

ABSTRACT

Molecularly imprinted polymers (MIPs) are kinds of powerful materials with promising selective molecule recognition abilities. However, the conventional MIPs have relatively low binding capacity. In order to improve this characteristic of MIPs, the modification monomer based on β -cyclodextrin (β -CD) and the essential of reversible addition-fragmentation chain transfer (RAFT) polymerization process were studied to generate potential MIPs. The study focuses on the characterization and adsorption behaviour of MIPs for selective recognition of benzylparaben (BzP) analyte. The potential of β -CD in MIP was investigated by synthesizing a reversible addition-fragmentation chain transfer molecularly imprinted methacrylic acid functionalized β -cyclodextrin polymer; RAFT-MIP(MAA- β -CD) based on methacrylic acid functionalized β -cyclodextrin (MAA- β -CD) monomer, which was then compared to a reversible addition-fragmentation chain transfer molecularly imprinted methacrylic acid polymer; RAFT-MIP(MAA) synthesized without β -CD. Both MIPs were prepared by the RAFT polymerization process in bulk polymerization method. The resulting MIPs were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Field Scanning Electron Microscope (FESEM) and Brunauer-Emmett-Teller (BET) analysis. The batch adsorption study that includes studying of the pH, kinetic, isotherm and thermodynamic was conducted. The essential of RAFT polymerization on MIP was studied by comparing RAFT-MIP(MAA- β -CD) with the molecularly imprinted methacrylic acid functionalized β -cyclodextrin polymer; MIP(MAA- β -CD) was synthesized without RAFT agent, and characterized by using FTIR, elemental analysis, FESEM and BET. The binding experiments demonstrated that the RAFT-MIP(MAA- β -CD) has a higher binding capacity and higher accessibility compared to RAFT-MIP(MAA) and MIP(MAA- β -CD) for selective of BzP, respectively. The β -CD and RAFT polymerization process improved the MIP's physical properties and

enhanced its recognition capacity, thus affecting the adsorption behaviour of RAFT-MIP(MAA- β -CD). The effects of RAFT polymerization process were also investigated by a reversible addition-fragmentation transfer molecularly imprinted hydroxyethyl methacrylate functionalized β -cyclodextrin polymer; RAFT-MIP(HEMA- β -CD). The RAFT-MIP(HEMA- β -CD) was synthesized based on the hydroxyethyl-methacrylate functionalized β -cyclodextrin (HEMA- β -CD) monomer and was prepared by the RAFT polymerization process in bulk polymerization method. The molecularly imprinted hydroxyethyl-methacrylate functionalized β -cyclodextrin polymer; MIP(HEMA- β -CD) without a RAFT agent was synthesized as comparison. A similar study to RAFT-MIP(MAA- β -CD) had also been carried out for RAFT-MIP(HEMA- β -CD). The effects of RAFT polymerization on RAFT-MIP(HEMA- β -CD) were contrasted with RAFT-MIP(MAA- β -CD). The compact and non-porous morphology of RAFT-MIP(HEMA- β -CD) reduces its binding capacity performance compared to MIP(HEMA- β -CD). Thus, this directly affected the RAFT-MIP(HEMA- β -CD) adsorption behaviour towards BzP. It was resulted that the RAFT polymerization had not improved the synthesis of RAFT-MIP(HEMA- β -CD). Careful choice of RAFT agent and monomer is essential in realizing good control over the RAFT-MIP polymerization process, and generating potential MIP.

ABSTRAK

Polimer molekul tercetak (MIPs) adalah penjerap yang terbaik, dengan menjanjikan keupayan kognitif molekul terpilih. Walau bagaimanapun, MIPs konvensional mempunyai keupayaan kapasiti pengikatan yang agak rendah. Bagi menambahbaik keupayaan MIPs, pengubahsuaian monomer berdasarkan β -siklodextrin (β -CD) dan keperluan proses pempolimeran fragmentasi rantai pindah boleh balik (RAFT) telah dipelajari untuk menghasilkan MIPs yang berpotensi. Fokus kajian adalah tertumpu kepada pencirian dan sifat penjerapan MIPs bagi keupayaan kognitif terpilih terhadap analit benzilparaben (BzP). Keupayaan β -CD di dalam MIP telah diselidik dengan mensintesis polimer tercetak molekul metakrilik asid berfungsi β -siklodextrin fragmentasi rantai pindah boleh balik; RAFT-MIP(MAA- β -CD) menggunakan monomer metakrilik asid berfungsi β -siklodextrin (MAA- β -CD), dan kemudian dibandingkan dengan polimer tercetak molekul metakrilik asid fragmentasi rantai pindah boleh balik; RAFT-MIP(MAA) yang telah disintesis tanpa β -CD. Kedua-dua MIPs telah disediakan melalui process pempolimeran RAFT dalam kaedah pempolimeran pukal. MIPs yang dihasilkan telah dicirikan menggunakan Spektroskopi Infra-merah Pemindahan Fourier (FTIR), Mikroskopi Imbasan Medan Elektron (FESEM) dan Brunauer-Emmett-Teller (BET) analisis. Kajian penjerapan merangkumi pH, kinetic, isotem dan termodinamik telah dijalankan. Keperluan proses pempolimeran RAFT di dalam MIP telah dikaji melalui perbandingan RAFT-MIP(MAA- β -CD) dengan polimer tercetak molekul metakrilik berfungsi β -siklodextrin; MIP(MAA- β -CD) yang telah disintesis tanpa agen RAFT, dan dicirikan menggunakan FTIR, analisis unsur, FESEM and BET. Eksperimen-eksperimen pengikatan telah menunjukkan bahawa RAFT-MIP(MAA- β -CD) mempunyai keupayaan pengikatan yang lebih tinggi berbanding RAFT-MIP(MAA) dan kebolehcapaian yang tinggi berbanding MIP(MAA- β -CD) terhadap pemilihan BzP. β -

CD dan proses pempolimeran RAFT dapat menambahbaik sifat fizikal dan meningkatkan prestasi kapasiti kognitif MIP, dan seterusnya memberi kesan terhadap sifat penjerapan RAFT-MIP(MAA- β -CD). Kesan proses pempolimeran RAFT juga, telah dikaji menggunakan polimer tercetak molekul hidrosietil metakrilat berfungsi β -siklodektrin; RAFT-MIP(HEMA- β -CD). RAFT-MIP(HEMA- β -CD) disintesis berdasarkan monomer hidrosietil metakrilik berfungsi β -siklodektrin dan disediakan melalui proses pempolimeran RAFT dalam kaedah pempolimeran pukal. Polimer tercetak molekul hidrosietil metakrilat berfungsi β -siklodektrin; MIP(HEMA- β -CD) disintesis tanpa agen RAFT sebagai perbandingan. Kajian yang sama seperti RAFT-MIP(MAA- β -CD) telah dijalankan terhadap RAFT-MIP(HEMA- β -CD). Kesan pempolimeran RAFT terhadap RAFT-MIP(HEMA- β -CD) adalah berbeza dengan RAFT-MIP(MAA- β -CD). Morfologi yang padat dan tidak porous pada RAFT-MIP(HEMA- β -CD) telah mengurangkan prestasi kapasiti pengikatannya berbanding MIP(HEMA- β -CD). Seterusnya, memberi kesan kepada sifat penjerapan RAFT-MIP(HEMA- β -CD) terhadap BzP. Ini menunjukkan bahawa pempolimeran RAFT tidak menambahbaik proses sintesis RAFT-MIP(HEMA- β -CD). Pemilihan yang teliti terhadap agen RAFT dan monomer adalah penting dalam merealisasikan kawalan yang baik terhadap proses pempolimeran RAFT-MIP, dan menjana MIP yang berpotensi.



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LIST OF ABBREVIATIONS

BET	Brunauer-Emmet-Teller
BJH	Barrett-Joyner-Halenda
BPO	Benzyolperoxide
BuP	Butylparaben
BzP	Benzylparaben
CDB	Cumyl dithiobenzoate
CD	Cyclodextrin
CTA	Chain transfer agent/RAFT agent
DBTDL	Dibutyltin dilaurate
DMAC	Dimethylacetamide
DR	Dubinin-Radushkevich
EtP	Ethylparaben
FRP	Free radical polymerization
HEMA	Hydroxylethyl methacrylate
HEMA- β -CD	Hydroxylethyl methacrylate
MAA	Methacrylic acid
MAA- β -CD	Methacrylic acid functionalized β -cyclodextrin
MAA- β -CD-BzP	Inclusion complex of methacrylic acid functionalized β -cyclodextrin with benzylparaben
MeP	Methylparaben
MIP(HEMA- β -CD)	Molecularly imprinted hydroxylethyl methacrylate functionalized β -cyclodextrin polymer

MIP(MAA)	Molecularly imprinted methacrylic acid polymer
MIP(MAA- β CD)	Molecularly imprinted methacrylic acid functionalized β -cyclodextrin polymer
MIPs	Molecularly imprinted polymers
NIP(HEMA- β -CD)	Non-molecularly imprinted hydroxyethyl methacrylate functionalized β -cyclodextrin polymer
NIP(MAA)	Non-molecularly imprinted methacrylic acid polymer.
NIP(MAA- β -CD)	Non-molecularly imprinted methacrylic acid functionalized β -cyclodextrin polymer
PrP	Propylparaben
RAFT	Reversible addition-fragmentation chain transfer polymerization
RAFT-MIP(HEMA- β CD)	Reversible addition-fragmentation chain transfer molecularly imprinted hydroxyethyl methacrylate functionalized β -cyclodextrin polymer
RAFT-MIP(MAA- β CD)	Reversible addition-fragmentation chain transfer molecularly imprinted methacrylic acid functionalized β -cyclodextrin polymer
RAFT-NIP(HEMA- β CD)	Reversible addition-fragmentation chain transfer non-molecularly imprinted hydroxyethyl methacrylate functionalized β -cyclodextrin polymer
RAFT-NIP(MAA- β CD)	Reversible addition-fragmentation chain transfer non-molecularly imprinted methacrylic acid functionalized β -cyclodextrin polymer
RDRP	Reversible deactivation radical polymerization
TDI	Toluene-2,4-diisocyanate
TRIM	Trimethylolpropane trimethacrylate
β -CD	β -cyclodextrin

LIST OF SYMBOLS

b	Langmuir constant
B_t	Boyd parameter
b_T	Temkin constant related to the heat of adsorption (J mol^{-1})
C_0	Concentration of the solute in the initial solution (mg L^{-1})
C_i	Initial concentration of solution (mg L^{-1})
C_f	Final concentration of solution (mg L^{-1})
C_e	Equilibrium concentration of BzP (mg L^{-1})
C_p	Amount of BzP per gram
C_t	Concentration of the solute in the liquid phase (mg L^{-1})
C_t	Equilibrium concentration of solution (mg L^{-1})
E	Mean free energy (kJ mol^{-1})
$h = k_2 q_e^2$	Initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$)
IF	Molecular imprinting effect
IP	Effect of the boundary layer thickness constant (mg g^{-1})
k_1	Pseudo-first order rate constant (min^{-1})
k_2	Pseudo-second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$)
K_d	Distribution coefficients
k_{ext}	Diffusion rate parameter for film diffusion model (min^{-1})
K_F	Freundlich constant for sorption capacity (mg g^{-1})
k_i	Particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{1/2}$)
K_T	Temkin constant related to the equilibrium binding energy
n	Freundlich constant for intensity
q_D	Maximum adsorption of BzP at the total specific micropore volume of the adsorbent
q_e	Amount of the BzP adsorbed at equilibrium (mg g^{-1})

q_t	Amount of the BzP adsorbed at any time (mg g^{-1})
Q_e	Binding capacity of BzP (mg g^{-1})
q_m	maximum sorption capacity (mg g^{-1})
q_t	Amount of the BzP adsorbed at time (mg g^{-1})
R	Universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$)
R_L	Separation factor
T	Temperature (K)
t	Time (min)
$t_{1/2}$	Half adsorption time (min)
V	Volume of solution (L)
w	Mass of adsorbent particles (g)
α	Initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$)
β	Rate for the extended surface coverage and activation energy for chemisorptions (g mg^{-1})
Δq	Normalized standard deviation (%)
ε	Polanyi potential

CHAPTER 1

INTRODUCTION

1.1 Background of research

Adsorption process is the most versatile and widely used method for the removal of various kinds of emerging compounds because of its low cost, simplicity of design, ease of operation and insensitivity to toxic substances. Various adsorbents such as activated carbon, ion-exchanger, and agricultural waste have been developed for this process. However, the qualification of these adsorbents is limited because of the non-selectivity and non-specificity properties. Therefore, molecular imprinting is a convenient technique for preparing polymeric matrix with molecule-specific recognition properties due to its simple preparation and stable nature (Li *et al.*, 2009). This polymer is advantageous for the treatment of trace contaminants because it can be specifically designed to remove one or a group of targetted compounds (Murray and Örmeci, 2012).

Molecularly imprinted polymers (MIPs) are advance materials with promising selective molecular recognition abilities. The monomer and cross-linker are copolymerized in the presence of a template molecule (Haupt and Mosbach, 2000). The removal of the template molecule from the obtained polymer by simple solvent extraction reveals the complementary binding sites that can recognize the template molecule from its structurally similar compounds (Alexander *et al.*, 2006). However, the conventional MIPs have low capacity and poor site accessibility for the template molecules. Most of the conventional MIPs only function in organic solvents, but limited to aqueous solvents (Xu *et al.*, 2013).

In order to overcome these limitations, an appropriate modification of the monomer with β -cyclodextrin (β -CD) has been made to improve the binding capacity of the MIP. β -CD is a cyclic oligosaccharide consists of seven glucose units residues linked with α -(1,4) bonds, which has the hydrophobic and hydrophilic cavities at interior and exterior sides, respectively. Due to its unique torus-shaped structure molecule, it ideally forms an inclusion compound with various analytes by “host-guest interaction”.

The modification of monomer with β -CD may be ascribed to the lack of sufficient specific binding sites in the cavities created by imprinting due to the linking of several functional groups of functionalized monomers to β -CD (Xu *et al.*, 2013). Hence, the orientation of the β -CD molecule residues in the MIPs is suitable for the cooperative binding of the templates (Xu *et al.*, 2007). The recognition abilities of the MIPs could be improved, thus enhancing the binding capacity of MIPs.

The MIPs are mostly prepared by free radical polymerization (FRP) technique because of its simple method and convenient experimental condition. However, the FRP has little control over its polymer chain process, resulting in polymer matrix with heterogeneous structures (Watabe *et al.*, 2005). The consequences towards MIPs product are broad binding site heterogeneity, low affinity and reduced selectivity (Pan *et al.*, 2009).

Reversible deactivation radical polymerization (RDRP) process is suitable to overcome the limitation of the FRP process. The problematic chain termination in FRP is minimized by using living radical initiators, which results a constant and slower rates for polymer chain growth (Hu *et al.*, 2012). Hence, it would improve the mismatch in the

chain growth and chain relaxation rates, leading to homogeneous polymer networks structure.

The reversible addition-fragmentation chain transfer (RAFT) polymerization process is one type of the RDRP processes was selected in this study due to its versatile and an applicable method (Chiefari *et al.*, 1998). It is compatible with almost all of the traditional radical polymerization monomers and the condition of RAFT process is similar to FRP (Chinthamanipeta *et al.*, 2008). The mechanism of RAFT process involves FRP of substituted monomers in the presence of a suitable chain transfer agent (CTA) which is called as RAFT agent.

In this study, two topics were discussed which were (1) the modification monomer of MIPs based on β -cyclodextrin (β -CD) and (2) the reversible addition-fragmentation chain transfer (RAFT) polymerization as a type of the MIPs polymerization process. Both studies were investigated to improve the adsorption capacity of MIPs. A benzylparaben (BzP) was used as a template model of MIPs.

1.2 Objectives:

1. To synthesize and characterize the molecularly imprinted polymers based on methacrylic acid, methacrylic acid functionalized β -cyclodextrin and hydroxyethyl methacrylate functionalized β -cyclodextrin monomer.
2. To study the effect of β -CD and RAFT agent on the properties and selective approach of molecularly imprinted methacrylic acid functionalized β -cyclodextrin polymer.

3. To study the effect of RAFT agent on the properties and selective approach of molecularly imprinted hydroxyethyl methacrylate functionalized β -cyclodextrin polymer.
4. To compare the effect of RAFT agent on RAFT-MIPs based on different monomers.

1.3 Significant of study

Molecularly imprinted polymers (MIPs) are significant in various applications especially in separation process. Therefore, there is a growing interest in the synthesis of molecularly imprinted polymers (MIPs) based on various preparation techniques to overcome several drawbacks of MIP system. MIPs are poor in certain aspects, and the most important drawback is its relatively low binding capacity. This has allowed us to use β -cyclodextrin (β -CD) functionalized with acrylic acid monomers as a new monomer and to prepare the MIP via reversible addition-fragmentation chain transfer (RAFT) polymerization process. The uniqueness of β -CD and the versatility of RAFT polymerization process have showed to be an excellent strategy. The characteristic and properties of MIPs have been studied in detailed.

CHAPTER 2

LITERATURE REVIEWS

2.1 Molecularly imprinted polymer (MIP)

2.1.1 The imprinting process

Molecularly imprinted polymers (MIPs) are materials that are prepared in the presence of a template that serves as a mould for the formation of a template-complementary binding site (Bonini *et al.*, 2007). The MIP is prepared by mixing the template molecule (targeted analyte) with monomer, cross-linker, and initiator in the presence of porogenic solvent. Subsequently, this pre-polymerization mixture is irradiated with UV light or subjected to heat in order to initiate polymerization.

During polymerization the complexes formed between the template molecule and monomers will be stabilized within the resulting rigid and highly cross-linked polymer. After polymerization and removal of the molecular template from the polymer matrix, the resulting rigid three-dimensional cavity will be complementary to the target analyte. Thus, it will enable the resultant polymer to selectively rebind the imprint molecule and its related compounds (Yan and Row, 2006).

The formation of the MIPs typically involves the copolymerization of a complex formed by the template and a monomer via three types of imprinting approaches, either non-covalent imprinting approach, covalent imprinting approach or semi-covalent imprinting approach (Figure 2.1).

Non-covalent imprinting approach is the frequently used method to prepare MIP due to its flexibility and easy conductive way (Mayes and Whitcombe, 2005). During polymerization, the specific binding sites are formed by the self-assembly between the template and the monomer, followed by a cross-linked co-polymerization. Removal of the template is usually accomplished by continuous extraction (Yan and Row, 2006). The imprint molecules interact with the MIP polymer during both the imprinting procedure and the rebinding process via non-covalent interactions.

The covalent imprinting approach is an interaction which makes the template and the monomer strongly assembled together by covalent linkage. This interaction possibly can prevent leakage of template molecules during polymerization. The hydrolysis process must be used to cleave the template molecule (template removal) from polymer matrix to form the specific binding sites. The MIPs rebind template molecules using the same covalent interactions (He *et al.*, 2007).

Semi-covalent imprinting approach is the hybridization between covalent and non-covalent imprinting approaches. This approach relies on a covalent bonding between the template and the monomer during the polymerization process. During the rebinding process, the imprint molecule and the MIP polymer interact via non-covalent interaction (Beltran *et al.*, 2010).

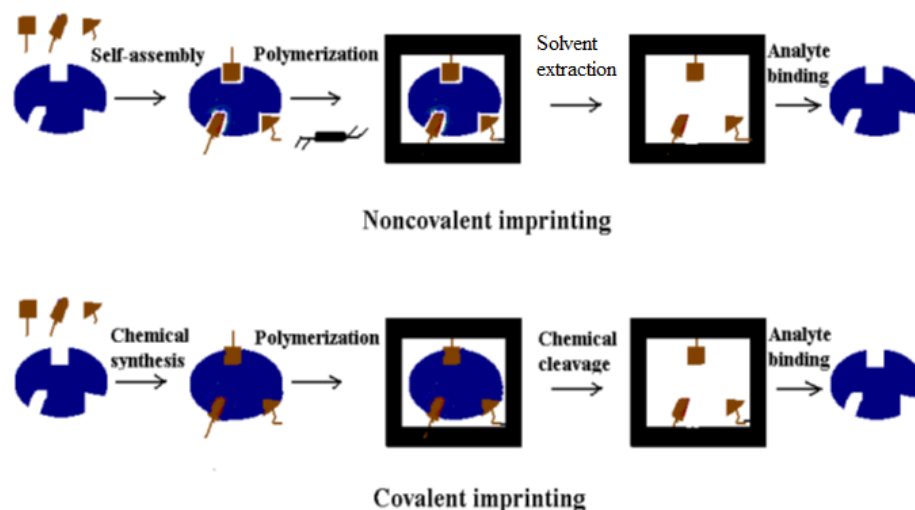


Figure 2.1: Schematic representation of covalent and non-covalent imprinting approach procedures (Yan and Row, 2006).

2.1.2 MIP components

In the synthesis of MIP, the selection of appropriate components including monomer, cross-linker, template, porogenic solvent and initiator is necessary.

2.1.2.1 Monomer

Monomers are responsible for the binding interactions in the imprinted binding sites. The careful choice of monomer is utmost important in providing complementary interactions with the template and substrates (Spivak, 2005). Typical monomers that are used include carboxylic acid, sulphonic acid, and heteroaromatic bases groups. Methacrylic acid (MAA) is a type of carboxylic acid group monomer that has been extensively used due to its hydrogen bond donor and acceptor characteristics, and its suitability for ionic interactions (Ye and Mosbach, 2001).

In non-covalent imprinting protocols, monomers are normally used in excess relative to the number of moles of template to favour the formation of template-monomer

assemblies (Vasapollo *et al.*, 2011). It is very important to match the functionality of the template with the functionality of the monomer in a complementary fashion (e.g. H-bond donor with H-bond acceptor) in order to maximize complex formation, thus maximizing the imprinting effect. The ratio of 1:4 and upwards for template to monomer is rather common for non-covalent imprinting (Cormack and Elorza, 2004).

Other examples, such as monomers based on polymerizable amidines and ureas have been developed for stoichiometrically imprinted polymeric receptor of β -lactam antibiotics (Urraca *et al.*, 2006), reducing non-specific adsorption. Lübke *et al.* (2000) have synthesized a bis(boronate-amide) monomer (carboxylate receptor) and a polymerizable chlorinated quinine (amine receptor) and used stoichiometric amounts of the two monomers in preparing MIPs that are capable of efficient binding of ampicillin from aqueous solution.

The co-monomers applied in MIP synthesis would give higher retention and resolution than that of a used single monomer, which is an indication of an increase in the affinity of the MIP (Yan and Row, 2006). In this way, a wide range of molecular interactions (ionic pairing, hydrogen bonding and hydrophobic forces) may be simultaneously exploited in applying non-covalent imprinting (Ye and Mosbach, 2001).

2.1.2.2 Cross-linker

In order to achieve high selectivity for the MIP polymer, types and amount of cross-linker are used in the imprinting process. The cross-linker is significant in controlling the morphology of the polymer matrix where it serves to stabilize the imprinted binding sites and imparts mechanical stability to the polymer matrix in order to retain its molecular recognition capability (Sellergren, 1999).

Different cross-linkers have been used in molecular imprinting. For example, ethylene glycol dimethacrylate (EGDMA) and trimethylolpropane trimethacrylate (TRIM) are widely employed as a cross-linker in non-covalent molecular imprinting. TRIM gives polymers more rigidity, structure order and effective binding sites than that of EGDMA (Vasapollo *et al.*, 2011).

High cross-link ratios are generally used in order to permanently access porous (macroporous) materials with adequate mechanical stability (Cormack and Elorza, 2004). Some researchers have found that cross-linker has a major impact on the physical characteristics of the polymers and much less effect on the specific interactions between the template and monomers (Shi *et al.*, 2007; Navarro-Villoslada *et al.*, 2004).

2.1.2.3 Template

Template is very important because it directs the organization of the functional groups pendent to monomers in all molecular imprinting processes. In terms of compatibility with free radical polymerization, templates should be chemically inert under the polymerization conditions, thus alternative imprinting strategies may have to be sought if the template can participate in radical or if it unstable the polymerization conditions (Yan and Row, 2006).

2.1.2.4 Porogenic Solvent

The porogenic solvent serves to bring all the components (template, monomer, cross-linker and initiator) in the polymerization into one phase. It plays an important role in the formation of the porous structure of MIP. The nature and level of solvent determine

the strength of non-covalent interactions and influence polymer morphology, and directly affect the performance of MIP.

The porogenic solvent should produce large pores to assure good flow through the properties of the resultant MIP. An increase in the volume of the solvents will enlarge the pore volume of the polymer. For this reason, the solvent is referred as the “porogen”. As usual, relatively low polarity solvents are used in MIP synthesis in order to reduce the interferences during complex formation between the imprint molecule and the monomer (Vasapollo *et al.*, 2011; Yan and Row, 2006).

In some reports, efficient MIPs have been prepared in polar solvents because strong template-monomer interactions have been observed. For example, water-compatible imprinted polymer with strong affinity for a polar 1-methyladenosine template has been synthesized in acetonitrile/water and successfully used as solid phase extraction (SPE) sorbent to extract analyte from spiked human urine samples (Scorrano *et al.*, 2010).

2.1.2.5 Initiator

Initiator is used to induce the initiation of polymerization process. Many chemical initiators with different chemical properties can be used as the radical source in free radical polymerization. Normally initiators are used at low levels compared to the monomer, e.g. 1 wt. % or 1 mol % with respect to the total number of moles of polymerizable double bonds (Cormack and Elorza, 2004). The rate and mode of decomposition of an initiator to radicals can be triggered and controlled in a number of ways including heat, light and by chemical/electrochemical means, depending on its

chemical nature. The commonly used initiators are benzoylperoxide, azobisisobutyronitrile, azobisdimethylvaleronitrile, and 4,4'-azo(4-cyanovaleric acid).

2.1.3 Preparation method of MIP

Different uses and applications of MIPs require different MIPs properties, thus many preparation methods of MIPs have been developed. Bulk polymerization is a conventional approach to prepare MIPs. The obtained MIP is grinded and successively sieved into the desired size ranges where the diameters are usually in the micrometer range (Baggiani *et al.*, 2005; Silvestri *et al.*, 2005). Nevertheless, the process to get the appropriate particle sizes is tedious and time-consuming and it produces particles that are highly irregular in size and shape (Turiel and Martin-Esteban, 2005). In addition, some interaction sites are destroyed during grinding, thus reducing the MIP loading capacity. This method suffers from high consumption of template molecules (Vasapollo *et al.*, 2011).

However, most imprinting publications are still based on bulk polymerization even though with the drawbacks insufficient control of the MIP physical form and difficulties in scaling up MIP production. Besides, this method is the most popular as it presents many attractive properties, especially to newcomers, in developing a new fundamental of MIP synthesis because it is a simple method and it does not require particular operator skills or sophisticated instrumentation (Yan and Row, 2006).

To overcome the limitation of the conventional bulk MIP, numerous research groups in molecular imprinting technology have attempted the production of MIP beads by using several preparation methods such as precipitation, suspension, dispersion, core-

shell emulsion, and seed/multi-step swelling. Table 2.1 summarizes each preparation method.

Table 2.1: Summary of molecularly imprinted polymer (MIP) prepared by different methods (Yan and Row, 2006).

MIP format	Benefits	Limitations
Bulk	Popular, Simplicity, no require particular skills or sophisticated instrumentation.	Tedious procedures of grinding, sieving and column packing, irregular particle in size and shape.
Precipitation	Imprinted microspheres, uniform size beads, high yields, and no need for additional stabilizer.	Large amount of template, high dilution factor, random aggregates product.
Suspension	Spherical beads, highly reproducible products, large scale possible.	Phase partitioning of complicate system, water is incompatible with most imprinted procedures, stabilizer (surfactant) required.
Dispersion	Simple technique, spherical, and near monodisperse beads.	Under developed in terms of molecular imprinting, stabilizer required.
Core-shell emulsion	Monodisperse beads, surface imprinting.	Complex, irreproducible.
Multi-step swelling	Monodisperse beads, well developed method.	Complex, need for aqueous emulsions.

2.1.4 Molecularly imprinted polymer in analytical applications

The main advantages of MIPs are their high selectivity and affinity properties for the target molecules used in the imprinting procedure. In addition, as compared to biological systems such as proteins and nucleic acids, MIPs have higher physical robustness, strength, resistance to elevated temperature and pressure. It also shows

inertness towards various acids, bases, metal ions and many organic solvents. The storage life endurance of the MIPs are very long and they can keep their recognition capacity for several years at room temperature (Sánchez-barragán *et al.*, 2007; Kielczyński and Bryjak, 2005). The peculiar properties of MIPs have made them versatile and become a promising adsorbent and highly interesting tool for different application areas especially in analytical techniques.

2.1.4.1 Solid-phase extraction

The application of MIPs in solid phase extraction (SPE) is the highest potential technique used in analytical chemistry field (Tamayo *et al.*, 2007). MIP for solid phase extraction (MISPE) is performed both in on-line or off-line procedures (Pichon and Chapuis-Hugon, 2008; Baggiani *et al.*, 2007). The MIPs particles are used as selective sorbent materials.

The on-line MISPE procedure is directly coupled with specific analytical systems such as high performance liquid chromatography (HPLC), thus minimizes samples manipulation and reduces the loss of analytes as well as the eventual contaminations (Garcia *et al.*, 2011). The off-line MISPE is the most effective procedure due to its simple methodology. Moreover, many solvents are easily handled regardless of their influence on the successive separation methods (Vasapollo *et al.*, 2011).

MISPE was successfully applied for extraction of many compounds in different sample matrices such as food analysis (Baggiani *et al.*, 2007; Puoci *et al.*, 2005), biological (Scorrano *et al.*, 2010; Caro *et al.*, 2006) and environmental samples (Caro *et al.*, 2004; Masqué *et al.*, 2001). MIPs have also been applied in other different selective extraction such as solid-phase microextraction (SPME) (Mullett *et al.*, 2001), stir-bar

sorptive extraction (SBSE) (Zhu *et al.*, 2006) and matrix solid phase dispersion (MSPD) technique (Crescenzi *et al.*, 2001).

2.1.4.2 Liquid chromatographic

Molecularly imprinted chromatography is another application of MIPs especially for liquid chromatography (LC) (Remcho and Tan, 1999; Kempe and Mosbach, 1995). The MIPs are used as a stationary phase and are prepared as tailor-made supports in LC due to their advantage of being able to be prepared with a predetermined selectivity for a targeted analyte (Vasapollo *et al.*, 2011). The MIPs are usually prepared by bulk polymerization process and then packed in a chromatographic column. However, this polymerization process results in irregular particles with board size distribution and lead to the packing of irreproducible quality particles which are not well suited for the preparation of chromatographic phases (Haginaka, 2008).

In order to overcome these drawbacks, many literatures have proposed several polymerization methods such as monoliths MIP (Sun *et al.*, 2009; Huang *et al.*, 2003) and spherical imprinted particles (Tamayo *et al.*, 2005; Turiel and Matrin-Esteban, 2005) to be used as chromatographic stationary phases. Matsui *et al.* (1993) was the first to propose a simple MIP synthesis called monoliths MIP.

The monolithic MIP is prepared directly inside the capillary columns or stainless steel column (Yin *et al.*, 2005; Matsui *et al.*, 1993). The obtained monolithic MIPs have fewer non-selective sites compared to conventional bulk MIP particles. Careful selection of porogenic solvent has been carried out in order to get a polymer with enough porosity to assure good flow-through properties (Haginaka, 2008).

In order to decrease heterogeneous size distribution, spherical imprinted particles are also prepared. To obtain a spherical MIP, several methods such as precipitation, suspension and multi-step swelling have been used as chromatographic stationary phases (Wei *et al.*, 2006).

2.1.4.3 Capillary electrochromatography (CEC)

MIPs have also been used as stationary phase for capillary electrochromatography (CEC). CEC is a hybrid separation technique that combines the stationary phase of LC with the electro-osmotically driven mobile-phase transport of electrophoresis (Vasapollo *et al.*, 2011; Turiel and Martin Esteban, 2005). The CEC is inherently more efficient chromatographic technique than the conventional HPLC. Moreover, CEC-mode separations lead to an improved performance of MIPs compared to that achieved in conventional LC (Andersson, 2000). The use of MIPs as stationary phase in CEC does not intrinsically differ from those described as conventional LC.

However, MIP columns have to fulfil some specific requirements according to the characteristics of CEC technique such as the used of capillary column, the necessity of electroosmotic driven flow and the possibility to carry out in-column detection (Turiel and Martin Esteban, 2005). The application of MIP based micro-column for CEC for separation of several compounds has been successfully realized (Turiel and Martin Esteban, 2005; Lämmerhofer *et al.*, 2000; Vallano and Remcho, 2000).

2.1.4.4 Sensors

IUPAC defines a chemical sensor as a device that transforms chemical information from the concentration of a specific sample component to total composition

analysis, into an analytical useful signal (Hulanicki *et al.*, 1991). The application of MIPs in chemical sensor is of growing interest in the field of analytical chemistry.

Recently, MIP is used as a sensor due to its highly selective and affinity recognition, high thermal, chemical and pressure tolerance, long-term stability, and insolubility in water and most organic solvents (Javanbakht *et al.*, 2008). Hedborg *et al.* (1993) was the first that reported the use of MIP as a sensor. They combined MIP membranes with field-effect devices as transducers to monitor chemical signals. Since then, the demand of interest in the generation of MIPs as a device sensor is grow.

MIPs application as a sensor include entrapping MIP particles into gels and immobilizing them on a platinum electrode for selective detection via amperometric measurements (Kriz and Mosbach, 1995), screen-printed electrodes functionalised with MIP layers for detecting herbicide compounds via differential-pulse and cyclic voltammetry (Krisch *et al.*, 2001; Kroger *et al.*, 1999).

Till date, MIPs have been successfully used with different types of transducers and several methods have been used to achieve a close integration of the transduction platform with the MIPs (Piletsky *et al.*, 2006). Such methods include as in-situ polymerization, photochemical process, thermal initiator process and surface grafting either with chemical or UV initiation (Henry *et al.*, 2008; Titirici and Sellergren, 2006; Piletsky *et al.*, 2000).

2.2 Polymerization process in Molecularly Imprinted Polymer

2.2.1 Free radical polymerization (FRP)

Free radical polymerization (FRP) process is the most widely used method for the industrial preparation of polymers. It is evidence that approximately 50 % of the world production of polymers is based on this process due to the fact that it is a robust process which is able to produce a range of materials with unique functions (Semsarilar and Perrier, 2010).

The advantages of FRP process is that it can be used with a large variety of monomers and tolerant to a wide range of functional groups such as OH, NR₂, COOH, CONR₂) and impurities in the system (e.g. water) (Moad *et al.*, 2005). Besides its fast chain growth, it also can generally be carried out under mild reaction conditions (ambient temperatures and atmospheric pressure) and wide production methods (in bulk, solution, suspension and dispersion). Thus, FRP is a simple method to implement and inexpensive commercially cost.

FRP is a process in which the propagating species is a long-chain free radical, initiated by the attack of free radicals derived from unstable materials called initiators (Semsarilar and Perrier, 2010). The high rates of polymerization process are consequences of the high reactivity of the radical species, which is responsible for the drawbacks of the technique. Instead of participating in the propagation process by addition of monomer, the radical species can undergo side-reactions leading to chain transfer or chain termination. The consequences are broad molecular weight distribution and lack of control over the chain-ends (Pound *et al.*, 2008).

The uncontrollability process does not only resulting polymer with broad molecular weight distribution (Li *et al.*, 2010b) but also provided heterogeneous structures of polymer networks (Wang and Zhu, 2005). The presence of heterogeneity within the network structures of the MIPs could have significant impact on the binding sites inside the networks, which might be responsible for some inherent drawbacks of the MIPs such as the broad binding site heterogeneity and the relatively low affinity (Pan *et al.*, 2009).

2.2.2 Reversible deactivation radical polymerization (RDRP)

Started in the mid-1990s, the polymer chemistry field has witnessed the volatile development of a number of procedures for conducting a reversible deactivation radical polymerization (RDRP) process (Braunecker and Matyjaszewski, 2007) known as a controlled or living radical polymerization process (Moad, 2014).

RDRP process can be advantageous in preparing polymers with well-controlled molecular weight, molecular weight distribution and well-defined structures (Fisher, 2001), in addition to controlled site-specific functionality and accessibility to complex architectures that were previously impossible to achieve using FRP process (Semsarilar and Perrier, 2010).

Since then, the problematic chain termination in FRP process can be minimized by using living radical initiators, which results in a much slower rate for polymer chain growth and a narrow molecular weight distribution for linear polymers (Boonpangrak *et al.*, 2006). Hence, it significantly improves the match in the chain growth and chain relaxation rates, which leads to homogenous polymer network structure (Pan *et al.*, 2009).

Furthermore, the RDRP process incorporates desirable features of traditional FRP (compatibility with a wide range of monomers, tolerance of many functionalities, and facile reaction conditions) (Semsarilar and Perrier, 2010). The major processes of RDRP are reversible addition-fragmentation chain transfer (RAFT) (Moad *et al.*, 2005), atom transfer radical polymerization (ATRP) (Kamigaito *et al.*, 2001; Matyjaszewski and Xia, 2001) nitroxide-mediated polymerization (NMP) (Nicholas *et al.*, 2013; Hawker *et al.*, 2001) and iniferter (Otsu, 2000). They have been developed in polymeric products due to their intrinsic advantages over FRP process.

The application of RDRP in molecular imprinting technology has successfully provided MIPs with improved binding properties, which is given a faster binding kinetics (Wei and Husson, 2007), higher binding capacities (Vaughan *et al.*, 2007; Boongpangrak *et al.*, 2006; Wang *et al.*, 2006) larger binding association constant (Salian *et al.*, 2012; Boonpangrak *et al.*, 2006) and higher affinity site densities (Pan *et al.*, 2009; Zu *et al.*, 2009).

2.2.3 Reversible addition-fragmentation chain transfer (RAFT) process

The reversible addition-fragmentation chain transfer (RAFT) polymerization process, which is one type of the RDRP methods, has been selected in this study. Among the RDRP types, RAFT polymerization has proven to be one of the most versatile technique (Chiefari *et al.*, 1998), which is applicable to a wide range of monomers (indeed, many of the monomers polymerizable by FRP) and reaction conditions without using metal catalyst, where no metal contaminants present in the final products (unlike ATRP process) (Cormack and Mehamod, 2013; Li *et al.*, 2010). RAFT mechanism involves the presence of a suitable chain transfer agent (CTA) (called RAFT agents) in the TRP of substituted monomers such as dithioesters, thiocarbamates, and xanthates.

The resultant polymer obtained by RAFT polymerization is end-capped by the moieties derived from the RAFT agent. As a result of which the functional groups can be easily introduced into the chain ends of the polymer by adjusting the structure of the RAFT agent used in the RAFT process (Lowe and McCormick, 2007). The mechanism of RAFT process involves FRP of substituted monomers in the presence of a suitable chain transfer agent (CTA) agent is shown in Figure 2.2.

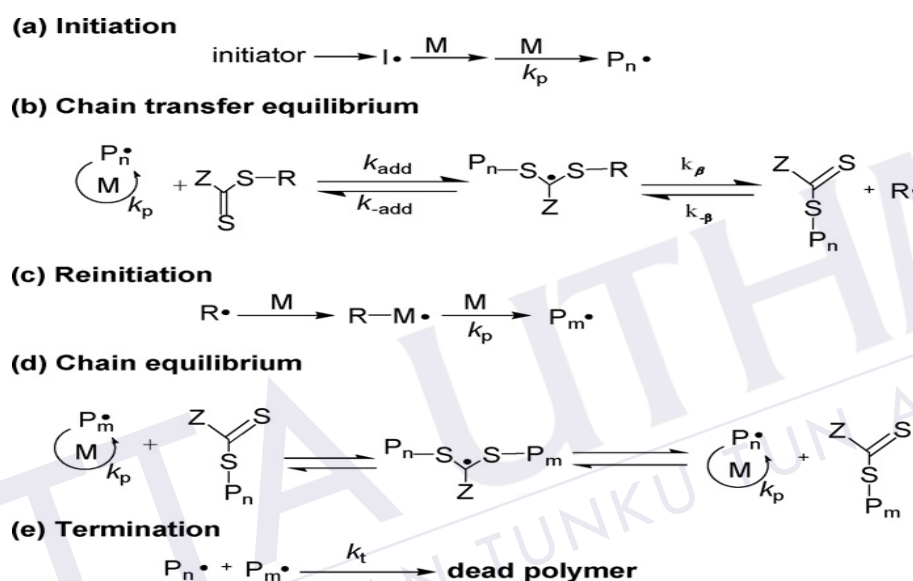


Figure 2.2: Mechanism of reversible-addition fragmentation chain transfer (RAFT) polymerization (Xu *et al.*, 2011a).

The initiation and radical-radical termination occur as in the conventional radical polymerization mechanism. At the stage of reversible chain transfer, the addition of a propagating radical ($\text{P}_n\cdot$) to the thiocarbonylthio compound $[\text{RSC}(\text{Z})=\text{S}]$ followed by fragmentation of the intermediate radical gives rise to a polymeric thiocarbonylthio compound $[\text{P}_n\cdot\text{S}(\text{Z})=\text{S}]$ and a new radical ($\text{R}\cdot$). Then, the reaction between the radical ($\text{R}\cdot$) and monomer forms a new propagating radical ($\text{P}_m\cdot$) in re-initiation stage. Then, the rapid equilibrium between the active propagating radicals ($\text{P}_n\cdot$ and $\text{P}_m\cdot$) and the dormant polymeric thiocarbonylthio compound provides equal probability for all chains to grow

and allows for the production of polymers with narrow polydispersity. When the polymerization is complete, most of the chains retain the thiocarbonylthio end group and can be isolated as stable materials (Xu *et al.*, 2011a).

The RAFT technique has been used by several researchers to produce MIP polymers on various substrates. For example, Titirici and Sellergren (2006) have introduced an approach to prepare thin films of MIP polymers which combines covalent immobilization of azo initiators with RAFT-mediated living radical polymerization on mesoporous silica beads.

Lu *et al.* (2007) formed a surface-imprinted core-shell nanoparticle using surface RAFT polymerization where the RAFT agent was functionalized onto silica nanoparticles in the presence of 2,4-dichlorophenoxyacetic acid as the template. Chang *et al.* (2010) synthesized core-shell MIP using the combination of RAFT polymerization and click reaction. The alkyne terminated RAFT chain transfer agents was firstly synthesized and then click reaction was used to graft RAFT agent onto the surface of silica particle which was modified by azide.

Southard *et al.* (2007) used a RAFT polymerization process to prepare a MIP for the luminescent sensing of pinacolyl methylphosphonate (PMP) compound. Recently, Zhang *et al.* (2013) synthesized MIPs using RAFT polymerization process in suspension polymerization method for selective recognition of vanillin.

2.2.4 RDRP challenges in MIP process

The RDRP in MIP process has been applied in several reports in recent years (Sasaki *et al.*, 2010; Vaughan *et al.*, 2007; Boonpangrak *et al.*, 2006). The MIPs prepared

using RDRP have been successfully developed with higher specific template binding and lower dissociation binding constant (K_d) than the MIPs prepared using FRP polymerization process. It can be concluded that the RDRP can improve the binding properties of MIPs.

Unfortunately, there are new reports which indicate that the MIPs prepared by RDRP have shown low binding capacities and template binding properties compared to the conventional MIPs (Ma *et al.*, 2013a; Zu *et al.*, 2010). These findings proved that the application of RDRP in molecular imprinting does not always improve the binding properties of the MIPs. However, an in-depth investigation is required before a definite conclusion can be reached.

2.3 Cyclodextrin

2.3.1 Properties of CDs

Cyclodextrins (CDs) are cyclic oligomers of α -D-glucopyranose units are produced during the transformation of starch by certain bacterias such as *Bacillus macrons* (Qi *et al.*, 2007; Jeang *et al.*, 2005). The preparation process of CDs consists of four principal phases; (i) culturing of the microorganism that produces the cyclodextrin glucosyl transferase enzyme (CGT-ase); (ii) separation, concentration and purification of the enzyme from the fermentation medium; (iii) enzymatical conversion of prehydrolyzed starch in mixture of cyclic and acyclic dextrins; and (iv) separation of CDs from the mixture, their purification and crystallization.

CGT-ase enzymes degrade the starch and produce intramolecular reactions without the involment of water molecule. In this process, cyclic and acyclic dextrins

are originated, which are oligosaccharides of intermediate size. The cyclic dextrins are formed by the link among units of glucopyranose through glycosidic oxygen bridges by α -(1,4) bonds as shown in Figure 2.3.

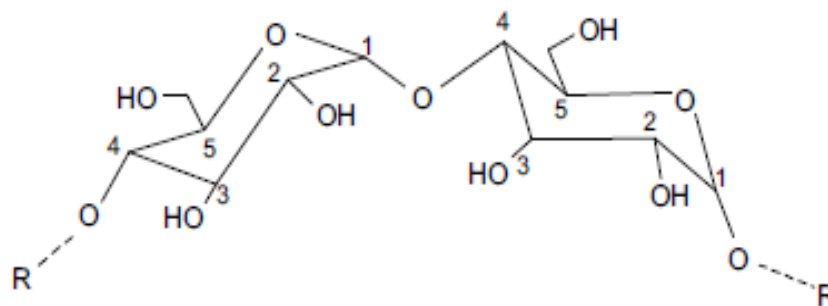


Figure 2.3: Glycosidic oxygen bridge α (1,4) between two molecules of glucopyranose (Astray *et al.*, 2009).

CDs which are well known non-toxic macrocyclic sugars of natural origin, excellent biocompatibility (Prabaharan and Mano, 2006), biodegradable (Lu *et al.*, 2008) and environmental friendly (Crini *et al.*, 2002) are considered to be helpful in many applications such as drug carrier and vitamins in pharmaceutical products, protecting foods and flavours in food industry, protecting natural colours in textiles industry, environmental protection and separation processes (Astray *et al.*, 2009; Del Valle, 2004; Radulovic *et al.*, 2001).

Due to these advantages, there was a progressive increase in the number of publications and patents related to the production of CDs (Singh *et al.*, 2002; Redenti *et al.*, 2001). CDs are of three types: α -cyclodextrin, β -cyclodextrin and γ -cyclodextrin. The α -CD comprises six glucopyranose units, β -CD comprises seven glucopyranose units and γ -CD comprises eight glucopyranose units (Figure 2.4) (Das and Jessup, 2000) which are torus-like macro-rings built up from glucopyranose units (Astray *et al.*, 2009).

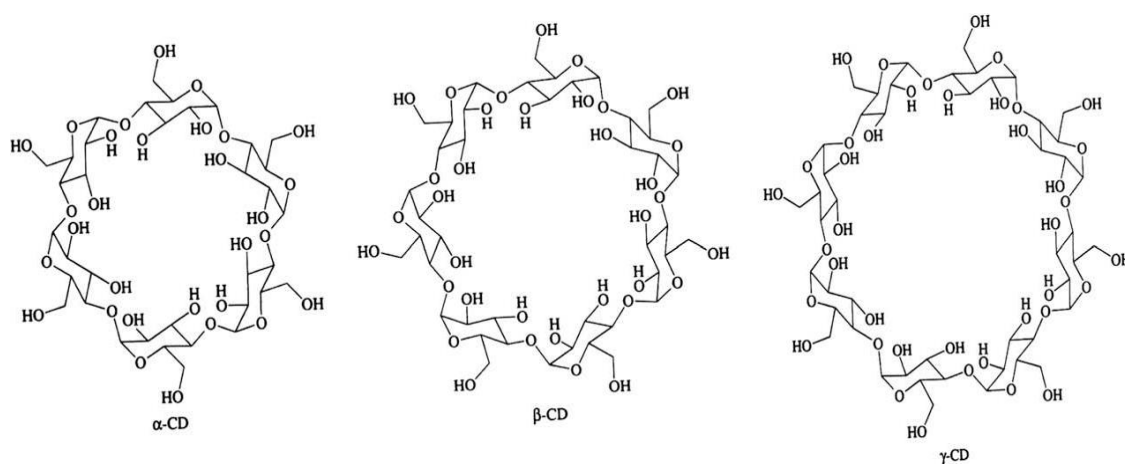


Figure 2.4: Chemical structures of α -CD, β -CD and γ -CD (Astray *et al.*, 2009).

The ring that constitutes the CDs is a conical cylinder, which is frequently characterized as a torus (doughnut shape) or wreath-shaped truncated cone (Figure 2.5). The cavity is lined by the hydrogen atoms and the glycosidic oxygen bridges. The non-bonding electron pairs of the glycosidic oxygen bridges are directed toward the inside of the cavity where they produce a high electron density and provide Lewis base characteristics (Saenger, 1983).

In the structure of CDs, the secondary hydroxyl groups (C_2 and C_4) are located on the wider edge of the ring and the primary hydroxyl groups (C_6) on the other edge and the apolar C_3 and C_5 hydrogens and ether-like oxygen are at the inside of the torus-like molecules. Because of this geometry, the interior of the cavity is relatively hydrophobic, described as a ‘micro heterogeneous’ environment, while the external of the cavity is relatively hydrophilic, which is soluble in water (Szejtli, 1898).

As the result of this cavity, CDs are able to form inclusion complexes with a wide variety of hydrophobic guest molecules. One or two guest molecules can be entrapped by one, two or three CDs called as “host- guest interaction” (Del Valle, 2004).

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