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Review
The effect of cyclodextrins on polymer preparation

JIE HU
Department of Polymeric Materials, Jiangsu University, Zhenjiang 212013, People's Republic of China; Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, People's Republic of China

ZHEN TAO
Department of Polymeric Materials, Jiangsu University, Zhenjiang 212013, People's Republic of China
E-mail: taozhen1975@hotmail.com

SONGJUN LI, BAILING LIU
Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, People's Republic of China

Cyclodextrins (CDs) and their chemically modified derivatives have been the subject of numerous investigations. These compounds have been applied in many fields, e.g. food chemistry, cosmetic and pharmaceutical industries due to their special structure. Recently, especially in the latest 5 years, there are many researches focused on the effect of CDs in polymer preparation. This article concluded in detail the successful application of CDs in polymer synthesis in aqueous solution. Some special aspects of cyclodextrins are found concerning the thermodynamic, copolymerization parameters, and chain transfer reaction.

Cyclodextrins (CDs) are a group of structurally related cyclic oligosaccharides that are formed by enzymatic cyclization of starch [1]. CDs having six, seven, and eight (α-1,4)-linked α-D-glucopyranose units are called α-, β-, γ-CDs, respectively. The CD molecules are cone-shaped with a somewhat hydrophobic central cavity and hydrophilic outer surface. The main properties of CDs are shown in Table I. And β-CD is the most accessible, the lowest-priced and generally the most useful.

CDs and their chemically modified derivatives have been the subject of numerous investigations [2–5]. These compounds have been applied in many fields, e.g., food chemistry, cosmetic, organic coating and pharmaceutical industries [6–9]. CDs exhibit a kind of cavity (Fig. 1) with the hydrophobic interior 'lined' with hydrogen atoms and lone pairs of glycosidic oxygen atoms. On the other hand, primary and secondary hydroxyl groups situated at the narrow and wider bases, respectively, endow them with hydrophilic character. Due to their relatively hydrophobic cavity and hydrophilic outer shell, they are able to form host-guest complexes with suitable hydrophobic molecules [10, 11] (Fig. 2). The formation of these complexes results in significant changes of the solubility and reactivity of the guest molecules, but without chemical modification. It is believed that hydrogen bonds and hydrophobic interactions are responsible for it.

Thus, water insoluble molecules may become completely water soluble simply by mixing with aqueous solutions of CDs, and it turned out that the complexed hydrophobic monomers can be successfully polymerized via free radicals in water. It has aroused great interests of many researches. For example, octadecyl methacrylate (OM) and dodecyl methacrylate (DM), highly hydrophobic monomers, are difficult to polymerize in aqueous media using traditional surfactant system. The difficulty is usually considered to be a consequence of the very low water solubility of OM and DM. The monomer must display some degree of water solubility in order that the essential process of monomer transport through the aqueous phase may occur [12]. One useful method is to use CD to form inclusion compounds with the guest hydrophobic species. In the presence of CD, these monomers can be successfully polymerized by emulsion polymerizations that do not involve the use of excessive levels of surfactant [13]. And using β-CD as a complexing agent, the relative hydrophobic monomer N-methacryloyl-11-aminoundecanoic acid can be polymerized radically in water without using any organic solvent or protective colloids. Compared to the

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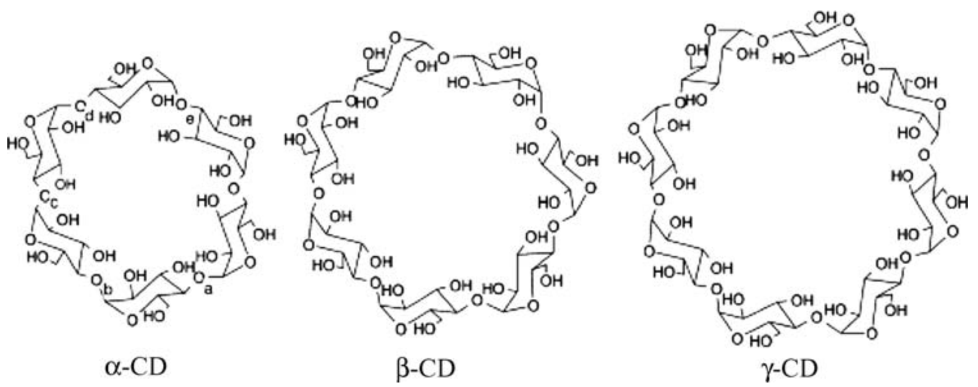

Figure 1 Structure of CDs.

polymerization of the uncomplexed monomer in a homogeneous DMSO/water solution under similar conditions, the precipitation polymerization of the monomer/CD pseudorotaxane in water occurs much faster, and the resulting molecular weights are relatively higher [14]. And it is also noticed that the storage stability of latexes increased with increasing CD concentrations; that is to say that latexes with lower CD concentrations displayed some settling over time, whereas, those with higher CD concentration remained well dispersed [15].

The polymerization of cyclodextrin complexes of commercial monomers like styrene and (meth)acrylic derivatives thus opens an alternative route to polymers simply from water without using surfactants [16]. Phillip H. Madison [17] researched the radical polymerization of tert-butyl methacrylate, cyclohexyl methacrylate, and 2-ethylhexyl methacrylate in the presence of methylated (1.8)-β-cyclodextrin. The resulting polymers exhibit number-average molecular weights as high as 140000 with PDI's as low as 3.2. Thus, hydrophobic, high molecular weight acrylic polymers are prepared in water with acceptable polydispersities and isolated yields as high as 86%. More interesting, 80–95% of the CD used in these reactions is recovered and ^{1}H NMR data and subsequent polymerization indicate that the carbohydrate can be recycled. Many other studies [18–20] also find that during the free-radical polymerization of the complexed hydrophobic monomers, the CD ring slips off step by step from the monomer during chain propagation and the polymer precipitates. The CD remains finally in the aqueous phase due to its high water solubility. This is grateful, especially in large-scale production.

The influence of the hydrophilic character of the monomers on the initial polymerization rate has also been investigated [21]. It could be found that the more hydrophobic the monomer, the higher the local concentration of monomer close to the active radical chain end of the polymer. This local concentration effect must lead to higher values of initial reaction rate. And they also observed that the overall polymerization rate is approximately proportional to the square root of the initiator concentration [16].

Recently, the free radical polymerization of hydrophobic monomers under semicontinuous conditions (the monomers are constantly added via syringes over a period of time) in water in the presence of randomly methylated-β-cyclodextrin is performed. Compared to batch polymerizations, where the water-insoluble polymer precipitates or produces high amounts of coagulum, this new method results in quantitative conversion of the monomers, and leads to stable latexes with nearly monodisperse polymer particle size distributions, which are very useful in many technical applications [22]. As shown in Fig. 3, the particle size distribution in the presence of CD is much narrower than that in absence of CD.

Just as above mentioned, due to the inclusion of the monomers into the CD-cavities, this new cyclodextrin-mediated polymerization method differs strongly from classical methods.

For one example, as an interesting observation, it is found that the reactivity ratios of the methylated β-CD complexed monomers isobornyl acrylate (a) and *n*-butyl acrylate (b) ($r_{a/\beta\text{-CD}} = 0.3 \pm 0.1$, $r_{b/\beta\text{-CD}} = 1.7 \pm 0.1$) differ significantly from the values of the corresponding uncomplexed monomers in the mixture of N, N- dimethylformamide (DMF)/H_2O ($r_a = 1.3 \pm 0.1$, $r_b = 1.0 \pm 0.1$) [23]. Some other researchers [24] also found that in the polymerization containing cyclodextrin, the free radical react quicker with butyl acrylate than with isobornyl acrylate. This phenomenon can be explained by the fact that acrylate monomers are incorporated into the cyclodextrin's cavity with their reactive double bond first, as could be proven by X-ray

TABLE I Cyclodextrins properties

Property	α-CD	β-CD	γ-CD
Number of glucopyranose units	6	7	8
Molecular weight (g/mol)	972	1135	1297
Solubility in water at 25°C (%, w/v)	14.5	1.85	23.2
Outer diameter (Å)	14.6	15.4	17.5
Cavity diameter (Å)	7.5–8.3	4.7–5.3	6.0–6.5
Height of torus (Å)	7.9	7.9	7.9
Cavity volume (Å)	174	262	427

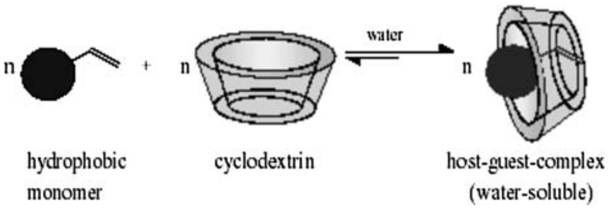

Figure 2 Scheme of the incorporation of a monomer into the cavity of cyclodextrin.

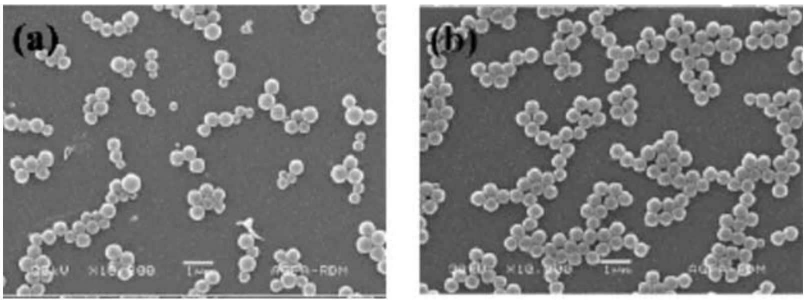

Figure 3 SEM images of polystyrene particles: (a) 0 wt% cyclodextrin, broad particle size distribution and (b) 5.6 wt% cyclodextrin, narrow particle size distribution.

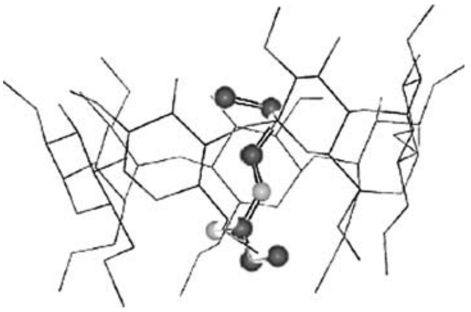

Figure 4 X-ray crystal structure of the butyl acrylate-β-CD complex.

spectroscopy (Fig. 4). The monomer has to leave the complex with CD to allow for a reaction at the reactive double bond. It can leave the cyclodextrin's cavity the easier, the weaker the interaction between monomer and CD is. A small monomer like butyl acrylate is bound weaker to the cyclodextrin and can thus polymerize faster than isobornyl acrylate which fills the cavity well and can therefore exert stronger interactions with the host molecule (Fig. 5).

Another example is the determination of the chain-transfer constants (Cs) [25]. To evaluate the results, the polymerizations of both uncomplexed monomers (methyl methacrylate (MMA) and styrene (St)) and monomers-CD complexes are carried out under similar conditions in the presence of chain-transfer agent N-acetyl-L-cysteine. Surprisingly, relatively high chain-transfer constants are found in the case of the complexed monomers in water ($\text{Cs}_{\text{MMA}/\beta\text{-CD}} = 1.7 \pm 0.3$, $\text{Cs}_{\text{St}/\beta\text{-CD}} = 2.6 \pm 0.3$). In contrast, the chain-transfer constants in DMF/H_2O mixture are significantly lower ($\text{Cs}_{\text{MMA}} = 0.7 \pm 0.1$, and $\text{Cs}_{\text{St}} = 0.7 \pm 0.1$). This means that the molecular weight of polymers obtained from complexed monomers can be controlled more effectively by hydrophilic thiol containing chain-transfer agents than in the case of polymerization of the corresponding uncomplexed monomers in organic medium.

Our group has also studied the effect of β-CD on the free radical polymerization of styrene and acrylate monomers [26]. However, so far, most viewpoints about the effect of CD on polymerization are still qualitative. Virtually, thermodynamics can quantitatively give much additional information involved by the polymerization process. So in the first time, according to the initial state and the final state of reaction molecules, our group studied the thermodynamic process involved by the polymerization in the presence of cyclodextrin [27]. From Table II, adding CD into the polymerization increases the enthalpy and the entropy. The most important is that the adding of CD decreases the free energy of the system by -4.28 kJmol^{-1}. This result, from thermodynamical viewpoint, explains quantitatively why the monomer conversion improves in the presence of CD. The increase of enthalpy and entropy may be responsible for the complexation of monomer with CD, and the change of zone concentration of monomer, respectively. For kinetic consideration, we defined a new symbol A_Γ as follows: $A_\Gamma = K_p^{CD}/K_p^{B}$, where K_p^{CD} and K_p^{B} are the rate constant in the presence of CD and absence of CD, respectively. Obviously, under comparable conditions, A_Γ may reflect the relative reactivity of monomer between polymerizations with CD and without CD. As shown in Table III, we found that CD produces significant effect on the monomer reactivity, and the higher content of CD correspondingly results in higher monomer reactivity. The increase of reactivity in the presence of CD may be responsible for the increase of polymerization rate.

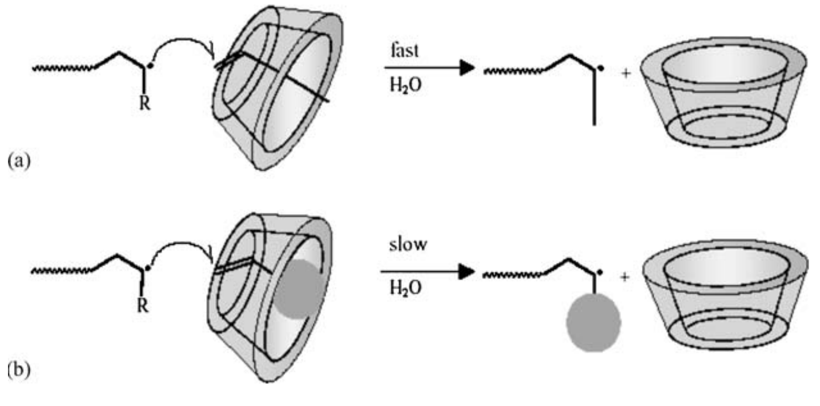

Figure 5 Dependence of polymerization kinetics on cyclodextrin complexation.

TABLE II Changes of thermodynamic parameters in polymerizations

	Changes of tharmodynamic parameter		
Polymerization system	Enthalpy (kJ mol^{-1})	Entropy (J mol^{-1} K^{-1})	Free energy (kJ mol^{-1}, 70°C)
Without CD	174.22	524.80	−5.78
With CD	322.69	970.16	−10.06
Effect of CD	148.47	445.36	−4.28

TABLE III Effect of CD on the monomer reactivity

CD content (%)	A_r
0	1
1.25	1.114
6.25	1.337
18.75	1.504

Using atom-transfer radical polymerization, host-guest complexes of methyl methacrylate and methylated β-CD are polymerized in aqueous medium [28]. 4,4′-di-(5-nonyl)-2,2′-bipyridyl is used as a very effective ligand, which was complexed with large excess of methylated β-CD in water (approximately 4-fold molar). The polymerization of methacrylate/ methylated β-CD complex is initiated by ethyl 2-bromoisobutyrate in the presence of copper bromide as the catalyst. It is found that the polymerization under these conditions has a living character, and the obtained polymer has a much lower polydispersity (PDI = 1.3–1.8).

It is know that the different solubilities of the monomers in water often make the copolymerization of water-soluble and water-insoluble monomers difficult by classical emulsion polymerization. For comparison, the copolymerization of hydrophobic monomer styrene with hydrophilic monomer N-isopropyl acrylamide in the presence of CD and absence of CD are carried out under similar conditions [29]. By means of the SEC data, it is found that, for all molar ratios of the incorporated monomer units, the weight averages of the copolymers obtained from complexed styrene and N-isopropyl acrylamide are about 3 to 7 times higher than that of the corresponding copolymers obtained from uncomplexed styrene. In all cases, UV- signal and RI-signal of SEC-elution of the monomodalic SEC curves deviated only slightly by about 10% of the maximum. Furthermore, the complex of styrene with CD is copolymerized with various molar ratios of sodium 4-(acrylamido)- phenyldiazosulfonate at 40°C [30]. In all cases, the azo content of the polymer is below that of the monomer feed. These results indicate that the diazosulfonate monomer is less reactive than the complexed styrene.

The synthesis of cyclic polymers with β-CD is another interesting example [31]. Generally, the basic synthetic approach to cyclic polymers is to form precursor polymers with two functional end groups and to react them intramolecularly. However, it is difficult to obtain prue cyclic polymers. β-CD has 7 primary hysroxyl groups on one side of the ring and 14 secondary hydroxyl groups on the other side. If vinyl groups are introduced into the secondary hydroxyl groups and the polymerization of vinyl groups is limited to the template monomer, both ends of the polymerized vinyl group will exist next to each other in the molecule. The closing of the ring in this monomer will be easier than for normal linear polymers. Because the number of vinyl groups in a β-CD is controlled, the degree of polymerization of vinyl groups and its distribution will be narrow. Fig. 6 showed the concept of the synthesis of cyclic polymers produce from cyclodextrin.

Recently, Flosbach C *et al.* [24] present an interesting way to synthesize powder clear coat resins by polymerization in aqueous solutions containing cyclodextrin. Generally, solid acrylic resins for powder clear coats are produced by solution polymerization. Much energy is consumed by distillation of organic solvents and grinding of the solidified polymer, which are inevitable steps in this process. For the new method, a radical polymerization is initiated in aqueous solution of a cyclodextrin-monomer complex. Upon polymerization, the resulting water-insoluble polymer cannot be complexated by CD due to sterical hindrance of the polymer chain. As a consequence, the free cyclodextrin remains in solution, whereas the resin separates from the aqueous solution; in case of a powder coat resin the polymer precipitates. Afterwards it can easily be filtered off the reaction mixture and is obtained free of CD after washing with water. Compared to the common

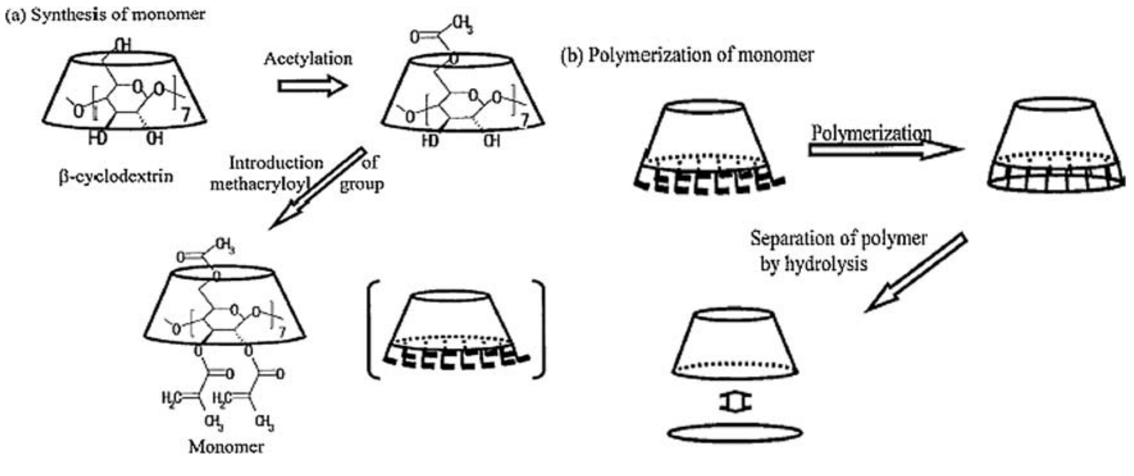

Figure 6 Scheme of the synthesis of cyclic polymer with cyclodextrin.

manufacturing of powder coat resins, no solvent is obtained as a byproduct, and the processes of distillation and crushing are also elided.

Another successful example of a cyclodextrin-mediated polymerization is the oxidative oligomerization of heterocyclic aromatic guests, such as pyrrol [32]. Due to the substantial Π-electron delocalization along their backbones, these polymers show interesting (nonlinear) optical properties and become good electric conductors when oxidized or reduced. Additionally, the use of cyclodextrin to polymerize phenol derivatives with water as the solvent is also investigated [33]. The enzyme catalyzed process is expected to be an alternative route for the preparation of phenol polymers without the use of toxic formaldehyde, which is a coupling comonomer for the synthesis of conventional phenolic resins. It is found that under similar condition only the presence of methylated β-CD enables the polymerization of the phenol in water, while only dimmers or trimers could be obtained in absence of methylated β-CD.

In conclusion, these investigations mentioned above indicate the successful application of CDs in polymer preparation in aqueous. Virtually, CDs have also been successful applied in many other fields, such as food chemistry, cosmetic and pharmaceutical industries etc., although did not be described in detail here. Due to their special structure, we believe that CDs are still one of the hot points in the next years.

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