed in the present work, to carry out the cyclic oligoester synthesis on a polymer-support which could subsequently be degraded, thus releasing the previously trapped cyclics which could then be removed and identified.

5.3 AIMS

The aims of the work described in the following section were as follows.

1) To synthesise cross-linked polystyrene networks which, when required, can be degraded to soluble fragments. The reagents used for the degradation must be neither strongly acidic nor strongly basic since such reagents would not be compatible with the presence of esters.

2) To synthesise networks which meet the requirements outlined in (1) but which also contains functionality which can be adapted for the synthesis of either cyclic oligoesters, oligoamides or oligo(amide-esters). The obvious functionality to meet this requirement is the chloromethyl group, which is easily incorporated into networks by using chloromethylstyrene (para- or para-/meta- mixed isomers) as a monomer.

3) To carry out the synthesis of cyclic oligoesters on a degradable resin. After thoroughly washing the resin to remove all free cyclics, to degrade it, and to remove any topologically trapped cyclic oligomers. The latter will then be removed and characterised.

CHAPTER 6

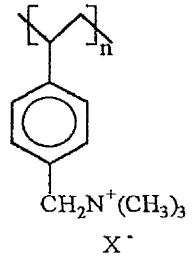
RESULTS AND DISCUSSION FOR RINGS TOPOLOGICALLY TRAPPED ON NETWORKS

6.1 AIMS

The primary aim of this project was to synthesise a degradable polymer network which could be used as a support for the synthesis of cyclic step-growth polymers. This could hopefully be achieved by incorporating double bonds into a polystyrene-based network. To accomplish this butadiene was chosen as co-monomer with styrene.

It has been shown before, that preformed cyclic polymers can be trapped in polymer networks, during network synthesis and this has even been used as a method of proving the cyclic nature of polymers.[117-120] This suggests that it should be possible to trap cyclic polymers in the support during a polymer-supported cyclisation. To best achieve this it was felt that the polymer support should be of the microporous type, i.e. those which swell to give very open networks and hence, the percentage cross-linking of this support should be kept reasonably low (approximately 1-2%).

To enable a polymer network to be used as a support for cyclisation reactions, it clearly needs to have the correct functionality to enable the step-growth monomers to be loaded on and then polymerised in a controlled manner to give cyclic products. Amberlyst A26 has been used to prepare cyclic polyesters.[115,121] This resin contains residues **(24)** and it was desirable to incorporate these moieties on the network.



Polymer Residue **(24)**

As a preliminary study to synthesising the required polymer network, a series of linear polymers were produced to acquire data on the co-polymerisation proportions, and to test the degradability of these polymers towards ozone, potassium permanganate or osmium tetroxide (all of which have been shown to cleave double bonds).[122-125]

The final stage was to produce a microporous polymer network with the required functionalities and to study this network as a polymer-support compared to Amberlyst A26. It should be possible to trap cyclic polymers within this network and then release them by degrading the polymer support.

This process is discussed in the following sections.

6.2 SYNTHESIS OF LINEAR STYRENE/BUTADIENE/ VINYLBENZYL CHLORIDE TER-POLYMERS

The synthesis of the linear ter-polymers, shown in Figure 78, was investigated to determine the percentage yields, composition and molecular weights of the products and hence, to determine the optimum reaction conditions. The results are summarised in Table 14. The following points are evident.

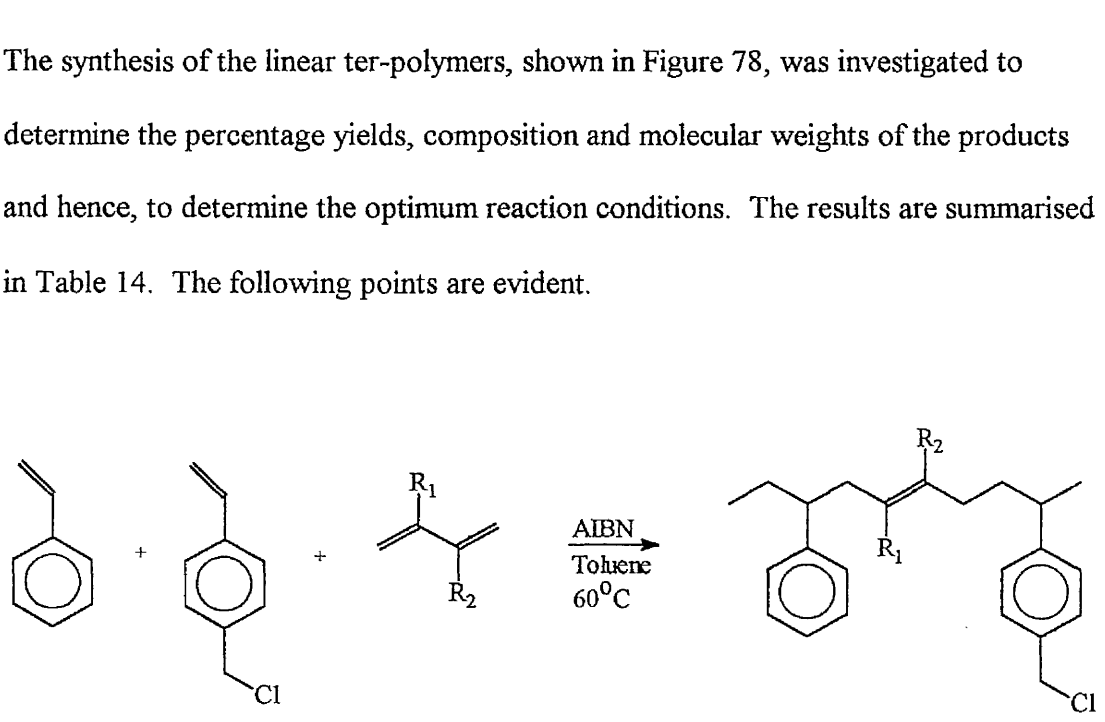


Figure 78

1) The addition of butadiene or vinylbenzyl chloride into the polymer changes both the percentage yield and molecular weight of the produced polymer.

2) The reactivity of the butadiene is greater than that of styrene whereas the reactivity of vinylbenzyl chloride is comparable to that of styrene. This means that in a ter-polymer of styrene, vinylbenzyl chloride and butadiene the percentage of the butadiene

in the final polymer is greater than that in the feed, whilst the ratio of styrene/vinylbenzyl chloride is approximately constant

4) The ratio of the butadiene in the feed / butadiene in the final polymer is decreased as the yield is increased. This seems to suggest that polymer formed early in the reaction will contain a higher percentage of butadiene than that formed in the later stages of the reaction.

The butadiene derivatives are introduced into the polymer to permit the controlled degradation of the polymer network using ozone gas. The butadiene units can be present in the polymer in three distinct ways as shown in Figure 79.

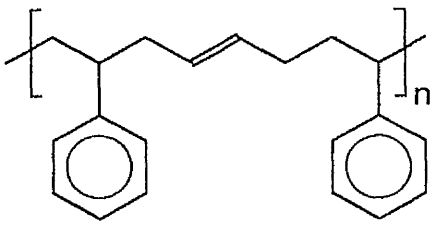
Oxidising the double bond of the trans-1,4- or cis-1,4-arrangements would degrade the polymer but cleaving the double bond of the 1,2-arrangement would not affect the polymer molecular weight. Hence it is necessary for the butadiene derivative to be introduced into the polymer in a 1,4-arrangement.

The vinylbenzyl chloride is introduced into the polymer so that consequently the chloromethyl residues can be transformed in to residues **(24)**.

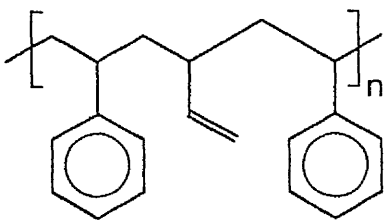
Table 14 - Synthesis of Linear Styrene Co-Polymers

Polymer Number	Co-Monomer	Co-Monomer in Feed (%)	Solvent Ratio	Reaction Time	Yield (%)	Co-Monomer in Polymer	Weight Average	Number Average	Polydispersity
25	None	0	1 Volume	24 Hours	25	0	243656	145430	1.68
26	Butadiene	5	1 Volume	24 Hours	15	10	284476	184724	1.54
27	Butadiene	5	1 Volume	72 Hours	24	8	64620	42513	1.52
28	Butadiene	5	1 Volume	2 Hours	4	11	84351	55674	4.52
29	Butadiene	5	5 Volumes	24 Hours	12	10	77632	51636	1.37
30	Butadiene	5	5 Volumes	72 Hours	21	9	108889	72643	1.5
31	Butadiene	25	5 Volumes	24 Hours	7	43	37066	25909	1.43
32	Butadiene	1	1 Volume	24 Hours	31	2	35299	23564	1.5
33	Isoprene	10	1 Volume	24 Hours	16	12	328729	241712	1.36
34	Isoprene	5	1 Volume	24 Hours	24	7	105208	68317	1.54
35	Isoprene	2.5	1 Volume	24 Hours	35	3	90451	68413	1.32
36	Dimethylbutadiene	10	1 Volume	24 Hours	18	10	317508	248053	1.28
37	Dimethylbutadiene	5	1 Volume	24 Hours	38	6	357913	250289	1.43
38	Dimethylbutadiene	2.5	1 Volume	24 Hours	34	3	307307	227635	1.35
39	Vinylbenzyl chloride	30	1 Volume	24 Hours	54	30	662401	447568	1.48
40	Vinylbenzyl chloride	50	1 Volume	72 hours	43	53	744804	490002	1.52
41	VBC / Butadiene	25 / 15	1 Volume	24 Hours	51	20 / 27	719955	514253	1.4
42	VBC / Butadiene	25 / 15	1 Volume	72 Hours	65	21 / 24	799368	547512	1.46
43	VBC / Butadiene	25 / 5	1 Volume	24 Hours	47	25 / 9	687330	464412	1.48
44	VBC / Isoprene	25 / 5	1 Volume	24 Hours	50	26 / 6	711237	504423	1.41
45	Vinylbenzyl Chloride / Dimethylbutadiene	25 / 5	1 Volume	24 Hours	57	28 / 5	760821	559427	1.36

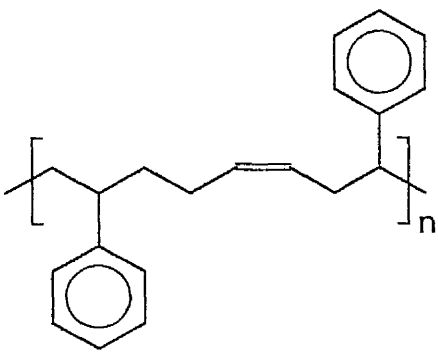
i) Co-Monomer in Feed - This is the percentage of the co-monomer used in the polymerisation
ii) Solvent Ratio - This is the number of volumes of toluene / volume occupied by total monomers
iii) Co-Monomer in Polymer - This is the percentage of co-monomer in the final polymer, detected by ^{1}H NMR
iv) By GPC relative to polystyrene standards



trans-1,4-arrangement



1,2-arrangement



cis-1,4-arrangement

Figure 79

6.3 CHEMICAL DEGRADATION OF LINEAR POLYMERS.

6.3.1 CHEMICAL DEGRADATION USING OZONE

The ozonolysis of linear polymers containing butadiene derivatives was investigated to ensure that it was possible to degrade the polymer cleanly using ozone. This was investigated by examining the ozonolysis products by GPC and ^{1}H NMR

spectroscopy. The results given in Table 15 are for a representative experiment using polymer **(26)**; all other polymers gave similar results.

The polymer was degraded by bubbling ozone gas through a solution of the polymer in chloroform for 4 hours at -78 °C. The resulting ozonide was decomposed using the appropriate reagents shown in Figure 80 to give oligomers with alcohol, acid or aldehyde end groups.

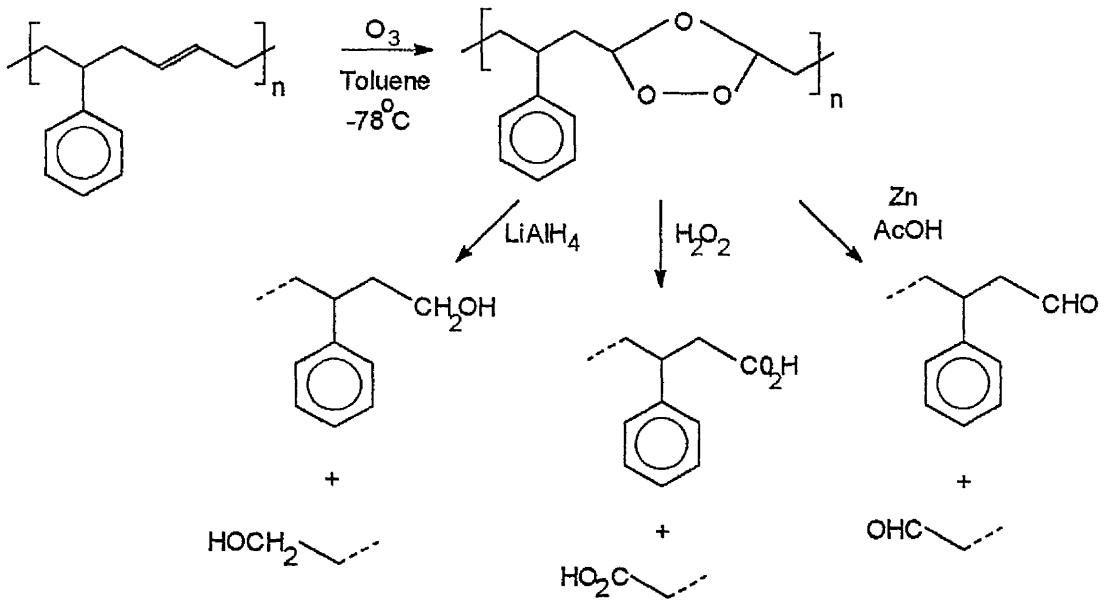


Figure 80

It is evident from the results in Table 15 that the ozonolysis successfully reduced the molecular weight of the polymer. Theoretically a polymer containing 10% butadiene, as polymer **(26)** does, which is evenly distributed along the polymer backbone would have a number average molecular weight around 1200 and a polydispersity of 2.00.

From the results shown in Table 15, it can be seen that the number average molecular weights and the polydispersities differ from the simple theoretical values and hence, either not all the double bonds are cleaved, or the butadiene cannot be randomly distributed along the polymer backbone with any low molecular weight oligomers being relatively volatile and soluble being lost. Examination of the ^{1}H NMR spectrum before degradation shows a signal at 5.0ppm due to the vinyl protons. This signal was no longer observed after the ozonolysis had been completed. This suggests that it is the random distribution of the butadiene and loss of low molecular weight oligomers that causes the polymers to exhibit higher than expected molecular weights.

Table 15 - GPC results for the ozonolysis of linear polymer (26) with Mn=284476 and Mw=184724.

Polymer End Group	Weight Average [a]	Number Average [a]	Polydispersity [a]
Alcohol	3198	1937	1.65
Acid	5121	2371	2.16
Aldehyde	4147	2194	1.89

a) By GPC relative to polystyrene standards.

Ebdon and co-workers have shown that the reaction of polystyrene polymers with ozone can cause the cross-linking.[126,127] They have shown that at a concentration of 2.5×10^{-2} g/cm^2 of polystyrene in chloroform there is no soluble material remaining after reaction with ozone for 2 hours at 0 or -60 °C for 2 hours. This is obviously not

true in the present case were the reaction was carried out at a concentration of 1×10^{-2} g/cm^2 at a temperature of -78 °C for 4 hours. Tanaka and co-workers report no cross-linking when the reaction was carried out at a concentration of 4×10^{-4} in dichloromethane at a temperature of -40 °C.[128] This suggests that it is the concentration of the reaction that is responsible for causing the cross-linking of the polymer.

6.4 SYNTHESIS OF 4-4'-DIHYDROXYSTILBENE NETWORKS.

4,4'-Dihydroxystilbene was synthesised by reacting chloroacetaldehyde diethylacetal with phenol in glacial acetic acid and concentrated sulphuric acid.[132] The resulting oil was then poured into a hot solution of diethyleneglycol bissodium salt, prepared by heating a mixture of sodium, methanol and diethyleneglycol to 190 °C whilst distilling off the methanol.

4,4'-Dihydroxystilbene was used to cross-link linear polymers containing chloromethyl residues, see Figure 81. It was hoped that this would enable the cleavage of the polymer networks to be carried out more efficiently and also at a later date, to enable the synthesis of polyrotaxanes, as a cross-linked polymer network containing double bonds only in the cross-links and not in the main chain will, upon degradation, yield a linear polymer. Any cyclics that where trapped in the original network will hopefully still be trapped on the polymer chain and hence, a polyrotaxane will have been synthesised.

A 1% cross-linked polymer network, containing double bonds in the cross-links as well as in the main chain, should be easier to degrade, as only relatively few of the cross-links need to be cleaved in order to render the network partially soluble.

6.5 DEGRADATION OF 4,4'-DIHYDROXYSTILBENE NETWORKS.

6.5.1 OZONOLYSIS OF A NETWORK WITH RESIDUES (46)

The ozonolysis of a network with chloromethyl styrene residues, residues **(46)** was completed with limited success. After a period of two weeks ozonolysis followed by two weeks treatment with hydrogen peroxide, a small amount of soluble material was obtained. It is necessary to degrade nearly all the double bonds in either the cross-links or the backbone in order to render the polymer soluble. Access to the double bonds is made more difficult in a polymer network and hence, the reaction time is greater than that for the ozonolysis of the linear polymers. The overall cleavage is a two-step reaction and therefore, the network is not opened up until both stages have been completed. For this reason many of the double bonds may remain inaccessible during the reaction and therefore, it may be necessary to repeat this procedure. This would be a lengthy procedure and therefore, an alternative method was used.

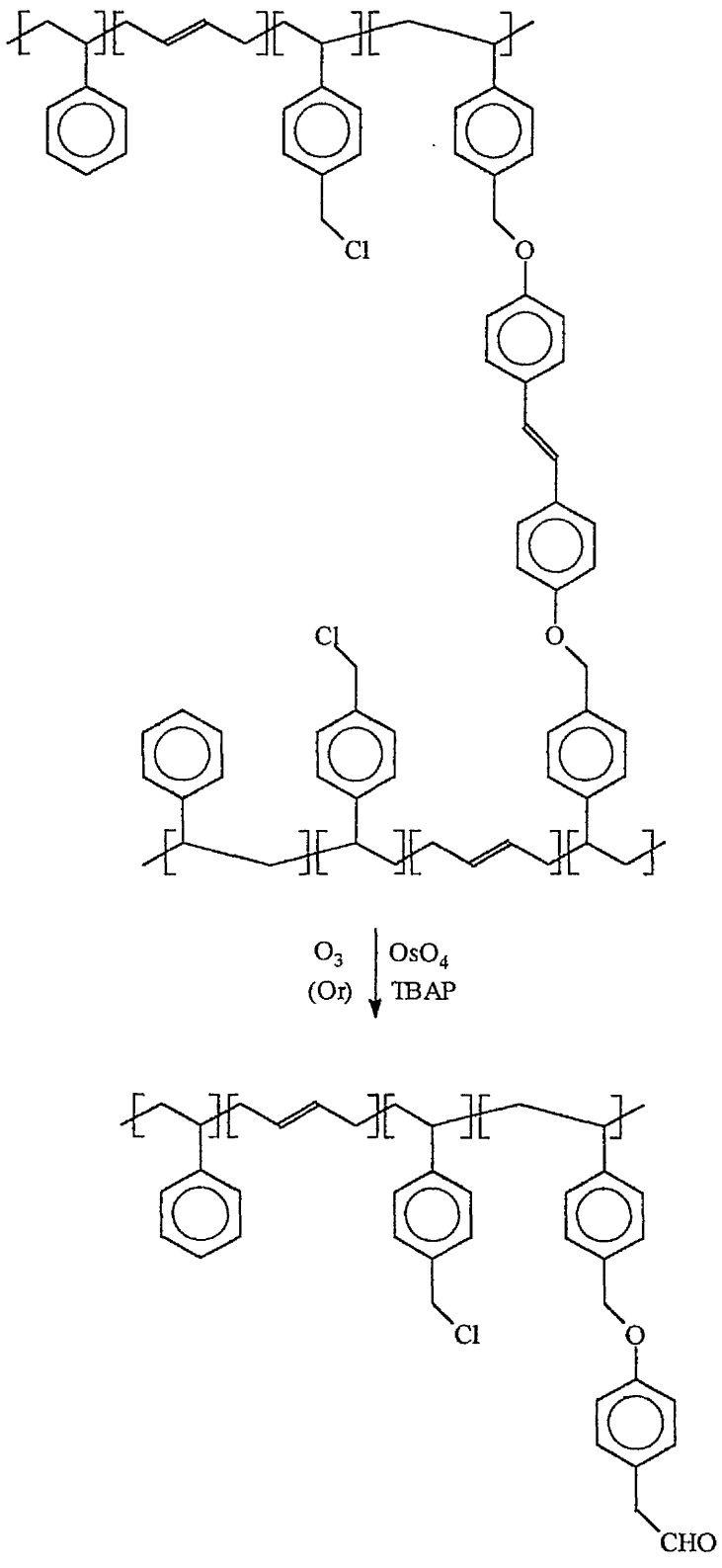


Figure 81

6.5.2 DEGRADATION OF A NETWORK WITH RESIDUES (46) USING OSMIUM TETROXIDE AND TETRABUTYLAMMONIUM PERIODATE.

The degradation of a network with residues **(46)** was carried out successfully using osmium tetroxide and tetrabutylammonium periodate. The tetrabutylammonium periodate was present to cleave the diol formed on osmylation and to re-generate the osmium tetroxide. With a reaction time of five days, 97% of the original network mass was found to be soluble. The reaction times are much shorter using this method due to two reasons.

1) The osmium tetroxide is much more reactive than ozone.

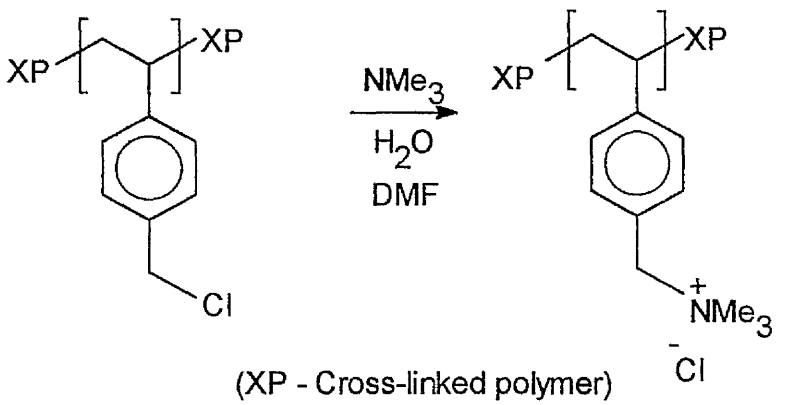
2) As the degradation of a network with residues **(46)** using osmium tetroxide is a one-pot reaction, then it follows that as the reaction proceeds, the network is opened up exposing more double bonds to possible degradation and hence, the rate of reaction increases.

6.6 CHEMICAL MODIFICATION OF A NETWORK WITH RESIDUES (46).

6.6.1 SYNTHESIS OF A QUATERNISED POLYMER-SUPPORT WITH RESIDUES (24).

To enable a network with residues **(46)** to be used as a polymer support it is necessary to introduce a functional group that will permit the loading of the required monomer.

The modification of a network with residues **(46)** to produce a quaternised network, i.e. one with residues **(24)**, was achieved by heating with trimethylamine at 100°C for 4 days.[130] The network obtained is similar to Amberlyst A26, which has been used extensively as a polymer support by groups working at both Manchester and York Universities. At the time the present work began, Amberlyst A26 appeared to be one of the best polymer supports for these types of reaction and hence, a good starting point for this work.



Residues **(46)** Residues **(24)**

6.7 CYCLISATION REACTIONS USING POLYMER SUPPORTS.

One of the aims of the present project was to trap cyclic polymers within the polymer supports. It is quite difficult to prove whether this has been achieved. The simplest method to obtain evidence for trapping, is to complete an accurate mass balance for the reactants used. If trapping occurs, then the recovered resin will be heavier than

expected on the basis of no trapping occurring. If there is a weight gain, then the network will be degraded to release any trapped cyclics which can then be recovered for analysis. These trapped cyclics should not include cyclic oligomers of DP 1-3 when 11-bromoundecanoic acid is used, because, these rings are too small to wrap around the polystyrene chain.

6.7.1 CYCLISATIONS USING AMBERLYST A26.

Refering to Figure 82, the following reactions could occur.

a) Chemical reaction of one loaded monomer unit to a neighbouring monomer unit to produce a polymer-supported chain of higher molecular weight.

b) Chemical reaction within one loaded monomer unit to produce a cyclic species in solution.

c) Chemical reaction within one loaded monomer unit, but where the chain wraps around the support polymer backbone to produce a trapped cyclic.

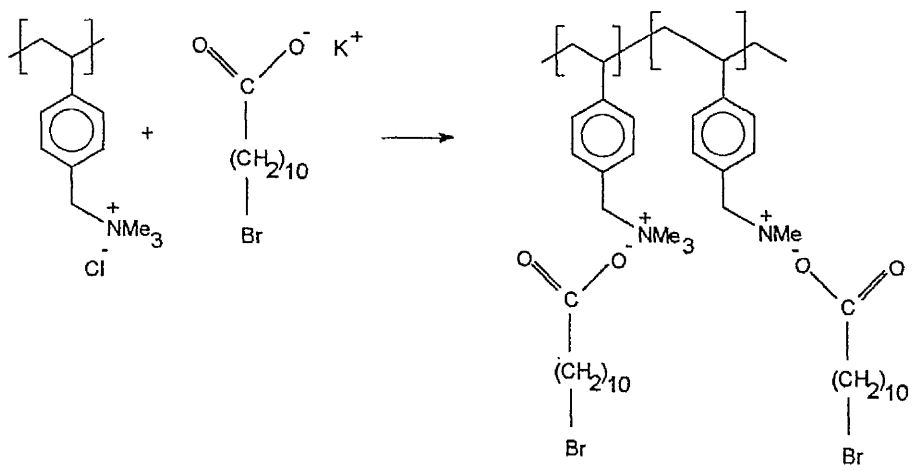


Figure 82

To gain familiarity with the reaction, the potassium salt of 11-bromoundecanoic acid was loaded onto Amberlyst A26 by ion exchange. The loaded resin was dried under vacuum at room temperature in an attempt to prevent premature cyclisation. It was found that 2.0g of the chloride form of Amberlyst A26 produced 2.8g of the loaded resin, i.e. 800mg (3mmol) of 11-bromoundecanoic acid was loaded onto 2.0g of Amberlyst A26. This gave 400mg (1.5mmol) of loaded monomer per gram of resin. The potassium salt of 11-bromoundecanoic acid was synthesised immediately prior to each loading, as it was found that it began to polymerise in the aqueous solution if left standing.[115]

The loaded resin was heated in toluene for 24 hours to effect cyclisation. This yielded 469mg (84mole%) of what appeared to be cyclic oligomers of 11-bromoundecanoic acid. A small amount of linear polymer could be detected by ^{1}H NMR. Approximately 14% of repeat units have detectable end groups (which could be CH_2Br, CH_2Cl or CH_2OH) by ^{1}H NMR, therefore, assuming an equal distribution of cyclics and linears, then for an average DP of ca. 3 ca. 42% of the recovered species are linear. The GPC of the assumed cyclics appeared to show that rings were present containing from one to eleven repeat units of 11-bromoundecanoic acid. The percentage by which each of these cyclics was present in the mixture increased as the ring size increased from one to three and then decreased as the ring size increased beyond this, see Figure 83.

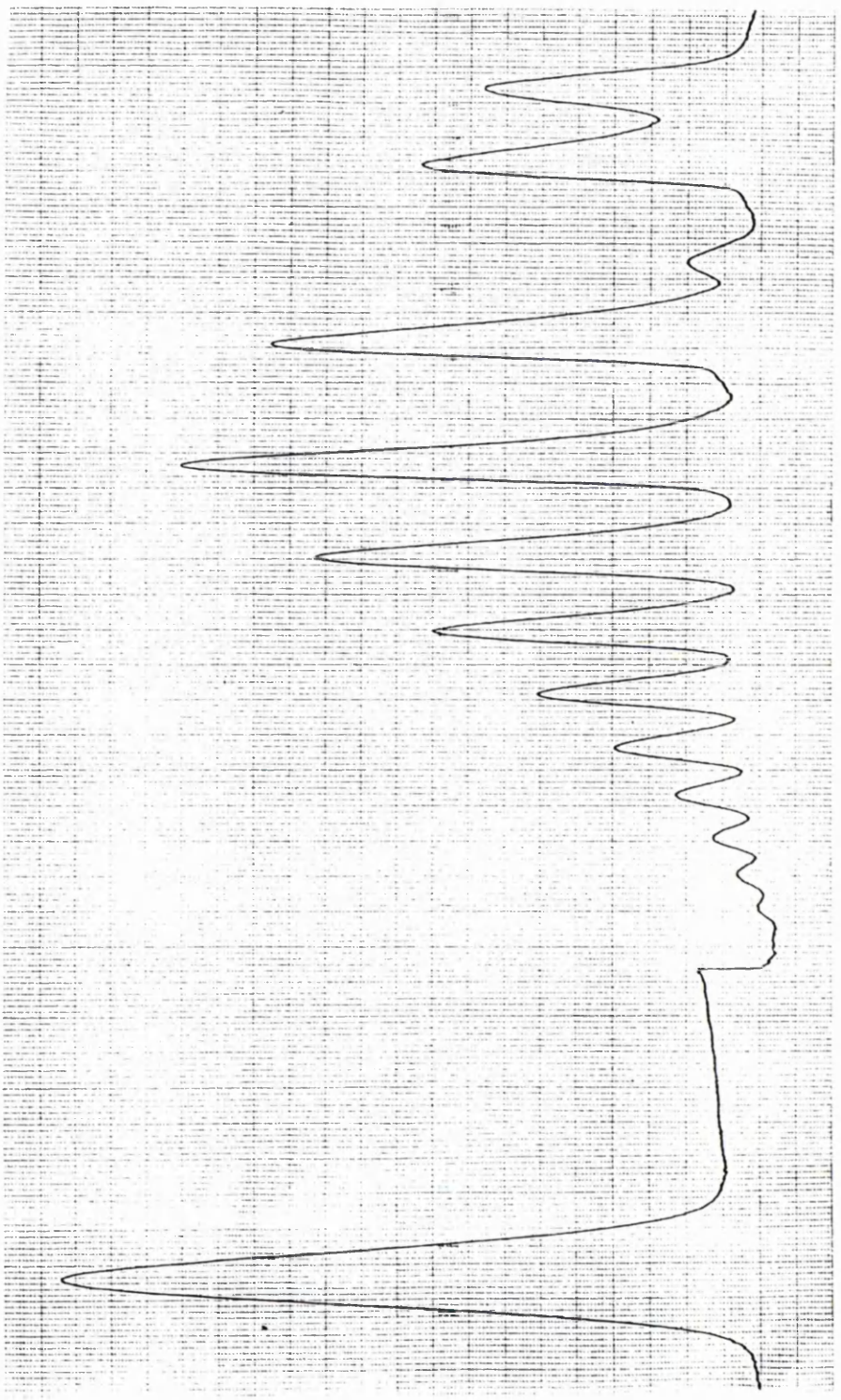


Figure 83

6.7.2 CYCLISATIONS ON A NETWORK WITH RESIDUES (24).

The potassium salt of 11-bromoundecanoic acid was loaded onto a network with residues **(24)** in the same way as for Amberlyst A26. The cyclisation reaction was carried out in toluene, in chloroform and in THF to observe any solvent effects. Any linears remaining attached to the network after the cyclisation reaction were removed by reaction with methyl iodide. This produces the methyl ester of the linear polymer of 11-bromoundecanoic acid and substitutes this for an iodide ion on the resin. The starting resin contained chloride ions and hence, the mass of the resin will have increased. To obtain an accurate mass measurement for the final resin and hence, observe any trapping that may have taken place, it was necessary at the end of the reaction to treat the resin with a vast excess of saturated sodium chloride solution to replace the iodide and bromide ions with chloride ions. The resin was then dried under vacuum at 60^{o}C over phosphorous pentoxide to remove all the water from within the polymer beads. The results are summarised in Table 16.

Table 16 - Weight gains from cyclisations using a network with residues (24).

Solvent	Mass of loaded monomers	Mass of cyclics	Mass of linears	Mass increase of resin
Toluene	1.00g (4.4mmol)	0.57g (3.1mmol)	0.29g (1.0mmol)	120mg (0.65mmol)
Chloroform	1.18g (5.2mmol)	0.78g (4.2mmol)	0.25g (0.9mmol)	110mg (0.59mmol)
THF	0.93g (4.1mmol)	0.55g (3.0mmol)	0.26g (0.9mmol)	120mg (0.65mmol)

It is evident that the use of a network with residues **(24)** produced much higher loadings of 11-bromoundecanoic acid, up to almost 50% higher than with Amberlyst A26. This is possibly due to the presence of the butadiene monomer units, which may open up the network making access to active sites easier and hence, increasing the efficiency of reaction.

The mass of what was assumed to be cyclics produced using a network with residues **(24)**, on average 0.32g / g of loaded monomer (75mole%) appeared to be lower than those produced using the Amberlyst A26. Could this be due to some of the oligomers being trapped in the network? The GPC of the collected soluble cyclics appeared to show a series of rings from one to eighteen repeat units of 11-bromoundecanoic acid, see Figure 84, and the ^{1}H NMR spectrum showed that 12% of the repeat units had detectable end groups ie. assuming an equal distribution of cyclics and linears, then for an average DP of ca. 3 this gives 36% of recovered species being linear.

The mass of retrieved linears from the network was quite low, on average 0.13g / g of loaded monomer (20mole%). Thus 5mole% of the loaded monomer is so far unaccounted for. Could this be trapped within the network?

After washing the network extensively with saturated sodium chloride solution in an attempt to return the network to its original form, the network was dried and re-weighed. It was found that all of the networks had gained weight, on average

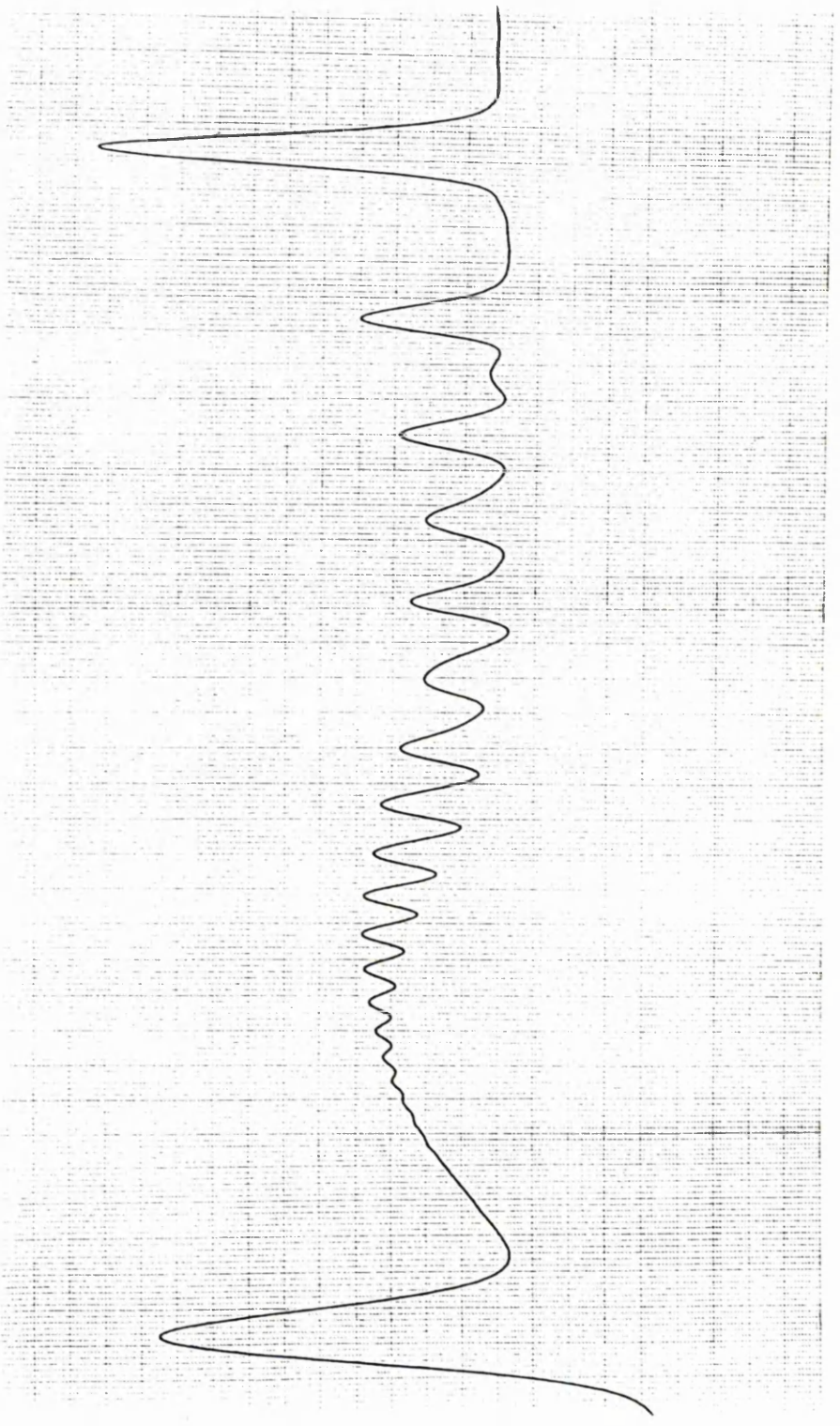


Figure 84

0.058g / g of loaded monomer (14mole% of the initial monomer units). This more than accounts for the remaining loaded monomer. The question still remains as to whether or not at least part of this gain in weight is due to trapped cyclics.

Theoretically all products from the cyclisation reaction that are not trapped within the network should have been removed, therefore, to prove the presence of any trapped products the network must be degraded.

6.7.3 REPEAT OF THE CYCLISATION REACTION USING A NETWORK WITH RESIDUES (24) IN AN ATTEMPT TO BUILD UP THE MASS OF TRAPPED CYCLICS.

Before degrading the network it was decided to attempt to build up the amount, if any, of trapped cyclics by repeating the cyclisation on the initial product, the results are shown in Table 17. When the cyclisation procedure was repeated it was found that the mass of 11-bromoundecanoic acid monomer that was possible to load was increased. The reasons for this are as yet unclear.

Table 17 - Weight gains from the repeating of the cyclisation procedure.

Repetition	Mass of loaded monomers	Mass of cyclics	mass of linears	Mass increase of resin
1	1.00g (3.8mmol)	0.57g (3.1mmol)	0.29g (1.0mmol)	120mg (0.65mmol)
2	1.07g (4.0mmol)	0.63g (3.4mmol)	0.26g (0.9mmol)	45mg (0.25mmol)
3	1.20g (4.5mmol)	0.72g (3.9mmol)	0.28g (1.0mmol)	20mg (0.10mmol)

When the cyclisation reaction was repeated the yield of oligomers obtained increased and the extent to which the network gained weight decreased. It is possible that as the cyclisation reactions are repeated and the number of rings trapped within the network is increased, then there will be less space within the network and hence the probability of trapping is decreased. In the cyclisation reactions a point should be reached where no more trapping will occur.

The mass of linears obtained from the reaction with methyl iodide remained reasonably constant. This suggests that the cyclisation reaction is not affected by any cyclics that may be trapped in the network.

6.8 DEGRADATION OF A NETWORK WITH RESIDUES (24) CONTAINING TRAPPED CYCLICS

After the final cyclisation reaction the loaded network was successfully degraded using osmium tetroxide and sodium periodate in DMF. DMF was used as the solvent to ensure the solubility of both the resulting quaternised linear polymer and any "trapped cyclics" that may be released.

^{1}H NMR spectral analysis of the DMF solution showed signals due only to the resulting linear quaternised polystyrene, no signals could be observed for any oligomeric esters of

11-bromoundecanoic acid. GPC analysis of the DMF solution showed a random mixture of oligomers similar to those observed for the degradation of a network with residues **(24)** alone. This, therefore, suggests that no cyclics have been trapped and that the gain in weight observed is due to other reasons, possibly the presence of different counterions in the network which may not have been swapped during the sodium chloride wash either due to a preference of the network to contain iodide counterions, or to a difficulty in the sodium chloride penetrating certain areas of the network. It may also be possible that some of the initial chloromethyl residues **(46)** in the network, were not quaternised with trimethylamine and upon reaction with methyl iodide, would be converted to iodomethyl residues which would not be re-converted to chloromethyl residues upon washing with sodium chloride. One final possibility although unlikely is that some of the sodium chloride used for washing has been trapped in the network. In order to investigate this more fully, it would be neccessary to use a network that initially contains iodide ions, produced by using iodomethylstyrene instead of chloromethylstyrene. Also 11-iodoundecanoic acid would have to be used as monomer instead of 11-bromoundecanoic acid. Both the iodomethylstyrene and 11-iodoundecanoic acid would have to be synthesised from chloromethylstyrene and 11-bromoundecanoic acid respectively using the Finkelstein reaction.

MALDI-TOF MS analysis of the apparent cyclic fraction showed a series of signals having mass $41+(184)_n$. MALDI-TOF MS has been shown to be accurate to 2-3 mass units and hence there are two possible explanations for the observed signals.

1) A series of cyclic oligomers have been synthesised and these have been launched in the MALDI-TOF MS with potassium ions.

2) A series of linear oligomers containg an an alcohol and a carboxylic acid end group, see Figure 85, have been synthesised and these have been launched in the MALDI-MS using sodium salts.

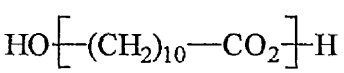


Figure 85

Dr Ruddick synthesised a series of linear hydroxy-acids by heating 11-hydroxyundecanoic acid in the absence of any catalyst in order to keep the molecular weight reasonably low, that is to obtain oligomers.[115] These linear oligomers were analysed by ^{1}H NMR spectroscopy and GPC and were found to be identical to some of the oligomers produced from the polymer support. It was shown that the higher oligomers especially were hydroxy-acid linears rather than cyclic oligomers.

Dr Ruddick also synthesised a series of cyclic oligomers by heating a dilute solution of linear polyundecanoate in chlorobenzene in the presence of dibutyltin oxide as a transesterification catalyst.[115] These oligomers were partially separated by preparative GPC and the cyclic dimer was isolated. An X-ray crystal structure was obtained to prove the cyclic nature. This series of cyclic oligomers along with the pure dimer have also been analysed by MALDI-MS. These oligomers show a series of signals of mass

$23+(184)_n$, consistent with that expected from cyclic oligoundecanoates launched using sodium salts. These cyclic oligomers were then analysed by GPC, and where shown to give a series of signals that had different retention times than some of the oligomers produced using the polymer support.

6.9 CONCLUSIONS AND FUTURE WORK

A polymer network has been synthesised that can be degraded to oligomeric fractions using osmium teroxide and sodium periodate. This network contains chloromethyl functional groups and so, in principle, it can be used to carry out many different polymer-supported organic reactions.

It was hoped to use this network as a support to carry out cyclisation reactions that may produce "trapped cyclics" which, upon degradation of the network, could then be released. The polymer-supported cyclisation procedure that we have followed has been shown to produce linear hydroxy-acid oligomers and not pure cyclic oligomers and therefore, a new method needs to be found.

More recent work has been succesful in producing cyclic oligomers and these methods are currently being further investigated.[114,115] If any evidence is found to suggest that any of these techniques may be producing "trapped cyclics" then it should be possible

to modify the current degradable polymer support to contain the required functionality for it to be used to repeat these methods.

CHAPTER 7

EXPERIMENTAL FOR RINGS TOPOLOGICALLY TRAPPED ON NETWORKS

Since most of the reactions carried out were examples of a few types only, a general example of each type is given in detail. Details of the other reactions are summarised in tabular form.

All products were dried under vacuum using a two-stage oil pump at 60 °C unless stated otherwise. When any washings were carried out a one bed volume was used unless stated otherwise.

The divinylbenzene (DVB) used was a commercial mixture of *meta* and *para* isomers in the ratio of 60:40.

The DMF used was dried over 4A activated molecular sieves and azeotroped with toluene before use.

The THF used was dried by distillation over sodium wire

7.1 SYNTHESIS OF LINEAR STYRENE POLYMERS, STYRENE CO-POLYMERS AND RELATED POLYMERS. [131]

Ter-polymerisations of styrene with buta-1,3-diene and chloromethylstyrene were carried out as follows.

A cylinder of butadiene gas was connected to a vacuum line so as to deliver the gas into a sealed vessel (of known weight) which was cooled in liquid nitrogen. The butadiene was introduced slowly so as to avoid a sudden pressure increase. Once the gas was collected the vessel was sealed and allowed to slowly warm to room temperature. This was then re-weighed and the required masses of the other monomers were calculated accordingly, placed in a second sealed vessel with an equal volume of toluene. AIBN (0.5wt%) was added and the resulting solution was degassed using standard freeze-thaw techniques. Both vessels were then connected to the vacuum line so as to transfer the butadiene gas into the reaction mixture. This was aided by cooling the receiving vessel in liquid nitrogen whilst gently warming the dispensing vessel by holding it in the palm of the hand. The reaction vessel was then sealed and allowed to warm to room temperature before being placed in a water bath at 80^{o}C for 24 hours. After this time the resulting solution was precipitated into methanol (1 litre). The resulting polymer was collected by filtration and dried.

Table 14 - Synthesis of Linear Styrene Co-Polymers

Polymer Number	Co-Monomer	Co-Monomer in Feed (%)	Solvent Ratio	Reaction Time	Yield (%)	Co-Monomer in Polymer	Weight Average	Number Average	Polydispersity
25	None	0	1 Volume	24 Hours	25	0	243656	145430	1.68
26	Butadiene	5	1 Volume	24 Hours	15	10	284476	184724	1.54
27	Butadiene	5	1 Volume	72 Hours	24	8	64620	42513	1.52
28	Butadiene	5	1 Volume	2 Hours	4	11	84351	55674	4.52
29	Butadiene	5	5 Volumes	24 Hours	12	10	77632	51636	1.37
30	Butadiene	5	5 Volumes	72 Hours	21	9	108889	72643	1.5
31	Butadiene	25	5 Volumes	24 Hours	7	43	37066	25909	1.43
32	Butadiene	1	1 Volume	24 Hours	31	2	35299	23564	1.5
33	Isoprene	10	1 Volume	24 Hours	16	12	328729	241712	1.36
34	Isoprene	5	1 Volume	24 Hours	24	7	105208	68317	1.54
35	Isoprene	2.5	1 Volume	24 Hours	35	3	90451	68413	1.32
36	Dimethylbutadiene	10	1 Volume	24 Hours	18	10	317508	248053	1.28
37	Dimethylbutadiene	5	1 Volume	24 Hours	38	6	357913	250289	1.43
38	Dimethylbutadiene	2.5	1 Volume	24 Hours	34	3	307307	227635	1.35
39	Vinylbenzyl chloride	30	1 Volume	24 Hours	54	30	662401	447568	1.48
40	Vinylbenzyl chloride	50	1 Volume	72 hours	43	53	744804	490002	1.52
41	VBC / Butadiene	25 / 15	1 Volume	24 Hours	51	20 / 27	719955	514253	1.4
42	VBC / Butadiene	25 / 15	1 Volume	72 Hours	65	21 / 24	799368	547512	1.46
43	VBC / Butadiene	25 / 5	1 Volume	24 Hours	47	25 / 9	687330	464412	1.48
44	VBC / Isoprene	25 / 5	1 Volume	24 Hours	50	26 / 6	711237	504423	1.41
45	Vinylbenzyl Chloride / Dimethylbutadiene	25 / 5	1 Volume	24 Hours	57	28 / 5	760821	559427	1.36

i) Co-Monomer in Feed - This is the percentage of the co-monomer used in the polymerisation
ii) Solvent Ratio - This is the number of volumes of toluene / volume occupied by total monomers
iii) Co-Monomer in Polymer - This is the percentage of co-monomer in the final polymer, detected by ^{1}H NMR
iv) By GPC relative to polystyrene standards

7.1.1 Poly(styrene/butadiene/vinylbenzyl chloride) ter-polymers

polymers (25) - (45)

IR: ν/cm^{-1} (Evaporated film) 1600 (aromatic) 1270 and 680 (CH_2Cl) ^1H nmr (δ/ppm): [signals due to styrene residues] 7.3-6.8 (3H, b, aromatic), 6.8-6.4 (2H, b, aromatic), 2.1-1.7 (1H, b, CH), 1.7-1.3 (2H, b, CH_2) [signals due to butadiene] 5.0-4.5 (2H, b, CH), [signals due to vinylbenzyl chloride] 7.3-6.8 (3H, b, aromatic), 6.8-6.4 (2H, b, aromatic), 4.5-4.0 (2H, b, CH_2Cl), 2.1-1.7 (1H, b, CH), 1.7-1.3 (2H, b, CH_2)

7.2 DEGRADATION OF LINEAR POLYMERS.

7.2.1 OZONOLYSIS OF POLY(STYRENE/BUTADIENE/ VINYLYBENZYL CHLORIDE) CO-POLYMER POLYMER (26) [122,123]

Polymer **(26)** (1.00g, 8.3mmol) in chloroform (100ml) was stirred at -78 °C and an ozone-air mixture containing approximately 1% ozone was bubbled through the solution for 4 hours. The ozonide formed was worked up as follows to give products with:-

a) alcohol end groups

b) acid end groups

or c) aldehyde/ketone end groups.

7.2.1.1 Reaction of Ozonide to Give Products with Alcohol End-groups [122,123]

A solution of the ozonide (1.00g) in chloroform (100ml) was added slowly to a suspension of lithium aluminiumhydride (55mg, 1.7mmol) in chloroform (20ml), and the mixture was stirred at room temperature for 18 hours. Water (0.5ml) was added slowly followed by sodium hydroxide solution (1.5ml of a 15% weight/volume solution) and finally water (1.5ml). The mixture was stirred for a further 1 hour and the resulting solid filtered off. The remaining solution was evaporated to dryness under reduced pressure to give polymer **(47)** with alcohol end groups.
Yield (0.87g, 87%) IR: ν/cm^{-1} (evaporated film) 3348 (OH), 3026 (CH), 2925 (CH_2), 2852 (CH), 1600 (aromatic) GPC weight average-3198, number average-1937, polydispersity 1.65. ^1H nmr (δ/ppm): 7.3-6.8 (3H, b, aromatic), 6.8-6.4 (2H, b, aromatic), 2.1-1.7 (1H, b, CH), 1.7-1.3 (2H, b, CH_2) no signals were observed at 5.0-4.5 which are characteristic of the double bond in butadiene.

7.2.1.2 Reaction of Ozonide to Give Products with Acid End-groups [122,123]

Hydrogen peroxide (0.5ml, 14.7mmol of a 100 volumes solution) was added to a solution of the ozonide (1.00g) in chloroform (100ml), and this was stirred for 1hour at room temperature. The resulting solution was shaken with potassium iodide followed by

sodium thiosulphate until no colour remained. The solution was then dried over magnesium sulphate and evaporated to dryness under reduced pressure to give polymer **(48)** with acid end groups.

Yield: (0.91g, 91%) IR: ν/cm^{-1} (evaporated film) 3428 (OH), 3025 (CH), 2923 (CH_2), 2854 (CH), 1706 C=O , acid), 1601 (aromatic) GPC weight average-5121, number average-2371, polydispersity-2.16 ^1H nmr (δ/ppm): 7.3-6.8 (3H, b, aromatic), 6.8-6.4 (2H, b, aromatic), 2.1-1.7 (1H, b, CH), 1.7-1.3 (2H, b, CH_2)

7.2.1.3 Reaction of Ozonide to Give Products with Aldehyde End-groups [122,123]

Glacial acetic acid (1ml, 4mmol) and zinc (catalytic amount), were added to a solution of the ozonide (1.00g) in chloroform (100ml) and this was stirred at room temperature for 1 hour. The zinc was filtered off and the remaining solution was evaporated to dryness under reduced pressure to give polymer **(49)** with aldehyde end groups.

Yield: (0.83g, 83%) IR: ν/cm^{-1} (evaporated film) 1713 C=O , aldehyde), 1601 (aromatic) GPC weight average-4147, number average-2194, polydispersity-1.89. ^1H nmr (δ/ppm): 7.3-6.8 (3H, b, aromatic), 6.8-6.4 (2H, b, aromatic), 2.1-1.7 (1H, b, CH), 1.7-1.3 (2H, b, CH_2)

7.2.2 DEGRADATION OF POLYMER (26) USING POTASSIUM PERMANGANATE. [124]

Potassium permanganate (0.32g, 2mmol) in water (2ml) was added to a solution of polymer **(26)** (1.0g, 10.1mmol) and sodium periodate (2.2g, 10.1mmol) in THF (30ml), and stirred at room temperature for 5 days. The THF was removed under reduced pressure, chloroform (50ml) was added and the resulting solution was washed with water (3 x 50ml) dried over magnesium sulphate and evaporated to dryness under reduced pressure to yield polymer **(50)** with aldehyde end groups.

Yield: 0.91g (91%) IR: ν/cm^{-1} (evaporated film) 1713 C=O , aldehyde), 1601 (aromatic) ^1H nmr (δ/ppm): 7.3-6.8 (3H, b, aromatic), 6.8-6.4 (2H, b, aromatic), 2.1-1.7 (1H, b, CH), 1.7-1.3 (2H, b, CH_2)

7.2.3 DEGRADATION OF POLY(STYRENE/BUTADIENE) USING OSMIUM TETROXIDE [125]

Osmium tetroxide (1ml, 39μmol of a 1% solution in tert-butanol), was added to a solution of Polymer **(26)** (1.0g,10.1mmol) and sodium periodate (2.2g, 10.1mmol) in chloroform (30ml), and stirred under nitrogen at room temperature for 5 days. The resulting solution was filtered through celite to remove the remaining osmium tetroxide and the filtrate was evaporated to dryness under reduced pressure to yield polymer **(51)** with aldehyde end groups.

Yield: 0.78g (78%) IR: ν/cm^{-1} (evaporated film) 1713 C=O , (aldehyde), 1601 (aromatic) ^1H nmr (δ/ppm): 7.3-6.8 (3H, b, aromatic), 6.8-6.4 (2H, b, aromatic), 2.1-1.7 (1H, b, CH), 1.7-1.3 (2H, b, CH_2)

7.3 SYNTHESIS OF CROSS-LINKED POLYMER NETWORKS

7.3.1 SYNTHESIS OF 4,4'-DIHYDROXYSTILBENE. [129]

I) A mixture of chloroacetaldehyde diethylacetal (91.50g, 0.6mol), phenol (113.0g, 1.2mol) and glacial acetic acid (400ml) were stirred in ice. Sulphuric acid (40ml) and glacial acetic acid (40ml) were added slowly over a period of 1.5 hours. The mixture was then stirred in ice for a further 6 hours, poured onto ice and extracted with ether to yield the intermediate product (i) as an oil.

ii) Sodium (76g, 3.3mol) was dissolved in methanol (850ml) and diethyleneglycol (400ml). The methanol was distilled off and the remaining solution heated under reflux until a bulb temperature of 190°C was reached. Product (i) was added slowly, and reflux maintained for 20 minutes until the evolution of hydrogen chloride gas ceased. The fluorescent yellow solution was poured into ice, and the mixture was acidified with 10% sulphuric acid. The precipitate was extracted with ether, the extract dried over magnesium sulphate, and evaporated to dryness under reduced

pressure to yield 4,4'-dihydroxystilbene as a white solid, which was recrystallised from glacial acetic acid.

Yield: 54g (42%) Mass Spec: M^+/Z: 212 (EI) mp 212°C (decomposes), lit [129] 212°C ^1H nmr (δ/ppm): 7.5 (4H, d, aromatic), 7.05 (2H, s, olefinic CH), 6.8 (4H, d, aromatic)

7.3.2 CROSS-LINKING OF POLY(STYRENE/BUTADIENE/ VINYLBENZYL CHLORIDE TER-POLYMER WITH 4,4'-DIHYDROXYSTILBENE.

A mixture of 4,4'-dihydroxystilbene (64mg, 0.3mmol, 1%), polymer **(41)** (3.00g, 30mmol) and sodium hydride (80mg, 2mmol) were stirred in dry DMF (30ml) at room temperature for 24 hours. The cross-linked polymer which formed, was filtered off and washed successively with 10% sulphuric acid, water and THF, then dried.

Yield: 95% IR: ν/cm^{-1} (KBr disc) 1600 (aromatic), 1270 and 680 (CH_2Cl)

7.4 CHEMICAL MODIFICATION OF CROSS-LINKED POLYMERS.

7.4.1 QUATERNISATION OF A NETWORK WITH RESIDUES (46) WITH TRIMETHYLAMINE. [130]

The cross-linked polymer **(46)** (10.0g, 100mmol) and trimethylamine (12.0ml, 91.2mmol of a 45% solution in water) in DMF (200ml) were heated at 100°C for 4 days. The cross-linked polymer was then filtered off, washed with water and THF and finally dried to yield the required quaternised network with residues **(24)** Yield: 14.92g IR: ν/cm^{-1} (KBr disc) 3210 (NH stretch), 1600 (aromatic), 1401(NH deformation) no signals were observed at 1270 and 680. Bands at these frequencies are characteristic of chloromethyl residues.

7.5 CYCLISATION REACTIONS USING POLYMER SUPPORTS.

7.5.1 POLYMER-SUPPORTED CYCLISATION OF 11-BROMOUNDECANOIC ACID USING AMBERLYST A26. [121]

a) Sodium hydroxide (2.33g, 41.5mmol) in water (50ml) was added to 11-bromoundecanoic acid (5.00g, 41.5mmol) in diethyl ether (50ml) the resulting two phase solution was shaken for 15 minutes and then the aqueous phase was

washed with diethyl ether. Amberlyst A26 resin (5.00g) was suspended in the aqueous phase and shaken for 18 hours. The resin was filtered off, washed with water (100ml), dried over phosphorous pentoxide under vacuum at room temperature for 2 days and re-weighed.

Mass of resin: 6.83g Increase in mass due to loaded monomers: 1.83g

b) The loaded resin was suspended in toluene (50ml) and heated at 60°C for 24 hours. The resin was then filtered off and washed with toluene (100ml) and chloroform (200ml). The combined washings were evaporated to dryness under reduced pressure to yield a white solid.

Yield: 1.07g ^{1}H nmr (δ/ppm): 4.05 (2H, s, CH_2), 2.30 (2H, t, CH_2) and 1.27 (16H, s, CH_2) GPC data is discussed in section 2 results and discussions.

c) After removal of the soluble product from (b), the resin was suspended in toluene (50ml) and methyl iodide (2ml) was added. The resulting suspension was heated under reflux at 110°C for 24 hours. The resin was filtered off and washed with toluene (50ml) and chloroform (150ml). The combined washings were evaporated to dryness under reduced pressure to give linear methyl 11-bromoundecanoate.

Yield: 460mg Mass spec M^+/Z 310 ^{1}H nmr (δ/ppm): 3.65 (2H, t, CH_2), 2.30 (2H, t, CH_2) and 1.27 (16H, s, CH_2) GPC data is discussed in section 2 results and discussions

7.5.2 POLYMER-SUPPORTED CYCLISATION OF 11-BROMOUNDECANOIC ACID USING A NETWORK WITH RESIDUES (24).

The same method was followed as for the polymer-supported cyclisation of 11-bromoundecanoic acid using amberlyst A26 with one addition. After the reaction of the resin with methyl iodide the resin was washed with aqueous saturated sodium chloride solution for 3 days, dried at room temperature under vacuum and re-weighed.

Table 16 : Cyclisations of 11-Bromoundecanoic Acid using Network with Residues (24)

Reaction Solvent	Mass of loaded monomers	Mass of cyclics	Mass of linears	Mass increase of resin
Toluene	1.00g (4.4mmol)	0.41g (2.2mmol)	0.25g (0.9mmol)	120mg
Chloroform	1.18g (5.2mmol)	0.58g (3.2mmol)	0.22g (0.8mmol)	45mg
THF	0.93g (4.1mmol)	0.46g (2.6mmol)	0.12g (0.4mmol)	20mg

In all above cases the starting mass of the resin was 2.00g.

7.5.3 REPETITION OF THE CYCLISATION OF 11-BROMOUNDECANOIC ACID USING NETWORK WITH RESIDUES (24).

The resin which had been cyclised in toluene was re-loaded and the cyclisation repeated a further two times.

Table 17 : Repetition of the Cyclisation using Network with Residues (24).

Repetition	Mass of loaded monomers	Mass of cyclics	mass of linears	Mass increase of resin
1	1.00g (3.8mmol)	0.41g (2.2mmol)	0.25g (0.9mmol)	220mg (1.2mmol)
2	1.07g (4.0mmol)	0.46g (2.5mmol)	0.21g (0.8mmol)	170mg (0.9mmol)
3	1.20g (4.5mmol)	0.62g (3.4mmol)	0.24g (0.9mmol)	90mg (0.5mmol)

(spectroscopic data is as for the initial cyclisation shown in section 7.5.1)

7.6 DEGRADATION OF 4,4^{l}-DIHYDROXYSTILBENE CROSS-LINKED POLYMERS

7.6.1 OZONOLYSIS OF A NETWORK WITH RESIDUES (46)

The same method was followed as for the ozonolysis of linear polymers except that the ozone mixture was bubbled through a suspension of a network with residues **(46)** in chloroform at -78° C for 14 days. The ozonide was worked up to give aldehyde end-groups. This gave no soluble material.

7.6.2 DEGRADATION OF A NETWORK WITH RESIDUES (46) USING OSMIUM TETROXIDE.

Osmium tetroxide (1ml, 39μmol) of a 1% solution in tert-butanol, was added to a suspension of a network with residues **(46)** (1.00g, 8.3mmol) and tetrabutylammonium periodate (12.5g, 39mmol) in chloroform (50ml). This was stirred under a nitrogen atmosphere in a sealed flask for 3 days. The resulting solution was filtered through celite to remove the remaining osmium tetroxide and the filtrate was evaporated to dryness under reduced pressure to give soluble linear poly(styrene/vinylbenzyl chloride) **(52)** with aldehyde end groups.

Yield 97% was retrieved as soluble material IR: ν/cm^{-1} (evaporated film) 3025 (CH), 2923 (CH_2), 2851 (CH), 1713 C=O , aldehyde), 1601 (aromatic) ^1H nmr (δ/ppm): 7.3-6.8 (3H, b, aromatic), 6.8-6.4 (2H, b, aromatic), 2.1-1.7 (1H, b, CH), 1.7-1.3 (2H, b, CH_2)

7.6.3 DEGRADATION OF A NETWORK WITH RESIDUES (24) USING OSMIUM TETROXIDE

The same method was used as for the degradation of network with chloromethylstyrene residues except that sodium periodate was used instead of tetrabutylammonium periodate and water was used as solvent instead of chloroform.

Yield 94% was retrieved as soluble material IR: ν/cm^{-1} (evaporated film) 3025 (CH), 2923 (CH_2), 2851 (CH), 1713 C=O , aldehyde), 1601 (aromatic) ^1H nmr

(δ/ppm): 7.3-6.8 (3H, b, aromatic), 6.8-6.4 (2H, b, aromatic), 2.1-1.7 (1H, b, CH), 1.7-1.3 (2H, b, CH_2)

7.6.4 DEGRADATION OF A LOADED NETWORK WITH RESIDUES (24) USING OSMIUM TETROXIDE

The same method was used as for the degradation of a network with residues **(24)** except that DMF was used as solvent instead of chloroform in order to ensure the solubility of both the resulting quaternised linear polymer and any "Trapped Cylics" that may be released.

CHAPTER 8

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