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# Synthesis of copolymers with cyclodextrin as pendants and its end group effect as superplasticizer

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ABSTRACT

In this paper, the efficient approach for the synthesis of β-cyclodextrin (CD) based functional monomers was described. Based on the monovinyl β-CD monomer (GMA-EDA-CD), a new type poly(AA-co-GMA-EDA-CD) (PCDs) copolymer bearing pendent CD groups was synthesized and used as superplasticizer. Their chemical compositions were characterized by FT-IR, NMR, MALDI-TOF and GPC. The effects of PCDs on dispersion and adsorption in cement mortars were detailed discussed. The results indicated that PCD copolymers behaved excellent dispersion ability and strong retarding effect. $PCD_2$ with molar ratio (%) for monomer (AA:GMA-EDA-CD = 80:20) had the best dispersion and dispersion maintaining abilities, which were mainly attributed to the synergistic effects of steric hindrance and electrostatic repulsive force, and the retarding effect of PCD copolymers resulted from steric hindrance repulsion of CD pendants and the large number of hydroxyl groups, which affected the hydration reaction of cement.



## 1. Introduction

It is well-known that cyclodextrins (CDs) are a series of natural cyclic oligosaccharides which are synthesized from starch via a simple enzymatic conversion and with negligible toxicity; it makes them appropriate for a broad range of applications and industrial production on the thousands-of-tons scale (Chen & Jiang, 2011; Miyauchi & Harada, 2004). These semi-natural compounds commonly comprise 6, 7 or 8 D-(+)-glucose units linked together by α-1,4-glycosidic bonds, and named α-, β- or γ-CD, respectively, are the most common ones. They possess a unique molecular structure with hydrophilic exterior surface and hydrophobic interior cavity which have been extensively studied as host molecules in supramolecular chemistry (Guo & Jiang, 2009; Kretschmann, Steffens, & Ritter, 2007; Tungala, Adhikary, & Krishnamoorthi, 2013; Wu, Ni, Zhang, & Zhu, 2010; Xiu, Yang, Zhao, Li, & Xu, 2013; Zou, Guan, Liao, Jiang, & Tao, 2009). CDs and their derivatives have been widely incorporated into dendrimers, microgels, block or star copolymers, polymeric brushes and gold surfaces which endow these materials with more interesting properties (Machín, Isasi, & Vélaz, 2012; Ping et al., 2011; Z.X. Zhang et al., 2008). CD-based polymers can be obtained by either polymer modification with CD-derivatives or polymerization of CD-based monomers. If a CD monomer contains reactive vinyl groups, CD polymers could be easily synthesized by homo- or copoly-merizations with other vinyl monomers. To date, a large number of published papers have reported about synthesis of multivinyl CD monomers and their homo- or copoly-merizations with other vinyl monomers; however, synthesis of a CD based polymer is a complicated work due to the parent CD molecule with large number active hydroxyl groups for reaction. It is well known that the preparation of linear CD-containing polymers may require monovinyl CD monomer, but only a few CD-containing polymers with linear structures were reported (Liu, Fan, & Gao, 2003; Wang & Jiang, 2006). The difficulties in preparing such CD-containing polymers are associated with the synthesis of monomers with monovinyl substitution of CDs. Therefore, it is necessary to develop a convenient and efficient technique to synthesize monovinyl CD monomers. This could lead to the preparation of many novel functional CD-containing polymers, and expand the scope of cyclodextrin chemistry.

A CD carrying multiple vinyl groups, which is easily produced, leads to highly branched or cross-linked polymers. It has been already proved that by introducing the easy leaving group p-toluenesulfonyl to get CD monomers carrying an unsaturated monovinyl group is one of the most effective measures. Petter et al. first reported the reaction between β-CD and p-toluenesulfonyl chloride in aqueous solution, but with low yield 11% (Petter, Salek,

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Sikorski, Kumaravel, & Lin, 1990). Matsui et al. first reported the reaction between β-CD and p-toluenesulfonyl chloride in pyridine with high yield to 28%, but the product involved in pyridine and other toxic organic solvent, and the process is complicated, so it has not been widely used (Matsui & Okimoto, 1978). In recent years, supramolecular self-assembly based on the inclusion complexation between cyclodextrins and various guest macromolecules have become the research hotspot, although many papers are more or less related to the preparation of CD based monomers, but most of them are briefly mentioned, up to date, there are few special studies on the synthesis of CD based monomers in detail (Brady, Lynam, O'Sullivan, Ahern, & Darcy, 2004; Gonil et al., 2011; Liu et al., 2003; Wang & Jiang, 2006).

During our study on the supermolecules and self assembles of CDs and their derivatives, our group have synthesized many CD based monomers. We successfully prepared and characterized OTs-CD, EDA-CD, and monovinyl substituted β-CD monomer (GMA-EDA-CD) which were all confirmed by FT-IR, $^1$H NMR, $^{13}$C NMR and MALDI-TOF measurements systematically, and further used GMA-EDA-CD for the synthesis of the poly (AA-co-GMA-EDA-CD) (PCDs) which were novel functional comb-like copolymers. It was found incidentally that PCDs could be used as superplasticizers and behaved excellent dispersion ability. This study offered a new approach to prepare superplasticizer from CDs and their derivatives, and expanded the scope of cyclodextrin chemistry. Moreover, to the best of our knowledge, this is the first report on the synthesis and characterization, adsorption and dispersion effect of PCDs as superplasticizers. Therefore, the overall goal of this study was to synthesize and characterize β-CD based functional monomers systematically, and then evaluated the dispersion and adsorption mechanisms of the PCDs in cement system.

## 2. Experimental

### 2.1. Materials

β-Cyclodextrin (β-CD) was acquired from Aladdin, and purified by recrystallization from water twice prior to use. Glycidyl methacrylate (GMA, >97%) was purchased from TCI, Japan. p-Toluenesulfonyl chloride (p-TsCl), ethanediamine (EDA), acrylic acid (AA) and azoisobutyronitrile (AIBN, 99%), were all purchased from Sigma, China. Tetrahydrofuran (THF) was initially dried over sodium wire and refluxed over potassium for 3 days before use, and the dried THF was stored over 4 Å molecular sieves at room temperature. N,N-dimethylformamide (DMF) was refluxed over $CaH_2$ before use. All other reagents were analytic grade made in China; they were used as received without further purification. The cement used in this study was an ordinary Portland cement (PO, 42.5R) was supplied by Guangzhou cement plant, China.

### 2.2. Synthesis of mono-6-OTs-CD (OTs-CD)

β-CD (24 g) was suspended in 180 mL of water, NaOH (2.623 g) in 20 mL of water was added dropwise over 30 min, and reacted under vigorous agitation at 0 °C for a period of 1 h then p-toluenesulfonyl chloride (4.032 g) in 20 mL of acetonitrile was added dropwise over 1 h, causing immediate formation of a white precipitate. After 3 h of stirring at 20 °C filtered off unreacted toluenesulfonyl chloride, the solution was neutralized with a pH of 7–8 by hydrochloric acid, and the filtrate refrigerated overnight at 4 °C. The white precipitate was recovered by suction filtration and recrystallization in water for at least three times. The sample obtained was dried at 60 °C for 48 h in a vacuum oven, and OTs-CD was obtained as a white solid (5.14 g, yield: 21.40%). IR (KBr, cm$^{-1}$): 3388 (s, OH), 2928 (w, $CH_2$), 1597 (s, Ph). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.42 (2H), 7.74 (2H), 4.75 (7H), 3.49–3.64 (28H), 3.28–3.36 (14H), 2.42 (3H). $^{13}$C NMR (DMSO): $\delta$ 144.9 (s), 132.7 (s), 129.9 (s), 127.6 (s), 102.3 (m), 81.5 (m), 71.9–73.1 (m), 69.8, 69.0, 59.5 (t), 21.3 (s) ppm. MALDI-TOF on CCA matrix (OTs-CD + Na$^+$) $m/z$ calcd for $C_{49}H_{76}NaO_{37}S$ (OTs-CD + Na$^+$) 1311.37, measured 1311.13.

### 2.3. Synthesis of mono (6-amino-6-deoxy)-β-CD (EDA-CD)

5.0 g of OTs-CD was reacted with excess amount of EDA (30 mL) in 20 mL DMF at 80 °C for 6 h. After the reaction was completed, the mixture was allowed to cool to room temperature, and then, 40 mL of cold methanol were added. Then added acetone slowly to precipitate, the precipitate was repeatedly dissolved in water and precipitate by acetone for three times for the removal of unreacted EDA. The sample obtained was dried at 40 °C for 72 h in a vacuum oven, and a white solid of EDA-CD were obtained (3.96 g, yield: 79.10%). IR (KBr, cm$^{-1}$): 3388 (s, OH, $NH_2$), 2928 (w, $CH_2$). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 4.85 (7H), 3.54–3.64 (28H), 3.27–3.41 (14H), 2.72–2.92 (4H). $^{13}$C NMR (DMSO): $\delta$ 102.0 (s), 81.6 (s), 72.1–73.1 (m), 60.0 (s), 40.1–39.5 (m) ppm. MALDI-TOF on CCA matrix (EDA-CD + Na$^+$) $m/z$ calcd for $C_{44}H_{76}N_2NaO_{34}$ (EDA-CD + Na$^+$) 1199.42, measured 1199.20.

### 2.4. Synthesis of monovinyl based β-CD (GMA-EDA-CD)

5.98 g EDA-CD was dissolved in 30 mL DMF and a small amount of 4-methoxyphenol was added as inhibitor. Then 2.49 g GMA with 10 mL DMF was added dropwise over 1 h. The reaction lasted 6 h at 70 °C. After the reaction was completed, the mixture was allowed to cool to room temperature, and then, 100 mL of acetone were added. A light yellow precipitate was filtrated and washed at least three times using a large amount of acetone, and finally, dried at room temperature for 3 d under vacuum. (4.90 g, yield: 82.0%). The synthetic route of β-CD based monomers is shown in Fig. 1. IR (KBr, cm$^{-1}$): 3388 (s, OH), 2928 (w, $CH_2$), 1720 (w, C=O). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 6.05 (2H), 4.81 (7H), 4.48 (1H), 3.54–3.62 (28H), 3.29–3.43 (14H), 2.72–2.92 (6H), 1.87 (3H). $^{13}$C NMR: (DMSO) $\delta$ 166.6 (s), 135.9 (s), 125.8 (s), 102.0 (s), 81.6 (s), 72.0–73.1 (m), 66.9 (s), 59.9 (s), 56.1 (s), 40.1–39.5 (m), 20.6 (t), ppm. MALDI-TOF on CCA matrix (GMA-EDA-CD + Na$^+$) $m/z$ calcd for $C_{51}H_{86}N_2NaO_{37}$ (GMA-EDA-CD + Na$^+$) 1341.48, measured 1341.09.

### 2.5. Synthesis of poly (AA-co-GMA-EDA-CD) (PCD)

Radical copolymerizations of AA and GMA-EDA-CD were initiated by AIBN. A typical experiment for the polymerization procedure is as follows: in a 100 mL three neck round-bottom flask, AA (1.18 g) and GCD (0.85 g) were mixed with 100 mL of DMF. The solution was bubbled under argon for 30 min at room temperature to remove free oxygen. The flask was then immersed in an oil bath thermo stated at 80 °C and the reaction was maintained for 10 h under argon. Copolymers were directly precipitated by acetone and washed at least three times using a large amount of acetone, and then dried at 50 °C under vacuum to yield a fine white powder. The synthetic route of free radical copolymerization between AA and GMA-EDA-CD is represented in Fig. 2.

### 2.6. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5100 spectrometer by KBr sample holder method in the fundamental region of 400–4000 cm$^{-1}$. Both $^1$H NMR and $^{13}$C NMR spectra were recorded on a DRX-400 MHz (Bruker) superconducting-magnet NMR spectrometer with DMSO-$d_6$ as solvents. The MALDI-TOF mass spectrum was recorded in the reflector mode on a Bruker autoflex III smartbean mass spectrometer using

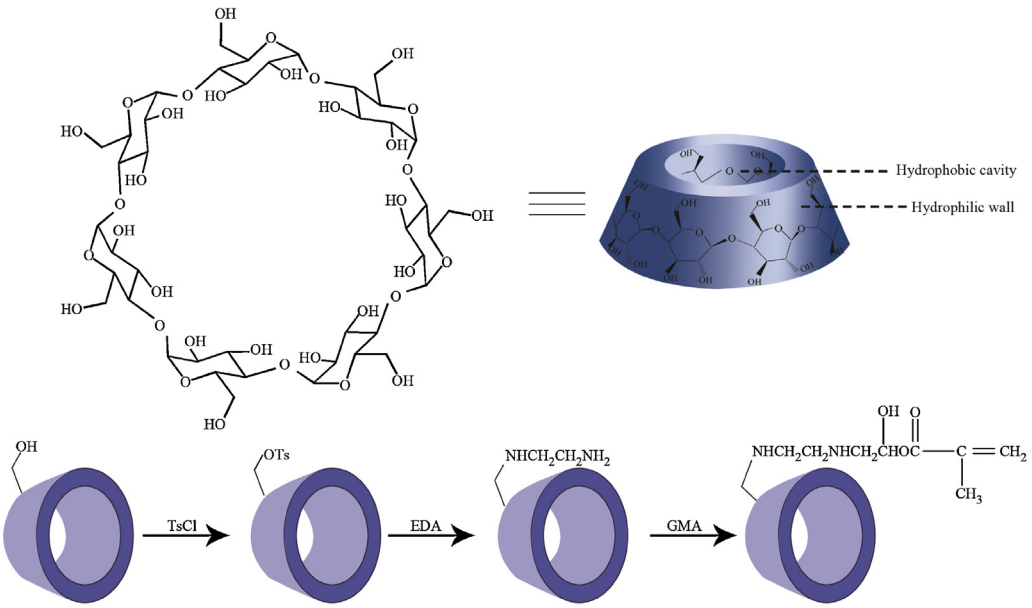


**Fig. 1.** Synthetic route of β-CD based monomers.

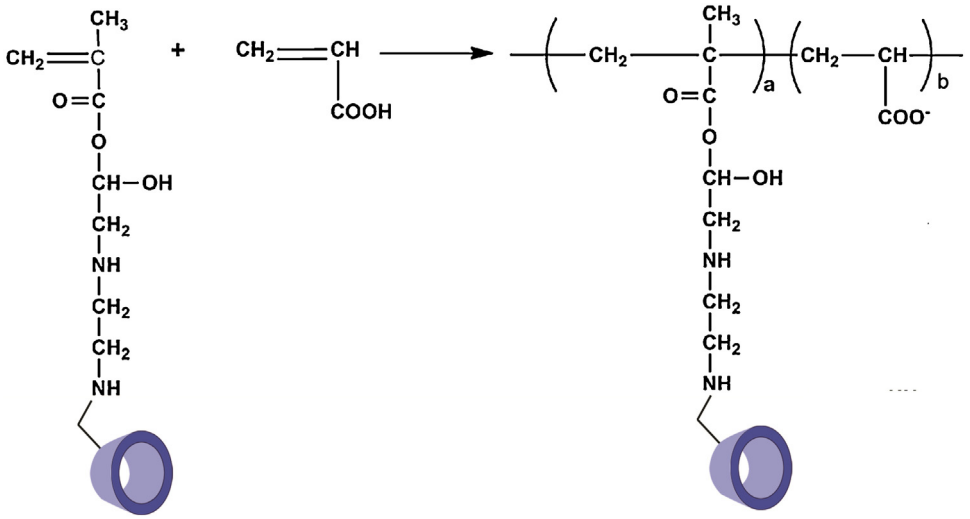


**Fig. 2.** Synthetic route of free radical copolymerization between GMA-EDA-CD and AA.

a nitrogen laser and α-cyano-4-hydroxycinnamic acid (CCA) was used as the matrix. The number-average molecular weight (Mn), weight-average molecular weight (Mw), and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) measurements using a Waters 515 chromatographic apparatus equipped with column ultrahydrogel 250, as well as a detector (Waters 2410). The mono-dispersive polyethylene glycols with various mo1ecular masses were used as calibration standards. DMF was used as the mobile phase at a flow rate of 0.2 mL/min at 45 °C. The characteristic properties of the PCDs obtained from GPC analysis are shown in Table 1.

### 2.7. Fluidities and setting times of cement pastes

The cement pastes with a water-cement ratio of 0.29 were prepared at 25 °C. The PCDs were added into water at a solid content ranging from 0.05% to 0.3% (weight percent of solid content to cement). The specimen of cement pastes were sealed in a container for 0, 30, 60 and 90 min before the measurement, respectively. The fluidities of cement pastes were measured using a minislump cone (a height of 60 mm, upper diameter of 36 mm and a bottom diameter of 60 mm). The initial and final setting times of cement paste were determined using a vicat analyzer. A homogeneous paste with great consistency is required. The initial setting occurred when the vicat needle was 4 ± 1 mm from the floor, and the final setting for a cement paste was when the vicat needle penetrated 0.5 mm into

**Table 1**
Molar masses and polydispersity index (PDI) of PCDs.

| PCDs | Molar ratio% (AA:GMA-EDA-CD) | Mw (g/mol) | Mn (g/mol) | PDI (Mw/Mn) |
|---|---|---|---|---|
| $PCD_1$ | 90:10 | 30,127 | 19,189 | 1.57 |
| $PCD_2$ | 80:20 | 28,419 | 19,465 | 1.46 |
| $PCD_3$ | 70:30 | 18,490 | 10,159 | 1.82 |

the cement paste. The processes were performed according to the Chinese standard GB/T 8076-2008.

### 2.8. Adsorption amounts of PCDs

The adsorption amounts of the PCDs on the surface of cement were measured by a total organic carbon (TOC) analyzer (Elementar liqui Toc analyzer, Germany). 30 mL of aqueous solution with various amounts of the PCDs and 10 g of cement were mixed by a magnetic stirrer for 10 min. Then, the suspension of cement paste was filled into a centrifuge at 4200 rpm/min for 20 min. The resultant solution was filtered by a 0.45 μm membrane using a vacuum pump and was decanted for TOC. Several aliquots of each sample were measured. The adsorption amounts of PCDs on the surface of cement can be calculated based on the difference between the amounts of PCD in aqueous phase before and after mixing.

## 3. Results and discussion

### 3.1. Synthesis and structure analysis of β-CD based monomers and PCD copolymers

β-CD based polymers can be obtained by either polymer modification with β-CD-derivatives or polymerization of β-CD-based monomers. However, only a few water-soluble β-CD-containing polymers with linear structures were reported. The difficulties in preparing such polymers are associated with the synthesis of β-CD with monovinyl substitution. A CD carrying multiple vinyl groups, which is easily synthesized, leads to highly branched or cross-linked polymers. In this work, we succeeded in obtaining monovinyl substituted β-CD monomer (GMA-EDA-CD), and based on GMA-EDA-CD monomer, poly(AA-co-GMA-EDA-CD)(PCDs) were also synthesized, which were all confirmed by FT-IR, $^{1}$H NMR, $^{13}$C NMR and MALDI-TOF measurements.

For the synthesis of OTs-CD monomer, compared to the literature (Petter et al., 1990), we succeeded in increasing the yield to 21.4% with a few modifications. For the synthesis of EDA-CD monomer, it was synthesized with yield to 79.10% compared to previous report (Liu et al., 2003), moreover, we succeeded in improving the separating process. First dissolved the crude product with methanol and added acetone slowly to precipitate, then dissolved the precipitate with the least amount of water (10, 30 and 70 mL, separately) and added acetone to precipitate separately, this process repeated at least three times for the removal of unreacted EDA, and be sure to control the adding amount of water to dissolve the crude product, otherwise it would need large acetone to precipitate. For the synthesis of monovinyl β-CD monomer, GMA is usually chosen as vinyl functional group because the reactivity of the epoxy group toward primary amine is reasonably high, and there are a few reports about the reaction of GMA and EDA-CD. However, it seems exist some contradictory conclusions for different reports (Liu et al., 2003; Wang & Jiang, 2006). In this paper, owing to its steric hindrance of CD pendants, in order to make EDA-CD completely reacting with GMA, GMA was used in excess. The results indicated that at molar feed ratio of 2.5–3:1 for GMA to EDA-CD, and reacted for 6 h at 70 °C, satisfactory results could be obtained.

As random copolymers composed of pendent bulky CD pendants and carboxylic groups, PCDs were expected to show some dispersion ability because both CD pendants are hydrophilic and with certain steric hindrance (Becer et al., 2008; Lv, Gao, Duan, Li, & Cao, 2012). The water soluble PCDs were prepared by free radical copolymerization of AA and GMA-EDA-CD in DMF solution, and with narrow molecular weight distribution shown in Table 1. However, it was noted that as the content of GMA-EDA-CD increasing the molecular weight distribution characterized by polydispersity index (PDI) of the PCD copolymers became relatively wide, this might be due to the steric hindrance of CD pendants decreased the reactivity of GMA-EDA-CD to AA. In this paper, poly (AA-co-GMA-EDA-CD) (PCDs) were obtained as new type copolymers including $PCD_1$, $PCD_2$ and $PCD_3$, just as shown in Table 1 the difference among $PCD_1$, $PCD_2$ and $PCD_3$ is their molar ratio.

### 3.2. Dispersion property

In this paper, it is evidently shown in Fig. 3 that PCDs were effective as cement dispersants and the fluidities increased with increasing the dosage of PCDs. Time dependant fluidity loss behavior of the PCDs was measured over a period of 1.5 h. According to the data, the fluidity maintaining abilities of the cement mortars with the PCDs were also effective.

Two important parameters of evaluating the performance of superplasticizers are the dispersion and dispersion maintaining abilities. While the dispersion maintaining ability is expressed by slump loss defined as the decrease in fluidity with time. Previous studies on cement-water-superplasticizers system revealed that polycarboxylate superplasticizers (hereinafter called PCEs) with the long side chains have better dispersion and dispersion maintaining abilities. Researchers also have generally accepted that the dispersibility of PCEs is mainly attributed to the steric hindrance of the side chains (Yamada, Hanehara, & Honma, 2000; Yoshioka, Sakai, Daimon, & Kitahara, 1997). Therefore, it could be inferred that the special molecular structures of PCDs also play important role in maintaining slump loss of cement mortars. As shown in Figs. 2 and 4, the difference of PCDs is the CD pendants at each side chain of PCD copolymers, in contrast to common PCEs with linear polyethylene glycol (PEG) side chains. When PCD copolymers

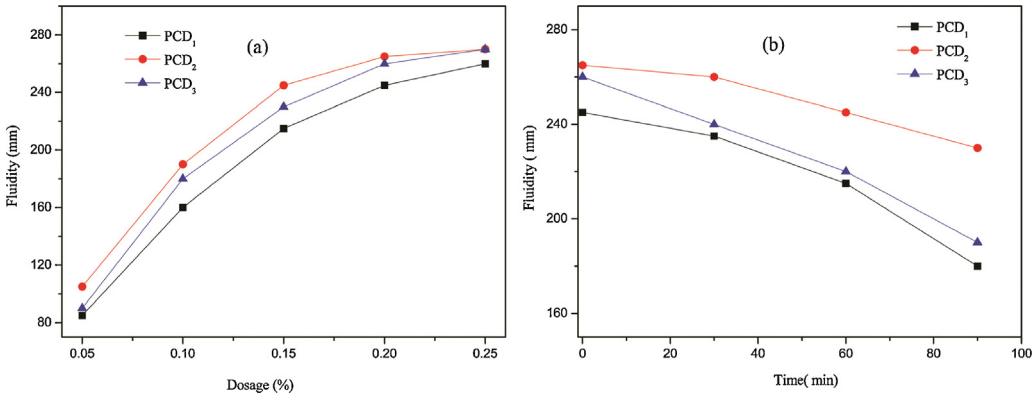


**Fig. 3.** Fluidity and fluidity loss behavior of cement paste with different PCDs.

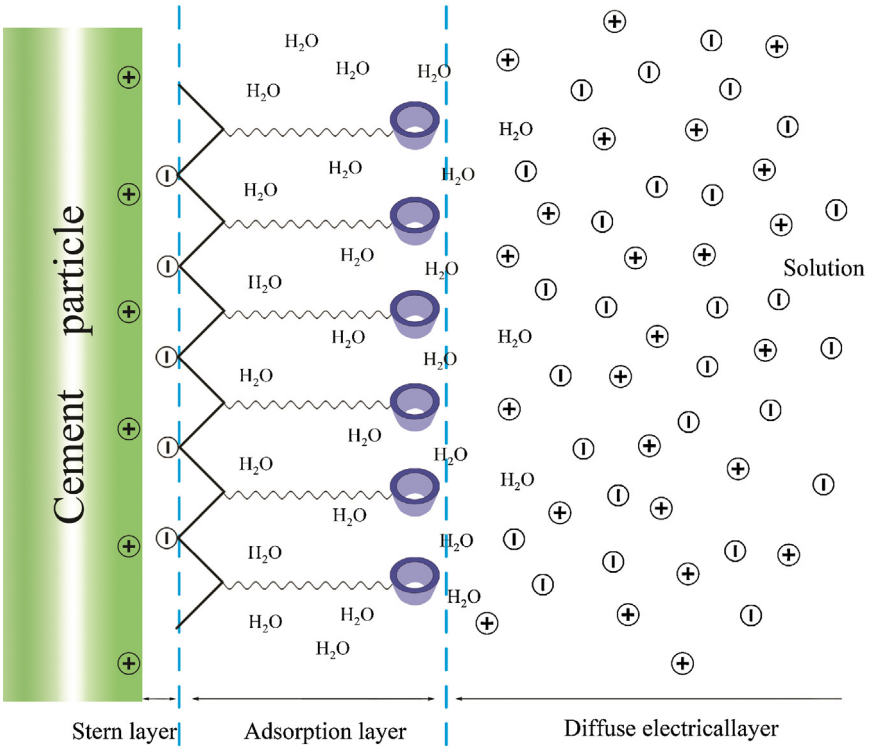


**Fig. 4.** Schematic figure for the dispersion and adsorption of PCDs on the cement surfaces.

used as superplasticizers, they also had much strong steric hindrance, so the dispersion and dispersion maintaining abilities of the PCDs improved significantly. However, as the content of GMA-EDA-CD increased to some extent, the dispersion abilities of PCDs decreased obviously; this could also be contributed to the steric hindrance of CD pendants. Just as the old saying says everything is a double-edged sword, the steric hindrance effect of CD pendants also reduced the reaction activity of GMA-EDA-CD to AA. Therefore, according to our experiment, only when molar ratio (%) of GMA-EDA-CD to AA is 20:80, the resulting $PCD_2$ had the maximum dispersion and dispersion maintaining abilities.

### 3.3. Adsorption behavior

Adsorption as one of the most effective measures to illustrate the interaction among admixtures, cement and other minerals, previous researchers concluded that the total admixtures present in cement pastes is either adsorbed onto cement particles or consumed in the formation of an organo-mineral phase. The dispersing action of superplasticizers is largely dependent on the adsorption of polymers onto cement particles, and results in changes in the ionic charge on the surface of cement particles and leads to electrostatic repulsion between the cement particles, meanwhile the adsorption capabilities and dispersion mechanisms vary with the molecular structure of the different superplasticizers (Qiu, Peng, Yi, & Deng, 2011; Yamada et al., 2000). The adsorption results of PCDs onto the surface of cement particles are shown in Fig. 5. The initial adsorbed amounts increased rapidly as the dosages increasing from 0.5–1.5 mg/g. Within this period, the surfaces of cement particles were more active and still contained empty sites, the adsorption could carry on continuously. While at higher dosages (>2.0 mg/g), the adsorption amounts increased slowly, and approached a constant value gradually. Previous studies found that at the same dosages, the adsorbed amount increased as the content of anchor groups (usually referred to as carboxylic groups) increasing, the higher the content of anchor groups provided, the stronger the adsorption onto the cement particles (Alonso, Palacios, & Puertas, 2013; Qiu et al., 2011). However, some obvious differences of the adsorption isotherms were observed. At lower dosages (0.5–1.5 mg/g), the adsorption of $PCD_2$ generally exhibited the highest values, followed by $PCD_1$ and $PCD_3$. At higher dosages (>2.0 mg/g), the adsorbed amounts of $PCD_2$ and $PCD_1$ increased more slowly than $PCD_3$.

To take a review of the results of the cement dispersion research, it could be inferred from these curves that besides the content of anchor groups, molecular structure and configuration of PCDs were largely responsible for the adsorption differences. $PCD_1$ had the highest carboxylate groups, followed by $PCD_2$ and $PCD_3$, while $PCD_3$ had the biggest steric hindrance, followed by $PCD_2$ and $PCD_1$,

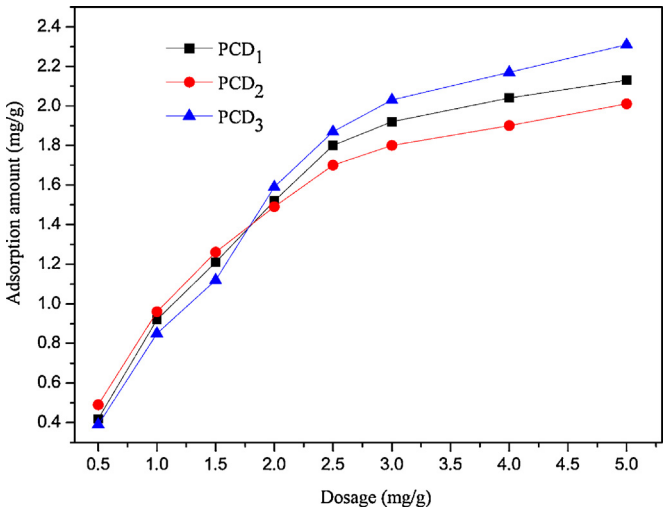


**Fig. 5.** Adsorption amounts of PCDs on cement surfaces.

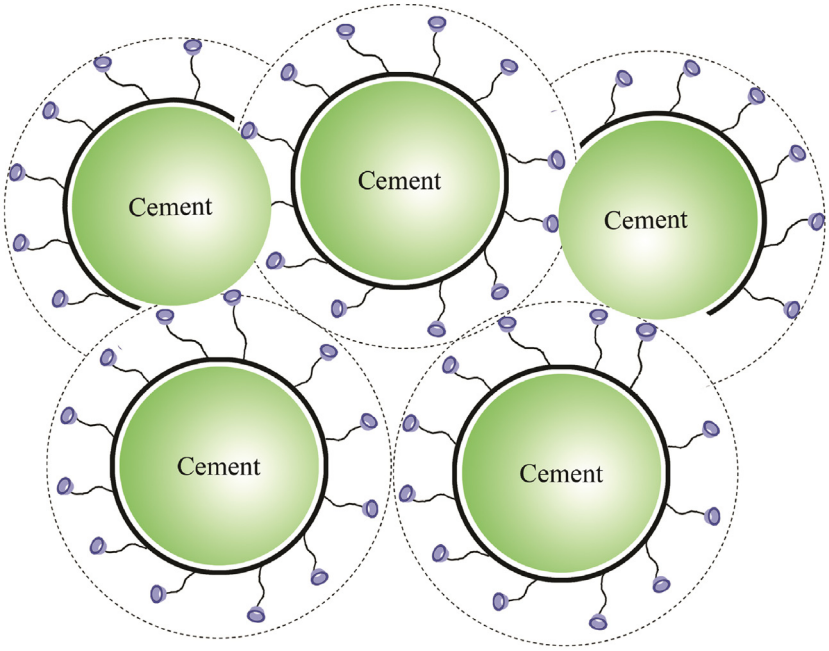


**Fig. 6.** Schematic figure of the retarding mechanism of PCDs.

but $PCD_2$ had the best dispersion and dispersion maintaining ability, followed by $PCD_1$ and $PCD_3$. These results indicated that as the hydration went on, only the $PCD_2$ with proper content of CD pendants and carboxylate groups could easily adsorb onto the cement particles and reach the adsorption equilibrium, and further confirmed why $PCD_2$ had excellent dispersion and dispersion maintaining abilities. For cement-water-superplasticizers system, most researchers have accepted that the effect of PCEs is mainly caused by steric hindrance (Flatt, Schober, Raphael, Plassard, & Lesniewska, 2009). For PCDs, as shown in Figs. 4 and 6, it could be inferred that during the absorbing process the anchoring group adsorbed on the surface of cement particles, formed electrical double layer, then the steric hindrance effect of CD pendants made the cement particles with adsorbed PCDs keep a distance.

### 3.4. Setting times and retarding effect

The effects of PCDs on the setting times of the cement pastes were studied at a superplasticizer dosage of 0.2 wt % and a water-cement ration of 0.29. The setting times of the cement pastes with PCDs are shown in Table 2. The initial setting times for all the cement pastes were greater than 2 h, the final setting times were less than 11 h, and the setting times increased with the contents of CD pendants increasing. The results indicated that the introduction of the CD pendants in the structure of PCDs improved their retarding effects. To take a review of the results of the cement dispersion research, although excessive CD pendants could cause outstanding retardation effect, the dispersion ability decreased obviously. Therefore, according to the actual need we could find a balance between the retarding effect and dispersion ability in engineering applications.

It has already been confirmed that retardation of cement pastes depends on connectivity of particles, which is influenced by many factors such as water-cement ratio (w/c), dosages and superplasticizer itself. In this paper, other experimental conditions were kept consistent, and investigated the effects of different PCDs on the setting times of cement mortars. The schematic figure of the retarding mechanism of PCDs is shown in Fig. 6. When adding PCDs, calcium chelate complexes of various compositions were formed and surrounded by PCDs, which prevented solid phase nucleation and hydration products growth, and resulted in retardation of cement hydration. Meanwhile, studies have already shown that polyhydroxy compound and its derivatives are often shown retarding effect, which are attributed to the active hydroxyl adsorption groups adsorbed on the surface of cement during the hydration process by hydrogen bonds, and the adsorptions also prevent and retard further hydration of cement (Lv et al., 2012; Pang, Qiu, Yang, & Liu, 2008; Zhang, Ju, Zhang, & Yang, 2008). As the complex cyclic oligosaccharides, CDs have large number of active hydroxyl adsorption groups, and make them easier adsorb on the surface of cement particles. Therefore, we could get reasonable explanation of the retarding effect of PCDs based on the effects of steric hindrance of CD pendants and electrostatic interactions of anchoring hydroxyl groups. Just the adsorption of PCDs with big steric hindrance and large amount hydroxyl groups prevented the hydration process of cement particles and showed outstanding retarding effect.

**Table 2**
Setting times of cement pastes with PCDs.

| PCDs | Setting time (min) | |
|---|---|---|
| | Initial | Final |
| $PCD_1$ | 380 | 510 |
| $PCD_2$ | 400 | 570 |
| $PCD_3$ | 460 | 630 |

## 4. Conclusions

In sum, series of β-CD based functional monomers were synthesized and characterized, and a new type poly (AA-co-GMA-EDA-CD) (PCDs) copolymer bearing CD pendants was synthesized and used as superplasticizer. It was found that PCD copolymers behaved excellent dispersion ability and strong retarding effect. The results indicated that the dispersion ability of PCD copolymers was mainly attributed to the synergistic effects of steric hindrance and electrostatic repulsive force, and the retarding effect of PCD copolymers

resulted from steric hindrance repulsion of the special hollow truncated cone structure and large number of hydroxyl groups of CD pendants, which affected the hydration reaction of cement. This study offered a new approach to prepare superplasticizer from CD and its derivatives, and expanded the scope of cyclodextrin chemistry and also provided an alternative to concrete engineering.

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## Appendix A.

See Figs. A1–A6.

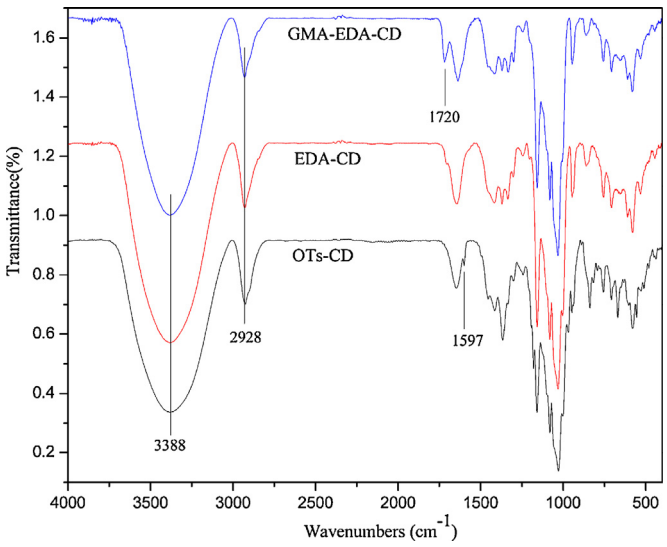


**Fig. A1.** FT-TR spectra of the OTs-CD, EDA-CD and GMA-EDA-CD.

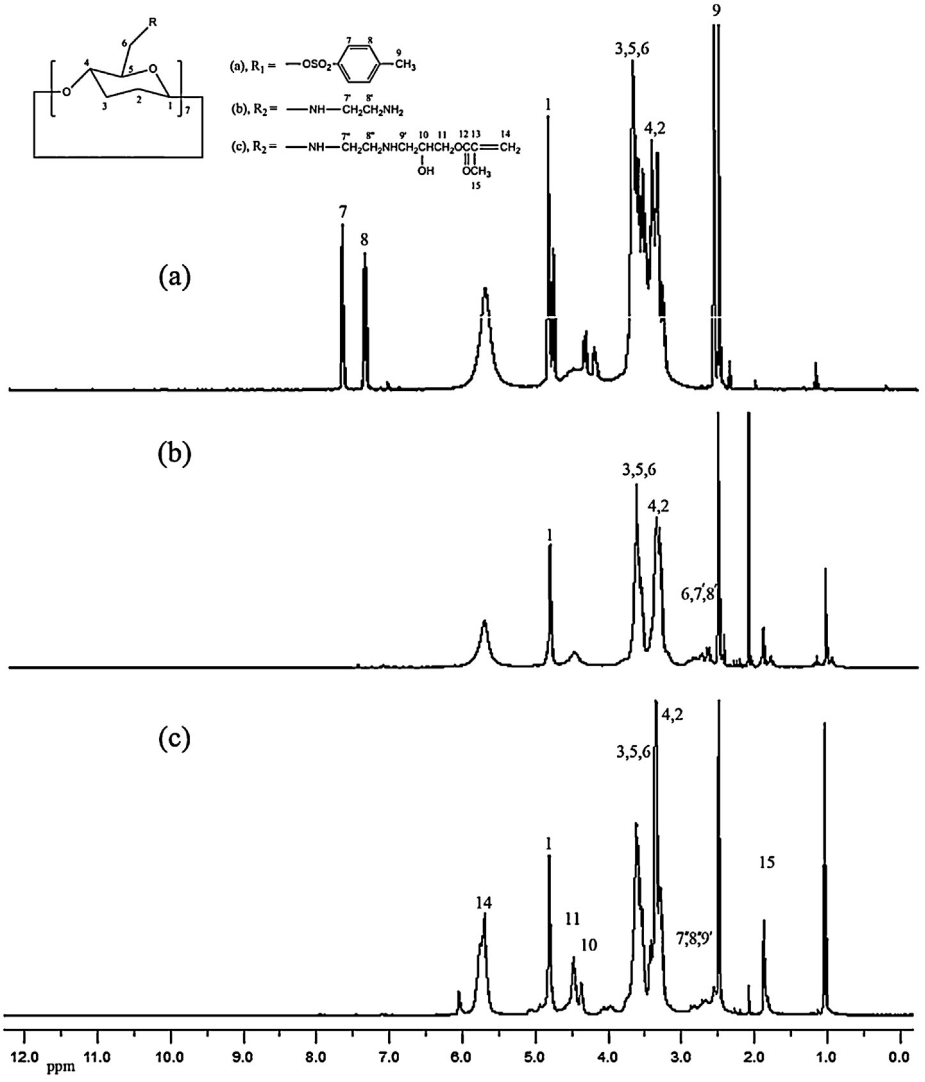


**Fig. A2.** $^{1}$H NMR spectra of the OTs-CD, EDA-CD and GMA-EDA-CD.

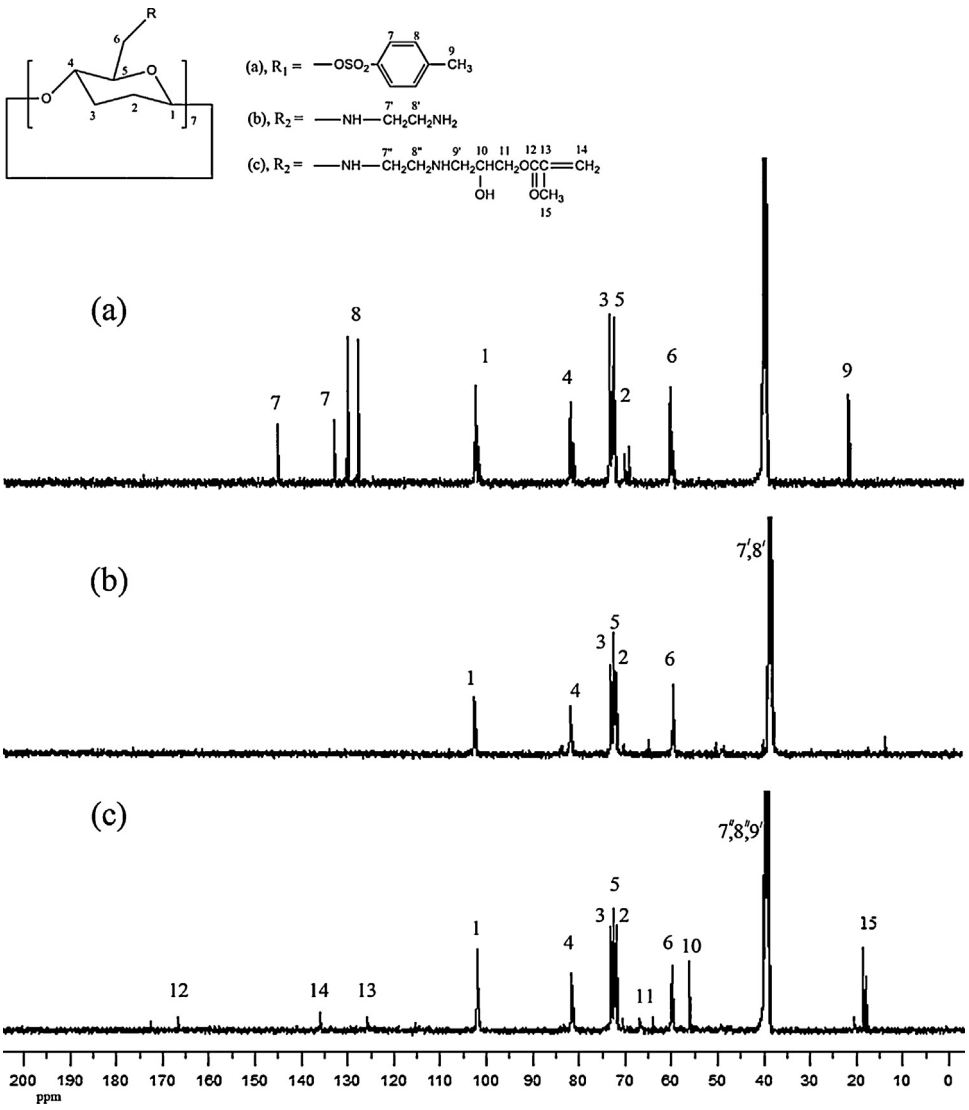


**Fig. A3.** $^{13}$C NMR spectra of the OTs-CD, EDA-CD and GMA-EDA-CD.

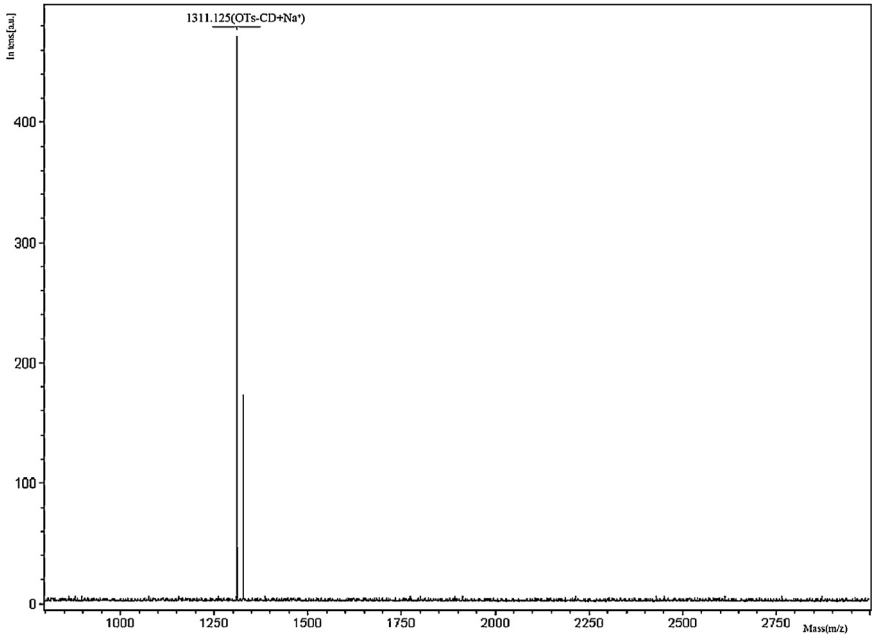


**Fig. A4.** MALDI-TOF spectrum of OTs-CD.

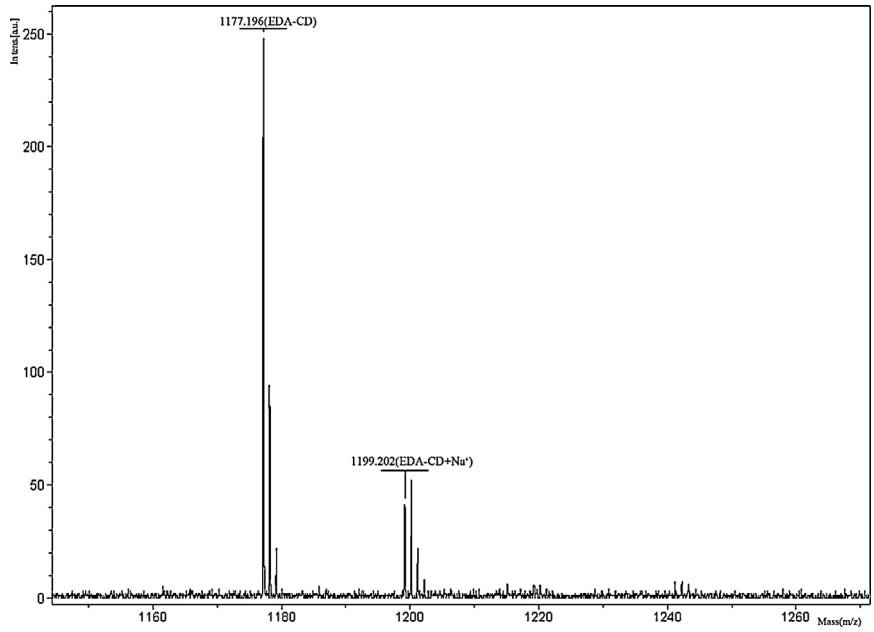


**Fig. A5.** MALDI-TOF spectrum of EDA-CD.

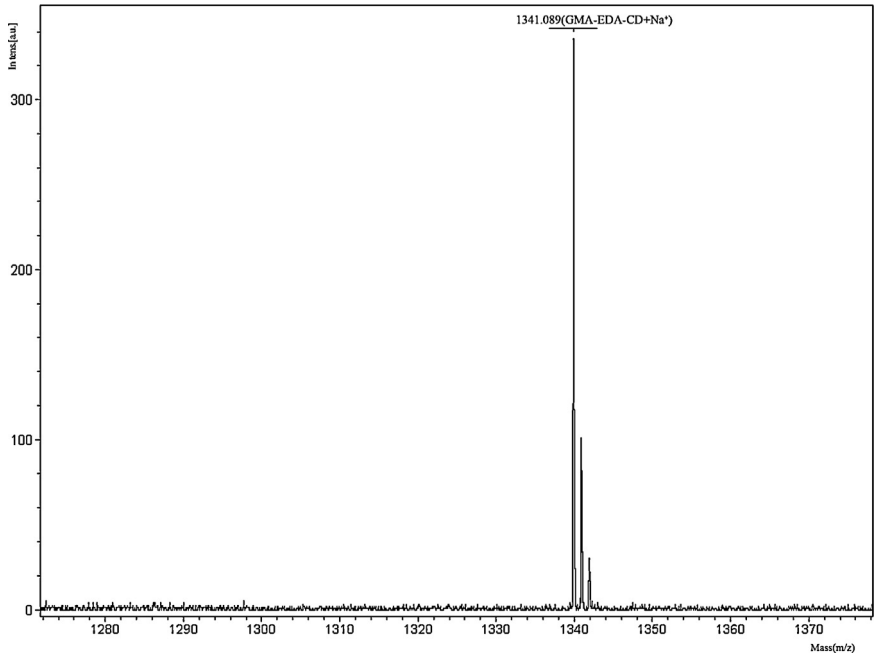


**Fig. A6.** MALDI-TOF spectrum of GMA-EDA-CD.

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