

Synthesis and MALDI-TOF Characterization of β -CD Core ATRP Initiators and RAFT Chain Transfers with Different Degrees of Substitution^{*}

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Abstract In this paper, three different kinds of β -CD derivatives were synthesized as atom transfer radical polymerization (ATRP) initiator or reversible addition-fragmentation chain transfer polymerization (RAFT) chain transfers. The degree of substitution for each derivative was carefully characterized through ¹H-NMR, ¹³C-NMR spectroscopy and matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS). The factors influencing the degree of substitution were discussed. Moreover, the comparison between ATRP and RAFT was shown in the polymerization of *N*-isopropyl acrylamide (NIPAM).

Keywords: β -CD core star polymers; MALDI-TOF; ATRP initiators; RAFT chain transfers; GPC.

INTRODUCTION

Star-shaped polymers exhibit versatile physical and chemical properties^[1–12] due to their different topologies^[13–19]. The past two decades have witnessed the rapid and fruitful development in the synthetic methodology of star-shaped polymers with various topologies^[20–23]. The strategies on star-shaped polymer synthesis are varied^[1, 6–11, 24–29]. The most natural tactic is utilizing an initiator with more than two active sites^[17, 18, 30–39]. Modified polyhydric alcohols are useful initiators^[40, 41]. Cyclodextrins (CDs) as a special kind of polyhydric alcohols with excellent supramolecular functions have been appealing to researchers^[3, 5, 42–52]. The hydroxyl groups in CDs makes it easy to be polysubstituted, as the esterification reactions provide mature and reliable methods for the further decoration.

On the other hand, CDs are widely used as the supramolecular linkers considering that large numbers of guest molecules can interact with their cavity form supramolecular inclusion complexes^[5, 45, 46, 48, 51, 53–57]. Sliding supramolecular polymer brushes^[58–65] or supramolecular block copolymers^[66–72] can be obtained by molecular recognition interaction between CD-core polymers and other guest polymers^[67]. The properties of such system can be regulated by the side chains bonded on the β -CD core. The density of the side chains, characterized by the degree of substitution in β -CD, will greatly affect the physical behavior of the polymers. Therefore, investigating the degree of substitution in β -CD core ATRP initiators or RAFT chain transfers obtained by different methods is of vital importance.

Poly(*N*-isopropyl acrylamide) (PNIPAM) is one of the most widely used thermo responsive polymers^[74–82]. It displays a critical solution temperature (LCST) near human body temperature in water. The combination of

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PNIPAM and β -CD would probably provide a temperature responsive building block for the construction of functional supramolecular polymers.

In this paper, we reported the synthesis of β -CD core ATRP initiators and RAFT transfers. $^1\text{H-NMR}$ spectroscopy and MALDI-TOF MS were utilized to characterize the degree of substitution in the products. The degree of substitution in β -CD core ATRP initiators and RAFT chain transfers were estimated through $^1\text{H-NMR}$. The degree of polymerization of star PNIPAM were characterized through gel permeation chromatography (GPC). However, the $^1\text{H-NMR}$ and GPC can only give out the general information or the arithmetic mean value. As the topology of such β -CD core star polymers is one of the most important influencing factors which affect their physical and chemical properties, there are much need to study the topology in detail, rather than think it is so. Naturally, the key points in controlled radical polymerization, the ATRP initiators or RAFT transfers, are also necessary to be fully characterized. To obtain more information about each molecule, MALDI-TOF-MS was adopted to indicate the distribution of molecules with different degree of substitutions. Peaks corresponding to diverse charge-to-mass ratio stand for the commensurate degree of substitutions. The overall consideration of information from $^1\text{H-NMR}$, GPC and MALDI-TOF-MS will make the structure of the initiator, the chain transfers, and the star polymers much more definite and reliable.

EXPERIMENTAL

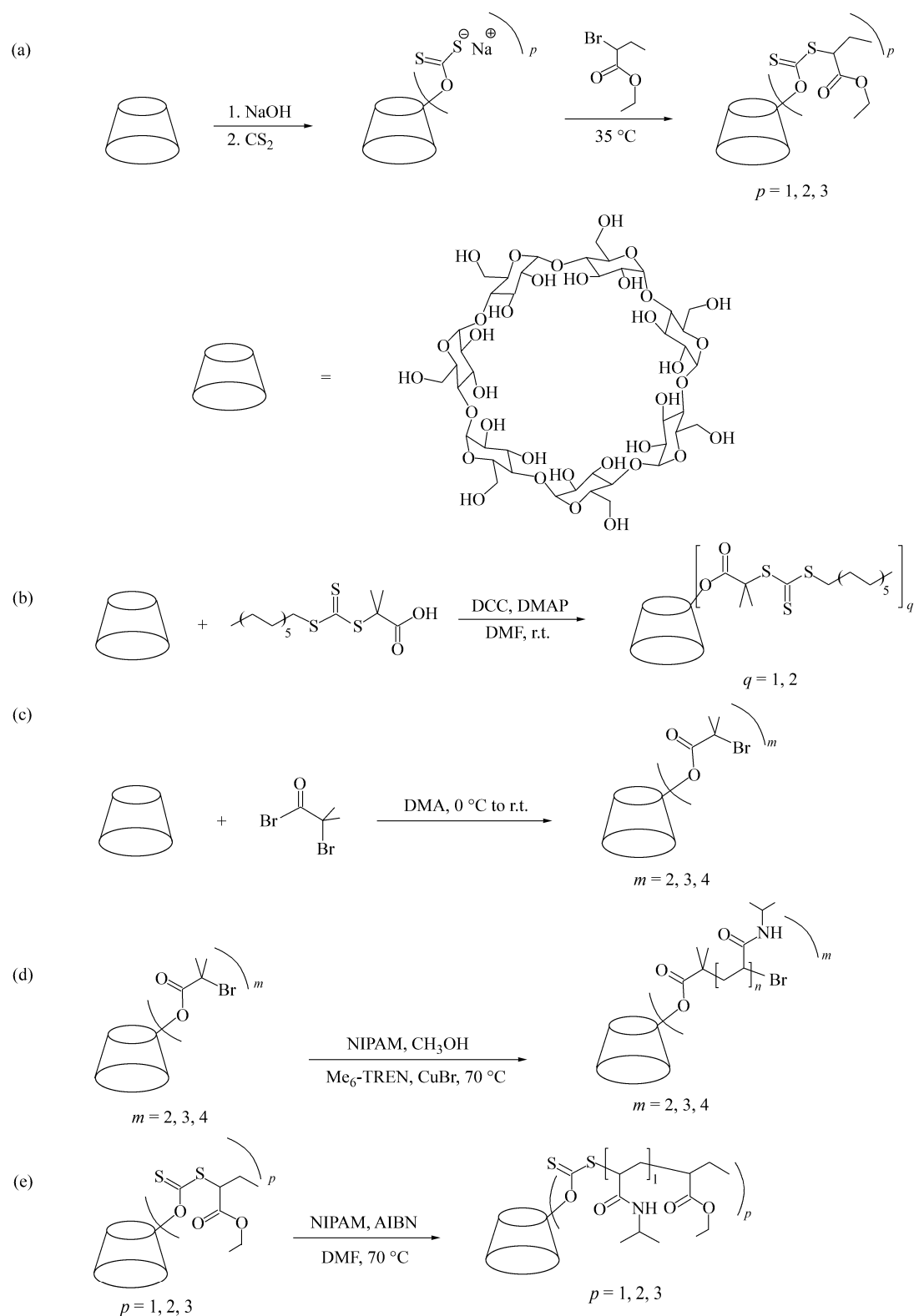
The synthetic routs are shown in Scheme 1. All of the β -CD core ATRP initiator and RAFT transfers were synthesized based on the relatively active 6-hydroxyl groups in β -CD. Three kind of bonding methods were used. For β -CD-xanthate, the key point is the nucleophilic addition between the deprotonated 6-hydroxyl groups and CS_2 . On the other hand, the β -CD-CTA and β -CD-Br were all synthesized through esterification of the 6-hydroxyl groups. β -CD-Br was gained through the addition of 2-bromo-isobutyric bromide while β -CD-CTA was synthesized after the activation of carboxyl group in CTA with DCC and DMAP. To make a comparison between ATRP and RAFT, a common monomer NIPAM was chosen to synthesize two kinds of β -CD core star polymer, β -CD-g-PNIPAM.

Materials

β -CD was procured from Kermel (China) and recrystallized for three times from water. *N*-isopropylacrylamide (NIPAM) was obtained from Acros and recrystallized for three times from toluene and hexane (1:3). 2,2-Azobis(isobutyronitrile) (AIBN) was got from Beijing Chemical Reagent Co., Ltd and recrystallized from ethanol for three times. 2-Bromoisobutyryl bromide, ethyl 2-bromobutyrate and copper (I) bromide were purchased from Acros (USA) and used as received. Dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) and tris(2-dimethylaminoethyl)amine ($\text{Me}_6\text{-TREN}$) were obtained from Alfa Aesar (USA) and used as received. Ethanol, actone, chloroform, isopropanol, ether, tetrahydrofuran, *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc) were received from Beijing Chemical Reagent Co. Ltd (China) and purified before use. All other reagents were commercially available and utilized without any further purification. Distilled water was used throughout the studies.

Characterization

$^1\text{H-NMR}$ spectra were recorded with a JEOL JNM-ECA400 NMR spectrometer with DMSO-d_6 , CDCl_3 or D_2O as the solvent. MALDI-TOF was recorded on an ABI MALDI-TOF mass spectrometry, using a nitrogen laser (337 nm) and cyano-4-hydroxycinnamic acid (CCA) as matrix. GPC measurements were carried out on a Waters e2695 GPC instrument with three column set (Styragel HR3 + HR4 + HR5), equipped with refractive index detector (Waters 2414), and DMF (containing $1\text{ g}\cdot\text{L}^{-1}$ LiBr) as eluent at $45\text{ }^\circ\text{C}$. PMMA was used as the calibration standard.



Scheme 1 Synthetic route of $\beta\text{-CD}$ -xanthate (a), $\beta\text{-CD}$ -CTA (b), $\beta\text{-CD}$ -Br (c), $\beta\text{-CD}$ -g-PNIPAM through ATRP (d) and $\beta\text{-CD}$ -g-PNIPAM through RAFT (e)

Synthesis of β -CD-xanthate

A typical procedure employed to synthesize β -CD-xanthate with the degree of substitution of 3 as the target was as follows^[70]. The β -CD (6.00 g, 5.29 mmol) was dissolved in 100 mL 20 wt% NaOH aqueous solution. Then CS₂ (1.2 mL, 19.8 mmol) was slowly added into the solution under stirring. Under room temperature, the solution turned orange gradually. After further stirring for more than 4 h until the CS₂ oil droplet disappeared, the solution was precipitated in ethanol. Then the crude resultant was dissolved in water and precipitated in ethanol for three times. After being dried under vacuum at 60 °C for 12 h, the product, light orange solid, sodium β -CD xanthate (β -CD-(XNa)_p), was obtained with 82% yield. Then, β -CD-(XNa)_p (4.00 g) was dissolved in 20 mL distilled water. Afterwards, ethyl 2-bromobutyrate (2.6 mL) was added dropwise into the solution, accompanied by stirring at 35 °C until light yellow precipitate appeared. The suspension was filtrated and washed with water and diethyl ether repeatedly. The product was obtained as β -CD-(xanthate)_p (Scheme 1a). Yield: 33%.

By adjusting the β -CD/CS₂ molar ratio from 1:3 to 1:12, four kinds of target products were synthesized for the study of degree of substitution. By changing the volume ratio of water and ethanol, the percentage of sodium β -CD xanthate with different degree of substitution will be affected.

Synthesis of a RAFT Chain Transfer Agent (CTA)

CTA was synthesized following these procedures^[81]. 1-Dodecanethiol (48.07 mL, 0.20 mol), acetone (120 mL), and tricaprylmethylammonium chloride (3.24 g, 0.008 mol) were added into a flask, then cooled to 0 °C under N₂ atmosphere with mechanically stirring. After that, a 50 wt% NaOH solution (8.38 mL, 0.21 mol) was added dropwise more than 1 h and stirred for 30 min. Then a mixture of carbon disulfide (12.07 mL, 0.20 mol) and acetone (24.54 mL, 0.33 mol) was added slowly in 1 h. After stirred for 30 min, 24.36 mL (0.30 mol) of chloroform was added over 40 min. The dropwise addition of NaOH (50%) solution (40 mL, 1.53 mol) was then in progress in 1 h. After 12 h stirring, 600 mL distilled water and 50 mL of concentrated HCl (38%) were added. The acetone was then removed by rotary evaporator. The obtained solid was suspended in 600 mL of 2-propanol and stirred for 2 h, and then the undissolved solid was filtered off. The 2-propanol solution was evaporated and the resulting solid was recrystallized from hexanes for three times (Scheme 1b). Yield: 37%.

Synthesis of β -CD-CTA

β -CD (1.14 g, 1.0 mmol, vacuum dried at 75 °C overnight before use), DMAP (0.17 g, 1.4 mmol) and CTA (5.10 g, 14.0 mmol) were dissolved in 15 mL of anhydrous *N,N*-dimethylformamide with stirring. DCC (5.77 g, 28.0 mmol) was dissolved in 15 mL of anhydrous *N,N*-dimethylformamide, and then added slowly into the solution. After the addition, the reaction was continued for 24 h. Then the mixture was filtered, accompanied by being precipitated with 400 mL ether and cooled to -20 °C overnight, and the light yellow solid was then collected by centrifugation and washed by cold ether (3 × 30 mL, -20 °C). The final product was dried under vacuum (Scheme 1c). Yield: 21%.

Synthesis of β -CD-Br

The macro monomer β -CD-Br was synthesized according to a previous report^[82]. β -CD (5.11 g, 4.5 mmol, vacuum dried at 75 °C overnight before use) was dissolved in 30 mL of anhydrous *N,N*-dimethylacetamide with stirring and then cooled to 0 °C. After that, a mixture of 2-bromo-isobutyric bromide (4.14 g, 18.0 mmol) and anhydrous *N,N*-dimethylacetamide (10 mL) was added dropwise to the solution over 1 h at 0 °C under N₂ atmosphere. The reacting temperature was maintained at 0 °C for 6 h and then allowed to reach slowly to room temperature. Then the reaction was continued for another 48 h. The final reaction mixture was precipitated with 600 mL ether. The resulting white powder was then collected by filtration. The crude product was suspended in 100 mL of distilled water, and stirred at room temperature overnight. The purified product was collected by filtration and dried under vacuum (Scheme 1d). Yield: 28%.

Synthesis of β -CD-g-PNIPAM through ATRP

As reported^[82], β -CD-Br (322.4 mg, 0.20 mmol), NIPAM (1.985 g, 17.5 mmol), methanol (10 mL) and Me₆-TREN (178.0 mg, 0.77 mmol) were added into a schlenk tube. Then the O₂ in the tube was removed by evacuation in liquid N₂ and melting under Ar atmosphere. Then, CuBr (91.8 mg, 0.64 mmol) was added and then the freeze-vacuum-thaw cycles circulated for three times to remove O₂. The mixture was then heated at 70 °C in an oil bath for 6 h. Then the tube was opened to stop the experiment because of exposing the catalyst to air. The final light green solution was diluted with 120 mL THF and passed through a short Al₂O₃ column to remove the copper catalyst. The resulting eluate was rotary evaporated to about 10 mL, and precipitated in 200 mL ether. The white product was collected by filtration, and then dissolved in methanol and precipitated in ether for three times. The final product was washed with ether, and dried under vacuum (Scheme 1e). Yield: 41%.

Synthesis of β -CD-g-PNIPAM through RAFT

In a similar way reported^[83], β -CD-xanthate (0.236 g, 0.3 mmol), NIPAM (1.93 g, 34.5 mmol), AIBN (2.69 mg, 0.0345 mmol) and 10 mL DMF were added into a 25 mL schlenk tube, followed by three freeze-vacuum-thaw cycles to remove O₂. The tube was heated in an oil bath at 70 °C with magnetic stirring for 6 h. Then the tube was quickly cooled in liquid N₂ to terminate the reaction. The solution was precipitated into 200 mL diethyl ether. The precipitate was then dissolved in 10 mL methanol and then precipitated again into 200 mL diethyl ether. The above dissolution-precipitation cycle was repeated for three times for purification. The final product was dried in vacuum (Scheme 1f). Yield: 49%.

RESULTS AND DISCUSSION

Synthesis of β -CD-xanthate

To study the influence of the molar ratio between β -CD and CS₂ on the degree of substitution in sodium β -CD xanthate, three ratios: 1:6, 1:9, and 1:12 were utilized in the synthesis processes separately. The degree of substitution was calculated through ¹H-NMR (Fig. 1) and MALDI-TOF (Fig. 2). However, the results obtained

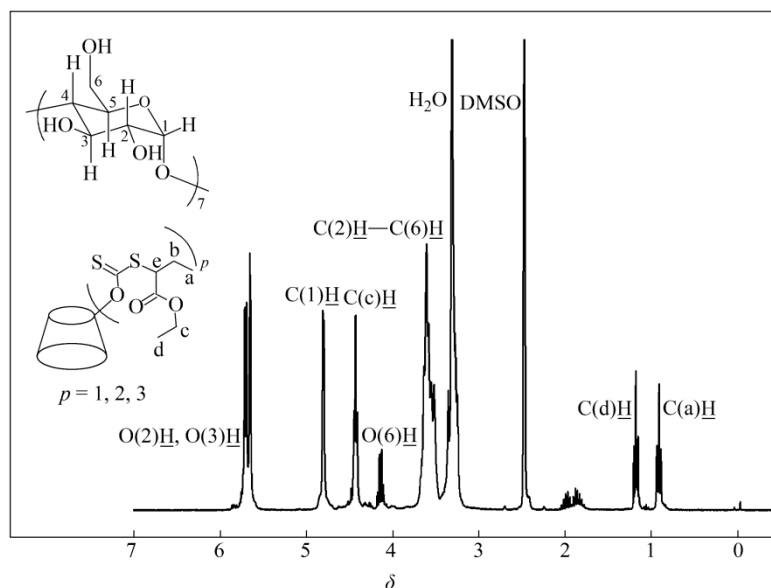


Fig. 1 ¹H-NMR spectrum of β -CD-(xanthate)

C(1)H was chosen as the standard, the integrals of the peak was set as 7, the other integral of the peaks were: 14.35(O(2)H, O(3)H), 6.83(C(c)H), 1.82(O(6)H), 27.39(C(2)H-C(6)H), 2.83(C(d)H), 3.05(C(a)H), the degree of substitution calculated was 1.

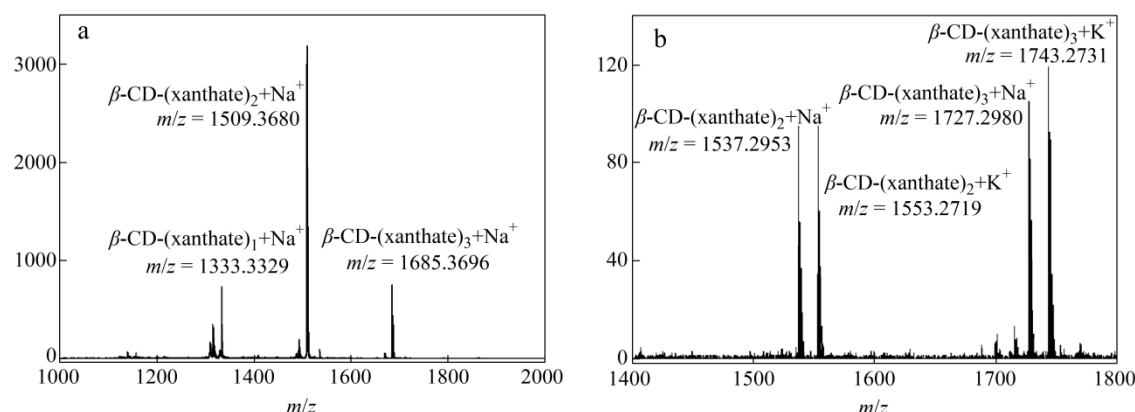
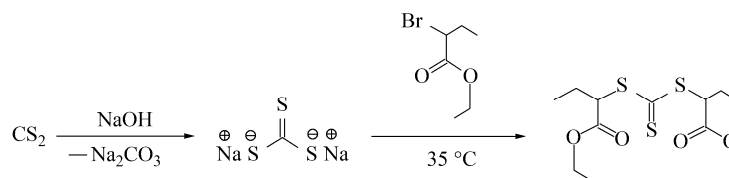


Fig. 2 MALDI-TOF MS spectra of β -CD-(xanthate) before (a) and after (b) stirring in distilled water. For spectrum (a) the molecular weights of β -CD-(xanthate)₁₋₃ are 1310 Da, 1486 Da, and 1662 Da, the $[M + Na]^+$ peaks are in accord with the MALDI-TOF-MS results. For spectrum (b) the molecular weights of β -CD-(xanthate)₂₋₃ are 1514 Da and 1704 Da, the $[M + Na]^+$ and $[M + K]^+$ peaks are in accord with the MALDI-TOF-MS results. The differences between the molecular weights of β -CD-(xanthate) in (a) and (b) are because of the ethyl butyrate residues, which were methyl ester in (a) and ethyl ester in (b).

from these two ways show a little difference: the $^1\text{H-NMR}$ shows the degree of substitution increases with the rise of the molar ratio of CS_2 while the MALDI-TOF shows the degree of substitution does not show obvious change when the molar ratio rises. Moreover, the MALDI-TOF shows the existence of three products: β -CD-(xanthate)₁, β -CD-(xanthate)₂, and β -CD-(xanthate)₃. The height of each peak can roughly show the content of each component: β -CD-(xanthate)₂ is the most while β -CD-(xanthate)₁ and β -CD-(xanthate)₃ have a similar content. The MALDI-TOF shows much more information of single molecules, while the $^1\text{H-NMR}$ shows the average information. That means, the highest degree of substitution in the product is three and there are some other components which cause the deviation of average degree of substitution.

One explanation for no products of which degree of substitution is higher than 3 is that one β -CD molecule has only seven 6-hydroxyl groups. When three of them transformed to sodium xanthate, the negative charge will hinder the deprotonation of their neighboring hydroxyl groups, which should be the first step in sodium xanthate formation. Considering that the degree of substitution is calculated by the ratio between the integrals of $\text{C}(1)\text{H}$ in β -CD and $\text{C}(a)\text{H}$ in ethyl butyrate residues, the most probable explanation is that the by-products have no β -CD structure but ethyl butyrate residues. As reported by the literature^[84], CS_2 itself will transform to sodium trithiocarbonate in NaOH solution (Scheme 2). So in later procedures, it will transform to another RAFT transfer with ethyl butyrate residues. However, its molecular weight is only 338 Da, which will be overlapped in the matrix peaks.



Scheme 2 Probable side reaction in the system

The product β -CD-(xanthate) is a mixture in which β -CD-(xanthate)₂ is the main component (Fig. 2a). Considering that the substituted xanthate groups are hydrophobic, which can reduce the solubility of β -CD in water, thus, we utilized distilled water in further purification to remove the products with lower degree of substitutions. After being washed by distilled water and dried in vacuum overnight, the further purified β -CD-(xanthate) was also characterized by MALDI-TOF, which shows that it was composed by a similar amount of

β -CD-(xanthate)₂ and β -CD-(xanthate)₃ without any β -CD-(xanthate)₁ (Fig. 2b). Such purification based on the positive correlation of the hydrophobic property of the products and their degree of substitution was also utilized in the later synthesis of β -CD-CTA and β -CD-Br.

Synthesis of β -CD-CTA

The products were also characterized by ¹H-NMR (Fig. 3) and MALDI-TOF (Fig. 4). The average degree of substitution calculated according to the ¹H-NMR results is 1.37, which means the existence of multi substituted components. The MALDI-TOF supports the results from the ¹H-NMR spectrum: the main product is mono substituted (β -CD-CTA₁), meanwhile the double substituted products (β -CD-CTA₂) can also be detected. However, the peaks corresponding to the products (β -CD-CTA₃₋₇) with degree of substitution higher than two cannot be observed.

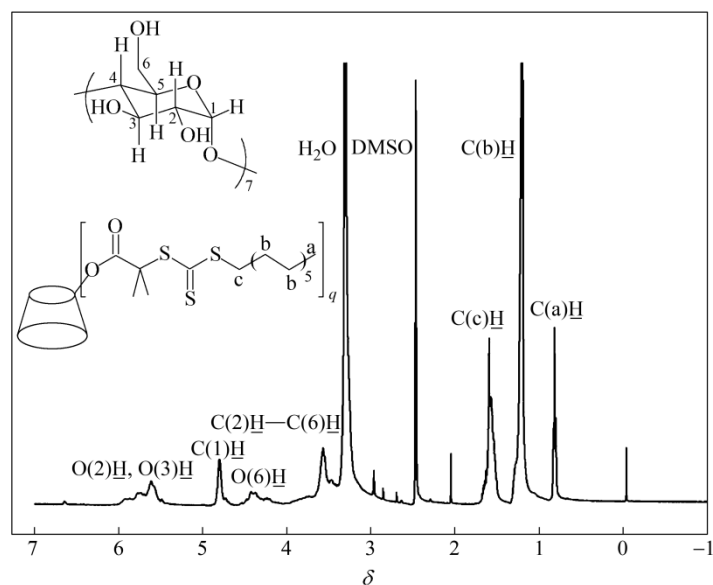


Fig. 3 ¹H-NMR spectrum of β -CD-CTA

C(1)H was chosen as the standard, the integral of the peak was set as 7, the other integrals of the peaks were: 8.97(O(2)H, O(3)H), 4.57(O(6)H), 28.27(C(2)H-C(6)H), 5.93(C(c)H), 61.85(C(b)H) and 9.05(C(a)H), the degree of substitution calculated was 3.

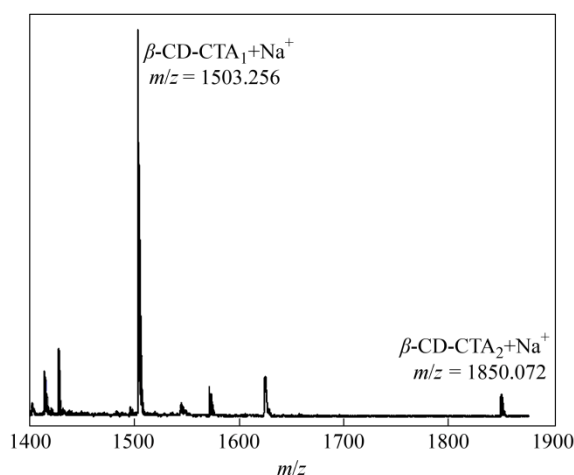


Fig. 4 MALDI-TOF MS spectrum of β -CD-CTA

The molecular weights of β -CD-CTA₁₋₂ are 1480 Da and 1827 Da, the $[M + Na^+]$ peaks are in accord with the MALDI-TOF-MS results.

The sample used in the characterizations above was synthesized with the molar ratio, 1:14 between β -CD and CTA. That means the molar ratio between 6-hydroxyl groups in β -CD and CTA is 1:2. It is abnormal to obtain products without any multi substituted β -CD components, even triple substituted β -CD-CTA. Since the DCC condensation is reliable and efficient, the main reason for such a result should not be due to the synthesis and purification.

The most possible reason for this should be the good solubility of CTA. Because of the long carbon chain in the molecule, it dissolves well in most organic solvents, even in the precipitant diethyl ether. Even the product (mainly β -CD-CTA) was obtained after overnight cooling at $-20\text{ }^{\circ}\text{C}$. A logical explanation is that products with high degree of substitutions cannot precipitate in the precipitant diethyl ether.

To further study the reaction, two reactions with the molar ratio between β -CD and CTA, 1:21 and 1:28 respectively, were conducted. Finally, no solid exists after precipitation, which can be treated as an indirect proof of such an explanation.

Synthesis of β -CD-Br

To obtain such a product, the procedures differ from the former ones. Because of the existence of one of the reactants, 2-bromo-isobutyric bromide, the 2, 3, and 6-hydroxyl groups show very similar activity in esterification reactions. Under these circumstances, it is of importance to know the exact binding sites of the functional groups. Thus, ^{13}C -NMR was conducted besides ^1H -NMR and MALDI-TOF. The ^1H -NMR (Fig. 5) and MALDI-TOF (Fig. 6) show similar results, the average degree of substitution is 3.2 and the MALDI-TOF reveals the peak of β -CD-Br₂, β -CD-Br₃, and β -CD-Br₄. That shows the effectiveness of washing by distilled water, and the product with low degrees of substitution was totally removed. What's more, the reaction should be conducted at lower temperature ($15\text{ }^{\circ}\text{C}$) for a longer time (48 h). Compared with the same reaction conducted at higher temperature ($25\text{ }^{\circ}\text{C}$) and shorter time (24 h), the high temperature products looked white and rarely dissolved in 100 mL of distilled water, while the low temperature products showed brown color and almost dissolved in water, which suggests the occurrence of side reaction and low degree of substitution products.

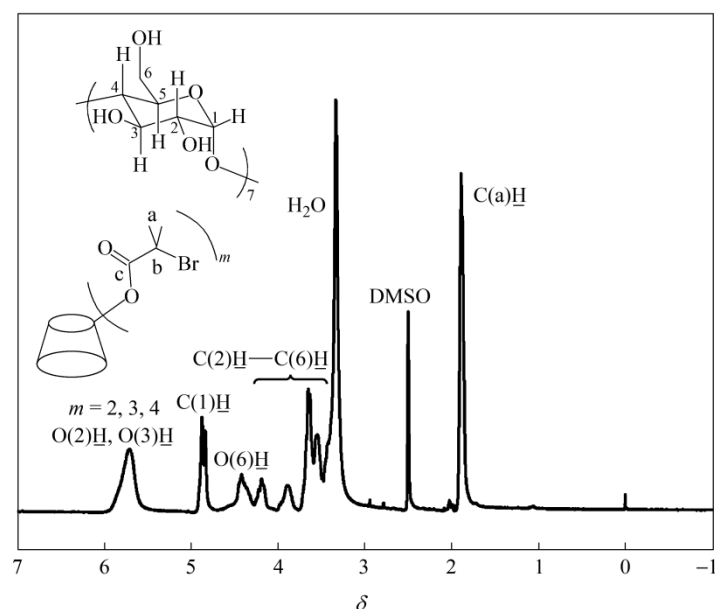


Fig. 5 ^1H -NMR spectrum of β -CD-Br

C(1)H was chosen as the standard, the integral of the peak was set as 7, the other integrals of the peaks were: 10.26(O(2)H, O(3)H), 5.03(O(6)H), 27.52(C(2)H-C(6)H) and 18.14(C(a)H), the degree of substitution calculated was 3.

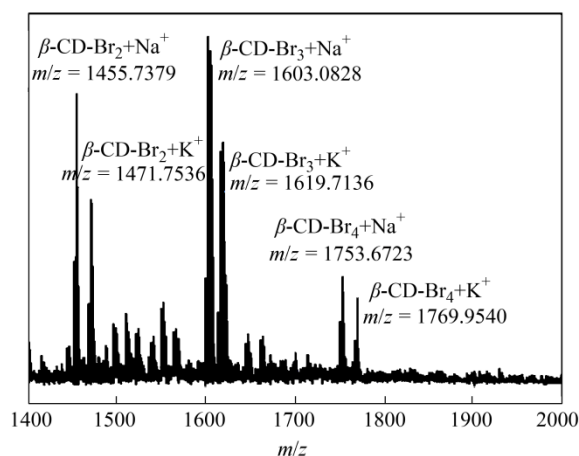


Fig. 6 MALDI-TOF MS spectrum of β -CD-Br

The molecular weights of β -CD-Br₂₋₄ are 1432 Da, 1580 Da and 1730 Da, the $[M + Na^+]$ and $[M + K^+]$ peaks are in accord with the MALDI-TOF-MS results.

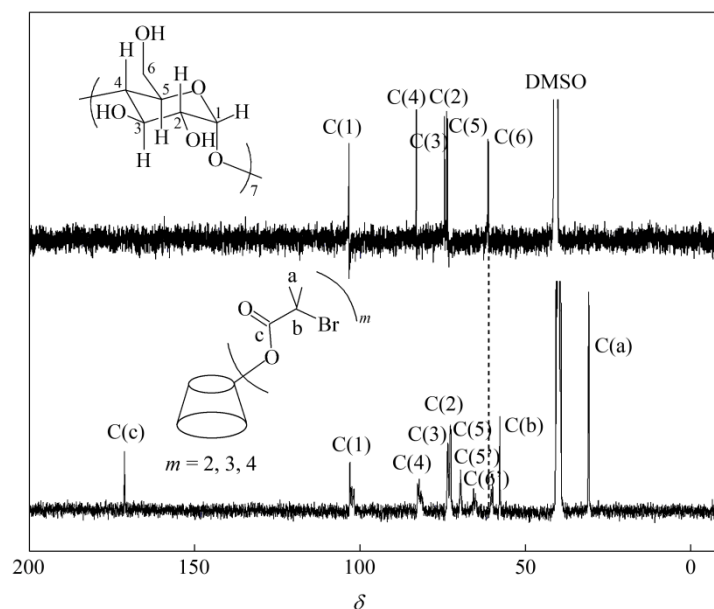


Fig. 7 ^{13}C -NMR spectrum of β -CD-Br

Meanwhile, ^{13}C -NMR (Fig. 7) result shows the binding sites of 2-bromo-isobutyric bromide residue is totally on the 6-hydroxyl groups. Compared with the ^{13}C -NMR of β -CD, the peaks existing in the ^{13}C -NMR of the product are only the C(a), C(b), C(c) in 2-bromo-isobutyric bromide residue and C(5'), C(6') in β -CD. That proves the 6-hydroxyl groups are the only binding sites for the functional groups.

Synthesis of β -CD-g-PNIPAM through ATRP and RAFT

From the review on RAFT polymerization^[84], the β -CD-(xanthate)₃ is not suitable for the polymerization of NIPAM. On the contrary, the β -CD-Br₃ with the high activity initiating system Me₆-TREN/CuBr shows good compatibility to NIPAM polymerization (Fig. 8). For these two systems, the feed ratio between initiator/transfer and monomer are always 1:50. After the same polymerization time, the products were characterized by ^1H -NMR and GPC to measure their number-average molecular weight (M_n) and polydispersity (PDI) (Fig. 9). The number-average molecular weight (M_n) based on GPC is smaller than that of ^1H -NMR. A reasonable explanation

is that the star polymer shows a smaller excluded volume than the linear polymer, which causes the decrease of M_n . As expected, the star β -CD-PNIPAM synthesized from β -CD-(xanthate)₃ displays higher PDI (1.37), while the star β -CD-PNIPAM synthesized from β -CD-Br₃ has a lower PDI (1.10) (Table 1), which shows the high controllability of the polymerization reactions. However, as one RAFT transfer maybe only suitable for specific monomers, such a result will change absolutely for other monomers^[80]. For example, *N*-vinylpyrrolidone (VP), or vinyl acetate (VA), the β -CD-(xanthate) will make a star polymer with low PDI while the β -CD-Br will lead to high PDI products or no reactions.

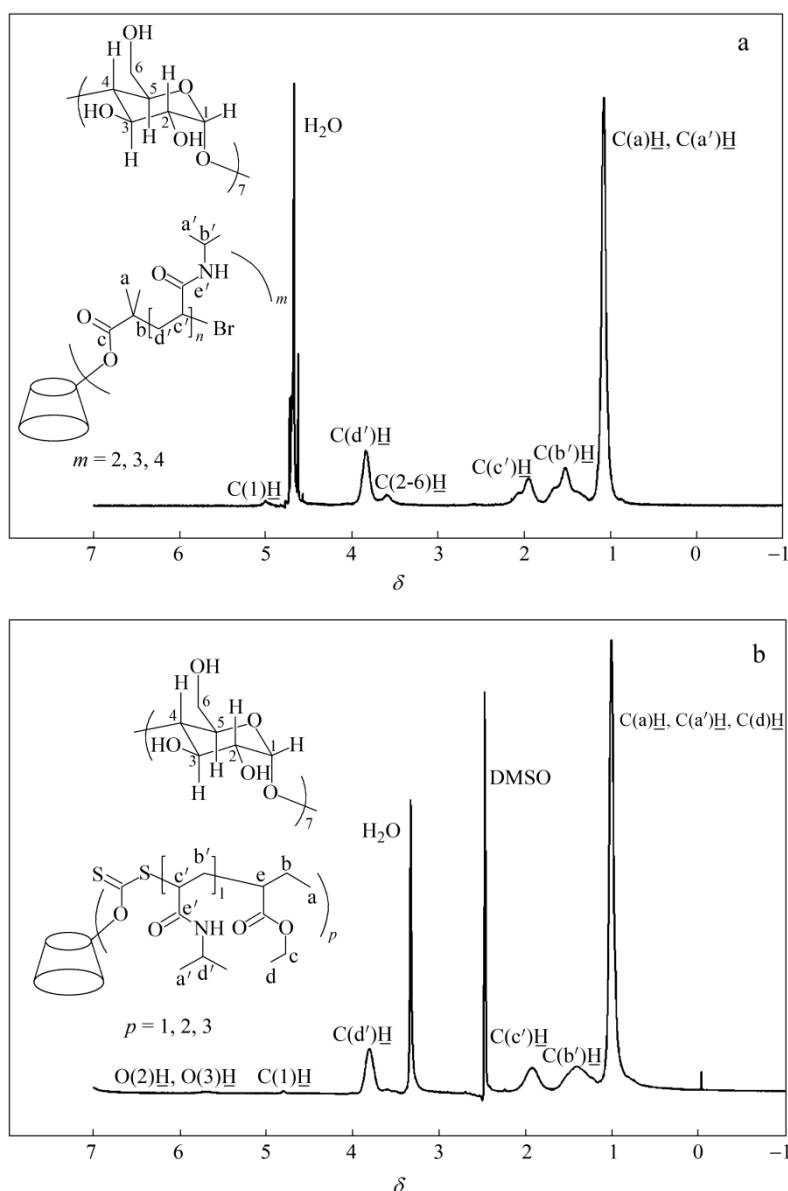


Fig. 8 ¹H-NMR spectra of β -CD-g-PNIPAM through ATRP (a) and RAFT (b)

For spectrum (a) C(1)H was chosen as the standard, the integrals of the peak was set as 7, the other integral of the peaks were: 142.98(C(d')H), 30.15(C(2-6)H), 118.48(C(c')H), 218.78(C(b')H), 767.16(C(a')H, C(a)H), the molecular weight calculated was 16000 Da. For spectrum (b) C(1)H was chosen as the standard, the integral of the peak was set as 7, the other integral of the peaks were: 6.35(O(2)H, O(3)H), 87.58(C(d')H), 75.99(C(c')H), 123.03(C(b')H), 608.95(C(a')H, C(a)H), the molecular weight calculated was 13000 Da.

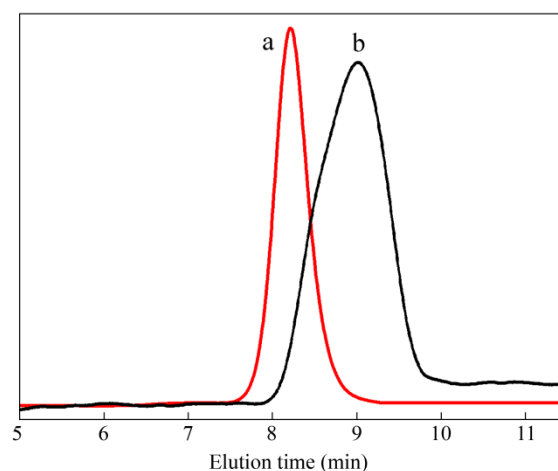


Fig. 9 The GPC elution curves of β -CD-g-PNIPAM obtained from ATRP (a) and RAFT (b)

Table 1. The molecular weights and molecular weight distributions of β -CD-g-PNIPAM obtained from ATRP and RAFT

	$M_{n,NMR}$	$M_{n,GPC}$	$M_{w,GPC}$	M_w/M_n
β -CD-g-PNIPAM (ATRP)	16000	7600	8500	1.10
β -CD-g-PNIPAM (RAFT)	13000	6600	9000	1.37

CONCLUSIONS

We have synthesized three kinds of β -CD based ATRP initiator and RAFT transfer with different degrees of substitution. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were utilized to character their chemical structures, degrees of substitution (average), and functional groups binding sites in each kind of products. Compared with other researchers, we utilized MALDI-TOF-MS to indicate the single molecule properties of β -CD core initiator and chain transfers to make up for the shortage of $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$. The combination of these characterizations shows much more definite information of the chemical structures of these β -CD based products. Moreover, we improved a purification method of the products. This work provides an easy way of synthesizing and characterizing the β -CD based ATRP initiator and RAFT transfer with definite structures. Further work on β -CD core star polymers based on these methods is still undergoing in our lab.

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