Cyclodextrins as Core Molecule in Supramolecular Assemblies and as Molecular Reinforcers in Polymer Coatings

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Contents

ABSTRACT

The inventions performed and discussed in this thesis relate in its entirety on cyclodextrins and cyclodextrin related compounds. Along the whole study, all the efforts were put in trying to exploit enormous opportunities that this biomolecule offers with synthetic chemistry.

Cyclodextrin-mediated polymerization of hydrophobic monomers, owing to the well-documented ability of the CDs to form inclusion complexes, in aqueous solutions has been exploited in this work. Physically-linked molecular structures namely, rotaxanes, opens a new window for polymer scientists in terms of polymer topology. As molecular composites, polyrotaxanes have indeed become an active field of research. This research also involves the development of mechanically interlocked polymer networks that incorporate CDs as one of their (ring) components. Difunctional acrylate and methacrylate monomers are complexed with CDs and polymerized in water leading to crosslinking systems incorporating CD. The discriminating influence of two kinds of cyclodextrins, α and β on the complexation and polymerization of afore mentioned monomers are studied. The complexes are analyzed by means of ^{1}H NMR, 2D ROESY spectroscopy and Job's curves which clearly revealed the discriminating characteristics of the two hosts towards complex formation. The obvious possibility of the smaller α-CD to form solid complexes leads to molecular packing structures of CD complexes in crystals. The crystal packing is determined by X-ray spectral analysis. More confirmations into the formation of interlocked polyrotaxanes are gathered from more spectral and thermal characterization. Relative spectral shifts in IR and a vast difference in T_g values of the interlocked polyrotaxanes as compared to their respective control polymers are recorded.

Taking steps further away from the conventional synthetic methodologies, this work has concentrated on utilizing microwave induced syntheses. An approach is to obtain new classes of both linear and branched polyrotaxanes, incorporating microwave assisted synthesis. The ring-opening polymerizations of ε-caprolactone in the vicinity of polymerizable cyclodextrins are monitored under microwave irradiation. A simultaneous ring-opening of the cyclic ester and a coupling reactions to the CD core is

observed, which results into the formation of a star polymer. GPC elugrams even revealed interesting insights into the formation of self-assemblies with time. Structure elucidations of the self-assemblies are performed by a competing complexation with adamantine as guest, which prevented any self-assembling by blocking the CD cavity. The effects of microwave energy into the formation of rotaxane and super structures by self-assembly is observed and are compared to similar reactions performed in conventional oil-baths. Trends in intrinsic viscosities of the star molecule and the supramolecule at precise intervals are recorded against reference poly(ε-caprolactone) that provided additional inputs into the entire reaction characteristics. Thermals analysis for each of the molecular species formed, served with influential confirmations. A total comparative study with respect to differently substituted CDs (hydroxypropyl and dimethyl) is carried out that provides a basis for understanding the mechanical and structural aspects of the supramolecules formed. A star polymer formation never occurred with the latter CDs, for many reasons, while an obvious complexation of the poly(ε-caprolactone) chains is evident with either of the alkyl substituted CDs.

An associated work on cyclodextrins involves the construction of novel functional polymeric systems of CDs that can be covalently incorporated into a polymer matrix. In effect, such functionalized CDs can serve as reinforcement in polymeric materials, especially coatings. When polymerizable cyclodextrins (PCDs) are incorporated into a polymer chain, molecular interactions between the polymer matrix and the rigid CD molecule comes into play. During this study on molecular reinforcing properties of CD, a variety of CD derivatives are prepared and mixed on to different polymer binder systems. Appropriately functionalized CDs incorporated into a coating in specified amounts produced crosslinked products, anchoring the polymer chains intact. The high crosslink density of these polymers gives greater strength, durability and dimensional stability. Evaluation of these coatings regarding their elasticity, hardness, scratch and chemical resistance are compared. A CD incorporated polymer coating is found to exhibit appreciable overall performance, suggesting a perfect substitute to conventional reinforcing systems.

1. Introduction

1.1 Concept of Supramolecular Chemistry

Supramolecular chemistry is a highly interdisciplinary field of science covering the chemical, physical and biological features of certain chemical species of greater complexity than molecules themselves that are held together and organized by means of intermolecular (non-covalent) binding interactions [1-3]. As defined by one of its leading proponents, Jean-Marie Lehn, a Nobel laureate, it is the "chemistry of molecular assemblies and of intermolecular bond" or more colloquially as the "chemistry beyond the molecule". Supramolecular species are characterized both by the spatial arrangement of their components, their architecture or suprastructure, and by the nature of the intermolecular bonds that holds these components together [4-6]. Various types of interactions may be identified, that offers different degrees of strength and directionality to the supramolecule. They could be electrostatic forces, hydrogen bonding, van der Waals interactions, donor-acceptor interactions etc [1,7,8].

A supramolecular self-assembly concerns the spontaneous association of either a few or many components resulting in the generation of either discrete oligomolecular supramolecules or of extended polymolecular assemblies. In its simplest sense it involves a kind of binding (non-covalent) or complexation event between two entities – a host and a guest [9-12]. Tremendous progress has been made, from the statistical and uncertain procedures of bygone days, to the predesigned and predictable syntheses based on molecular recognition phenomena, in host-guest chemistry of the present day.

1.2 Host - Guest Chemistry

A complexation event could be considered when a molecule (a 'host') binds another molecule (a 'guest') to produce a host-guest complex or a supramolecule. Commonly, the host is large molecule or aggregate such as an enzyme, or synthetic cyclic compound possessing a sizeable, central hole or cavity and the guest can be either a monoatomic cation, a simple inorganic anion or even sophisticated molecules like hormones, pheromones etc [13]. Formally, a host is defined as the molecular entity possessing

convergent binding sites and the guest possesses divergent binding sites. The resulting host-guest complex composes either of the constituents held together in unique structural relationships by electrostatic forces other than those of full covalent bonds [14-17].

A key division within host-guest systems relates to the stability of the host-guest complex in solution and to the topological relationships between the guest and host. *Cavitands* are hosts possessing intramolecular cavities which are strictly an intramolecular property of the host and exists both in solution and solid state. Conversely, *clathrands* possess extramolecular cavities, often a gap between two or more hosts, that is relevant in crystalline or solid state (Figure 1.1) [12,16-18].

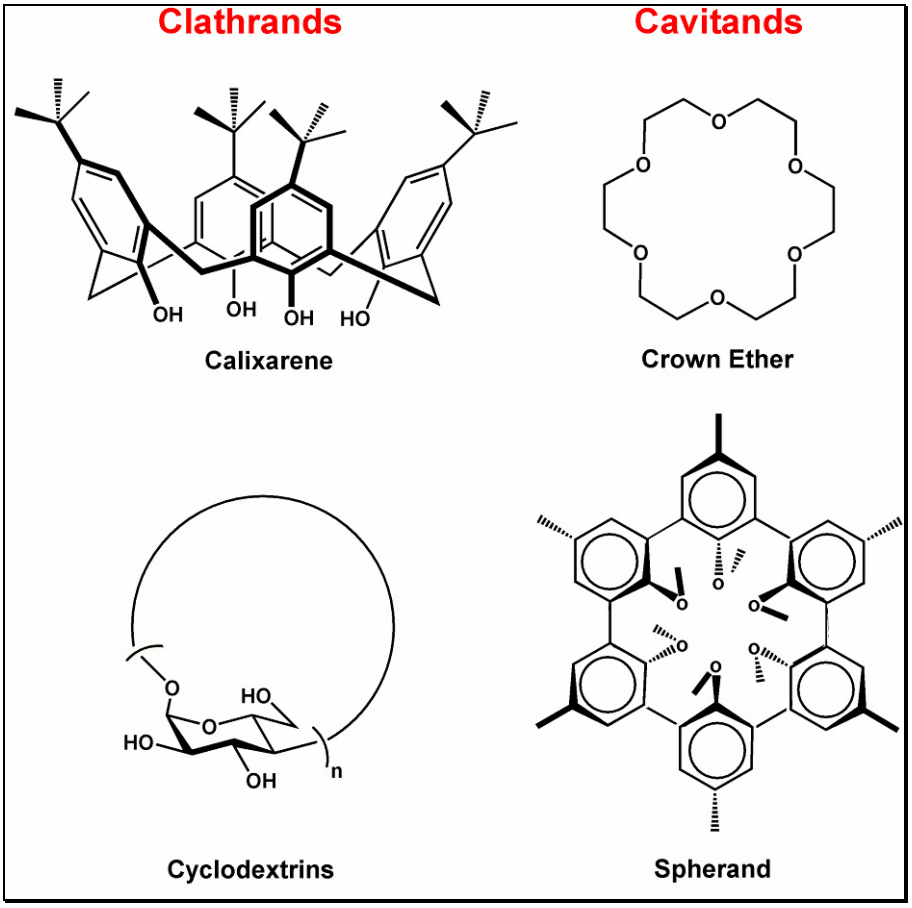


***Figure 1.1**: Classification of neutral host-guest compounds*

1.3 Cyclodextrins as Supramolecular Hosts

Among all potential supramolecular hosts, cyclodextrins (CDs) seem to be the most important ones, for the following reasons [19-22]:

(1) They are seminatural products, produced from a renewable natural material, starch, by a relatively simple enzymic conversion.
(2) They are produced in thousands of tons per year by environmentally friendly technologies.
(3) High production led to their initially high prices dropping to levels where they become acceptable for most industrial purposes.
(4) Any of their toxic effect is of secondary relevance and can be eliminated by selecting the appropriate CD type or derivative or mode of application.
(5) Consequently, CDs can be consumed by humans as ingredients of drugs, foods, or cosmetics.

Befittingly, naturally occurring cyclodextrins were the first receptor molecules whose binding properties towards organic molecules were recognized and extensively studied, yielding a wealth of results on physical and chemical features of molecular complexations.

1.3.1 Cyclodextrins: Structural and Functional Features

Cyclodextrins (CDs), as they are known today, were called cellulosines when first described by Villiers in 1891, islolating it by digesting starch from certain enzymes of bacterial origin, *Bacillus macerans* being the earliest source. Later, Schardinger identified the naturally occurring analogues and were referred to as Schardinger sugars [22-23].

Cyclodextrins are cyclic oligosaccharides comprising usually, six to eight D-glucopyaranoside units, linked by a 1,4-glycosidic bond. The three most important members of the cyclodextrin family are α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin, which possess, respectively 6, 7 and 8 glucopyranoside units. The shape of a CD ring is of a tapering torus or truncated funnel. The primary hydroxyl groups are located on the narrow end of the torus and secondary hydroxyl groups on the broader side. The six-membered D-glucopyranoside rings are linked edge to edge, with their faces all pointing inwards, towards a central hydrophobic cavity of varying dimensions. A functional scheme of cyclodextrin anatomy along with the cavity sizes is shown in Figure 1.2 [20,23,24].

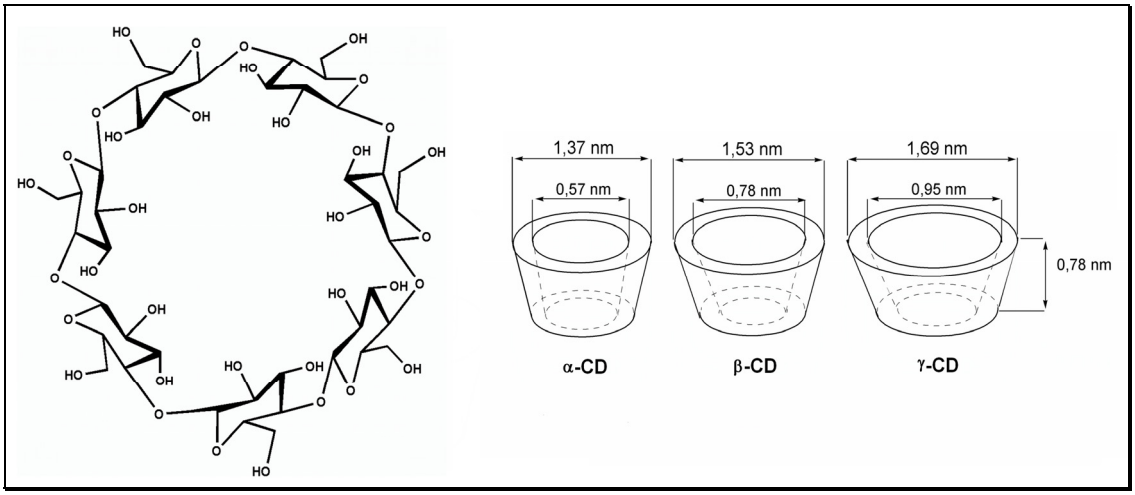


***Figure 1.2**: Structure of β-CD and geometric dimensions of α-, β-, and γ-CD molecules*

Apart from those previously mentioned reasons, there are a set of structural and functional features that makes CDs a preferred candidate in host-guest complexations (Figure 1.3). They could be summarized as follows:

(1) Steric complementarity
(2) Interactional complementarity
(3) Large contact areas
(4) Multiple interaction sites
(5) Strong overall binding

These are obvious reasons for cyclodextrins to serve as organic host molecules, wherein the internal cavity is able to accommodate one or two guest molecules. Conversely, suitable guest molecules can also be used to thread one, two or many CD rings in solution resulting in certain supramolecular structures. This opens up an area of mutually interlocked and intertwined molecular architectures, the existence of which had not been realized until relatively recent times [25-27].

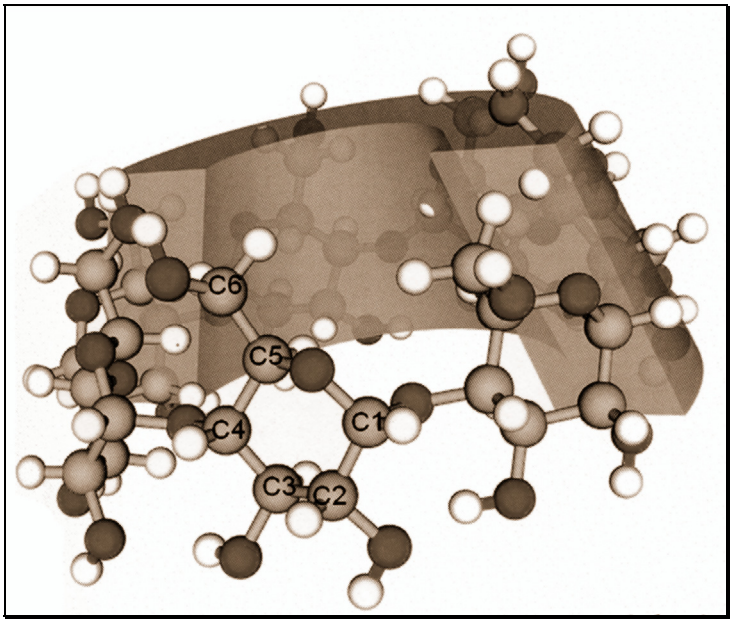


***Figure 1.3**: X-ray model showing position of atoms in β-Cyclodextrin*

Rotaxanes catenanes and have captured the imaginations of a wide spectrum of the scientific community not only because of their undisputed beauty, but also a result of the potential applications that might be addressed by incorporating the aspect of entanglement into chemical systems [28-30]. For this reason, as well as for the improved methods of their synthesis, the last few years have witnessed an explosion in research carried out into the creation of rotaxane and catenane superstructures.

1.4 Rotaxanes and Catenanes

Catenanes, from the Latin *catena* meaning chain, are molecules which contain two or more interlocked rings, which are inseparable without the breaking of a covalent bond. Rotaxanes, from the Latin *rota* meaning wheel, and *axis* meaning axle, are comprised of a dumbbell-shaped component, in the form of a rod and two bulky stopper groups, around which there are encircling macrocyclic components. The stoppers of the dumbbell prevent the macrocycles unthreading from the rod. When these stopper groups are absent from the ends of the rod, or if the bulky groups are of insufficient size to stop equilibration of the bead, we refer to the corresponding complexes as pseudorotaxanes (Figure 1.4) [31-34].

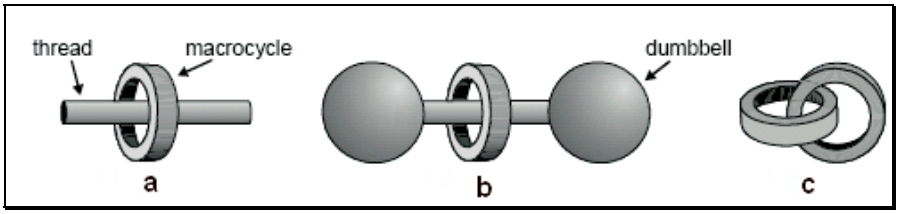
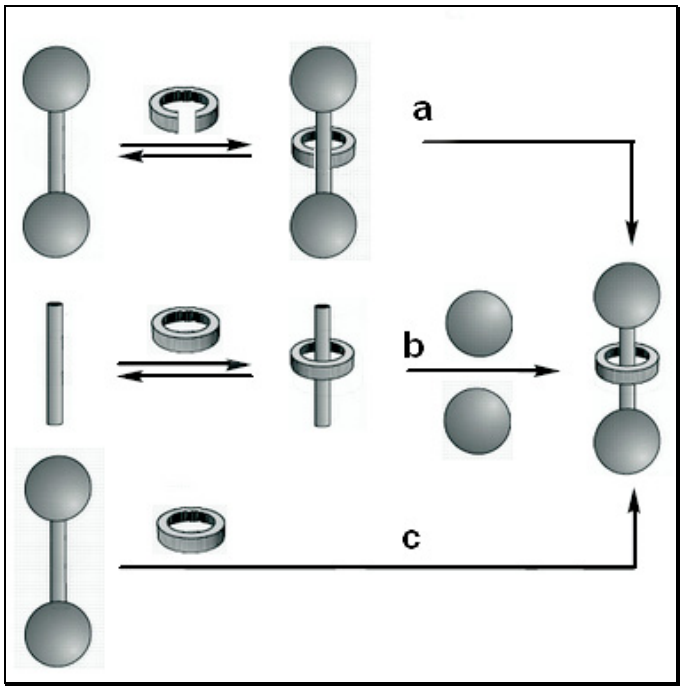


***Figure 1.4**: Schematic representation of (a) pseudorotaxane, (b) rotaxane and (c) catenane*

The current work primarily focuses on rotaxanes and pseudorotaxanes based on cyclodextrins which shall be discussed specifically thenceforth.

1.4.1 Cyclodextrin-Based Rotaxanes and Pseudorotaxanes

The well-documented ability of the parent CDs to form inclusion complexes with a very wide range of guest species in aqueous solutions has been exploited in the construction of rotaxanes and pseudorotaxanes. However, there exists only a thin line between rotaxanes and pseudorotaxanes enabling similar synthetic approaches.



***Scheme 1.1**: Different approaches to rotaxane synthesis:(a) "clipping" (b) "threading" (c) "slippage"*

At least three different mechanisms for the construction of rotaxanes can be identified (Scheme 1.1) [35-37]. Although the "clipping" approach (a) is not an efficient way to the self-assembly of CD-containing rotaxanes, both the "threading" (b) approach and "slippage" (c) approach appear to provide possible mechanisms, particularly since the CDs possess remarkable abilities to form inclusion complexes with a very wide range of guest molecules in aqueous media. The different cavity sizes of the CDs (ca. 5.7, 7.8, and 9.5 Å for α-CD, β-CD, and γ-CD, respectively) assist in this broad spectrum of guest molecular recognition [38-40].

A few examples of cyclodextrin-based rotaxanes considering the diversity of possible structures and on the method employed can be discussed further.

The idea of self-assembling rotaxanes, incorporating CDs as the ring components, was achieved for the first time by using transition metal complexes as "stoppers" at the ends of bisfunctionalized threadlike guests encircled by the CDs. In 1981, Ogino reported the use of the reaction between *cis*-$[CoCl_2(en)_2]Cl$ (en denotes ethylenediamine)and α,ω-diaminoalkanes as a way to construct the dumbbell components of rotaxanes incorporating either α-CD or β-CD (Figure 1.5) [41,42].

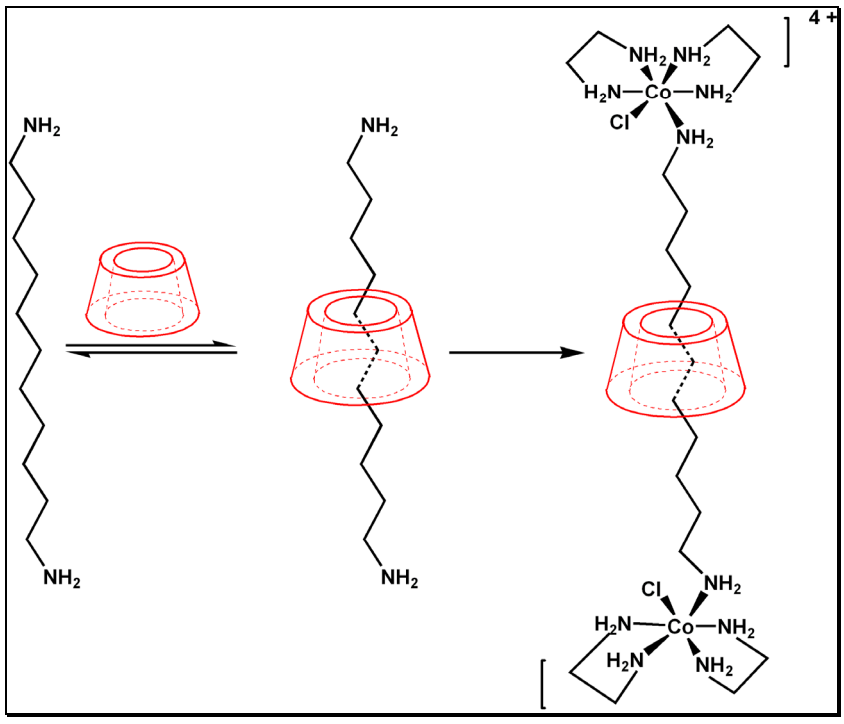


***Figure 1.5**: Self-assembly of a rotaxane using a "threading" procedure*

CD-based rotaxanes incorporating dumbbell components with "stoppers" covalently linked to the threads could be considered the ultimate molecular structures in view of their unquestionably higher stabilities. However, since the covalent bond-forming reactions have to be carried out in aqueous solutions, the efficient attachment of "stoppers" to "threads" when they are complexed by CD rings is quite a challenge.

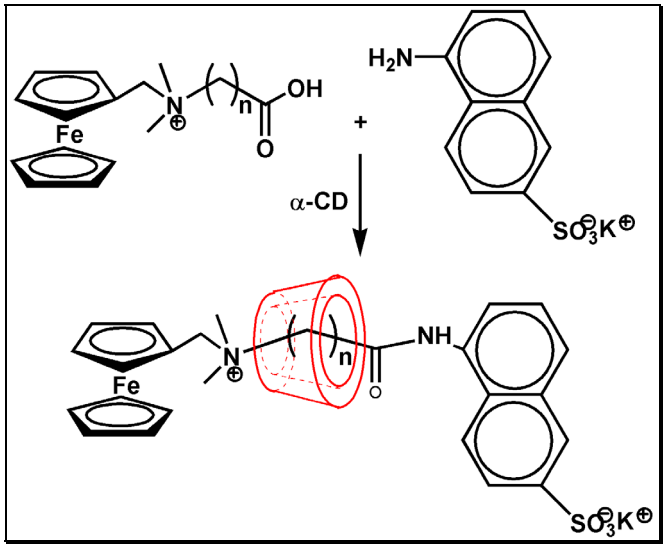


***Figure 1.6**: Self-assembly of zwitterionic rotaxanes using a "threading" procedure*

Employing functional groups with relatively high nucleophilicities -such as NH_2 or S^- at the termini of the "threads" is one possible solution to this problem. In one such reaction, a carboxylic acid polymethylene chain is attached via a tetrasubstituted ammonium site to a ferrocenyl methyl unit which ultimately serves as one of the "stoppers" in the rotaxanes. The other "stopper" is derived from potassium 5-amino-2-naphthalensulfonate which forms amide bonds in water with carboxylic acid terminated polymethylene chain (Figure 1.6) [43-45].

Pseudorotaxanes with considerable lifetimes can be achieved by increasing the steric bulk of the "stoppers" on the dumbbell components up to sizes that match closely the diameters of the CD cavities (Figure 1.7). A pseudorotaxane of α-CD of that kind has been described recently where a "slippage" mechanism is attempted [46,47].

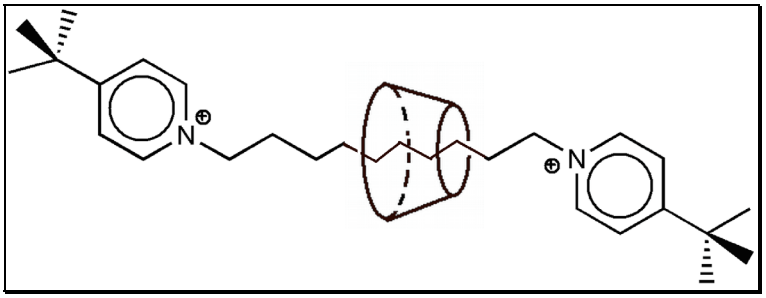


***Figure 1.7**: a-CD based rotaxane prepared using a "slippage" procedure*

A rather unique kind of superstructure has been observed in the solid state for a monosubstituted β-CD derivative that behaves both as a host and as a guest, such that a $-CH_2NH(CH_2)_6NH_2$ side chain on the primary face of one molecule enters into the cavity of the β-CD ring of a neighbouring molecule and so on in a linear fashion (Figure 1.8). The monosubstituted β-CD derivatives are arranged spirally, forming a polymer-like superstructure [48-50].

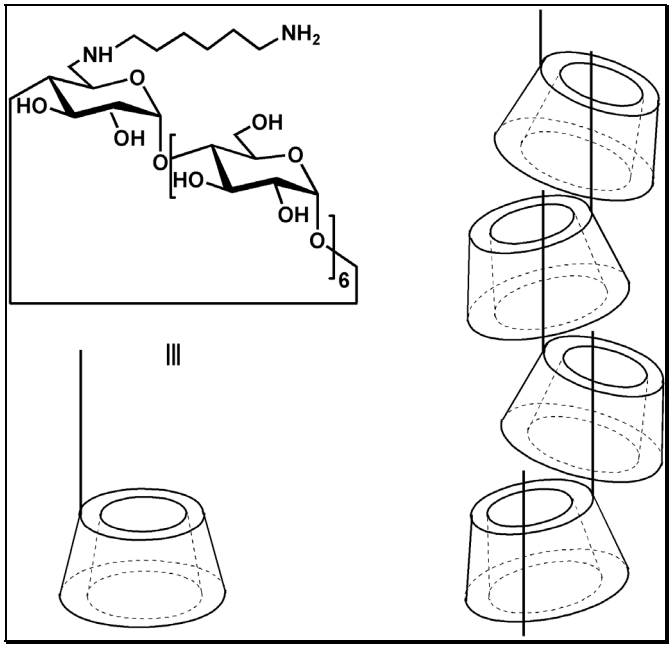
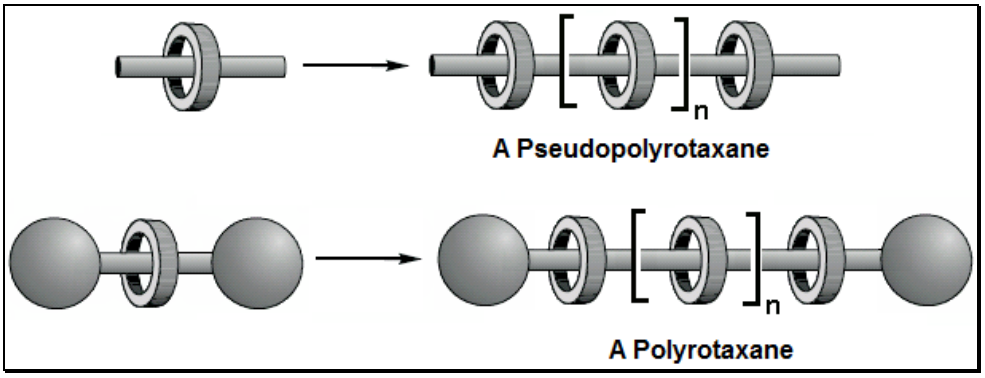


***Figure 1.8**: Structural formula of a monosubstituted β-CD (left) that forms a continuous supramolecular polymer.*

1.4.2 From Rotaxanes to Polyrotaxanes and Pseudopolyrotaxanes

It is appreciated that, the most obvious way to prepare a rotaxane from a pseudorotaxane is to attach a bulky substituent group to the open

ends of the threaded molecule. Evidently, pseudorotaxanes are considered necessary precursors to rotaxanes and any boundary between them are not well-defined. Thus, a species which is a rotaxane at ambient temperature might well be a pseudorotaxane at elevated temperatures. Even a solvent change can turn a rotaxane into a pseudorotaxane at the same temperature.



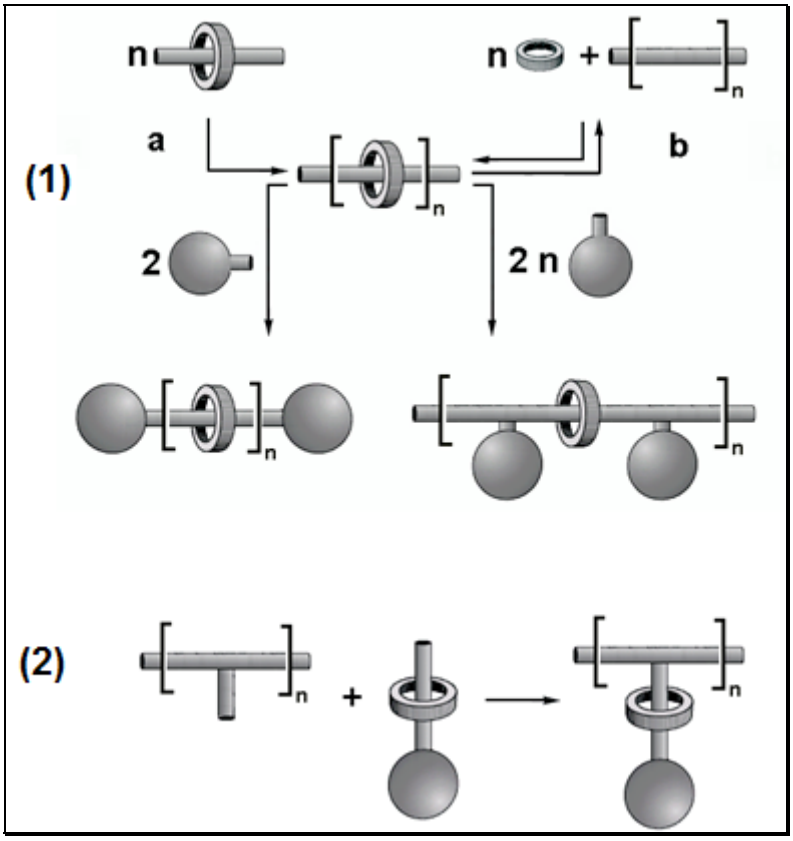
***Scheme 1.2**: Polymeric systems due to rotaxanation*

Interestingly, the two interlocked macrocycles opens up possibilities to their polymeric counterparts, creating supramolecular interlocked architectures at the macromolecular level. A clear illustration of such Polyrotaxane and Pseudopolyrotaxane polymeric systems can be represented as in Scheme 1.2 [25].

1.4.3 Polyrotaxanes and Pseudopolyrotaxanes of Cyclodextrins

Polyrotaxanes can be prepared by reaction between axial polymeric inclusion compounds with blocking groups or by polymer-analogous reactions of polymers with monomeric inclusion compounds. In the former case the rotaxane axis lie along the polymer main chain while in the latter they branch off from its side chains.

These two kinds, main-chain polyrotaxanes and side-chain polyrotaxanes, can be clearly demonstrated as in Scheme 1.3, considering the synthetic approaches employed to obtain either of them [51-53]



***Scheme 1.3**: (1) Two different routes 'a' and 'b' for main-chain and (2) side-chain polyrotaxanes from the appropriate components*

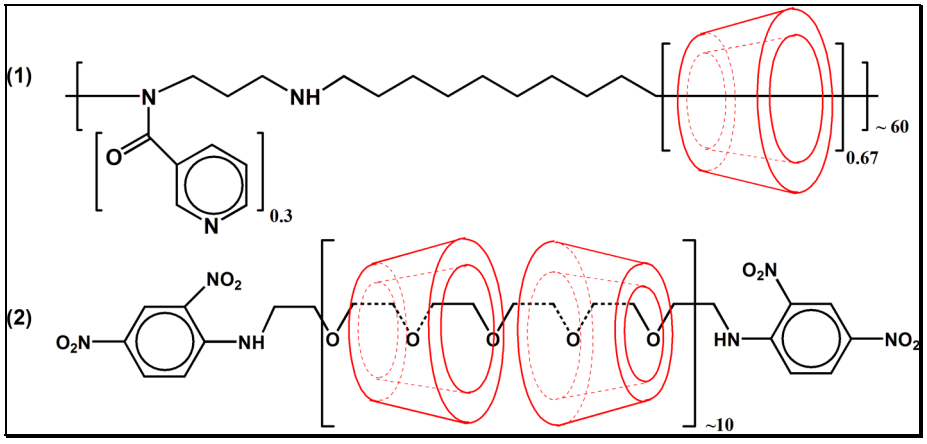


***Figure 1.9**: Main-chain polyrotaxanes with (1) a smaller and (2) a larger blocking group*

Wenz and Keller reported water-soluble main-chain α-CD and β-CD based polyrotaxanes with polyamines (poly(iminoundecamethylene) and poly(iminotrimethylene iminodecamethylene) by partial polymer-analogous reaction of the amino groups with nicotinoyl chloride. In the case of β-CD, the nicotinoyl groups are too small to block the larger ring cavity, and larger

blocking group like 2,4-dinitro 5 aminophenyl groups were used instead [54,55]. A similar polyrotaxane with about twenty rings on the main chain by reacting the terminal amino groups of a polyethylene oxide was synthesized by Harada et al (Figure 1.9) [56]

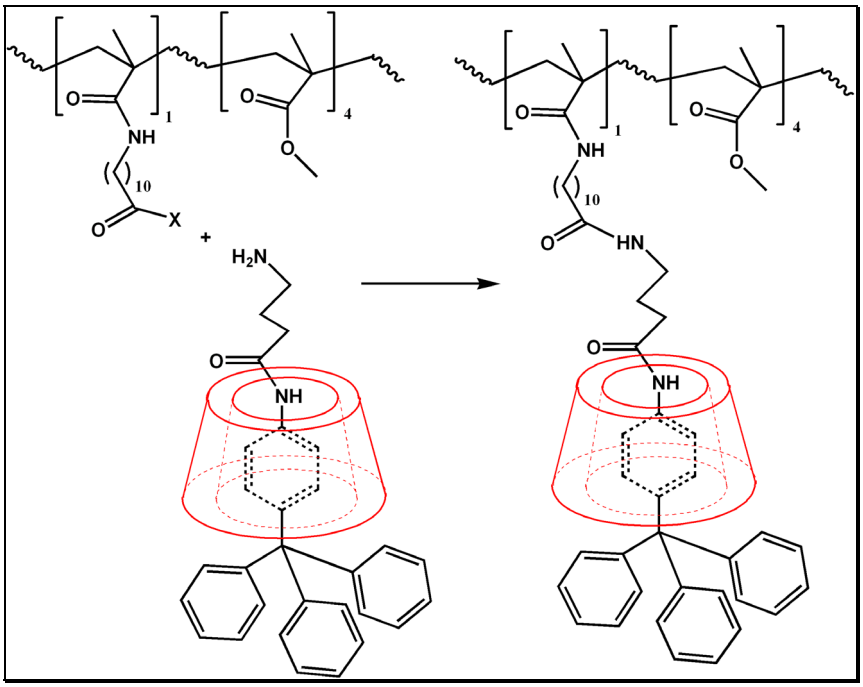


***Figure 10**: A side-chain polyrotaxane from methylated β-CD. (X = O-COOEt)*

In addition to the above main-chain polyrotaxanes, cyclodextrin was also successfully used for the preparation of side-chain polyrotaxanes. The first kind of side-chain polyrotaxanes were reported by this working group (Figure 1.10). Ritter et al. performed inclusion complexation of 2,6-di-*O*-methyl β-CD and a monofunctional stopper group as guest, in water and chloroform to afford a monorotaxane [57]. The isolated intermediate was then reacted with a preformed copolymer based on poly(methyl methacrylate) in organic solvents to derive side chain polyrotaxanes.

Harada and coworkers have done extensive research on cyclodextrin complexations with various polymeric backbones including poly(ethyleneoxide), poly(propyleneoxide) and polyisobutylene [58-59]. An identical polyrotaxane prepared from poly(ethyleneoxide) and α-CD created an extended column structure of stacked CD rings (Figure 1.11). To prevent threaded rings from slipping off the backbone, dinitrophenyl amino moieties were introduced at the chain ends as stopper [60]. The resulting polyrotaxane was used as a template to obtain tubular polymers by

treating with epichlorohydrin and subsequently cleaving the stopper function.

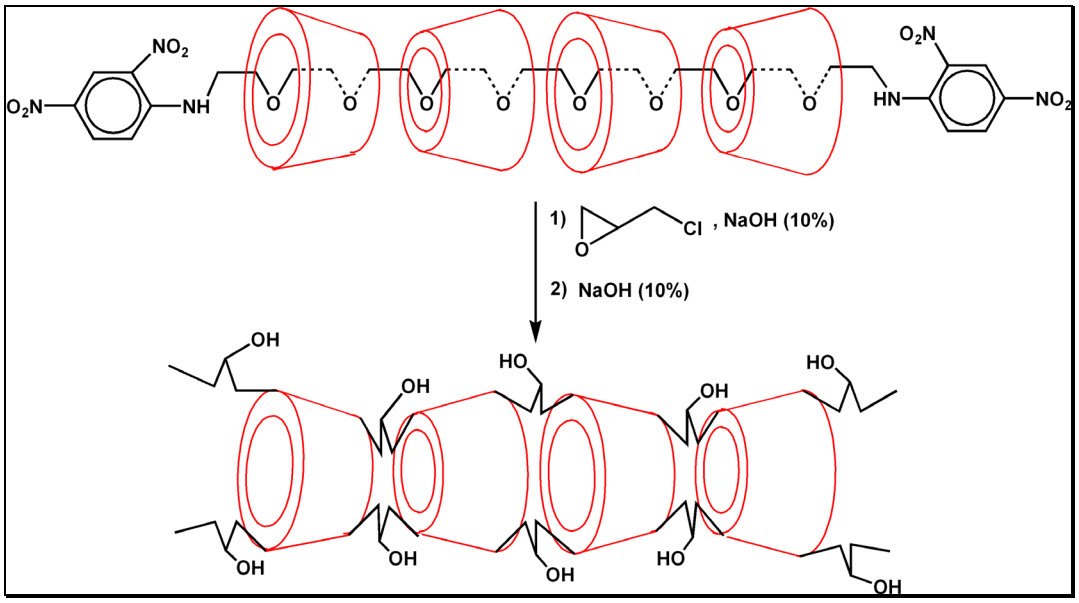


***Figure 1.11**: Synthesis of a tubular polymer of a-CD units from stacked polyrotaxane rings*

1.4.4 Cyclodextrins in Star Polymer Synthesis

An extension to the versatile research possible on cyclodextrins is in the field of star polymers and/or hyperbranched polymers. Star polymers attain significance primarily due to their lower solution and melt viscosities compared to analogous linear polymers with similar molecular weights [61-63]. Star polymers produced with the core-first method and with atom transfer radical polymerization (ATRP) as controlled radical polymerization have already been reported by few research groups [64,65]. The control of the architecture is obtained by the use of a well-defined core usually by this method.

Cyclodextrins are one of the best candidates as a core molecule, on account of its well-defined cyclic structure with fixed numbers of primary and secondary hydroxyl groups, which are utilized for selective modification. The substitutable hydroxyl groups on the peripheral surface of CD rings provide the possibility to make an initiator-core to form star polymers with varying number of arms [22,25].

Xiao et al reported a range of novel cationic star-like polymers through atom transfer radical polymerization (ATRP) by core-first method, using a β-cyclodextrin initiator with 21 initiation sites, based on the cationic monomer, [2-(methacryloyloxy)ethyl] trimethyl ammonium chloride (MeDMA) (Figure 1.12). Polymerization was performed in aqueous phase, using the cationic monomer MeDMA directly to eliminate the toxicity brought by a postquaternization procedure [66,67]. Moreover, the polymerization was well controlled to render the polymers water soluble for the sake of the biomedical applications. The synthesized cationic star-polymers are reported to have great potential as DNA vectors for gene therapy [68]. Starting from a similar CD macroinitiator, star polymers with polyelectrolyte arms that removes organic hydrophobic compounds as well as metal ions from polluted water was reported by Reynaud et al [69].

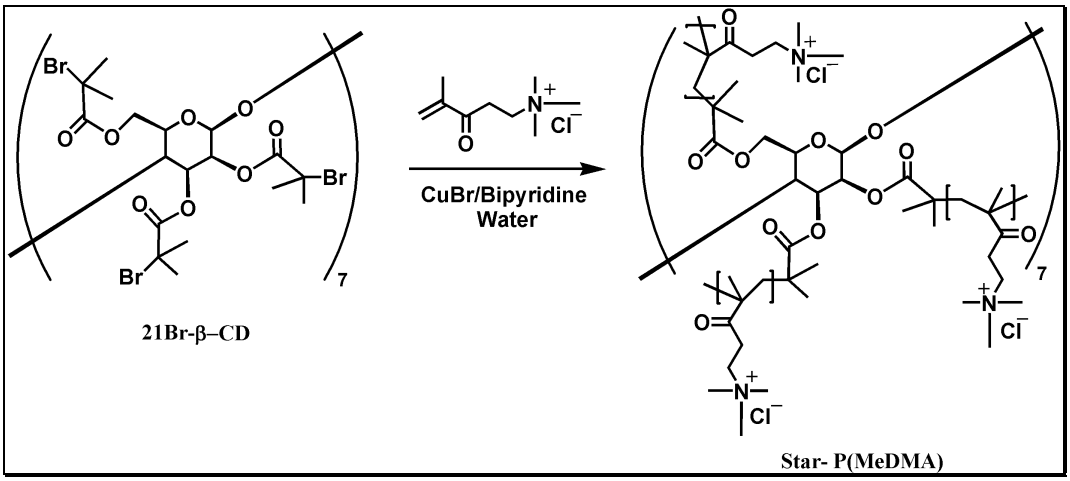


***Figure 1.12**: Synthesis of a 21 arm β-CD cationic star polymer*

Kakuchi et al extended controlled radical polymerization to the synthesis of a core-functionalized well-defined star polymer using a multifunctional initiator based on β-cyclodextrin (Figure 1.13). They synthesized acetylated β-CD bonded with TEMPO adducts at C-6 positions to obtain the seven arms multifunctional initiator [70,71]. Styrene was polymerized with the initiator to afford products with a trimodal molecular weight distribution. On fractionation the crude product yielded the desired star polymer, along with low molecular weight and high molecular weight byproducts. The star polymer on deacetylation formed a symmetric star with seven polystyrene arms at C-6 and 14 hydroxyl groups at C-2 and C-3.

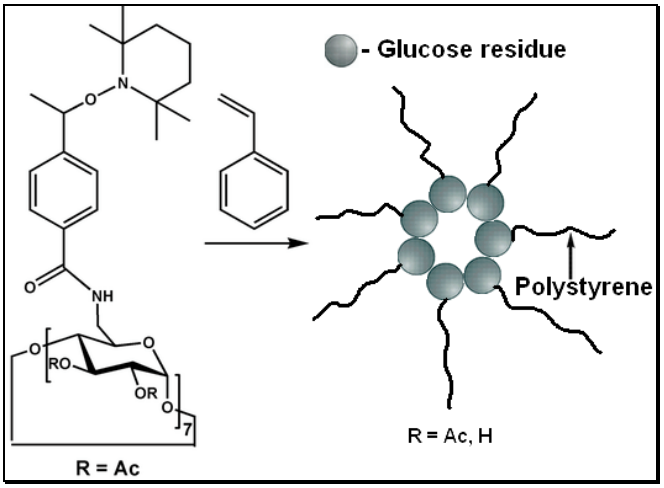


***Figure 1.13**: Seven-arm star polystyrene with β-CD core using TEMPO*

Stenzel et al extended the synthesis of polystyrene star polymers by RAFT polymerization, where the core of the stars comprised a trithiocarbonate heptafunctional β-cyclodextrin ring (Figure 1.14). Such a RAFT agent is dissolved in styrene by selectively protecting the remaining hydroxyl groups.

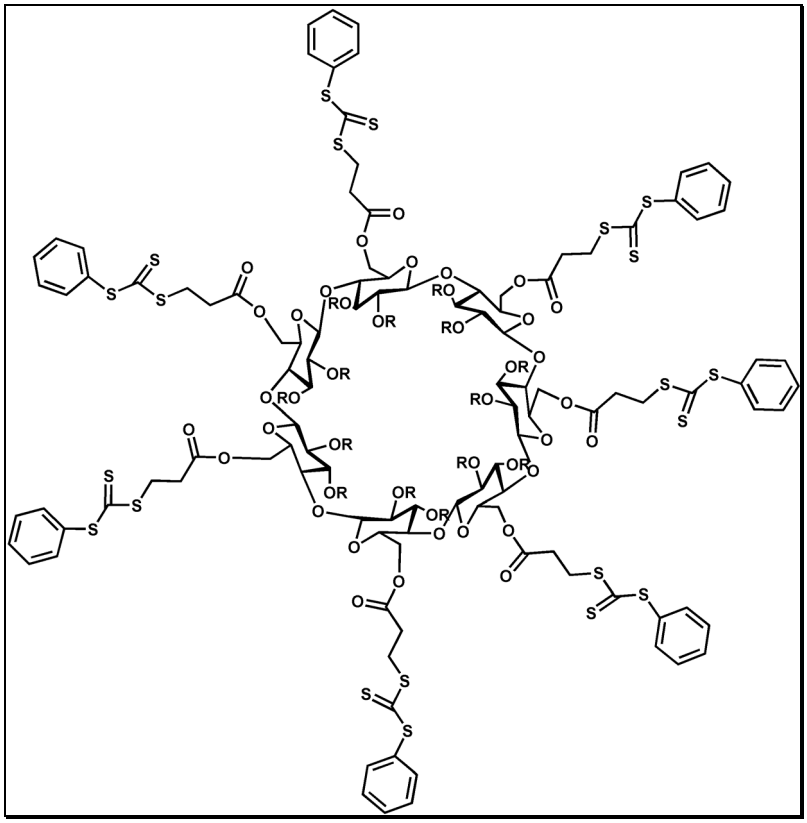


***Figure 1.14**: β-Cyclodextrin derived RAFT agent (R=Ac)*

The benzyl leaving group initiates polymerization with styrene accompanied by a transfer to the RAFT agent. As the polymerization proceeds as the RAFT agent transforms, so that the leaving group consists of a growing polymer chain [72].

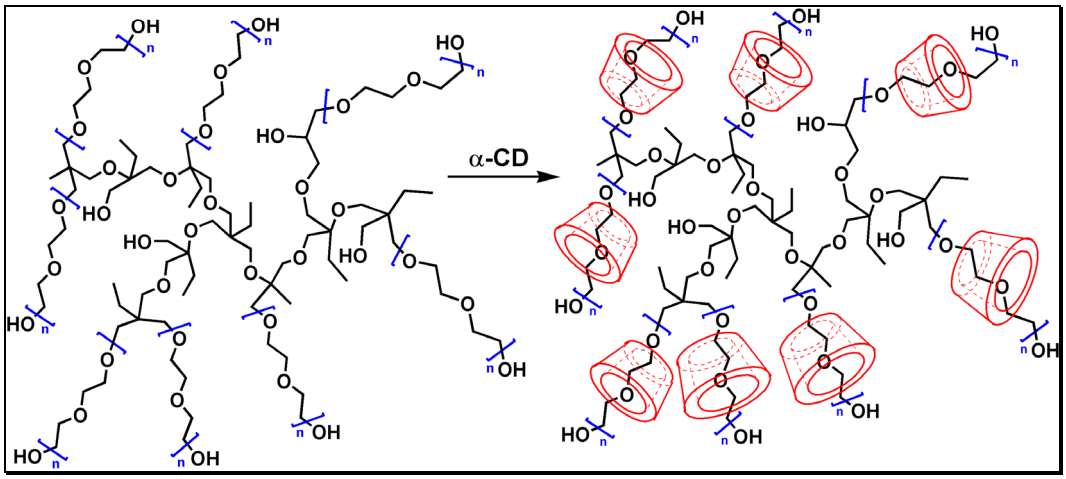


***Figure 1.15**: Synthesis of multiarm semipolyrotaxanes with a hyperbranched core*

On a different note, a new class of a new class of polyether-based semipolyroxatanes, multiarm inclusion complexes with hyperbranched cores, are prepared, and the inclusion complexation and supramolecular selfassembly processes are reported by a Chinese research group (Figure 1.15) [73]. A clear indication to the existence of noncovalent intermolecular forces between CDs and polymers that play a very important role in the formation of these complex architectures are evident in such a structure [74,75].

1.5 Concept of Molecular Reinforcement

High-stiffness high-strength polymer materials are always in demand for a broad range of applications. Routes towards such high performance polymers are achieved more commonly by the reinforcement of thermoplastic or thermoset matrices by fibers, whiskers or even particulates [76,77]. In simple terms, any discrete inclusions used to improve the structural characteristics of a material could be recognized as reinforcement. This method has been commonly employed combining plastics and reinforcers resulting in versatile materials with unusual

characteristics. On a macroscopic scale, reinforcements permanently combined with a material are referred to as composites. Promising efforts were accomplished of late, to introduce the idea reinforcement on a molecular level to design successful materials of so called “next-generation” polymeric materials [78,79].

The great potential of molecular reinforcement over fiber reinforcement, as innovative structural materials for industrial applications is largely due to the following main reasons [80].

(1) The processing of fiber reinforced materials is complicated, expensive and restricted, while guarantees fewer processing steps, easier access to isotropically reinforced materials and the use of a variety of processing techniques.

(2) Fiber reinforced materials are restricted in their application due to their inhomogeneity. Molecularly reinforced materials are characterised by their homogeneity, offering crucial advantages.

(3) Single molecule fibers behave as perfect fibers since the synthetic control of the chemical structure of single molecules will be easier than the minimization of fiber defects during the processing.

Molecular reinforcement procedure is thus regarded as a mere translation of fiber reinforcement to the molecular level where the adhesion between the fiber and the matrix is replaced by molecular interactions between a matrix and rigid molecules. Nevertheless, the parameters accountable for reinforcement in the former case, like the aspect ratio (length/diameter), play the same role with the rigid molecules in molecular reinforcement. The underlying assumption is that a rigid molecule dispersed in a polymer matrix will lead to an increase of modulus along its direction of orientation in a way similar to the case of a macroscopic fiber [81,82].

Computer simulations on the basis of a force field approach are used to test the concept of molecular reinforcement and to get an insight into the factors controlling the reinforcement effect. The finding is that molecular reinforcement may be as effective as fiber reinforcement. Additionally, these calculations have predicted the demand for intrinsically rigid rods for effective molecular reinforcement. Rigid rods as single molecule fibers hold the key to exchange Van der Waals interactions by covalent bonds as the molecular origin for strength and stiffness. Stiffness and strength values, which can be obtained by covalent bonds, may be increased by several orders of magnitude in relation to properties based on Van der Waals

interaction. In Figure 1.16 some suitable rigid segments that most sources tend to use for reinforcement are displayed [83-86].

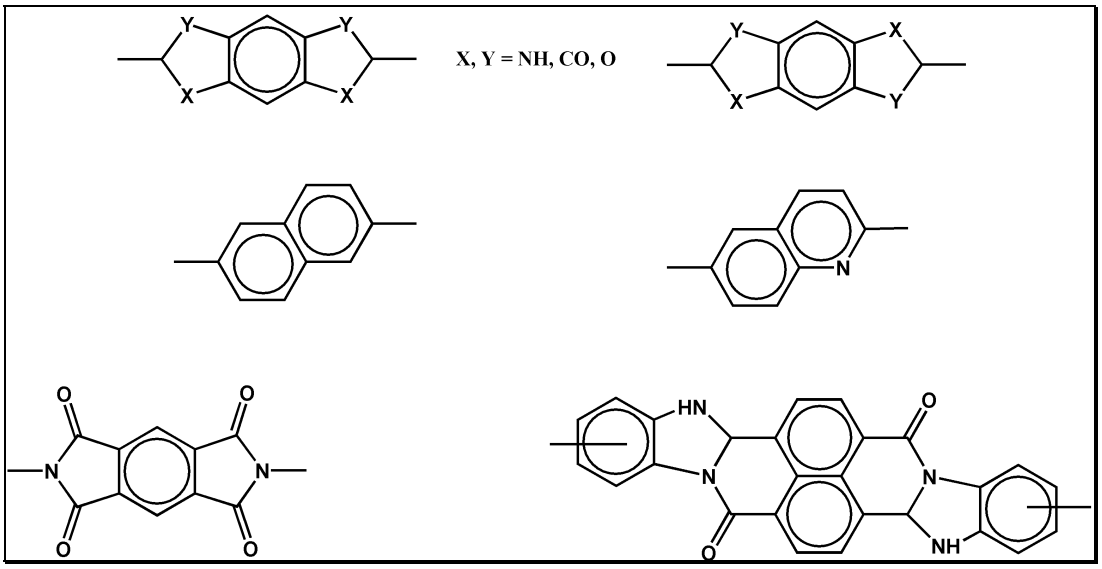


***Figure 16**: Examples of rigid segments to build up intrinsic rigid-rod molecules*

1.5.1 Advanced Structures for Molecular Reinforcement

The experimental verification of the concept of molecular reinforcement often turns out to be a tedious task. The principal obstacle which has to be circumvented in this approach is the inherently string immiscibility of rigid and flexible chain molecules originating from entropy effects. Yet, there are ways around this problem. These involve, among others, the introduction of side chains of specific interactions or copolymerization between the constituent segments. The concept to use covalent bonds between flexible and rigid components to hinder or even to rule out the molecular mobility, which determines a phase separation, leads also to the idea to use network structures. Indeed, in the case of rigid and flexible segments fixed in a network structure, the chance to rule out the phase separation totally seems realistic [81-83]. The covalent bond between rigid and flexible structures presents a strong enough interaction to overcome the immiscibility. On account of this, the different possible polymer architectures possible for a rigid-flexible molecular pairs shall be considered further [87,88].

Rigid multipodes (or rigid star molecules) were indicated to be a promising means of molecular reinforcement based on lattice calculations by Wendorff et al. The calculations showed that, though rigid molecules display strong tendency towards immiscibility with flexible chain molecules, compatibility exists if the arms pointing in the three orthogonal directions are of same length [83-87]. The approach was based on the idea that isotropic structures although rigid, diminishes or eliminates any tendency to build up an orientational order caused by anisotropy of rigid rods. These theoretical considerations were justified because multipodes display an enhanced solubility both in low molar mass solvents and in polymer matrices. Furthermore, the rigid and complex structures seem to be able to prevent aggregation into an ordered phase caused by the strongly hindered molecular dynamic. Most notable is that the prediction is not restricted to the variety of rigid star like molecules based on one central core but it does also apply to more dendrimeric systems as represented in Figure 1.17.

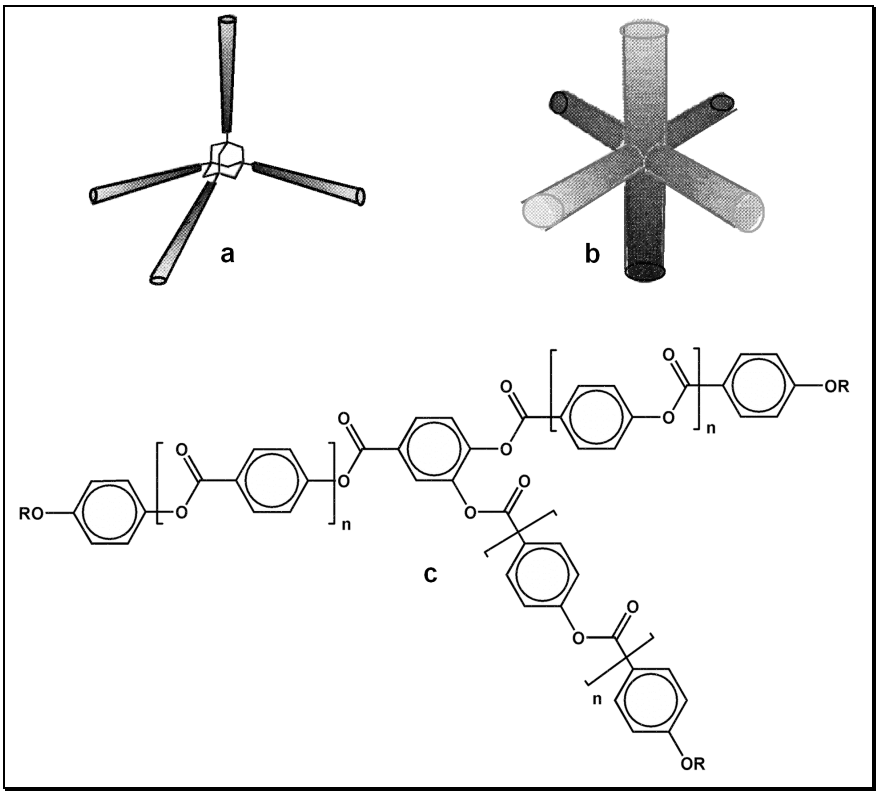


***Figure 1.17**: Rigid multipode systems for reinforcement; (a) adamantane core, (b) 6-orthogonal arm star and (c) benzene core*

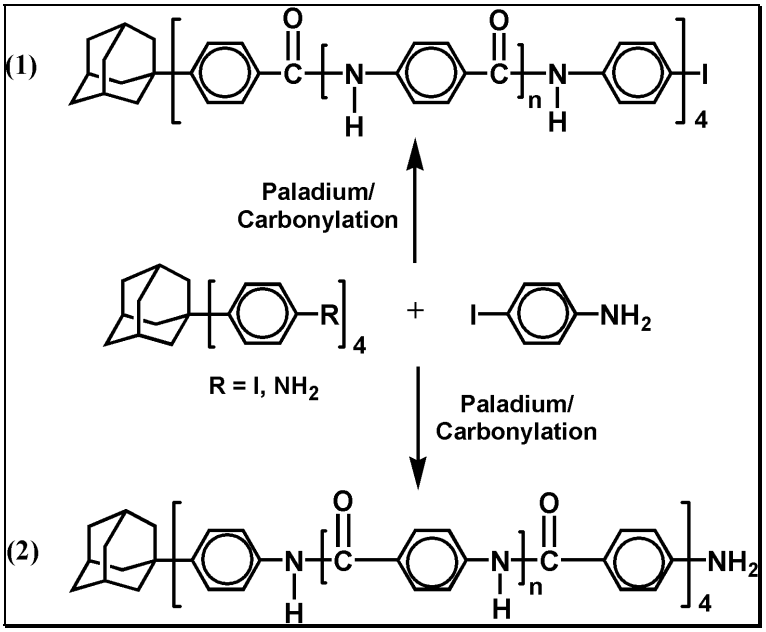


***Figure 1.18**: Star aramid formation from adamantane core units with (1) R = I and (2) R = NH_2*

Mathias and Reichert incorporated rigid, tetrafunctional adamantane cores with intrinsic tetrahedral symmetry into rigid-rod aramid systems to form dendrimeric and hyperbranced polymers with high-performance properties (Figure 1.18). Appropriate dervatives of 1,3,5,7-tetraphenyl adamantine are ideal three-dimensional core units for these branched polymers due to their high symmetry and thermal stability [89,90]. Paladium caltalysed tail-linked and head-linked polymerisation of 4-iodoaniline and 3,5-dibromoaniline gives respectively three dimensional star aramids and highly branched analogues.

Rigid-rod aromatic heterocylic polymers of poly(p-phenylene benzobisthiazole) (PPBT) and poly(p-phenylene benzobisoxazole) (PPBO) are thermo-oxidatively stable polymers, employed in various aerospace application requiring high specific strength and modulus. However improved applications of these polymers are hindered by the difficult processibility of these polymers due to their difficult solubility and complete infusibility. Evers et al modified the relatively rigid aramide polymer backbone by grafting flexible polymer chains of propylene oxide via the abstraction of an acidic proton from the amide group (Figure 1.19) [91,92].

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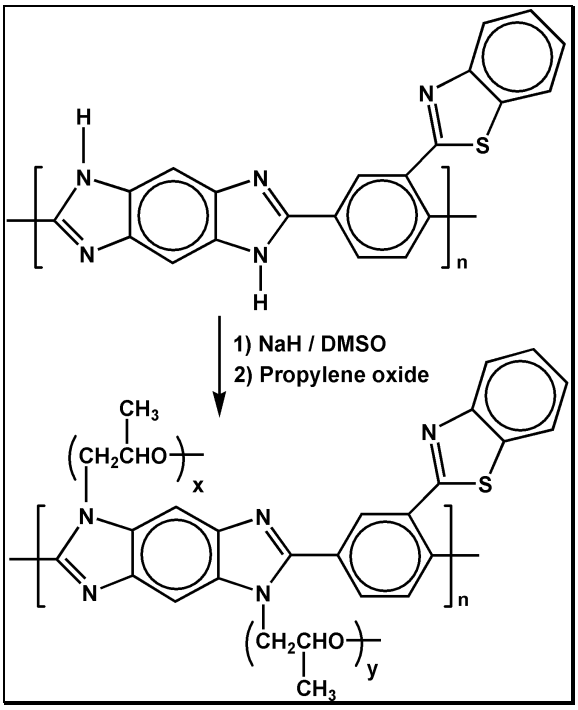

***Figure 1.19**: Poly(propylene oxide) grafted PPBT*

In a different attempt, Tsai et al synthesised a series of novel ABA block copolymers containing a rigid-rod (B) block for reinforcement and a flexible coil (A) block as the matrix [93,94]. Poly(p-phenylene benzobisthiazole) (PPBT), was the rigid block (B) used in this study and polymerised in such a way to provide carboxylic end-groups. The carboxy terminated PPBT was copolymerised with two AB monomers, 3,4-diamino benzoic acid and 4-amino-3-mercapto benzoic acid chlorides generating benzimadazole or benzthiazole (A) block(Figure 1.20).

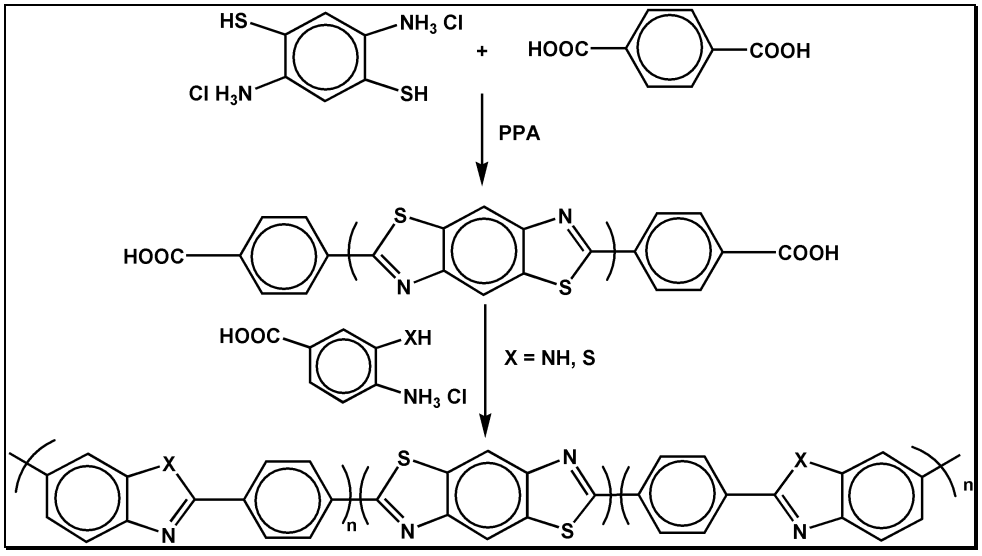

***Figure 1.20**: Reinforced ABA block copolymers*

The low solubility of rigid-rod polymers and phase separation are frequently dealt with while experimenting molecular reinforcement. Both these factors limit processing conditions of the resultant polymer and subsequently cause reduction of mechanical properties [95]. In one of their works, Lee et al. tried to increase the solubility of Polyamide/Polyimide (PA/PI) block copolymers, a lyotropic amine-terminated polyamide prepolymer was copolymerized with an amine-terminated polyimide via a coupling reaction using terephthaloyl dichloride to form the resultant block copolymers (Figure 1.21) [96].

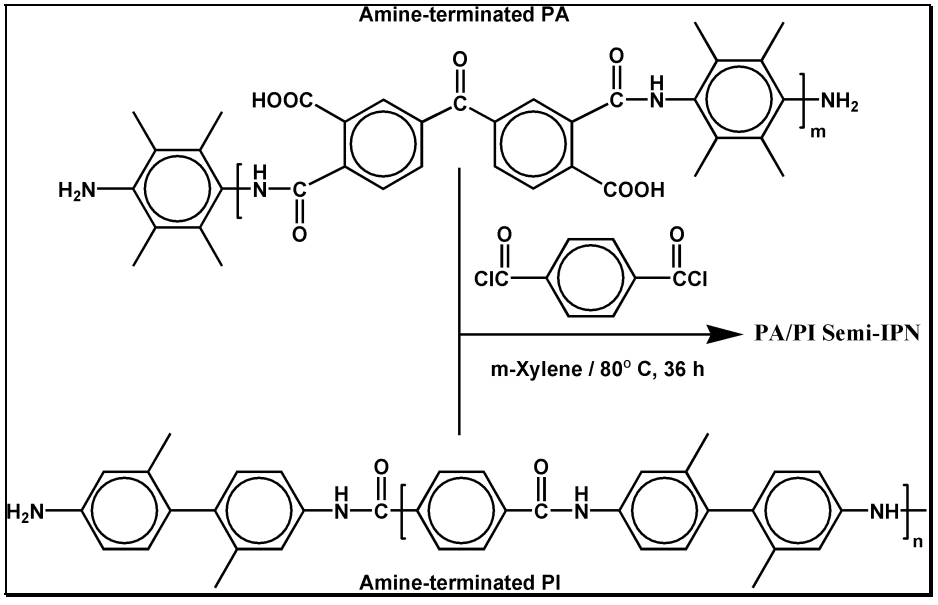

***Figure 1.21**: PI/PA prepolymers forms LC-Semi-IPN block copolymers*

Interestingly, such an approach created a semi-interpenetrating polymer network of rigid polyamide and flexible polyimide and the rigid amide segment maintained its liquid- crystalline behaviour in spite of being a block in the copolymer.

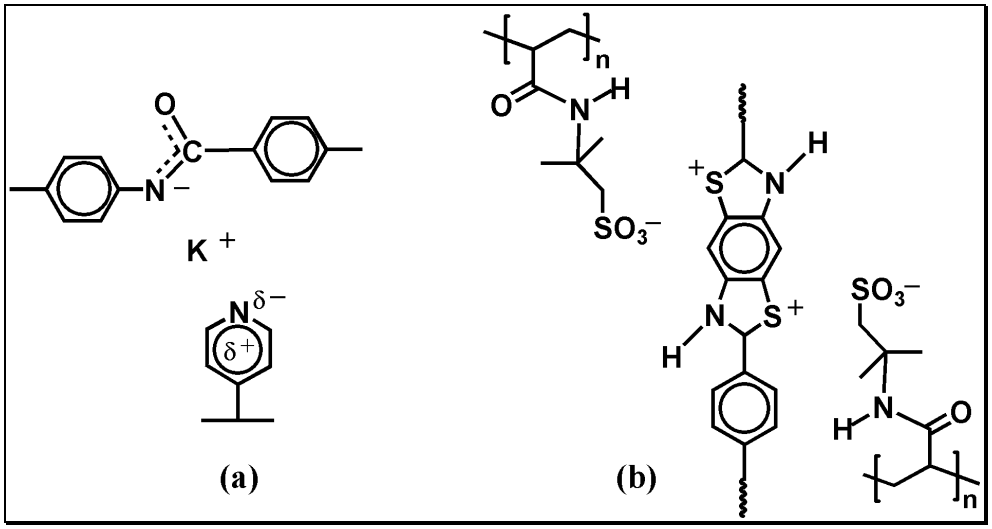

***Figure 1.22**: Reinforcement due to (a) ion-dipole and (b) ion-ion interactions between rigid and flexible components.*

Apart from those mentioned, different chemical binding forces are nominated to enhance the miscibility of the component flexible polymers (Figure 1.22). Among these, intermolecular forces (hydrogen bonding, charge-transfer complexation, etc.), ionic interactions are known to be the strongest [97,98]. Molecular reinforcement by ion-ion interaction enhanced miscibility for poly(2-acrylamido-2-methylpropanesulfonicacid)/PPBT components [99]. The strong coulomb interactions between the protonated thiazole rings and pedant sulfonated groups enhance miscibility. Similarly, strong ion-dipole interactions were identified for few types of ionic PPTA blended with various polar polymers like poly(4-vinylpyridine) (PVP).

1.5.2 Reinforcement in Polymer Coatings

Any liquid compositions when applied to a surface, dries up to form a well-adhering thin continuous layer, are generally termed as a coating. A coating can only conserve a material if it is durable itself. Furthermore, the coating film must not become detached from the substrate to be protected if lasting protection is to be obtained. The main objective of applying coating is to prepare protective, durable, decorative films in an economical way on

wood, metals, plastics, or mineral building materials. In reality, no single coating is able to satisfy all requirements.

The large variety of coatings allows many ways of classification. They can be divided according to use (automotive or can coatings), according to application method (spray or dip coatings), according to processing state (solvent or water-based), according to drying behaviour (air or cold curing), or according to the chemical nature of the binder (alkyd resin, polyurethane). Several of these features including the specification of the binder determine the working properties and performance of the coating. In most cases a single coat cannot satisfy the manifold demands regarding decorative appearance and protective effect. Several coating films are therefore applied one on top of the other and each layer is specially designed for a particular purpose. For instance, a suitable primer should adhere well to its substrate and provide protection against corrosion while the top coat has to give high gloss, scratch resistance and weathering stability. It is appropriate that a coating material normally consists of a physical mixture of numerous components such as binders, pigments, extenders, additives and solvents, each constituent contribution its part to the total performance of the coating.

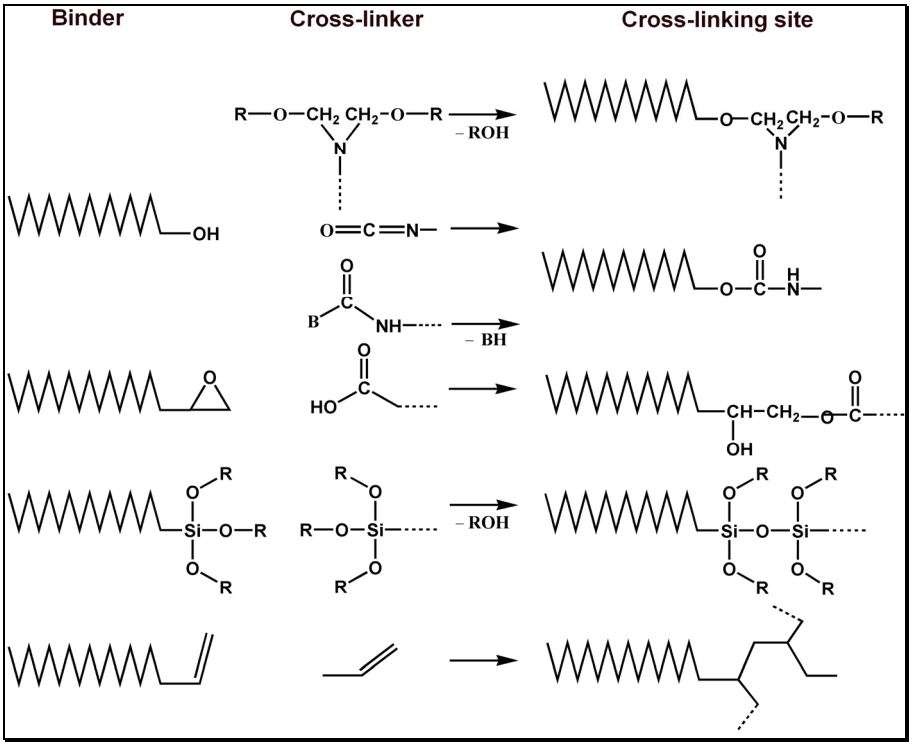

***Figure 1.23**: Different cross-linking mechanisms in automotive coatings*

Cross-linkable coatings are the most important among numerous kinds, as they are largely considered high-performance, practically convenient paint systems (Figure 1.23) [100,101]. They usually contain binders with unsaturated components (unsaturated polyester resins), ethoxy groups (epoxy resins), and hydroxyl groups (polyesters, alkyd resins, acrylic resins, vinyl resins). A wide range of cross-linking agents are available for a variety of applications [102]. Reinforcement of the coating material is additionally achieved by cross linking agents like phenolic or amino resins and polyfunctional isocyanates which exclusively finds application in automobile and plastic industry. Cross-linking materials for automobiles have to satisfy particularly stringent requirements like high gloss, colour durability and maintenance-free behaviour for few years [103].

Photopolymerization of multifunctional monomers is a commonly used process for producing cross-linked automotive coatings. The usefulness of the final polymer product depends on the material properties of the polymer such as storage modulus, glass transition temperature, structural (or spatial) heterogeneity and double bond conversion as well as kinetic properties such as polymerization rates. As a polymer becomes more highly cross-linked, the storage modulus and glass transition temperature tend to increase while the achievable conversion decreases because the mobility of the system decreases. The extent to which a settlement between strength, rate and conversion required is determined by the progression of the polymer network. Thus, it is necessary to understand the effects of monomer functionality and structure on the network formation in order to achieve the desired material and kinetic properties [104,105].

The colour of a car is one of its important selling features, so it should come as no surprise that automakers fret over the performance of their multilayer coatings. Starting from the electrodeposition layer put on the steel to the primer surfacer applied, followed by the coloured base coat and then the clear coat, new technologies and new products are constantly on the rise. Lower cost, reduced air pollution and better performance continue to be the key drivers in automotive coatings. Industries are willing to totally transform the painting process to achieve these goals, and for those unwilling one's, the auto paint industry has more modest alternatives as well.

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2. Research Objectives and Scope

The complete research associated with cyclodextrins (CDs) is aimed at exploiting all the versatile research that CD offers. Cyclodextrins present both enormous opportunities and challenges to synthetic chemists. Opportunities are provided when CDs serve as exquisite molecules that can be invaluable in investigations ranging from stereoselective synthesis, dual phase catalysis and binding or in the development of supramolecules by rotaxane chemistry. Challenges are provided by the presence of the hydrophobic cavity and a large number of hydroxyl groups along the CD toroid.

Cyclodextrin-mediated polymerization of hydrophobic monomers, owing to the well-documented ability of the CDs to form inclusion complexes with a very wide range of guest species, in aqueous solutions has been exploited in this work. Physically-linked molecular structures namely, rotaxanes, opens a new window for polymer scientists in terms of polymer topology. As molecular composites, polyrotaxanes have indeed become an active field of research. This research also involves the development of mechanically interlocked polymer networks that incorporate CDs as one of their (ring) components. Difunctional acrylate and methacrylate monomers are complexed with CDs and polymerized in water leading to crosslinking systems incorporating CD. The discriminating influence of two kinds of cyclodextrins, α and β on the complexation and polymerization of afore mentioned monomers are studied. The obvious possibility of the smaller α–CD to form solid complexes leads to molecular packing structures of CD complexes in crystals. The crystal packing is determined by X-ray spectral analysis. More confirmations into the formation of interlocked polyrotaxanes are gathered from more spectral and thermal characterization. As a result, it is possible to draw some conclusions into the range and stability of the two cyclodextrin kinds and their effects on these kinds of monomers.

Taking steps further away from the conventional synthetic methodologies, this work has concentrated on utilizing microwave induced syntheses. Microwave-assisted syntheses are characterized by the strong accelerations produced in many reactions as a consequence of the peculiarity of the

dielectric heating, which cannot be reproduced by classical thermal heating. Higher yields can be afforded, milder reaction conditions and shorter reaction times can be used and many processes can be improved. Thermal effects are strictly correlated to the possibility to achieve, under microwave irradiation, very high temperature in very short time.

Another approach is to obtain new classes of both linear and branched polyrotaxanes, incorporating microwave assisted synthesis. This is also an effort to overcome potential obstacles with minimal expense, as the entire research is directed towards the replacement of traditional organic solvents. The ring-opening polymerizations of ε-caprolactone in the vicinity of polymerizable cyclodextrins are monitored under microwave irradiation. The effect of microwave energy into the formation of rotaxane and super structures by self-assembly is observed. A total comparative study with respect to differently substituted CDs (hydroxypropyl and dimethyl) is carried out that provides a basis for understanding the mechanical and structural aspects of the supramolecules formed. Each of these reactions are compared with products obtained at normal oil bath conditions to examine the extent of deviations for each system. Evaluating the impact of microwave and its specific effects on the ring-opening reaction is a daunting task. Nevertheless, both correlations and contradictions are seemingly significant for either of the reaction methods. Time scales for both the methods is a major factor, when the target molecule is obtained at the shortest possible time with microwaves. Kinetic details throw evidence into the existence of a growing macrostructure, while preferential complexation reaction with the fitting guest molecule, adamantine, stops such a self-assembling process by rotaxanation. Interesting observations are also recorded for other alkyl CD derivatives.

In terms of the size, shape and availability of chemically useful functional groups, native cyclodextrins offer limited utility. But then, it attains much prominence when the hydroxyl groups are selectively converted to desired functionalities. An associated work on CDs involves the construction of novel functional polymeric systems of that can be covalently incorporated into a polymer matrix. In effect, such functionalized CDs can serve as reinforcement in polymeric materials, especially coatings. This phenomenon

is analogous to the concept of fibre reinforcing where high performance thermo and thermosetting plastics are obtained.

When polymerizable cyclodextrins (PCDs) are incorporated into a polymer chain, molecular interactions between the polymer matrix and the rigid CD molecule comes into play. CD ring being a distinct structural unit and the cyclodextrins are situated in favourable positions, they can be expected to behave cooperatively in binding the polymer matrix. With appropriate polymerization conditions and in presence of suitable initiators, curing would subsequently form a three dimensional crosslinked polymeric network to provide improved bonding between the substrate material and overlying polymer coating. Substituents located on the rims of the CD ring, occupies a so-called quasi-random configuration since all the reaction sites of CD are not equally reactive. Such a quasi-spherical configuration of these high-volume crosslinking monomers is the basis for providing compactness after curing.

During this study on molecular reinforcing properties of CD, a variety of CD derivatives are prepared and mixed on to different polymer binder systems. On one end of the spectrum, there are highly substituted or derivatised cyclodextrins containing many polymerizable groups, for example, methacrylate or acrylate ester moieties, plus or minus other organophilic groups to provide coating formulations with organophilic characteristics. Evaluation of these coatings regarding their elasticity, hardness, scratch and chemical resistance are compared. A CD incorporated polymer coating is found to exhibit appreciable overall performance suggesting a perfect substitute to conventional reinforcing systems.

3. Cyclodextrins in Polymerization

3.1 Cyclodextrins in Rotaxane Formation

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

Cyclodextrins are well known for their inclusion complexation behaviour with a large variety of organic molecules. The capability to include diverse compounds into its apolar cavity allows cyclodextrin (CD) to be a favorable host. These molecular host-guest systems have achieved enhancing importance in industry. Polymerization reactions mediated through the formation of a so called pseudorotaxanes have been a revelation in synthetic polymer chemistry [1-3]. There has been an increased extent of research done in these particular host-guest systems over the last decade. In addition to obtaining optimal polymerization conditions, the properties and nature of the resultant polymer is controlled through cyclodextrin mediated polymerizations. An effective reason for these is that the inclusion phenomenon leads to significant enhancement in solution properties and influences reactivity of the guest molecule. Many suitable hydrophobic molecules are thus made completely soluble in an aqueous solution of cyclodextrin without any chemical modification of the guest involved. [4-5]

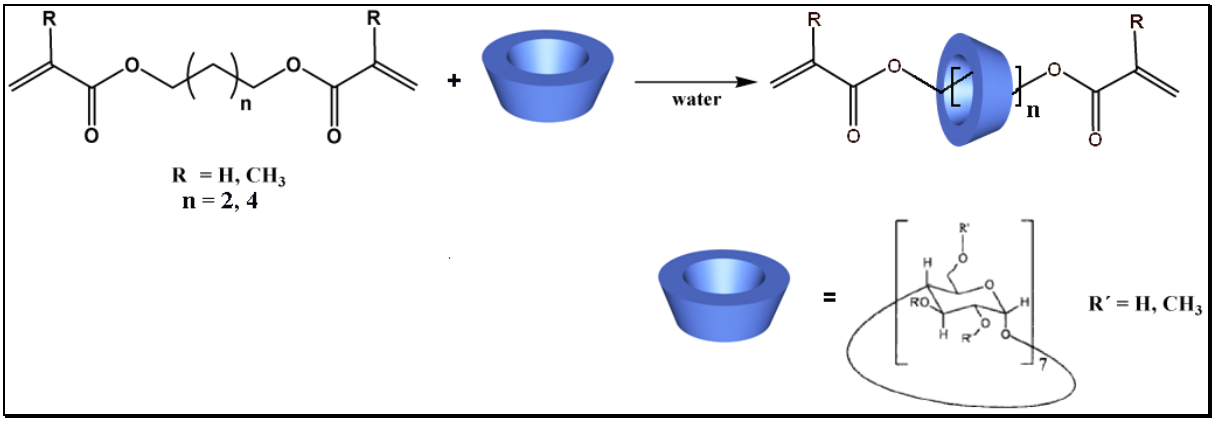
Extensive research on cyclodextrin mediated polymerizations, involving a broad range of monomers, leading to polyrotaxanes had already been reported.[6-7] Nevertheless, the following study was the first attempt with difunctional monomers, in which we report initial results of polymerization for diacrylate and dimethacrylate monomers *via* cyclodextrin complexation. Additionally, the axial inclusion of a linear guest molecule is of special interest since it refers to a one-dimensional transport process as reported by Wenz and Keller. [8] The major objective of this work was the development of a new class of mutually interlocked molecules, which unlike classical molecular structures consists of two separate components which

are not connected by covalent bonds. The desired polyrotaxanes are expected to show different physical, and mechanical properties compared to classical polymers due to topological differences. It is significant also to understand the influence of two different forms of CDs, alpha and beta, over the complexation and polymerization of the above monomers.

3.2 Supramolecular Rotaxane Networks of Cyclodextrin

This segment deals with the design, synthesis and characterization of novel supramolecular networks where the CD guests non-covalently occupy the polymer chains due to inclusion complexation and subsequent polymerization of the monomers are compared.

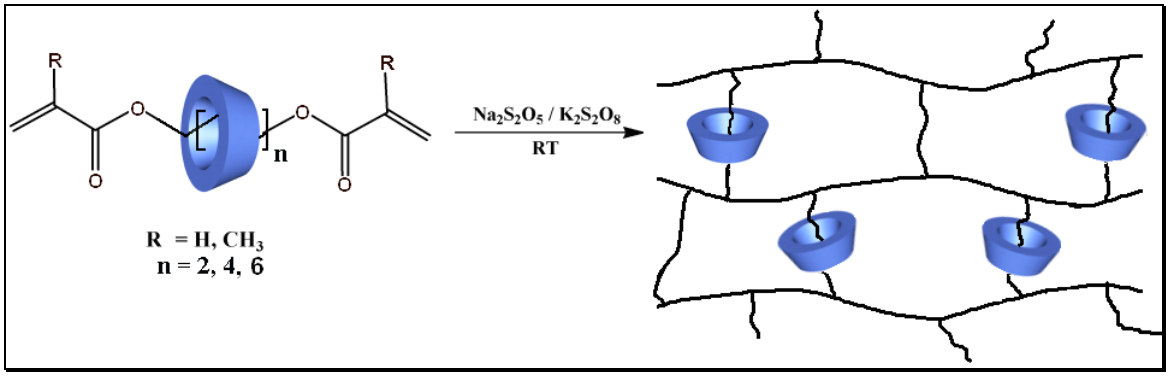
In aqueous solution, the slightly apolar cavity of CD molecules are filled by water molecules which are energetically unfavored (polar-apolar interaction) and are therefore readily substituted by appropnate "guest molecules" that are less polar than water. The driving forces involved in the inclusion complex formation are van der Waals interactions hydrogen bonding hydrophobic interaction release of ring strain in the CD molecule and change in the solvent-surface tension. All these parameters effectively coincide in a favorable complexation process.



Scheme 3.1*: Complexation of acrylate and methacrylate monomers with Me-β-CD in aqueous medium*

A general complexation mechanism follows Scheme 3.1, a 1:1 complexation with Me β-CD is shown in this case [9]. The monomer-Me β-CD complexes in water are polymerized at room temperature utilizing a set of redox

intiators, adding each of them one after the other (2.5 mol equivalents), under nitrogen. The unthreading of the CD component must preferentially occur during the approach of the monomers of to the growing chain end groups. During polymerization, the CD slips off the growingpolymer chain, exposing the unsaturated group to the growingradical chain. Polymerization is instantaneous in this case and the mixture gels to a solid mass immediately. Water is added to dilute the mixture and filtered out. The polymer obtained is repeatedly washed with methanol and water to remove any residual Me β-CD. (Scheme 3.2)



***Scheme 3.2**: Proposed Structure of the Crosslinked Polymers obtained by the Redox Polymerization of the Me-β-CD Complexed Monomers*

Molecular host-guest systems of α-cyclodextrin (α-CD) and methylated β-cyclodextrin (Me β-CD) with diacrylates and dimethacrylates of 1,4-butanediol and 1,6-hexanediol at varying stoichiometries are formed. These hydrophobic monomers form solid inclusion complexes with α-CD that separates out from the aqueous solution, while forming highly water soluble complexes with Me β-CD which, obviously remains in solution. The very fact that unmethylated α-CD complexes precipitates out compared to soluble complexes of methylated β-CD, could be attributed to the extent of their complex stability and to the tendency of crystal formation. [10] Furthermore, the complex with unmethylated α-CD has a homogeneous geometrical feature that leads to the formation of stable crystals. Accordingly, it has to be considered that the stability of a host-guest complex is enhanced with the geometrical fit of the guest into the CD cavity. The respective internal dimensions for α-CD and β-CD cavities are 0.57 nm and 0.78 nm in

diameter and 0.78 nm in length. The included guest is a long molecule with a maximum diameter of about 0.45nm for the methacrylate.[11,12] It is found that despite the realtively huge CD ring, the pseudo-rotaxane could be homopolymerized very easily in water. The cavity dimension for each of the rings are a determinanent factor in the differntial complexing abilties of either of the cyclodextrins towards the acrylate and methacrylate monomers.

With regard to polymerization, complexed monomers are polymerized using a redox initiator system in water. The polymerization is so immediate that the complexed system seems to react sensitively to the presence of cyclodextrin. Rapid precipitaion of the corresponding water soluble polymers is observed during the polymerization reaction. The polymers are separated by filtration, washed, dried and characterized. However, in the absence of cyclodextrin these monomers polymerized in 15 minutes, at 60^{o}C in bulk.

3.2.1 Analysis of Pesudo-Rotaxane Formation

The most preferred method to investigate the complexes is through the use of NMR spectroscopy. [11,12] . The inclusion properties Me β-CD towards each of its guest monomers are studied and compared by this method, since the monomer complexes had good solubility in deuterium oxide (D_2O). Usually, guest molecules included in CD cavities give rise to chemical shifts in ^{1}H NMR spectra.

For instance, a comparison of the NMR spectra of 1,6-hexanediol dimethacrylate monomer with 1:1 and 1:2 complexes of Me β-CD , revealed significant shifts of the protons of the long alkyl chain to lower fields (Figure 3.1). We observed considerable shifts from 1.57 ppm to 1.73 ppm for the beta methylene protons (5,5') and from 1.29 ppm to 1.47 ppm for the gamma methylene protons (6,6') for the uncomplexed and 1:1 complexed monomer respectively, though the chemical shifts for 1:2 complexed are not very far from 1:1 type. Interestingly, the chemical shift for the terminal methyl group of the monomer is very much the same (1.89 ppm) in all the cases. The NMR spectra of various complexes revealed shifts in the proton frequencies corresponding to the alkyl chains of the guest monomers to

lower fields due to the included cyclodextrin ring. Typical shifts are also induced by the guest monomers on the CD protons, particularly the inner CD protons which are shifted to a higher field clearly indicating the existence of monomer molecule within the cavity of cyclodextrin ring.

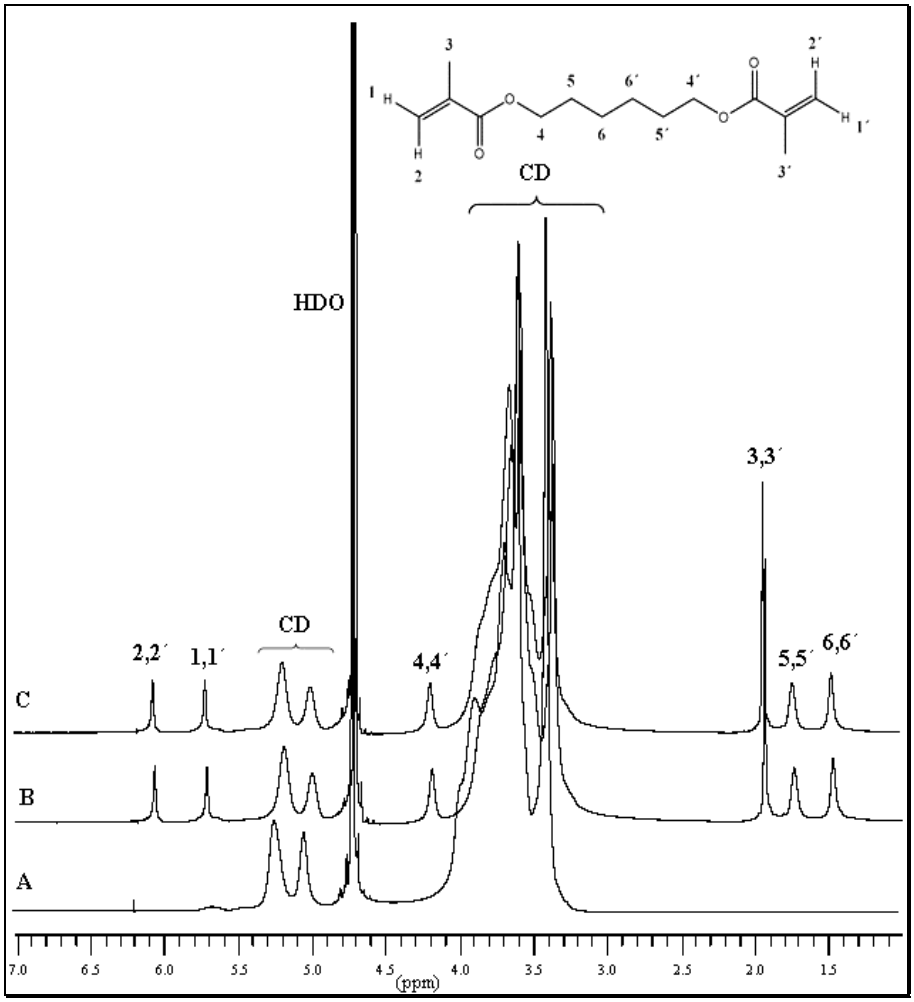


Figure 3.1*:[1]H NMR spectra for Me β-CD (A) is compared to a 1:1 (B) and 1:2 (C) stoichiometric 1,6-hexanediol dimethacrylate-Me β-CD complexes showing realtive shifts in proton singnals*

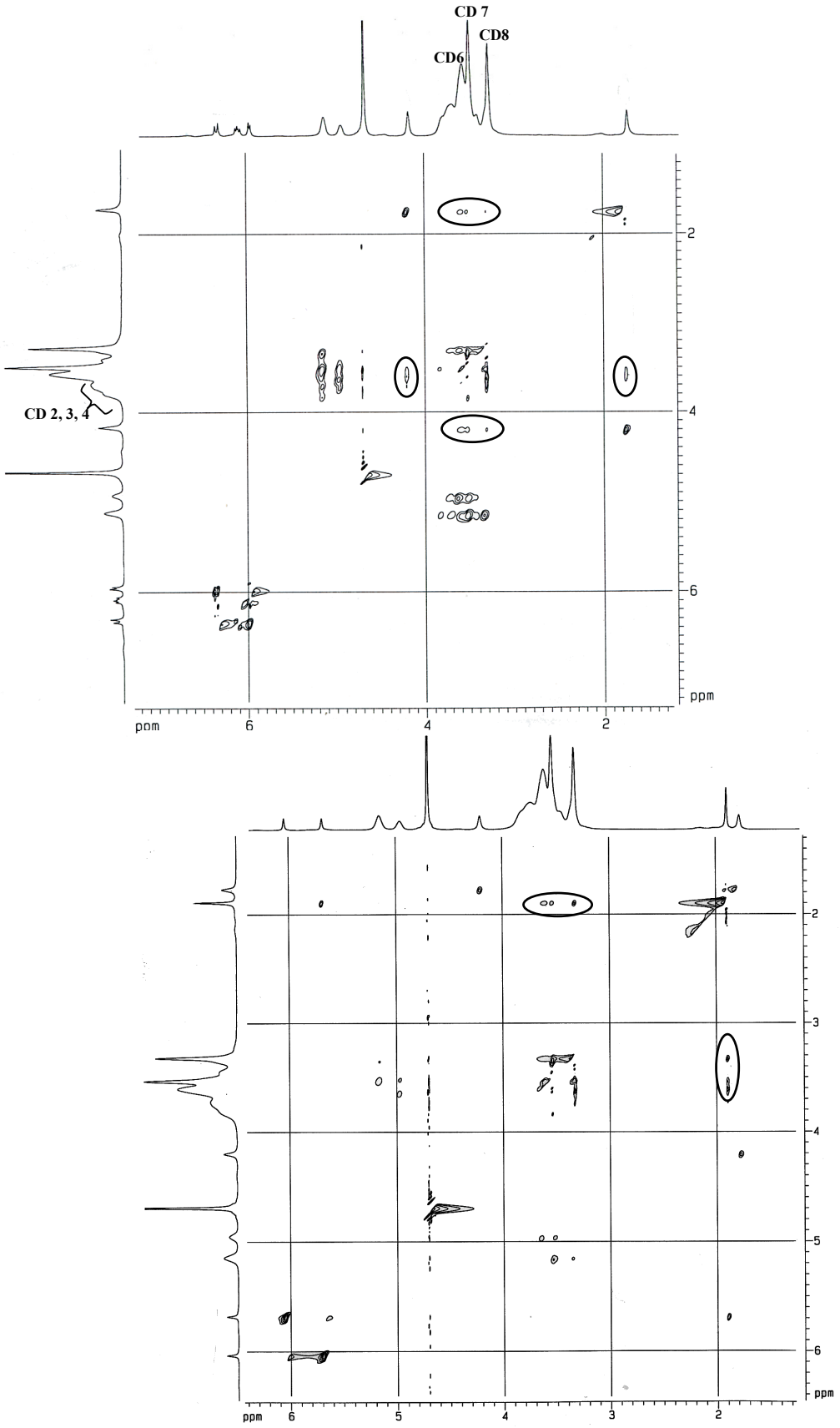


***Figure 3.2**: 2D ROESY spectrum in D_2O showing proton correlations.for a) a 1:1, 1,4-butanediol diacrylate-Me ß-CD complex b) a 1:1, 1,4-butanediol dimethacrylate-Me ß-complex*

A more contrasting observation is made, to our anticipation, when we tried to investigate the topology of the pseudorotaxane formed. [13] A 2D ROESY spectrum of the Me β-CD complexes in D_2O is measured. For instance, ROESY spectrum of stoichiometric 1:1 complex of 1,4-butanediol diacrylate and 1,4-butanediol dimethacrylate implied the formation of a perfectly included and partially included complex structures respectively. The ROESY spectrum of 1,4-butanediol diacrylate showed cross-peaks between the alpha and beta methylene protons at 4.20 ppm and 1.76 ppm of the monomeric guest and the $C_2C_3C_4$ cyclodextrin protons at 3.89 – 3.78 ppm (Figure3.2a). This is likely, provided there is an interaction between the interior CD protons and the methylene chain of the guest, which purely arise when the guest molecule penetrates completely into the cyclodextrin cavity. On the contrary, there is no evidence of any correlation between the above protons and the interior CD protons in 1,4-butanediol dimethacrylate-Me β-CD complex. Nevertheless, there is a clear indication of interaction between the terminal methyl proton of the methacrylate function at 1.89 ppm with the CD protons (Figure 3.2b). Obviously, it could be assumed that the cyclodextrin ring is located at the terminal end of the guest for this complex.

3.3 Determination of Stoichiometry of the CD-Monomer complex

The most probable stoichiometry of the complexes were evaluated using Job's method of continuous variation. [14,15] Different volumes of the host and the guest are mixed such that the total volume remains constant every time while [Host]/[Guest] varies in small steps. The relative proton NMR spectral intensities (Δδ) of these mixtures are a linear function of the molefraction (X) of each species under these conditions. A plot of these parameters yields a curve whose maximum determines the complex stoichiometry.

Job's curves plotted against Δδ and molefraction of the guest (X) for 1,4-butanediol diacrylate monomer with Me β-CD and α-CD as the host is shown in Figure 3.3. For 1,4-butanediol diacrylate-Me β-CD pair, a sharply symmetrical curve with a maximum at 0.5 (a) was obtained suggesting a 1:1 stoichiometry while for 1,4-butanediol diacrylate-α-CD system, the curve (b)

showed a maximum around 0.3 indicating a 1 monomer to 2 CD (1:2) complex structure.

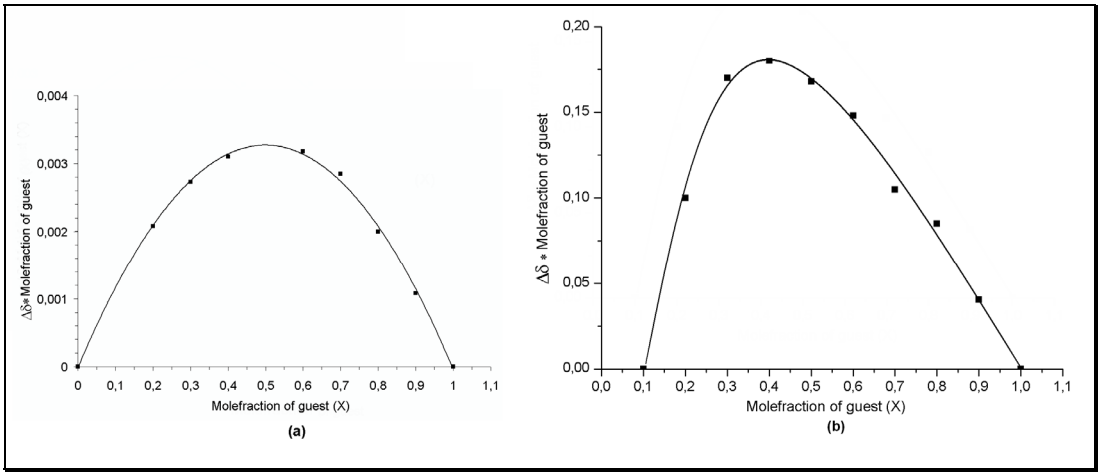


Figure 3.3*: Job's plot showing stoichiometry of complexes*
a) a 1:1, 1,4-butanediol diacrylate-Me β-CD complex
b) a 1:2, 1,4-butanediol diacrylate-α-CD complex

3.3.1 Crystallographic Analysis of the CD-Monomer Complex

Crystallographic analysis of the inclusion complexes reveals the molecular packing structures of CD complexes in to crystals and such a molecular ordering are dependent on the structures of guest molecules. Suitable crystals for X-ray data collection are obtained from the aqueous solution of the respective inclusion complexes, crystals are generated by slow evaporation of these solutions at 25 °C. In this context, the x-ray crystal structure for the stoichiometric 1:2 - 1,6 hexanediol dimethacrylate and α -CD actually confirms the existence of two host α -CD rings along the monomer length (Figure 3.4a).

These X-ray structure clearly shows how the monomer chain occupy the cavity of the CD ring, with different positions relative to the primary and secondary hydroxyl groups, along the CD ring resulting a molecular packing in the crystal structure. In effect, the dimethacrylate monomer is found to form a 1:2 inclusion complex with α-CD, regard-less of the molar ratio of the host to the guest charged, giving rise to a head-to-head dimer structure. The

head-to-head dimer can further self-assemble to form one dimensional channel-type polymeric supramolecules supported by hydrogen bonds between the dimers (Figure 3.4b). Two α -CDs in a head-to-head dimer arrangement are connected by 12 hydrogen bonds from the hydroxyl groups on the secondary sides of the α-CDs.

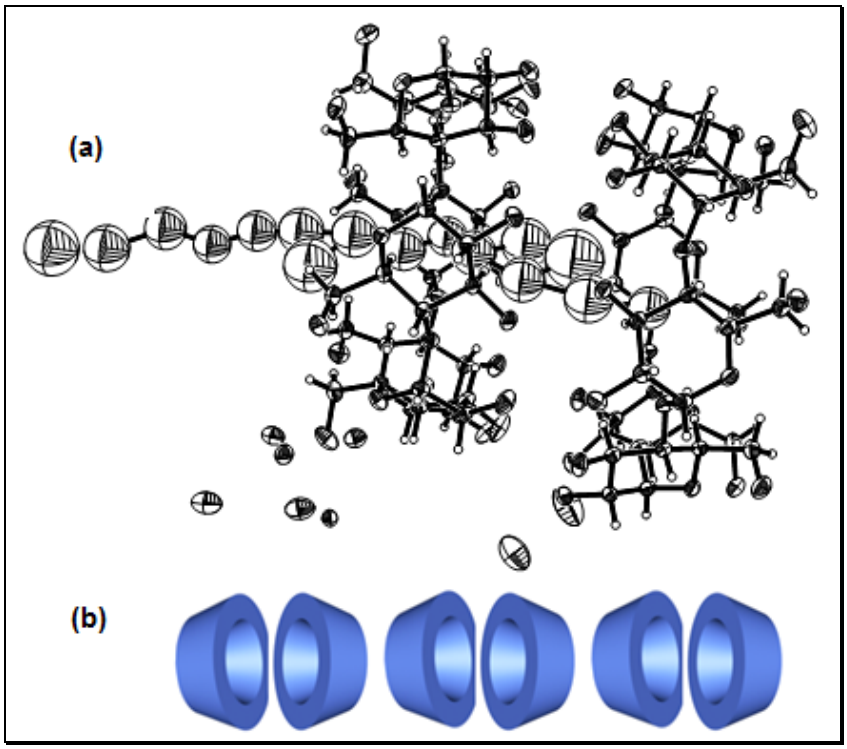


***Figure 3.4**: X-ray crystal structure showing stoichiometry*
a) 1:2 - 1,6-hexanediol dimethacrylate-a-CD complex
b) head-to-head representation of the CD rings as stacked in its crystal

3.4 Spectral and Thermal Correaltions to Stable Rotaxanes

FTIR spectra of the proposed rotaxanted crosslinked polymers showed peaks of constant intensity corresponding to cyclodextrin after repeated extractions, particularly the broad peaks due to CD-OH. Moreover, shifts in the spectral frequencies were observed for the carbonyl ester function in the polyrotaxane compared to the reference polymer prepared without CD. This shift was attributed to replacement of intramolecular hydrogen bonding in native α-CD by intermo-lecular hydrogen bonding between the guest molecule and α-CD.

These shifts are induced by the bulky CD ring present in the network. [16,17] Table 3.1 shows the spectral shifts in the carbonyl frequencies (υ_{CO}) for crosslinked polyrotaxanes obtained from two different monomers.

Type of Polymer	1,4-butanediol diacrylate	1,6-hexanediol dimethacrylate
Without CD	1719	1713
1:1 Me β-CD	1726	1720
1:2 Me β-CD	1728	1721
1:1 α-CD	1729	1723
1:2 α-CD	1731	1725

Table 3.1*: IR spectral shifts in the carbonyl frequency (υ_{CO} / cm^{-1}) for polyrotaxnes from two different monomers*

As a consequence of the crosslinking reaction, the signal characteristic of the carbonyl group of the monomer is significantly shifted to higher frequencies. The spectral shift for poly(1,4 butane diacrylate) varied from 1719 cm^{-1} to the range 1731 cm^{-1} when polymerized via its CD-inclusion complex, as shown in the table above.

Furthermore, spectral shifts were also observed in the same carbonyl frequency (υ_{CO}) for the guest monomers in their complexed and uncomplexed forms. The crosslinked polyrotaxanes are also washed with trifluoro acetic acid, and the resulting IR spectra showed no trace of cyclodextrin indicating a complete disruption of all the glycosidic linkages by the acid. These observations provide a hint towards the existence of crosslinked rotaxanes which represent a novel type of single-molecule supramolecular architecture.

Thermal measurements by use of differential scanning calorimetry (DSC) are carried out to verify the crosslinking process. The glass transition temperature of the polymers (T_g) is found to be greatly influenced by cyclodextrin mediated polymerization. In the case of both diacrylate and dimethacrylate monomers the glass transition for the polymers obtained is found to gradually increase with the increasing amount of cyclodextrin used for complexation. The results of these measurements are shown in Table 2.

For instance, the T_g increased roughly by 7 degrees for the 1,4-butanediol dimethacrylate polymer derived from 1:2 Me β-CD complex while a

substantial increase of 15 degrees is observed for the same polymer obtained from 1:2 α-CD complex. This trend is noticeably evident with the other monomers as well, where α-CD had a predominant increasing effect on the glass transition of the polymers compared to Me β-CD. These observations indicate the true existence of a rotaxane type structure of crosslinked polymers bearing CD rings. In scheme 2, a typical structure for such a crosslinked polymer is proposed as previoulsy represented in Scheme 3.2

Type of Complex	1,4-butanediol diacrylate	1,6-hexanediol diacrylate	1,4-butanediol dimethacrylate	1,6-hexanediol dimethacrylate
Without CD	47	36	40	45
1:1 Me β-CD	52	41	43	49
1:2 Me β-CD	54	45	47	53
1:1 α-CD	51	44	48	54
1:2 α-CD	57	48	55	58

***Table 2**: Glass transition temperature (T_g / °C) values for polymers derived from different complexes*

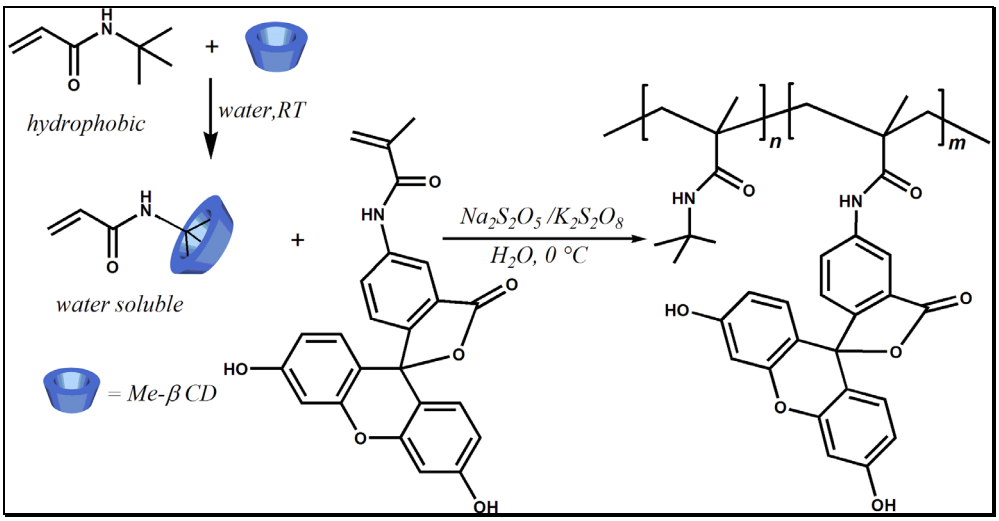
The contribution towards the T_g of the polymer network is greatest for α-CD than with the Me β-CD, suggesting the significant presence of the much smaller α-CD ring in comparison to the bigger Me β-CD ring in the respective polymers. As the non-covalently included CD ring reduces the mobility of the polymer segments, it is obvious that the smaller α-CD ring has a greater influence on the mobility which is reflected in the higher T_g value. Hence, it is worthwhile to predict an exceedingly stable rotaxane formation by α-cyclodextrin than by methylated β-cyclodextrin.

Thus, it has been demonstrated that α-cyclodextrin and methylated β-cyclodextrin behave differently to diacrylate and dimethacrylate monomers. There is a spontaneous formation of complexes in both cases, a sparingly soluble inclusion complex for α-CD and highly soluble complex in water for Me β-CD. The nature of complex formation looked contrasting with α-cyclodextrin, for the monomers 1,4-butanediol dimethacrylate and 1,4-butanediol diacrylate. A true inclusion geometry can be suggested for the latter and a partial inclusion occurs in the former. Job's plot measurements determined the stoichiometries of the complexes. An effective evaluation to

the effect of cyclodextrin rings on the resulting polymers is monitored. The effect on their glass transition is very dominant and distinct for either of the two host CDs.

3.5 Hydrophobic Fluorescent Polymer Synthesis Mediated by Cyclodextrin

Fluorescent polymers find potential application as sensors in studying the mechanism of thickeners and as tracers or monitors for understanding the behaviors of biological macromolecules[4]. Typical fluorescent polymer synthesis involves two approaches-either a chemical modification of polymers by fluorescent molecules[5-7] or by polymerization of fluorescent monomers.[8-10] This work utilizes 5-(methacryloylamino)-fluorescein (5-MAF) as fluorescent monomer to synthesize fluorescent polymers. 5-MAF is an efficient member among fluorescent monomers which is water-soluble and effectively fluoresces in alkaline media. It's fluorescence changes sensitively with the basicity of the aqueous solution, the more alkaline solution exhibiting stronger fluorescence within a pH range of 6 to 12. In addition, the presence of a salt in solution has a diverse influence on the fluorescence of 5-MAF.



***Scheme 3.3**: Hydrophobic fluorescent polymer synthesis in water in presence of CD via redox-initiators*

The inclusion complexation of the fluorescent species by β-CD hosts not only induces the fluorescence enhancement and peak shifts but also leads to significantly elongated fluorescence lifetimes in the hydrophobic environment.5-MAF copolymerizes with hydrophobic comonomers forming corresponding hydrophobic fluorescent polymers as well. Copolymerization of 5-MAF with a hydrophobic monomer like *N*-(*tert*-butyl)acrylamide in water mediated through inclusion complexation into a methylated β-cyclodextrin ring to obtain hydrophobic fluorescent polymers is performed in this work.
Hydrophobic polymers exhibiting fluorescence property are obtained successfully in aqueous medium (Scheme 3.3). The property of methylated β-cyclodextrin to form highly water soluble inclusion complexes with hydrophobic molecules is utilized to dissolve a completely insoluble monomer like *N*-(*tert*-butyl)acrylamide in water [18,19].

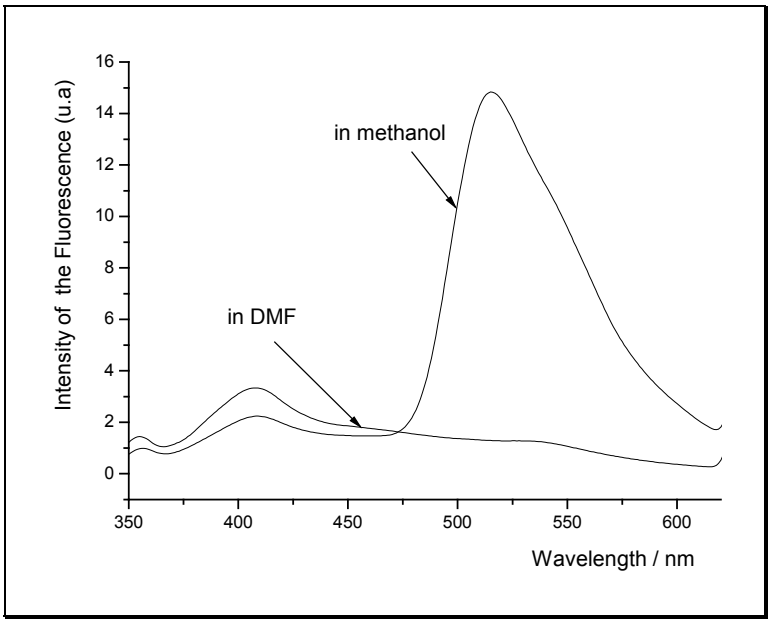


Figure 3.5*: Fluorescence spectra of hydrophobic polymer in methanol and DMF*
The concentration of the polymer amounts to 1 g/L

The fluorescencing monomer 5-MAF in a relatively low proportion (only 0.5 wt.-%) was added to the *N*-(*tert*-butyl)acrylamide-Me-β CD complex and copolymerized at 0°C yielding the polymer in a considerable yield. The obtained yellow solid polymer has a glass transition temperature of 147.3°C. The measurement of SEC shows an average number molecular weight of 4600 with a polydispersity of 2.22. The polymer exhibited strong

fluorescence in solid state and also in organic solvents. The fluorescence ability changes just as the monomeric 5-MAF with the polarity of the solvent, showing a intense fluorescence band at υ_{max} 515 nm in methanol and a comparatively weak fluorescence band at υ_{max} 408 nm in DMF. The relative fluorescence spectra for these two solvents are shown in Figure 3.5 . A similar polymer obtained from a stoichiometric 1:2 *N*-(*tert*-butyl)acrylamide-Me-β CD complex using the same amount of the fluorophore exhibited the same property suggesting a zero-effect on the fluorescence property of the polymer with increasing amounts of Me-β CD used for complexation.

3.6 Experimental

3.6.1 Complexation of diacrylate and dimethacrylate monomers

2g of α-cyclodextrin was dissolved in 16ml of water, and the solution was flushed with nitrogen for about 15 minutes. Equimolar amounts of the monomers are added to this aqueous solution of α-cyclodextrin, when an immediate formation of the complex was observed. The suspension was further allowed to stir, under a slow stream of nitrogen, for a couple of hours more, allowed to settle and filtered out. The resulting white powder was washed with 20 ml of cold water and dried at room temperature. Similar complexation was performed with a molar ratio of 1:2 (monomer:α-cyclodextrin), and the precipitated inclusion complexes were separated and dried.[8]

Highly water soluble inclusion complexes are obtained when the monomers are complexed using Me β-CD. To a 50-wt% aqueous solution of Me β-CD, equimolar amounts of respective monomers are added, after flushing the solution with a stream of nitrogen gas. The mixture is continuously stirred under nitrogen for about 2hrs, yielding a homogenous, colorless solution of the complexed monomers in water. Stoichiometric 1:2 monomer-Me β-CD complexes are also prepared likewise.

3.6.2 Polymerization of complexed monomers in water

Homopolymerization of the solid α-CD-monomer complexes were carried out by dissolving 1g of each of the complex in 20ml of water at 50°C, followed by adding the redox initiators, first $Na_2S_2O_5$ followed by $K_2S_2O_8$ (2.5 mol equivalents each), in presence of nitrogen. The corresponding polymers, obtained in about 10 minutes, were simply filtered off, washed with hot water and methanol and dried. [10]

3.6.3 Synthesis of water-insoluble fluorescent polymers

Copolymerization of 5-MAF with the hydrophobic monomer N-(tert-butyl)acrylamide was performed in the presence of Me-βCD. To a 50wt% aqueous solution of Me-βCD (11mL), equimolar amounts of N-(tert-butyl)acrylamide was added, after flushing the solution with a strong stream of nitrogen gas. The solution mixture was stirred continuously under nitrogen for nearly 2 h to obtain a homogenous, colorless solution of the complexd monomer in water. 5-MAF (0.5wt%) is added to this complexed solution, and stirred again for 30mins. Polymerization is then carried out under ice using redox initiators $Na_2S_2O_5$ and $K_2S_2O_8$ (2mol equivalents each). The resulting polymer gets precipitated in about 2h reaction time, and was recovered by centrifugation. The fluorescent polymer in about 85% yield was washed repeatedly with water to remove the residual Me-βCD. A polymer corresponding to a stoichiometric 1 : 2 monomer/Me-βCD complex was also prepared likewise.

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4. Cyclodextrin Self-assemblies under Microwave Irradiation

4.1 Microwave vs Conventional Synthesis

Microwave assisted organic synthesis (MAOS) approach was executed for the synthesis of cyclodextrin(CD) based star polymers. Microwave irradiations are electromagnetic waves (frequency range of 0.3 to 300 GHz) which are known for their efficient heating of materials by "microwave dielectric heating" effects. As an alternative to conventional heating techniques, microwave irradiation provides an effective, selective, and fast synthetic method by heating the molecules directly through the interaction between the microwave energy and molecular dipole moments of the starting materials. This internal heating is believed to produce an efficient reaction because the reactive sites, which have strong dipole moments, are the primary source of activation in the microwave electromagnetic field (Figure 4.1). Considerable efforts have been devoted to investigating the advantages of microwave irradiation over conventional heating techniques in polymer synthesis.

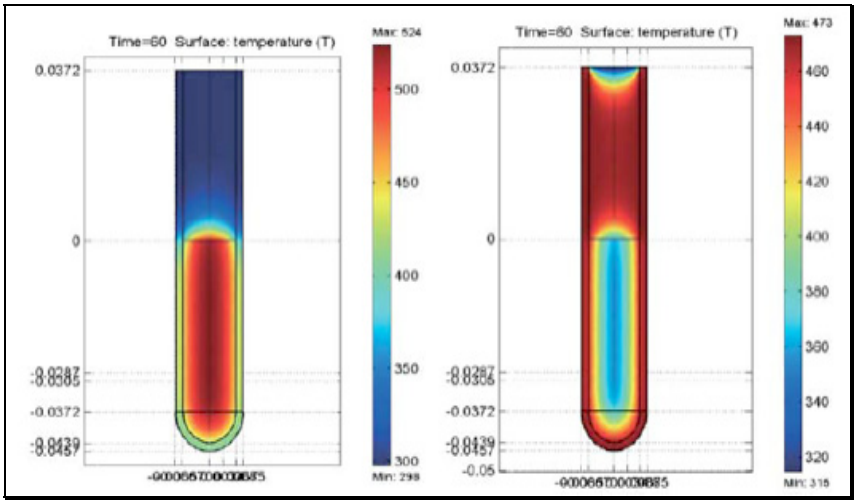
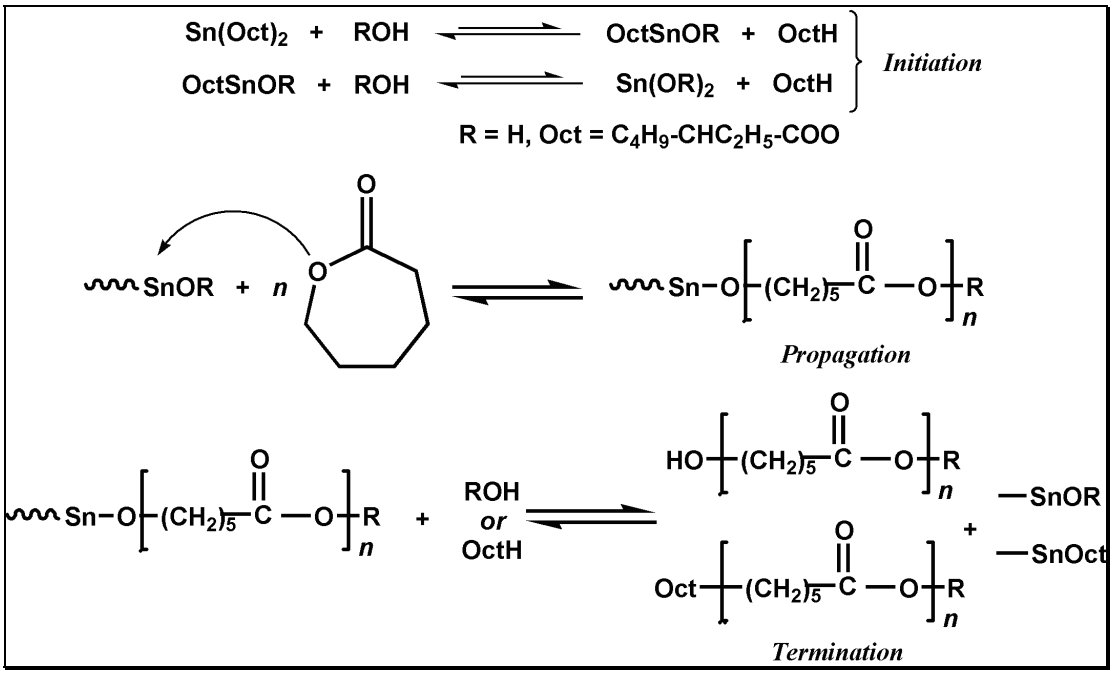


Figure 4.1: Temperature gradient comparisons, thermal heating (right) Vs microwave irradiation (left)

4.2 Supramolecular Rotaxanated Star Polymers from Cyclodextrin Core

Energy conservation and environmental consideration aspects have prompted this investigation on the application of microwave energy in the polymerization of ε-caprolactone. This cyclic ester undergoes ring opening polymerisations to form homo and copolymer adducts. Ring-opening polymerization (ROP) of ε-caprolactone was performed in the microwave oven with a lower forward power system considering the monomer was in the liquid state. All the polymerization reactions were performed using tin(2)-ethylhexanoate [$Sn(oct)_2$] as the catalyst. [$Sn(oct)_2$] is one of the agents most widely used for initiating the ring-opening polymerisation particularly of lactones. ε-Caprolactone was dried under vacuum for 3 days before reaction to remove water molecules and kept under inert atmosphere prior to the reaction. Yet, any trace amount of water from the catalyst or in the reaction system can act as the initiator. The accepted mechanism for a similar polymerisation under microwave irradiation using [$Sn(oct)_2$] catalyst and traces of water as initiator can be summarised as in Scheme 4.1.



Scheme 4.1: Mechanism of a ring opening polymerization (ROP) of ε-caprolactone in presence of catalyst

The choice of cyclodextrins as an adduct along with ε-caprolactone was very appropriate since both are interesting contenders for biodegradable polymer materials. A simultaneous ring-opening polymerisation and coupling reaction was aimed at while performing this reaction under the microwave energy assistance. A polymerizable derivative of β-cyclodextrin was synthesized by reacting it with appropriate molar amounts of methacrylic anhydride. This methacrylated β-cyclodextrin derivative had an average degree of substitution 7-8 implying that, most of the identical secondary hydroxyl functionalities are still free and will be offering coupling sites for the poly(ε-caprolactone) (PCL) chains or the hydroxyl functionalities might serve as initiators for the polymerisation mechanism. In addition, CD-ring provides the possibility of forming inclusion complexes with poly(ε-caprolactone) chains. The chance of linear poly(ε-caprolactone) chains to complex with the hydrophobic cavity of β-CD cannot be ruled out, though instances of linear high-molecular weight polymers are cited which are unable to include into CD cavities. A suitable reason for this effect would be due to the difficulty to disperse high-molecular weight polymers in water, since the afore mentioned complexation reactions were performed in water.
On the other hand, the ring-opening of ε-caprolactone was carried out under no-solvent conditions in an open system. Water as a solvent for this reaction, may also effect the hydrolysis of the resultant PCL chains. Any such possibility was avoided in bulk. It was also considered that any native forms of cyclodextrins were hardly soluble in ε-caprolactone while most of CD derivatives were appreciably soluble in the cyclic ester which prompted a no-solvent reaction condition to be followed. The methcrylated β-cyclodextrin derivative was accordingly mixed with quantitative amounts of ε-Caprolactone and dissolved in it under a mechanical stirrer over few minutes time. Catalytic amounts of $Sn(Oct)_2$ was added to this homogenous mixture and reaction system was subjected to the microwave irradiation at the CEM microwave apparatus for 30 minutes time.

4.3 Analysis of Microwave Assisted Ring-Opening Polymerization

The per-methacrylated β-cyclodextrin derivative with all their primary hydroxyl functions substituted by a methacryl group was used as a

coupling core for poly(ε-Caprolactone) chains. After microwave irradiation, the colour of the crude product varied from pale at shorter reaction times to light brown at longer times. This is indicative of any oxidative degradation that probably occurs during synthesis inside the open-system. Purification of the crude product was accomplished by extraction which removes any unreacted CD derivative, monomer, low molecular weight species and even the dark colour. A solid residual product was isolated as a white powder which was further subjected to various analytical methodologies. GPC analysis over a polystyrene (PS) standard of the resulting product was performed.

4.3.1 Molecular Weight Analysis of the Microwave Products

Molecular weight analysis of the pure products by gel permeation chromatography over a polystyrene standard in DMF revealed interesting insights into the reaction pathways. The observed molecular weights are not the absolute values since the self-assembled supramolecules and the liner PS standard differ in their hydrodynamic volumes. Yet, the trends in M_w and M_n values can be fittingly predictable.

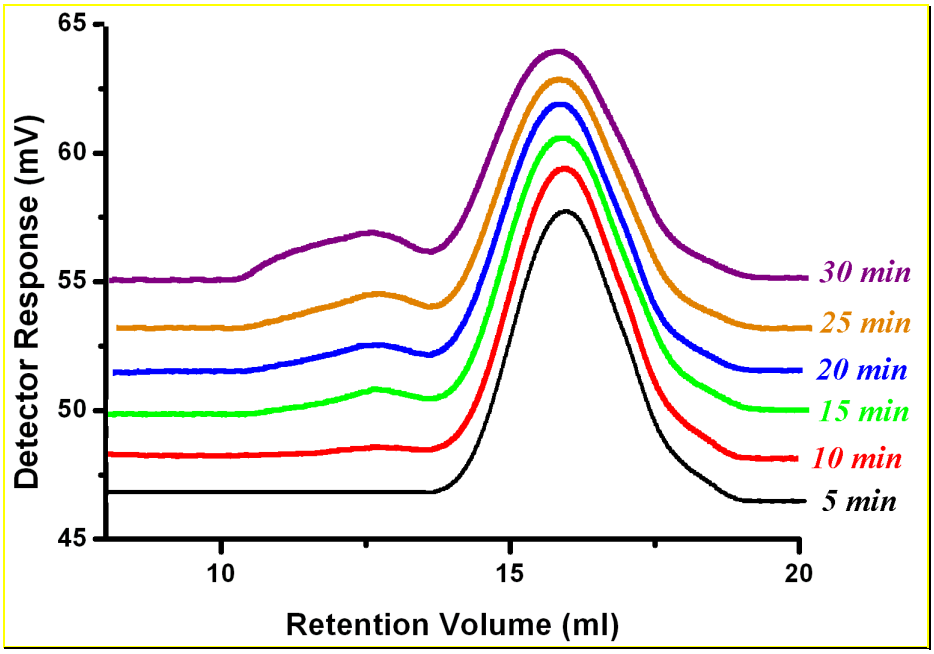


Figure 4.2: GPC elugrams for microwave ROP at precise time intervals showing gradual low and high molecular weight build-up

The GPC elugrams displayed bimodal peaks, one corresponding to a very high molecular weight and lower molecular weight components at retention volumes in the range of 12.7 ml and 15.8 ml respectively. Later, kinetic analyses of the same reaction at varying times under the same experimental conditions were performed and evaluated using GPC. These series of experiments each time revealed the apparent formation of the high molecular weight fraction getting increased with time corresponding to the very same retention volume whereas the lower molecular weight fraction largely remained unaltered (Figure 4.2). A time-dependent formation of a high molecular weight species, so called supra molecule, is evident from these GPC elugrams. The high molecular weight build-up is markedly maximum at 30 minutes time and literally nil at 5 minutes.

4.3.2 Mn and Mw Correlations

Efforts to clearly estimate the possible reaction pathways for this reaction system was the task in hand. Going by the most probable reaction mechanism for the ring-opening polymerization of ε-caprolactone it is easy to conclude that the poly(ε-caprolactone) chains have coupled with the free hydroxyl groups of per-methacrylated cyclodextrin. A model reaction of the same kind with methyl methacrylate in place of the CD- derivative did not yield any trans-esterification product, virtually refuting such a possibility. Consequently, a star like polymer architecture with the CD ring as the core and the growing poly(ε-caprolactone) chains as its arms hence can be postulated. A clear indication to this conclusion is provided by molecular weights (M_n and M_w) values and polydispersity indices of the obtained star polymers for the same reaction corresponding to varying times.

Table 4.1 shows the molecular weights and polydispersity data for the star polymer at retention volume 16.2 ml and for the apparent supramolecule at lower volumes (between 12.7ml – 13.6ml). Clearly, there is always a limit to which M_n and M_w reaches and remains nearly a constant for the star structure and polydisperisty values largely remains a constant for the entire reaction time. These observations can be indicative of the maximum available/probable free -OH functions in the CD core are utilised for coupling with the poly(ε-caprolactone) chains, reaching a limit until a star

Reaction Time (minutes)	Star polymer (At retention volume ~15.8ml)			Supramolecule (At retention volume ~12.7ml)		
	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
5	9791	14,689	1.502	-	-	-
10	9703	15,625	1.610	254,695	402,013	1.578
15	10,904	18,935	1.736	296,358	568,541	1.918
20	10,803	18,463	1.709	333,537	733,385	2.199
25	11,881	21,280	1.791	418,115	1,004 e^6	2.401
30	11,602	21,770	1.876	460,110	1,239 e^6	2.694

Table 4.1: Representative Mn and Mw values for the proposed star and supramolecule at specific reaction times under MW conditions

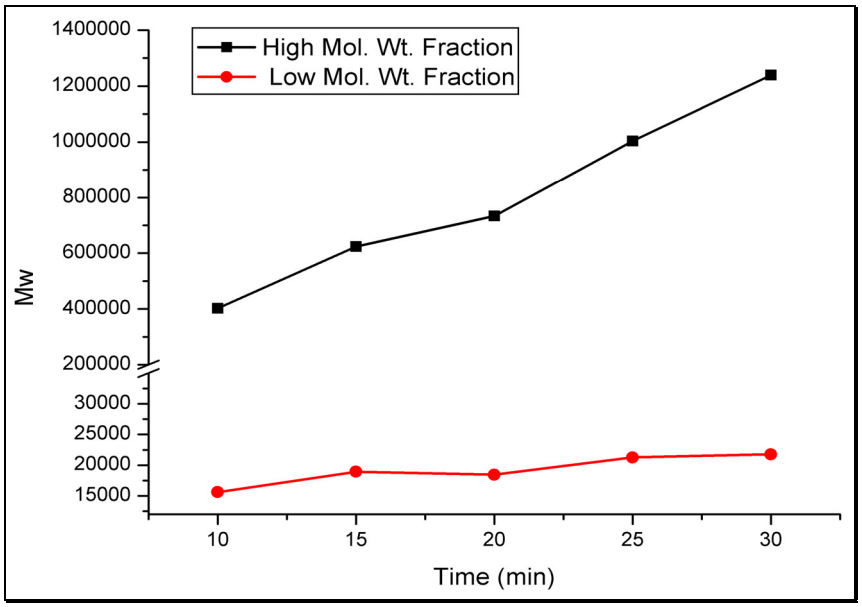


Figure 4.3: M_w vs time trends for the high and low molecular weight MW polymers

structure with sterically favourable numbers of poly(ε-caprolactone) arms was formed. However, there is a geometric progression in M_n and M_w values immediately after its initial formation at 10 minutes reaching the very maximum at the end of the reaction suggesting a supramolecular formation.

The polydispersity values prominently suggest such a gradual molecular build up in the molecule. The entire reaction performance can be graphically represented, for instance, plotting M_w against the reaction time as in Figure 4.3.

4.3.3 Thermal Analysis and Viscosity Evidences to Self-assembling

Differential scanning calorimetry (DSC) provides a rapid method for determining polymer crystallinity based on the heat required to melt the polymer. From the DSC measurements of the microwave products at different reaction times, strong melting peaks for the poly(ε-caprolactone) are observed. The corresponding polymer crystallinities are determined with DSC by quantifying the heat associated with melting (fusion) of the polymers. This heat is reported as percent crystallinity by normalizing the observed heat of fusion to that of a 100 % crystalline poly(ε-caprolactone) sample. As authentic samples of 100 % crystalline polymers are rare, literature values are often used for this value. For instance, the melting enthalpy of pure poly(ε-caprolactone) in the completely crystalline state is 139 J/g according to the literatre. Crystallinity % calculated for a reference poly(ε-caprolactone) against the two different microwave products are shown in Table 4.2. The crystallinity for the polymer at 30 minutes (MW/30min) is lower since higher amounts of the CD core present in the supramolecular structure, apparently lowering the crystallinity of poly(ε-caprolactone). The polymer at MW/5 minutes is slightly better, since it had much lower CD content.

Polymer	*T_m (^oC)*	*ΔH (J/g)*	*Crystallinity (%)*
Poly(ε-caprolactone)	55.53	64.14	46.14
MW / 5 minute	48.43	38.62	27.78
MW / 30 minute	45.60	36.89	26.53

Table 4.2: Percentage crystallinity for MW polymers at 5 and 30 minutes calculated from their respective heat of fusion (ΔH)

The formation of the supramolecule molecule with time is accompanied by the gradual increase in molecular weight and intrinsic viscosity [η] as suggested by GPC. The molecular weight is maximum at 30 minutes and practically nil at 5 minutes. Appealing trends are observed with the intrinsic viscosity values for the individual polymers. The dependence of intrinsic viscosities of the polymers on its relative molecular weights is measured by applying Mark-Houwink equation, which in its simplest form can be represented as,

$$\text{Intrinsic Viscosity, } [\eta] = K \cdot M^{a}$$

where, K and *a* are constants for a particular polymer and M is its corresponding relative molecular weight.

Plots of Log M vs Log [η] are drawn for polymeric products at precise time intervals. For instance, figure 4.4 demonstrates the molecular weight correlations with intrinsic viscosity for the reaction times, t = 5, 10 and 20 minutes. The intrinsic viscosity values for the supramolecules at t = 10 and 20 minutes are effectively lower when compared to those of poly(ε-caprolactone) while at t = 5 minutes, the intrinsic viscosity is seemingly higher than the intrinsic viscosity of poly(ε-caprolactone).

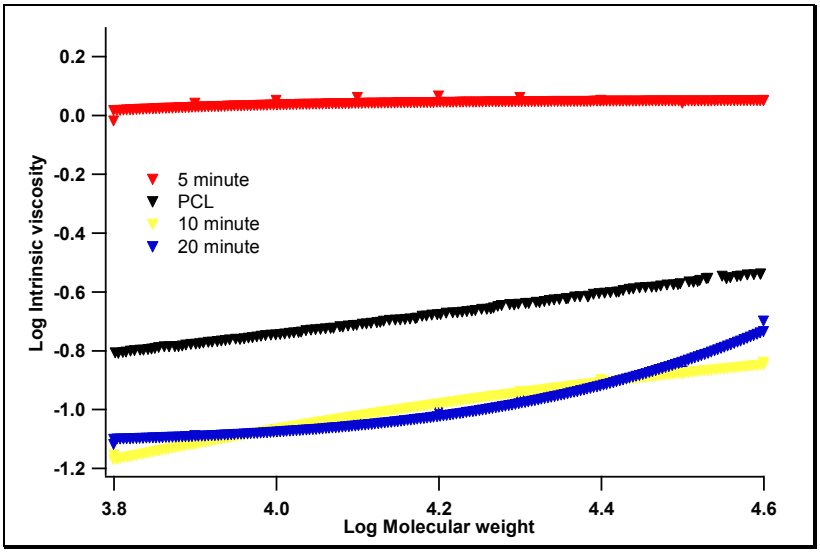
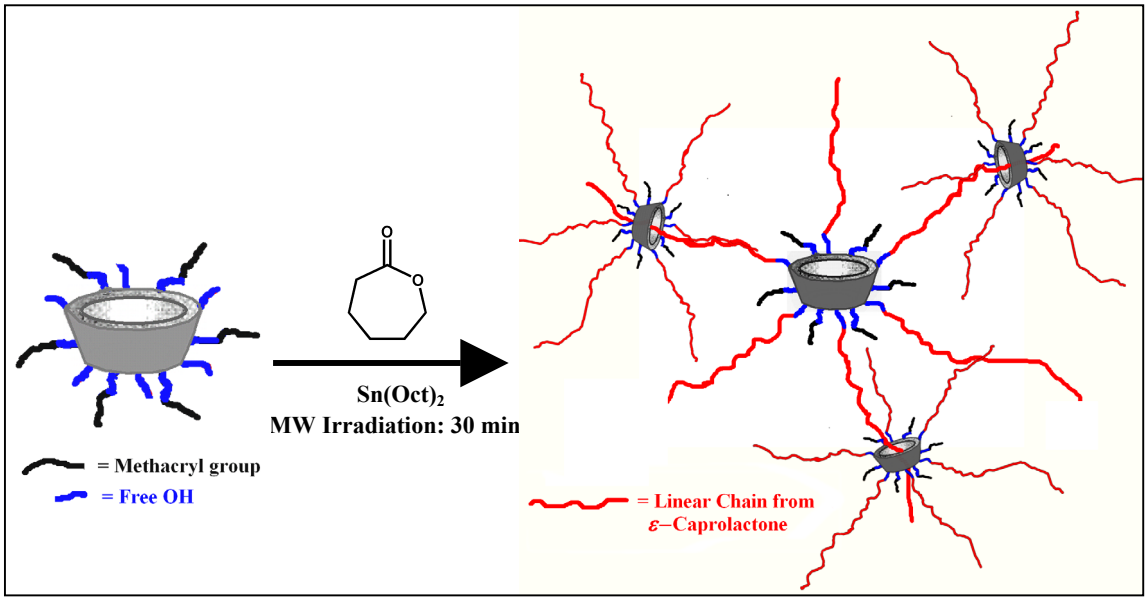


Figure 4.4: Intrinsic viscosity comparisons for MW products at 5, 10 and 20 minutes with poly(ε-caprolactone) (PCL)

An effective reason to this behaviour is that the growing poly(ε-caprolactone) chains of the star molecule can act as suitable guests for the CD core leading to inclusion complex structures. This inclusion tendency is least observed at shorter reaction time (t = 5 minute) while continuing/gradual inclusion occurs with time, reaching maximum at longer reaction times (t =10, 20, 30 minutes.). As the change in polymer hydrodynamic volumes and conformational properties vary, subsequent changes in viscosity characteristics also occurs. Such viscosity effects are well documented for inclusion complexes and reported. At t = 10 and 20 minutes, there is maximum increase in hydrodynamic volume and conformational parameters which understandably lowers the intrinsic viscosity with respect to poly(ε-caprolactone) while at t = 5 minutes, either of the parameter changes are nil or minimum. Perhaps, at t = 5 minutes, since the resulting star polymer formed had few long poly(ε-caprolactone) arms, it imparts higher intrinsic viscosity than the reference.

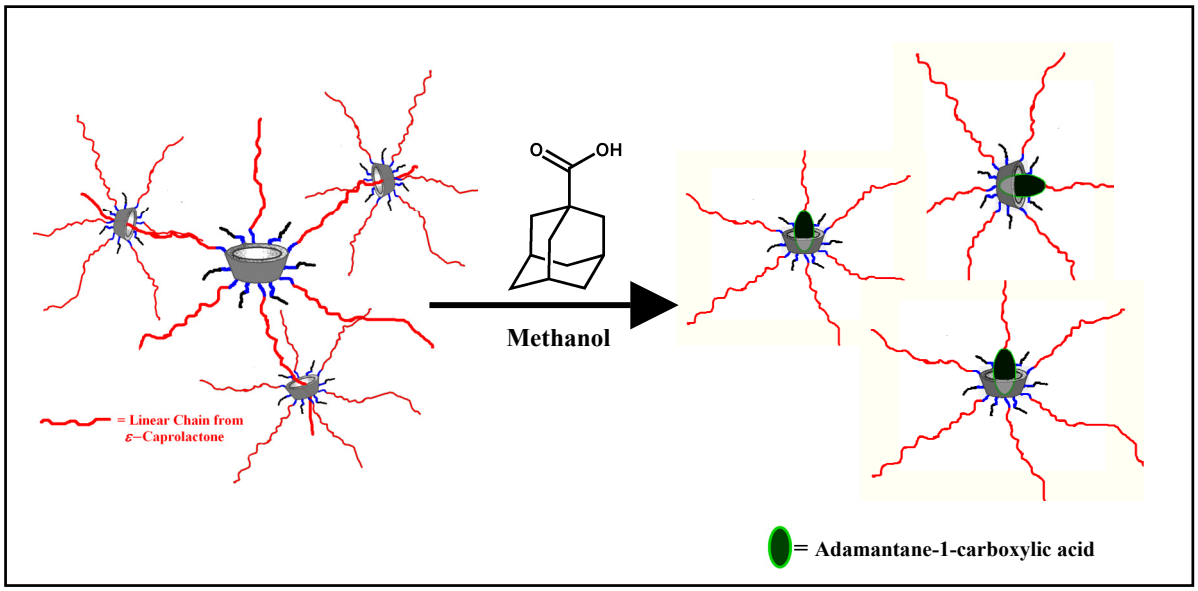


Scheme 4.2: Proposed formation of a self-assembled poly pseudo-rotaxane under MW assisted ROP of ε-Caprolactone

Ultimately, this leads to each of the arms of the adjacent star molecules forming pseudo-rotaxanated complexes with each other's CD core resulting in pseudo-rotaxanated star self assemblies. Based on the above hypothesis,

the overall reaction sequence resulting into the formation of a self-assembled pseudo-rotaxanated star-shaped macrostructure can be drawn as in Scheme 4.2.

In this context, it is also worthwhile to consider that the poly(ε-caprolactone) chains will behave as a loose-fitting guest for the CD host. These polymeric chains run freely inside the larger CD core, that a de-rotaxanation is always a nearest possibility whereas any molecule which fits perfect into the CD cavity forms stable rotaxanation. These assumptions were found to hold true, when a stable guest molecule like adamantane-1-carboxylic acid was stirred for long hours in methanol with the pseudo-rotaxanated star product obtained at maximum time. The suspension was filtered out and dried to obtain a powdery mass for which the GPC elugram was virtually similar to the star polymer obtained at 5 minutes time. This observation suggests that adamantine ring being stiff and stable preferentially complexes with the CD core than the poly(ε-caprolactone) chains, in that way, preventing any self-assembling leading to growth of a pseudo-rotaxanated star macrostructure. The de-rotaxanation is depicted as in Scheme 4.3.



Scheme 4.3: De-rotaxanation of the self-assembled star polymers by competing complexation with adamantane

4.3.4 Spectral Details to Pseudo-rotaxanes and their De-rotaxanation

Structure elucidation of the high molecular weight supramolecular component was achieved by a competing complexation reaction. An effective and visible reasoning to the formation of an adamantine ring complexed with the CD core is provided by NMR spectra. Figure 4.5 compares a region in the spectra of the self assembled supramolecule obtained at 30 minutes time (a), with the same supramolecule in its complexed state after stirring 3 hrs with the fitting guest, adamantane carboxylic acid (c). The NMR spectrum for adamanatane carboxylic acid is also shown as a reference (b). The region between 1.7 ppm and 2.0 ppm is largely blank in the uncomplexed state of the growing supramolecule. A clear indication to the presence of peaks at 1.70-1.80, at 1.95 ppm and at 2.0 ppm corresponding to each of the axial and equatorial hydrogens of the adamantine ring in the supramolecule severely indicates the existence of adamantine in its complexed state with CD ring.

After repeated extractions of the complexed supramolecule with methanol the similar NMR spectrum was obtained, which is an indication to a perfect host-guest pair that adamantine and cyclodextrin creates. Presence of peaks at 1.40 ppm, at 1.65 ppm relates to the methylenic protons along the poly(ε-caprolactone) chain while the alpha methylene protons are observed at 2.7 ppm. The PCL peak intensities are effectively higher in the adamantine complexed –CD/PCL star (c), while for the CD/PCL pseudo-rotaxane peak intensities are comparatively lower (a) possibly due to the complexed state of PCL chains masking its presence. Sharp peaks are seen at 2.06 ppm (-CH_3 of methacrylate), peaks in the range 2.80 ppm to 5.50 ppm (contributions from CH_n protons in the CD ring) and more significantly two singlets at 5.65 ppm and 6.20 ppm (=CH_2 of the methacrylate moiety in the CD ring) confirmed the existence of cyclodextrin ring in the supramolecule. The effectiveness of the afore mentioned de-complexation reaction can be clearly elucidated out of the spectral details obtained. On the contrary, the entire de-complexation process can prevent a cyclodextrin star polymer into gradually self-assembling to a growing supramolecule by blocking the complexing cavity of the cyclodextrin ring.

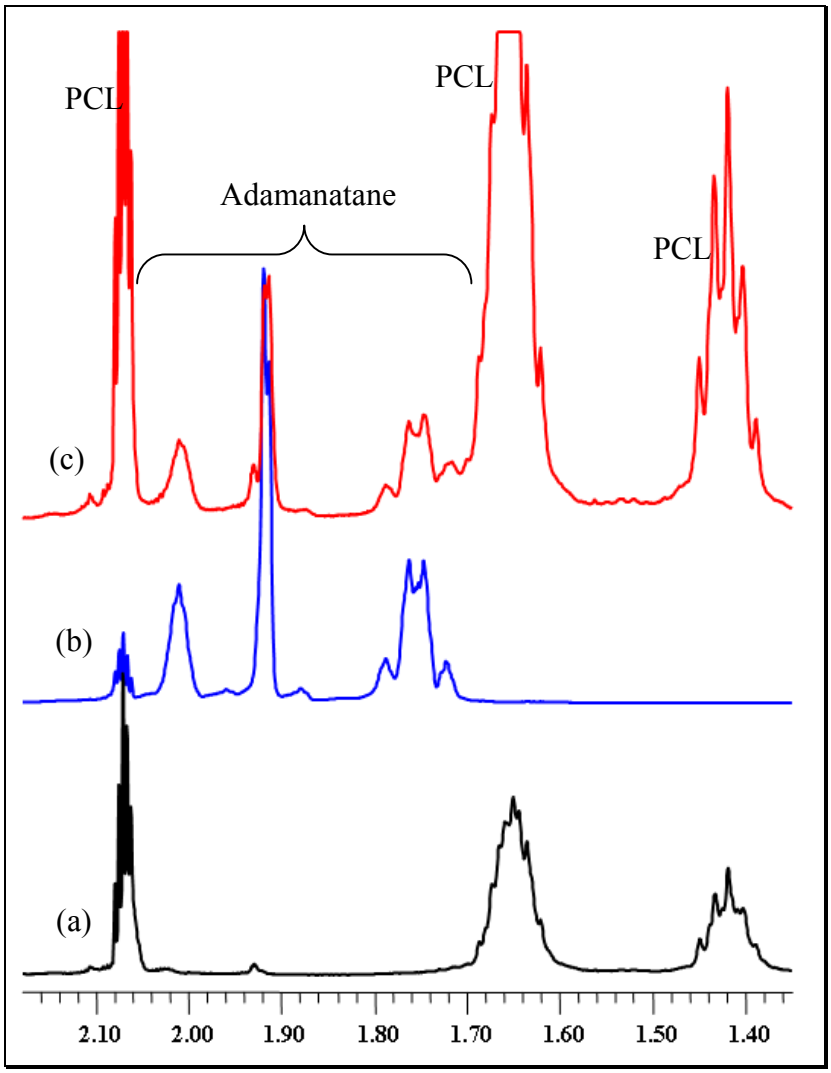


Figure 4.5: ^{1}H NMR for the (a) CD-PCL poly pseudo-rotaxane (b) Adamantane 1- carboxylic acid and (c) Admantane-complexed CD-PCL

4.4 Analysis of Ring-Opening Polymerization (ROP) by Conventional Heating

Trial reactions of the previous kind involving the ring-opening polymerization of ε-caprolactone in presence of per-methacrylated β-cyclodextrin derivative were also performed under conventional heating in an oil bath. The actual temperature of the reaction vessel during microwave irradiation was recorded previously over a period of time. The aim was to strictly reproduce, as far as it was possible, equivalent conditions of

temperature and heating rate of the MW assisted reactions also for the polymerizations performed in oil bath.

The temperature is monitored using an infrared (IR) pyrometer that measures the temperature on the outside of the reaction vessel. This, however does not really reflect the temperature inside the reaction mixture due to different interactions between MW, the glass vessel and the reaction mixture and to the short reaction time that does not allow the system to reach a thermal equilibrium. To overcome this situation, a calibration curve of the infrared pyrometer with an external digital thermometer is plotted.

The results obtained under MW irradiation are compared with those of the reactions carried out under normal thermal heating. A good number of reactions on the ring-opening polymerization of ε–caprolactone under normal heating demonstrate the reaction to proceed to a minimum of 20-24 hours. Accordingly, the model reaction to synthesise poly(ε–caprolactone) is also performed for 24 hours at 100°C in bulk. Kinetic studies are also performed under oil bath conditions, removing polymer samples at definite intervals of time and subjecting them to GPC measurements. Unlike in microwave conditions, the elugrams displayed prominently 3 peaks, at varying time scales relating to the existence of poly(ε-caprolactone), star polymer and a supramolecule in the reaction system. (Figure 4.6)

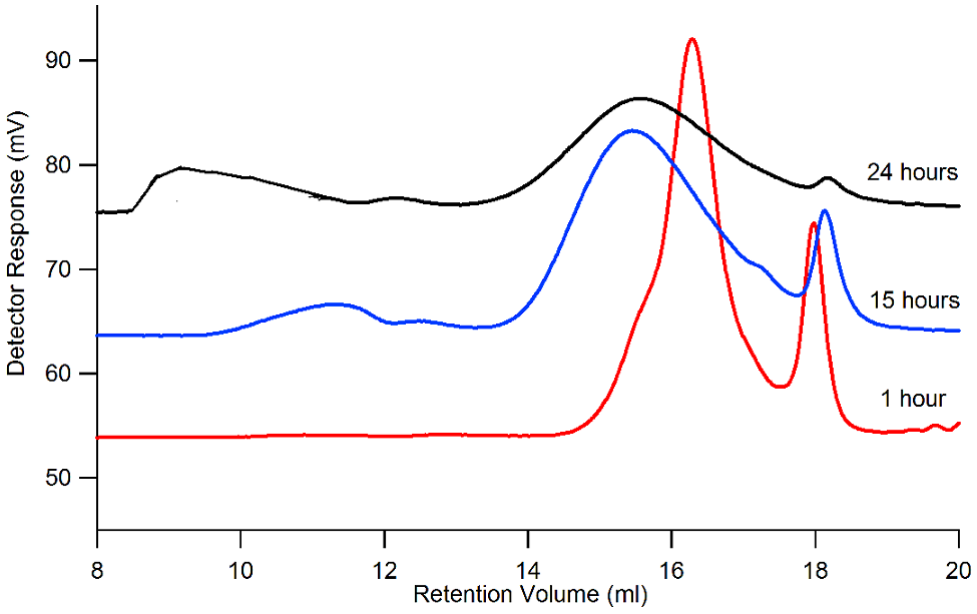


Figure 4.6: GPC elugrams for conventional ROP in oil bath showing high molecular weight build-up after 24h

The GPC elugrams conveys few insights into the possible mechanism leading to the formation of the supramolecule under these conditions. Except, for the large presence of poly(ε-caprolactone) at shorter times corresponding to minimal or no presence of the supramolecule, the GPC profiles are virtually similar. Initial traces of a self assembled polymer are seen at 4 hours time, during which the growth of the considerably long poly(ε–caprolactone) chain had been complete which is confirmed from their constant M_n and M_w values as in Table 4.3

Much higher M_n and M_w values are observed for the star polymer than those from MW irradiation, which might suggest that the arms of this particular star polymer is long enough than the previous case. This indirectly conveys the ring opening polymerization of ε-caprolactone precedes the coupling reaction to the CD core where as simultaneous coupling and ring opening occurs under MW where the poly(ε- caprolactone) chains grows from the CD core ultimately reaching a limit. Lower M_n and M_w values for the supramolecule might be due to minimal complexation owing to the longer arms of the star at shorter times. But, after longer reaction times there is considerable complexation reaching maximum M_n and M_w values, yet not reaching the same molecular weights obtained with microwave. (Figure 4.7)

Reaction Time (hours)	*Star polymer (At retention volume ~15.62ml)*			*Supramolecule (At retention volume ~12.55ml)*		
	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
1	9784	11,421	1.167	-	-	-
4	12,399	18,813	1.517	270,714	324,249	1.198
7	13,479	21,545	1.598	324,138	363,926	1.123
10	13,187	21,295	1.615	302,637	333,773	1.103
15	10,351	19,095	2.287	312,784	352,954	1,128
24	8638	21,461	2.484	458,951	571,589	1.245

Table 4.3: Representative Mn and Mw values for the proposed star and supramolecule at specific reaction times under oil bath

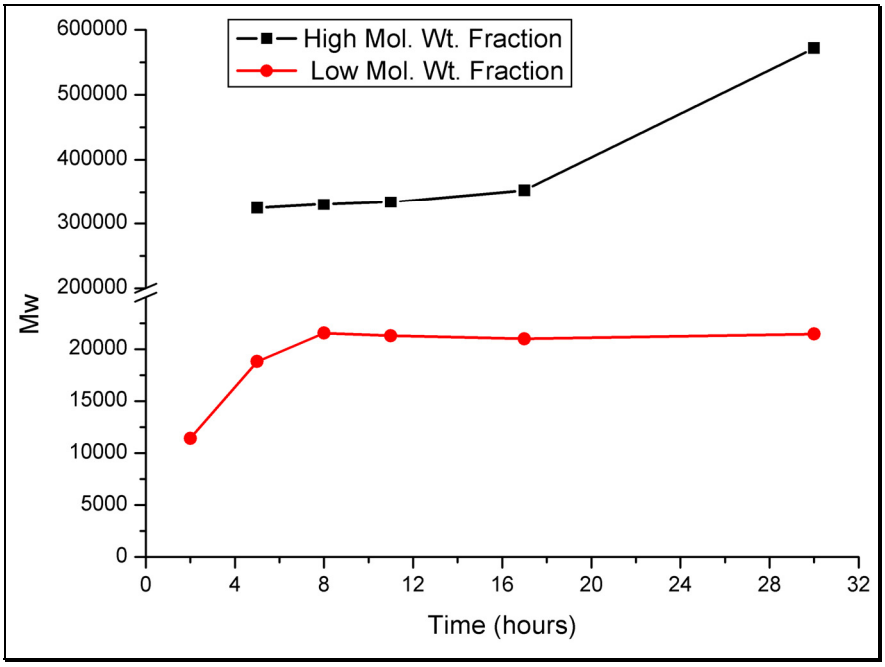


Figure 4.7: M_w vs time trend for the high and low molecular weight polymers synthesized in oil bath

4.4.1 Intrinsic Viscosity Inferences

Log Intrinsic viscosity vs Log Molecular weight peaks for the reaction system clarifies the assumption that ring-opening polymerization precedes the coupling reaction to the CD-ring. Longer poly(ε-caprolactone) chains hence constitute the arms of the star polymer, exhibiting higher intrinsic viscosities than the poly(ε-caprlactone) reference. Interestingly, the intrinsic viscosity values are closing on to its reference at higher reaction times, owing to the gradual dominance of the hydrodynamic volume and conformational influences at higher time scales. Figure 4.8 explains this behaviour, when the intrinsic viscosity at 1 hour reaction time is seemingly higher than poly(ε-caprolactone) and at a longer reaction time of 24 hours the intrinsic viscosities for the polymeric system closes on to the viscosity of its reference.

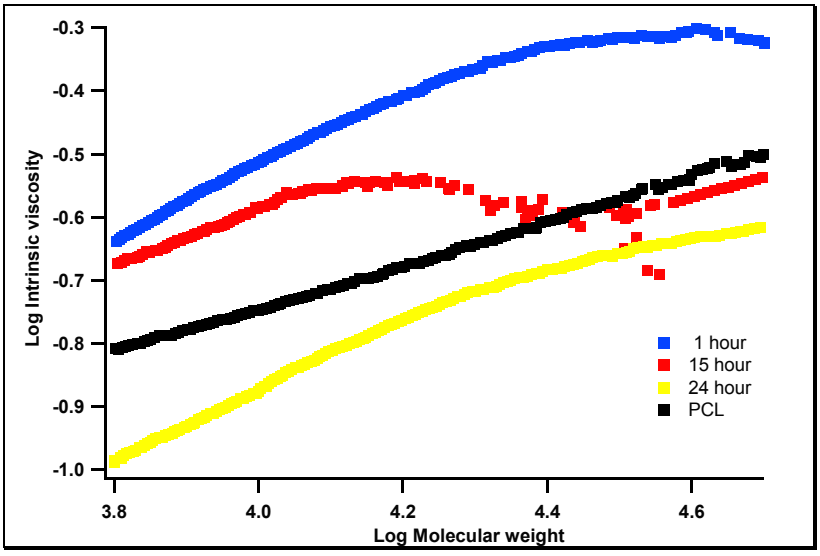


Figure 4.8: Intrinsic viscosity comparisons for oil bath products at 1, 15 and 24h with poly(e-caprolactone) (PCL)

4.5 Analysis of Conventional ROP vs Microwave ROP

The assumption that the ring-opening polymerization of ε-caprolactone precedes the coupling reaction in oil bath holds true because, under MW irradiation, -OH groups of the CD core being microwave absorbers activates the core enhancing coupling reaction concurrently with the ring opening. This confirmation could account for the presence of a specific microwave effect. On the other hand, interesting diversity is observed under classical heating method when the coupling reaction to the core initiates only when ring-opening polymerization of the lactone was apparently completed. Nevertheless, there had been numerous similarities in either of the reaction strategies with the major products in each case is typically a relatively low molecular weight star molecule and a reasonable high molecular weight supramolecule. GPC elugrams showing virtually the same retention volumes for the star (~15.7 ml) and the supramolecule (12.6 ml) and NMR data for both the products under microwave and non-microwave reaction conditions respectively indicate to the formation of seemingly identical molecules in both techniques. But then, the extent, the probability and the kinetics of formation of each of the entities are miles different. Highly probable and rapid is the formation of the supramolecule under microwave (less than 30

minutes) when long hours are needed to actually start a supramolecular formation in an oil bath. However, in each case the growth of the star polymer is largely stagnant throughout the reaction time, while the supramolecular formation under microwave is a gradual steady step-growth process in contrast to an abrupt rapid-growth at longer times under oilbath. These effects are virtually agreeable with the intrinsic viscosity characteristics observed at distinct time intervals for the microwave and non-microwave reaction products.

4.6 Microwave Effects on Other Modified Cyclodextrins

Analogous ring-opening polymerization reactions of the same kind were performed with modified β-cyclodextrins that contains, few of their identical secondary hydroxyl functionalities still free. Two alkyl derivatives of β-CD, one with all the primary hydroxyl group substituted by hydroxypropyl moieties (6 hydroxylpropyl β-CD) and another a randomly dimethylated β-cyclodextrin (2,6 dimethyl β-CD) are used as the core molecules in the analogous reaction. Ring-opening polymerization conditions for ε-caprolactone, under microwave irradiation, is reproduced in these reactions, even retaining the catalytic amounts of $Sn(oct)_2$.

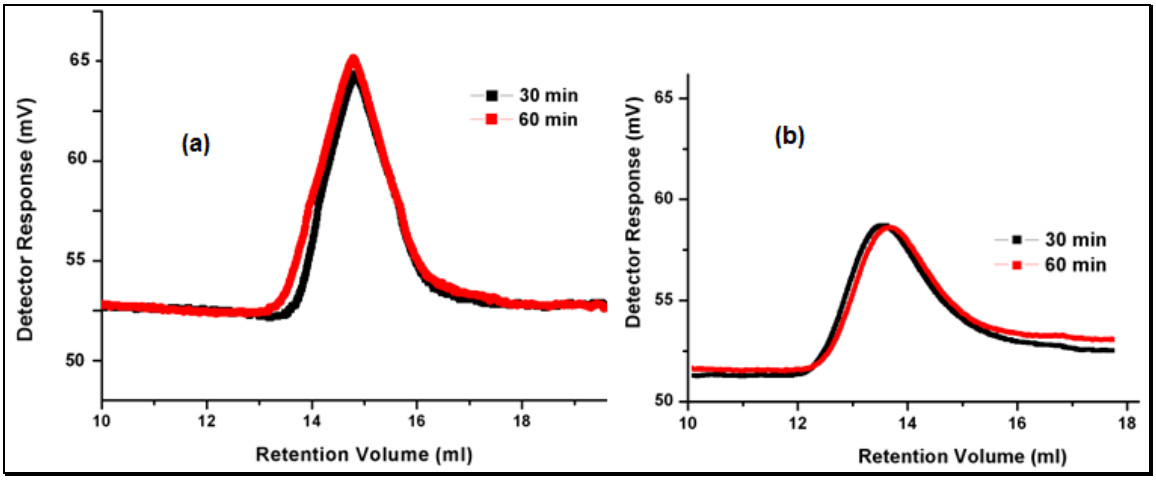
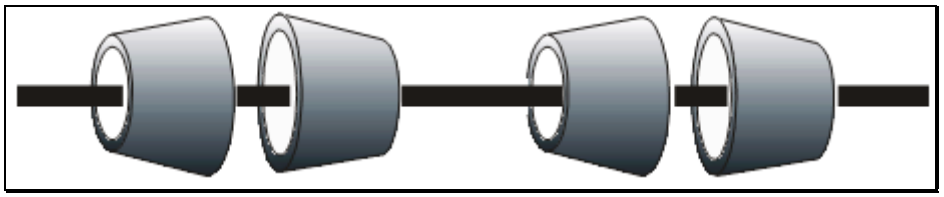


Figure 4.9: GPC elugrams for the ROP of ε-caprolactone with (a) hydroxypropyl and (b) dimethyl β-cyclodextrins

GPC traces, for the reactions are monitored at specific time intervals for each of the CD derivatives. The resultant elugrams revealed, a mono-modal peak for either of the methyl and hydroxypropyl derivatives, even after a prolonged reaction time of 1 hour inside the microwave reactor. The peak for hydroxylpropyl β-CD (at ~14.8 ml) is much intense than that observed for the randomly methylated β-CD derivative (at ~16.1 ml). Figure 4.9 represents the behaviour of both the CD derivatives.

A sensible hypothesis to the above performance of hydroxypropyl and dimethyl CD derivatives can be effected such that none of the two alkyl derivatives can promote a coupling reaction of the poly(ε-caprolactone) chains to their CD core. The fact that too little number of secondary -OH groups are present and exposed on the cyclodextrin torus, virtually deny any possibility of coupling reaction. Moreover, any such exposed –OH groups are masked by the steric hindrances arising from their hydroxypropyl and dimethyl substituents along the CD ring. Additionally, both hydroxypropyl and methyl moieties are no better microwave absorbers unlike the methacrylate groups in the polymerizable CD derivative. Hence the possibility of a star formation with a CD core and poly(ε-caprlactone) arms are unfeasible.



Scheme 4.4: A head-to-head configuration of alkyl-β-CDs along the poly(ε-caprolactone) chain

Nevertheless, the most likely possibility of the poly(ε-caprolactone) chains getting included into the cyclodextrin cavity is always open. Inclusion complexations of this kind are reported comprehensively by many. The likelihood of a pseudo-polyrotaxane between the modified β-CD host and poly(ε-caprolactone) guest will thus lead to the well documented head-to-head or tail-to-tail packing of the CD ring along the polymer chains resulting in “molecular tubes” as schematically shown in Scheme 4.4.

4.6.1 Molecular Weight Analysis of the Pseudo(polyrotaxanes)

From the MALDI-TOF mass spectral analysis, of the pseudo(polyrotaxane) derived from hydroxypropyl β-CDs, it is possible to identify the "template polymer" in the pseudo(polyrotaxanes). In the event of a non-existence of a pseudo(polyrotaxanes) between poly(ε-caprolactone) and hydroxypropyl β-CDs, no peaks corresponding to the guest template polymer would have been observed in the MALDI-TOF spectrum. Randomly methylated- β-CD also formed such a pseudo(polyrotaxanes) with poly(ε-caprolactone). Though, the molecular weight of the compounds themselves could not be determined precisely by MALDI-TOF, probably due to fragmentation of the cyclodextrins in the MALDI procedure, the method can provide ample proof to the existence of included template polymers into the CD cavity

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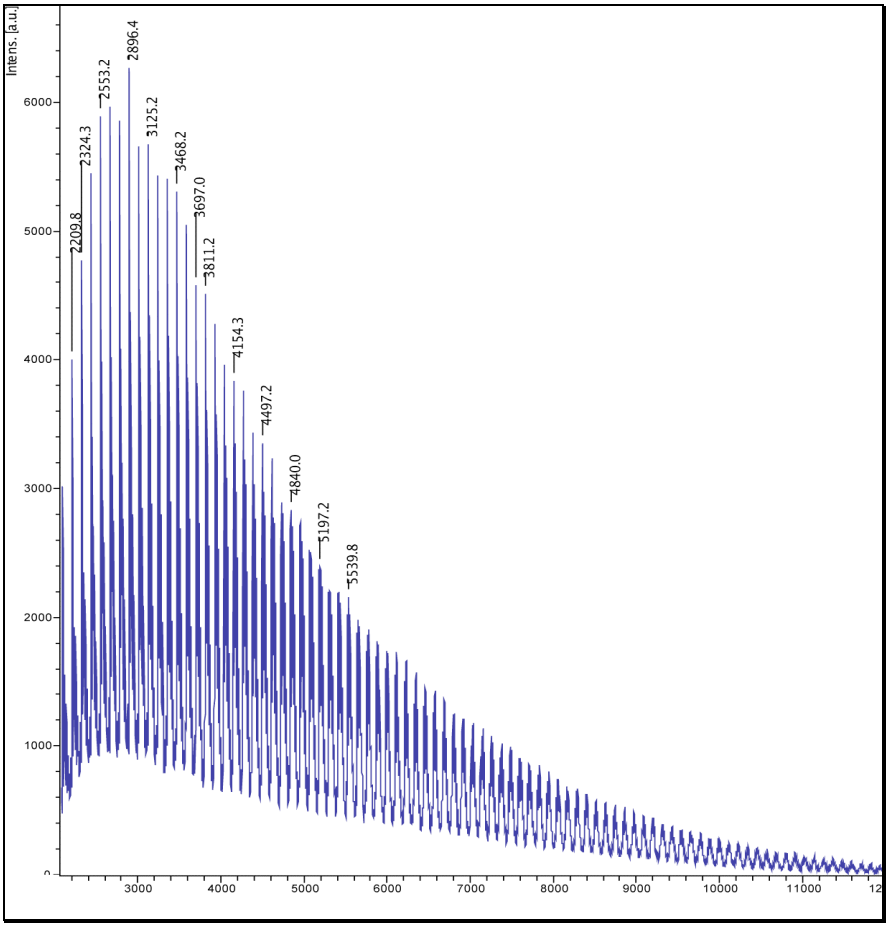

Figure 4.10a: MALDI-TOF spectra for the PCL / dimethyl β-CD poly pseudo-rotaxane

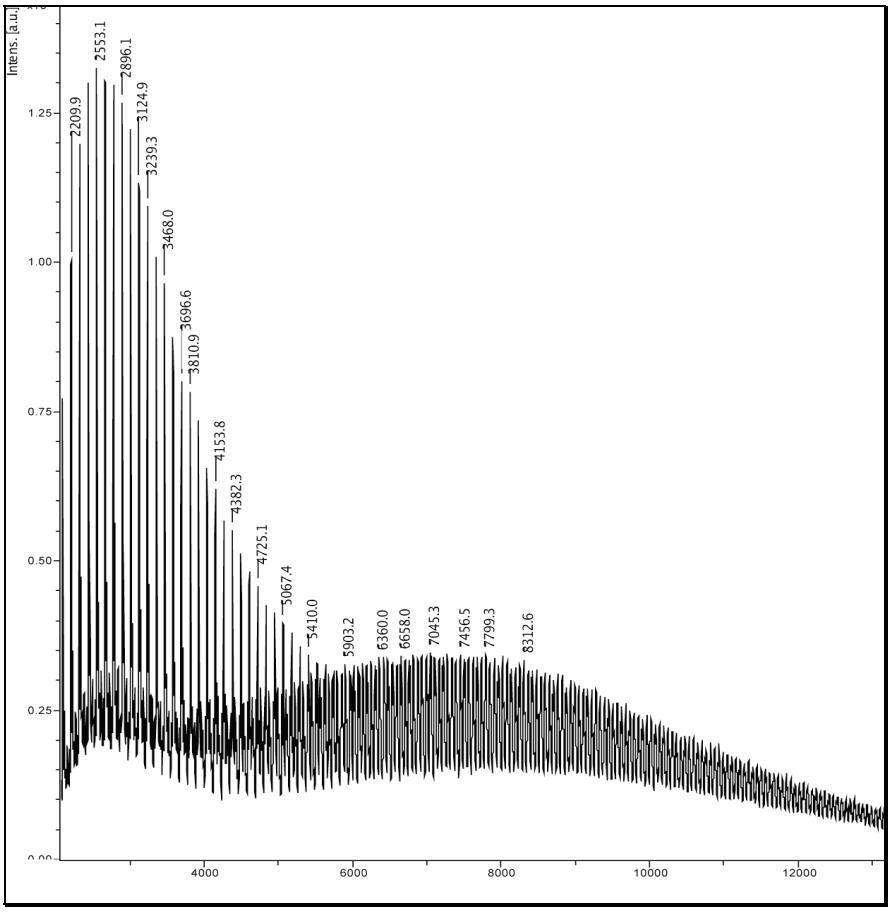

Figure 4.10b: MALDI-TOF spectra for the PCL / hydroxypropyl β-CD polypseudo-rotaxane

Figure 10a and 10b reveal the MALDI-TOF spectrum for the pseudo(poly rotaxanes) derived from hydroxylpropyl and dimethylated β-CDs. It has to be noticed that each signal in the spectrum appeared at 114 amu intervals or multiples of it, where 114 amu corresponds to the ε-caprolactone monomer unit.

Representative molecular weights, M_n and M_w obtained from GPC, for the pseudo(polyrotaxanes) obtained from both the alkyl derivatives may also suggest their potential towards rotaxanation. In fact, it has to be considered that, many CD derivatives behave differently with respect to their ability to form inclusion complexes with poly(ε-caprolactone) under microwave conditions. Similar findings are observed by Harada where the complexing abilities of native CDs and their derivatives are studied.

Reaction Time (minutes)	Hydroxypropyl-β-CD (At retention volume ~14.8 ml)			Methyl-β-CD (At retention volume ~15.9 ml)		
	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
15	30,031	35,159	1.171	5764	10,387	1.802
30	29,481	35,095	1.190	7326	12,779	1.744
60	30,479	35,545	1.166	8906	12,433	1.396

Table 4.4: Representative M_n and M_w values for the proposed pseudo(polyrotaxanes) of hydroxypropyl and dimethyl β-CDs with PCL

In this context, it can be assumed from the M_n and M_w values that (Table 4.4) the feasibility of forming a pseudo(polyrotaxane) complex with poly(ε-caprolactone is higher for hydroxypropyl β-CD than its dimethyl analogue. But then, for either of the CD derivatives, the M_n/M_w values remain largely constant as time passes, which might possibly owing to a threshold to which rotaxanation is possible. Beyond the threshold limit, no inclusion of the CD ring was possible even at extended reaction times for either of the hosts.

4.6.2 Viscosity and Thermal Analysis Correlations

With regard to the intrinsic viscosity, the intrinsic viscosities for the poly(ε-caprolactone)- alkyl β-CD pseudo(polyrotaxane) products are much lower than poly(ε-caprolactone) alone (Figure 4.11). Obviously, this arises due to the stiffening and binding effects exerted by the inclusion of the bulky cyclodextrin core into the poly(ε-caprolactone) chains. This finding is well supported by thermal analysis by DSC where the percentage crystallinity for the two kinds of pseudo-polyrotaxanes, after 60 minutes reaction time, are found to be different from poly(ε-caprolactone) (Table 4.5). The more is the stiffness of the polymer chain due to a favourable inclusion, the less will be the crystallinity, as observed for hydroxypropyl β-CD derivative.

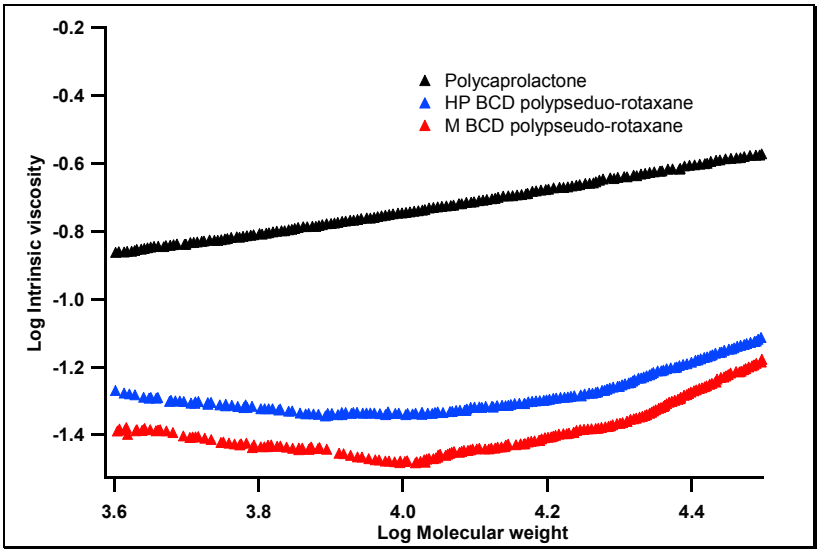

Figure 4.11: Intrinsic viscosity comparisons of poly pseudo-rotaxanes derived from modified-β-CDs with poly(e-caprolactone) (PCL) under MW

The % crystallinity for the dimethyl β-CD-poly(ε-caprolactone) polyrotaxane is slightly on the higher side, as the bulkiness effect due to CD ring is less in comparison to the previous case. This also throws light at the lesser ability of dimethylated β-CD to form a pseudo(polyrotaxane) over the hydroxypropylated β-CD as discussed before.

Polymer	*T_m (°C)*	*ΔH (J/g)*	*Crystallinity (%)*
Poly(ε-caprolactone)	55.53	64.14	46.14
MB-CD / PCL	49.71	50.76	36.52
HP-CD / PCL	46.95	47.14	33.91

Table 4.5: Percentage crystallinity calculated from the respective heat of fusion (ΔH) for the pseudo(polyrotaxanes) after 60 minutes reaction

4.7 Experimental

All the syntheses carried out under MW irradiation were performed under power control to assure a constant energy transfer during the entire reaction time.

4.7.1 Synthesis of methacrylated β cyclodextrin

20 gm (0.018 mol) β-cyclodextrin, 0.8 gm butylated hydroxytoluene (BHT), 0.4 gm dimethyl aminopyridine (DMAP) and 0.4 gm potassium methacrylate were dissolved in 55 ml dimethyl formamide (DMF). When the solution was homogenous 110 ml of methacrylic acid anhydride was slowly dropped on to the reaction mixture via a dropping funnel over 40 minutes time. The reaction was then further continued at 120^{o}C for 2 hours. The CD derivative was recovered by precipitating the mixture into methanol. Repeated precipitations yielded high purity. The product was filtered out and dried in vacuum.

^{1}H NMR ($CDCl_3$) δ (ppm): 6.2 – 3.0 (m, CH_n(cyclodextrin), CH_2(methacrylate), 1.88 (s, CH_3 (Methacrylate)

MALDI-TOF: m/z = 1733 amu, 8 methacrylic groups

4.7.2 Ring-opening polymerization in microwave reactor

ε-Caprolactone (1gm) was weighed out to the vial and added 0.176 gm of methacrylic β-CD. The CD derivative was dissolved in the mixture using a stirrer. 0.05 ml of tinoctoate was added to this mixture and stirred until homogenous. The vial was then loaded onto the microwave reactor. The reactor was set at 80W power and 150^{o}C. Several such sample reaction mixtures were prepared and the reaction was allowed to run for 5, 10, 15, 20, 25 and 30 minutes time. Tetrahydrofuran was added to the vial to dissolve unreacted CD derivative and polycaprolactone formed. The remaining solid was dried and characterized.

Similar reaction was performed under an oil bath mostly maintaining the temperature profiles for microwave. Here the reactions were allowed to go until 24 hours, aliquots were examined at every hour interval.

ε-Caprolactone was also homopolymerized to obtain a reference for the entire reaction products. The homopolymerization was performed in bulk for 25 hours at 100°C.

The ring-opening reaction was reproduced with hydroxypropyl and dimethyl β-CD derivatives as well.

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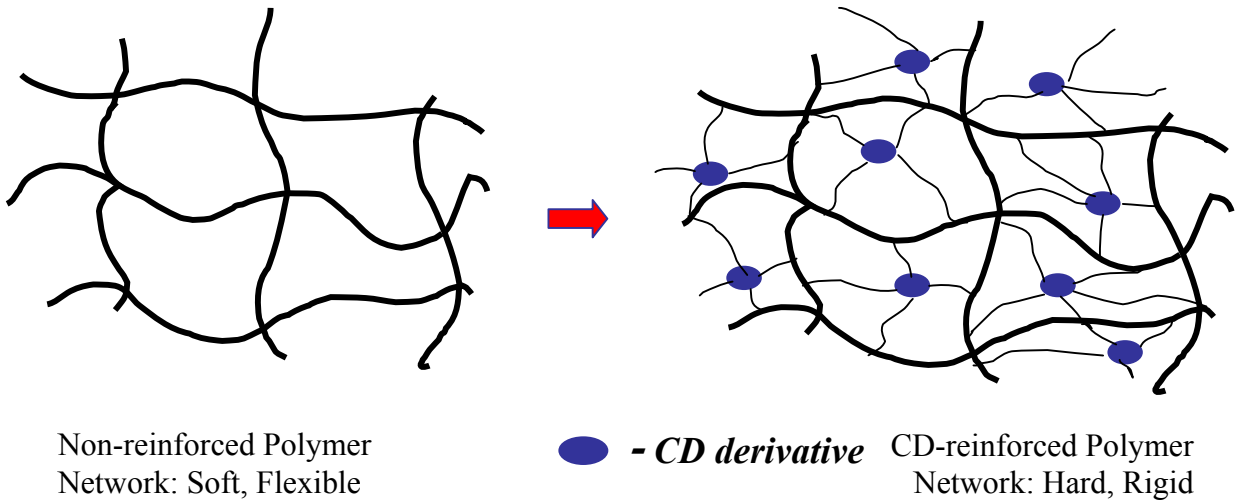
5. Polymerizable Cyclodextrin Derivatives for Molecular Reinforcement

5.1 Molecular Reinforcing Features of Cyclodextrin

A conventional route towards high performance polymers are based on the reinforcement of thermoplastic and thermoset matrices by fibres. The concept of molecular reinforcement originates from this idea where a rigid molecule replaces the fibre in the polymer matrix. Consequently, the adhesion forces between fibre and the matrix in the case of fibre reinforcement is replaced by molecular interactions between the polymer matrix and the rigid molecule. Thus, the assumption is that a rigid molecule dispersed in a polymer matrix will lead to an effective increase in the modulus of a polymer and the finding is that molecular reinforcement is as effective as fibre reinforcement.



Scheme 5.1: Molecular reinforcing effects of a cyclodextrin derivative on a polymer network

This research task tries to establish molecular reinforcing effects exploiting the rigid, toroid structure of cyclodextrin (CD) molecule. Cyclodextrins with polymerizable groups can be crosslinked to a polymer matrix generating a

highly crosslinked polymer network. This could appreciably change the overall performance of the polymers offering it greater strength, adhesion properties, dimensional stability etc. The general reinforcement behaviour of a cyclodextrin derivative can be represented as in the Scheme 5.1.

Though the strategy of modification depends on the purpose of the final product, the general reinforcement behaviour of a CD derivative depends mainly on two parameters, the appropiate selection of functional group and the degree of derivatization. Many different chemical moieties may be introduced into the cyclodextrin molecule by reaction with the hydroxyl groups lining in the upper and lower ridges of the toroid. The unique characteristics of cyclodextrin prompted this study to determine the feasibility of synthesizing polymerizable cyclodextrin derivatives. This invention generally relates to polymerizable CD monomers that have a multiplicity of functional groups, which compositions are useful components of industrial coating formulations for a number of specific applications. The principle focus is on functionalised methacrylated cyclodextrins and their derivatives, preferably beta-cyclodextrins because of their availability and economic considerations.

5.2 Functional Cyclodextrins for Polymer Coating Reinforcement

In conjunction with this task on functionalized polymerizable derivatives, few cyclodextrin derivatives have been synthesised to be investigated and applied to a polymer coating. Experiments and analysis have clearly shown a reinforcing effect due to the cyclodextrin molecule. The detailed synthetic procedures and reinforcing effects for the new CD derivatives along with the methods employed for their performance evaluation will be discussed.

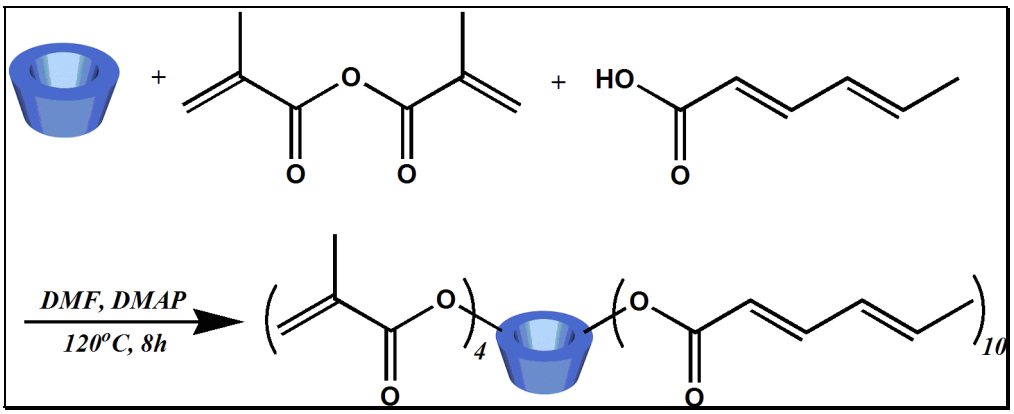
5.2.1 Performance Analysis of Coatings

Among a set of performance detection methods, initial measurements are focused mainly on determining the hardness, elasticity and resistance conducts of the polymerizable CD loaded coating. Hardness is detected by an instrument consisting of a pendulum which is free to swing on two balls resting on a coated test panel. The pendulum hardness (PH) test is based on

the principle that the amplitude of the pendulum's oscillation will decrease more quickly when supported on a softer surface. The hardness of any given coating is given by the number of oscillations made by the pendulum within the specified limits of amplitude determined by accurately positioned photo sensors. An electronic counter records the number of swings made by the pendulum. The effectiveness of the coatings are well evaluated by calculating the PH, after swelling the coating with xylene, and monitoring the PH variations at fixed time intervals. The xylene test gives a good understanding of the resistance to aromatic solvents and curing density gained by the coating. An additional chemical resistance test, the sulphuric acid drop test, in which each minute a new drop of 36% sulphuric acid was placed on the coating panel during a 30 minute period. Swelling and etching time scales for the respective coatings are directly observed from the visible marks on the panels. Elasticity was identified with an "Erichsen indentation tester", where a sphere is pressed from the backside against the coated panel. The depth of indentation at which the paint film does not crack is stated which correlates with the elasticity of the coating.

5.2.2 Synthesis of Polymerizable Cyclodextrin Methacrylates

The abundant –OH groups along a CD ring can be derivatized to yield a highly functional super crosslinker. Methacrylate derivatives of CD which are already used in UV curable tooth fillings, enhancing their mechanical properties like surface hardness by increasing the polymer crosslink density. The development of the current varieties of polymerizable CDs was targeted at their application in automotive clear coats that requires the combination of high etch and high scratch resistance. For high etch resistance the cross-linking is the key factor, while scratch resistance is mainly influenced by the cross-linking density and the flexibility of chains between net-points. By combining these parameters high etch and scratch resistant clear coats can be formulated. Additionally, coatings loaded with polymerizable CDs were analysed in UV curable coating systems for their strength and chemical resistance characteristics.



***Scheme 5.2**: Representative synthetic route to β-CD with methacryl and sorbic acid functionalities*

A multi functionalised CD derivative containing methacrylic group as the polymerizing function along with sorbic acid was synthesised following the Scheme 5.2. MALDI-TOF spectrum confirmed the empirical molecular weight and the degree of substitution for each of the substituent along the CD ring. The ring on an average, consisted of 4 methacrylic and 10 sorbic functionalities Figure 5.1

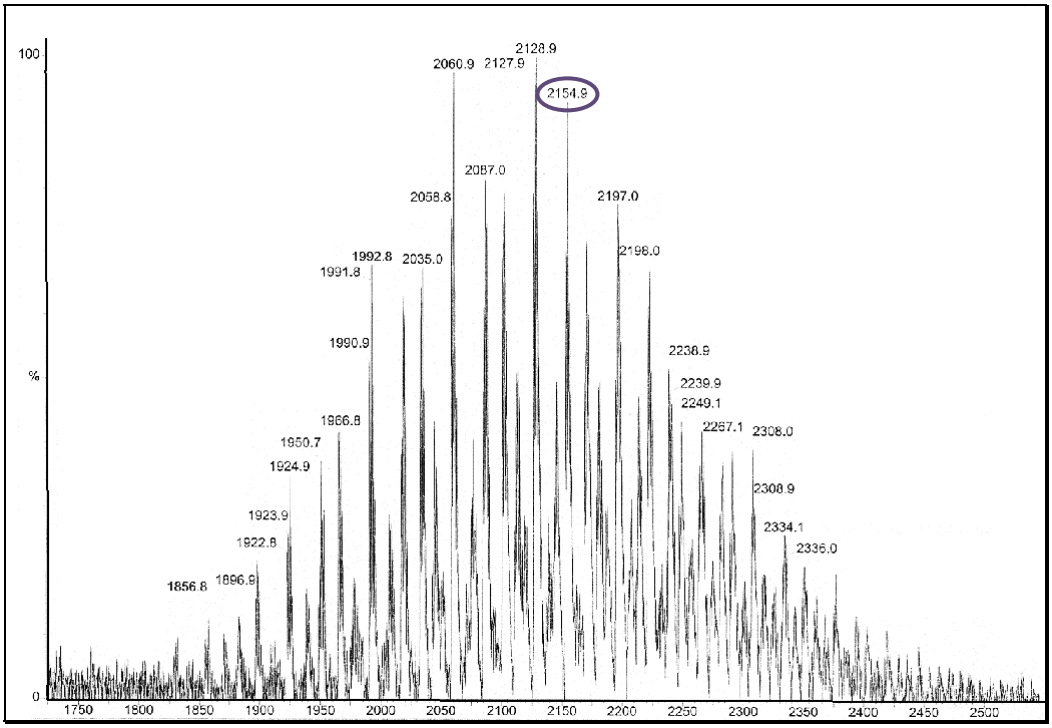


***Figure 5.1**: MALDI-TOF spectrum for β-CD with methacryl and sorbic acid functionalities, DS 4 and 10 respectively*

The resulting mixed ester derivative was a white solid which decomposed only at temperatures as high as 250°C. In a thermally initiated copolymerization with methyl methacrylate using AIBN, crosslinking and gelation effected within 2 minutes which apparently proved the effectiveness of the CD-derivative. The CD crosslinker was used as an additive in a UV-curable coating system and films of them were tested concerning hardness, elasticity and resistance features. Pendulum hardness (PH) for the films before and after swelling with xylene was recorded and of the values were found to be higher than for the reference coating while increasing amounts of CD derivative loaded had concomitant effect on the hardness characteristics too. Table 5.1 summarises the evaluation results for the coating with 10% and 20% additive amounts of CD derivative, compared to a reference coating.

Test	Reference	10% β-CD	20% β-CD
Pendulum hardness	15	33	64
Xylene test (PH after 15´)	12	18	26
Xylene test (PH after 2h)	13	23	41
Erichsen Indentation (mm)	9.0	8.1	8.2
Acid test (mark/etch)(min)	1/15	2/15	6/16
Yellowing (b*)	-2.46	-2.25	-2.42

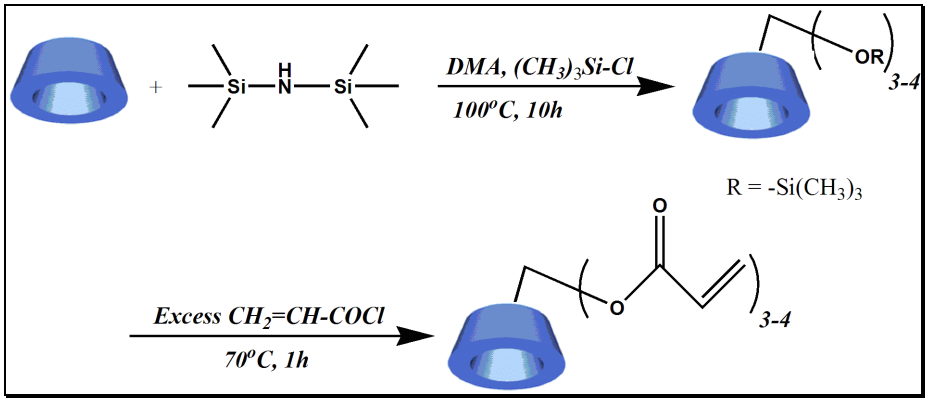
Table 5.1*: Test methods and performance comparisons for coatings with different loads of methacryl-sorbinic β-CD*

The absorption of UV light by the polymer coating provides the energy to break key bonds such as C=C, C-H or C=O near the surface of the exposed coating and creating free radicals. These free radicals react with oxygen and form peroxy radicals, which attack molecules in the coating. The absorption of UV light therefore induces minimum degradation along with crosslinking.

5.2.3 Synthesis of Polymerizable Cyclodextrin Acrylates

In comparison to the methacrylic derivatives, acrylic CDs have a much higher activity in UV-curing coating systems. The attachment of acrylic groups to CD ring was hence of much significance and a tempting task.

Acrylic derivatives of both α and β-CDs are prepared via the trimethyl silyl CD derivative (Scheme 5.3)



***Scheme 5.3**: Synthesis of CD-acrylates via the trimethyl silyl-CD derivative*

It was possible to achieve an average substitution of 3-4 acrylate groups on both α-CD and β-CD. Alpha and beta cyclodextrin acrylates are tested for their crosslinking effect on a polyurethane acrylate binder. 5 and 10 weight percent each of the derivatives are added to the binder and tested. The results are shown compared to a reference in Table 5.2

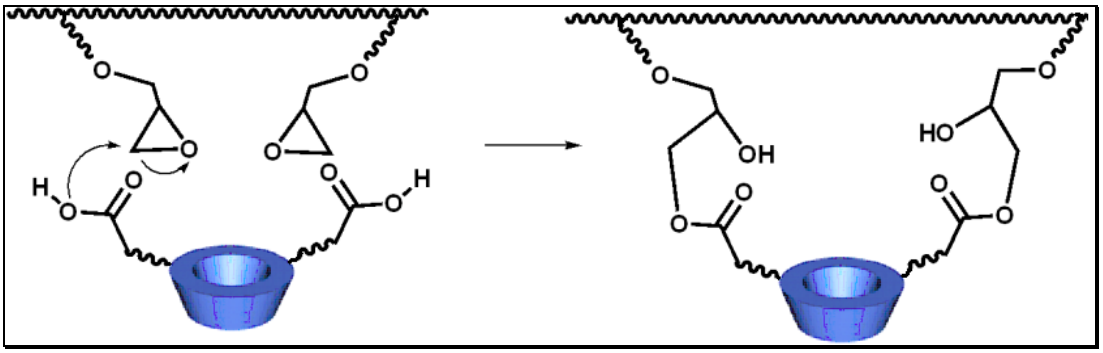
Test	0%	5% α-CD	10% α-CD	5% β-CD	10% β-CD
Pendulum hardness	15	25	32	23	29
Xylene test (PH after 15´)	10	18	23	19	20
Xylene test (PH after 2h)	11	24	29	21	27
Erichsen Indentation (mm)	8.8	9	9.2	9.5	9.2

***Table 5.2**: Performance comparisons for coatings with different loads of α-CD and β-CD acrylates*

5.2.3 Carboxy-Epoxy Crosslinking of Cyclodextrin Derivatives

Acidic and acid derived ligand groups can be attached on to the CD-ring, by reacting them with cyclic mono-anhydrides in presence of tertiary amines. The addition reaction of the cyclic substituent also results in ester substituents that retain free carboxyl groups. The free carboxyl group provide ligand functions with affinity for substrate sites and also allows

having a wide range of miscibility. Such CD derivatives can undergo carboxy-epoxy crosslinking on curing with an epoxy binder as represented in the Scheme 5.4.



***Scheme 5.4**: Carboxy-epoxy crosslinking initiated by a carboxyl functionalised CD*

For applications requiring high hydrophile-lipophile ratio, involving an application onto hydrophilic surfaces, synthesis utilizing appropriate proportions of cyclic anhydrides per CD molecule is used. Two such derivatives of β-CD functionalised with succinic and maleic moieties, (degree of substitution = 4), was added on to an epoxy binder and made into films. The coated films are subjected to pendulum hardness measurements and each of the films displayed higher hardness characteristics compared to the binder alone. Figure 5.2 displays the PH variations before and after xylene test for either of the coating kinds.

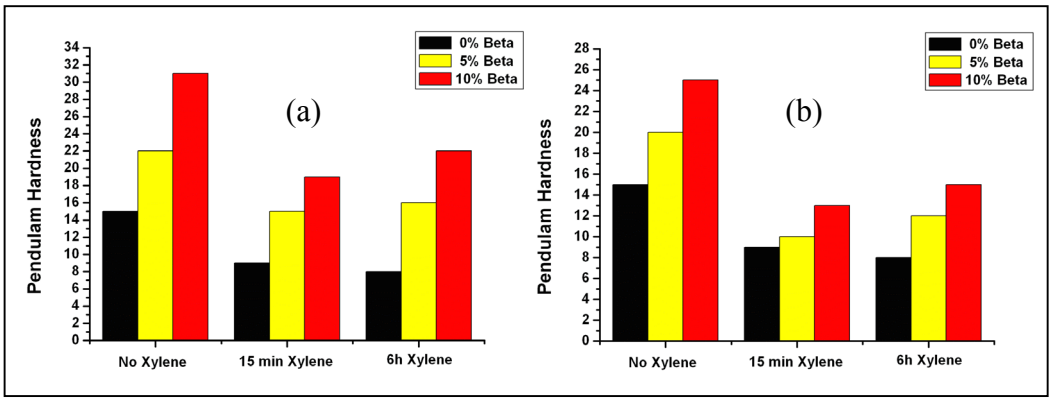


***Figure 5.1**: Pendulum hardnes comparisons for carboxyl β-CDs derived from a) succinic anhydride and b) maleic anhydride*

5.3 Experimental

5.3.1 Synthesis of methacrylic-sorbinic functionalised β-cyclodextrin

6.7 gm β-cyclodextrin was dissolved in 19 ml of DMF. To this was added 0.34 gm BHT, 0.16 gm DMAP and 0.16 gm potassium methacrylate. The entire solution was stirred to homogeneity and then added 2.25 gm sorbic acid. After dissolving the entire constituents, methacrylic acid anhydride was dropped into the solution under stirring. The whole mixture was heated in oil bath for 2 hours at 120^{o}C. It was then cooled and then poured into water for precipitating, filtered and dried. Reprecipitation by dissolving in minimum amounts of methanol and pouring into water ensured maximum purity.

^{1}H NMR ($CDCl_3$) δ (ppm): 6.2 – 3.0 (m, CH_n (cyclodextrin), CH_2 (methacrylate), CH (sorbic) 1.88 (s, CH_3 (Methacrylate), 1.91 (s, CH_3 (sorbic)
MALDI-TOF: 2154 amu, 4 methacryl and 10 sorbic acid groups on CD

5.3.2 Synthesis of cyclodextrin acrylates

Acrylic esters of Cyclodextrins were prepared via their trimethylsilyl derivatives. Dried β-cyclodextrin (10 g) was dissolved in 80ml dimethyl acetamide. hexamethyl disilazane (16.5 ml) was dropped slowly in over 40 minutes to this solution under stirring. Catalytic amounts of trimethylsilyl chloride(0.6 ml) was dropped and the mixture was refluxed at 100^{o}C for 10 hours under nitrogen. After the reaction was complete the mixture was concentrated to half its original volume and poured into 300 ml methanol. To this clear solution 30 ml water was dropped very slowly at intervals, when silylated cyclodextrin precipitates. The compound can be purified by dissolving it in acetone and re-precipitating in water.

Trimethylsilyl cyclodextrin derivative (5g) was added under nitrogen atmosphere to 2.5-5 equivalents of acrylic acid chloride. The mixture was heated for 60 minutes at 70^{o}C and the resulting chlorotrimethylsilane was completely distilled off. The residue was dissolved in minimum quantity dry methanol and precipitated in water. The precipitated cyclodextrin-acylate ester was filtered and dried at 40^{o}C under vacuum.

^{1}H NMR ($CDCl_3$) δ (ppm): 6.2 – 3.0 (m, CH_n (cyclodextrin), CH_2 (2s, acrylate), CH (s, acrylate).

5.3.3 Synthesis of carboxyl CD derivatives

β-Cyclodextrin (5 gm) was dissolved in dried DMF. 0.34 gm of DMAP and 1.3 ml of diethyl methylamine was slowly dropped to this mixture over some time and stirred for few minutes. The cyclic anhydride, maleic acid anhydride was added in 3 portions. The viscous mixture was then heated at the oil bath for 3 hours at 100^{o}C. At the end, the pale green solution was precipitated in acetone when white powder like product forms and settles on allowing to stand. Filter and recover the product in better purity. Any unreacted anhydrides can be removed by stirring longer in acetone, carefully avoiding any moisture presence. Final product was obtained after vacuum drying.

A similar method was used with succinic anhydride as well.

^{1}H NMR ($CDCl_3$) δ (ppm): 8.7 (s, COO*H*), 6.2 – 3.0 (m, CH_n (cyclodextrin), CH_2 (m, maleic), CH (s, maleic).

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6. Conclusive Remarks

The inventions performed and discussed in this thesis relate in its entirety on cyclodextrins and cyclodextrin related compounds. Along the whole study, all the efforts were put in trying to exploit enormous opportunities that this biomolecule offers with synthetic chemistry dealing with, complexation, polymerization, self-assembling to macrostructures and even as molecular reinforcing agents-something which has not been documented to date. Additionally, incorporating the possibilities of microwave assisted green synthetic methods along with the much greener choice of cyclodextrins as the target compound in these studies, all convenient and benign methods and motives are executed in the total research work.

This study tries to open up prospects for the future as well. The most tempting combination of cyclodextrin chemistry together with microwave assisted synthetic methodologies will be largely inspiring. There are reported to be over 10,0000 citations regarding cyclodextrins, their derivatives concerning all aspects of complexation, polymerization, catalysis etc, but extensively on conventional chemical synthesis. However, there are apparently no or minimum discovery or recommendations to the use of microwave synthesis in cyclodextrin chemistry. Apparently, a 'library' of different permutations and combinations involving CDs and their combination with microwaves is the need of the hour.

With regard to the chemistry discussed herein, the first recommendation would be a direct extension of the current work. In order to fully comprehend the polymerization effects on difunctionalised monomers, a study of the effect on a range of monomers, both aliphatic and aromatic should be undertaken. The examination of the effects of each of the cyclodextrin kinds (α, β and γ) into forming interlocked polyrotaxane networks will be an interesting avenue. Initial experiments are pursued in this work; however, the results of these experiments are preliminary and inconclusive. Future reactions of the same kind should be performed to apply these mechanisms for the construction of new topological polymers, design and prepare new types of main-chain, side-chain and three dimensional network polyrotaxanes by self assembly and in the synthesis

of other polyrotaxanes with versatile backbones carrying non-covalent CD rings.

Microwave induced coupling reactions and subsequent self-assembling has opened possibilities for 'supramolecules' at short reaction times. In this context, cyclodextrins as a catalyst and core to initiate polymerization of cyclic lactones already studied can be extended to many other lactones and lactides. In these reactions, CDs combine their act as a catalyst and also as a supporting architecture similar to certain proteins and enzymes in living systems. The mechanism is similar to that of an enzyme because the substrate is non-covanetly bound to the active site in forming a self-assembly, and they are concurrently released from the active site under appropriate circumstances. The entire reaction with lactone and CD reaching up the level of a supramolecule thus creates an ideal biomimetic polymerization system.

This study also involved combining and reacting polymerizable cyclodextrin derivatives with binder coatings so as to create molecular interactions between the polymer matrix and the CD derivative. Such molecular reinforcing effects presents functionalized cyclodextrins as a "super crosslinker", when appropriately derivatized. A heavily substituted CD incorporated into a coating in specified amounts will produce crosslinked products, having substituents located in 'quasi-random' configurations on one or both of the two rims of the various cyclodextrin molecules, anchoring the polymer chains intact. The high crosslink density of these polymers gives greater strength, durability and dimensional stability. As a result, a novel combination of properties of polyfunctional CD monomers and their formulations provides for an unprecedented variety of potential uses. Cyclodextrin derivatives may well be a substitute to the trivial fiber reinforcing methods opening a more workable bio-alternative in crosslinking chemistry.

7. General Experimental Notes

If not otherwise stated, all reagents were commercially available and used as received. The solvents were distilled and, when the case, conveniently dried before use.

^{1}H-NMR and ^{13}C-NMR spectra were performed using a Brucker Advance DRX 500 spectrometer at 500.13 MHz for proton and 125.77 MHz for carbon, using $(CD_3)_2SO$, D_2O or $CDCl_3$ as solvents. The δ-scale relative to TMS was calibrated to the deuterium signal of the solvent as an internal standard. Infrared spectra were recorded on a Nicolet 5SXB FT-IR spectrometer.

Gel permeation chromatography (GPC) was performed on a GPC-system consisting of a Waters 486 tunable absorbance detector at 275 nm and a Waters 410 differential refractometer, using THF as eluent. The system was calibrated with polystyrene standards with a molecular weight range from 580 to 1 186 000 D. The flow rate was 1 mL·min^{-1}. 100 µL of a 0.125% (wt./wt.) polymer solution was given to a HEMA-column-combination consisting of a pre-column of 40 Å and main columns of 40, 100, and 300 Å porosities.

GPC was also performed on a GPC-system consisting of a Viscotek VE 3580 differential refractometer and a Viscotek viscometer model 250, using DMF as eluent. The system was calibrated with polystyrene standards with a molecular weight ranging from 580 to 1 186 000 D. The flow rate was 1 mL·min^{-1}. 100 µL of a 0.125% (wt./wt.) polymer solution was given to a SDVB based ViscoGEL column-combination consisting of a pre-column HHR-H and two main columns GMHHR-M.

Glass transition temperatures (Tg) were determined using a Mettler Toledo TC15 TA Controller apparatus at a heating rate of 10 °C per minute. The Tg values are reported as the average of three measurements using the midpoint method. The same instrument was also used to perform the syntheses in normal thermal heating conditions (§ 2).

A monomode microwave reactor (CEM-Discover) operating at a maximum power of 300W equipped with an infrared pyrometer and a fiber optic contact thermometer was used. The calibration curve of the infrared pyrometer was built using a digital thermometer Heidolph EKT 3001.

The fluorescence spectra were recorded with a JASCO FP-6200.
MALDI-TOF-MS was performed on a Bruker Ultraflex time-of-flight mass spectrometer equipped with a 337-nm nitrogen laser.

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Die hier vorgelegte Dissertation habe ich eigenständig und ohne unerlaubte Hilfe angefertigt. Die Dissertation wurde in der vorgelegten oder in ähnlicher Form noch bei keiner anderen Institution eingereicht. Ich habe bisher keine erfolglosen Promotionsversuche unternommen.

Düsseldorf, den 10.05.2009

Mahesh Kumar Sarvothaman