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ARTICLE TYPE

High grafting density of cyclodextrin polymer for fast removal of aromatic compounds from water

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Abstract: A side-group *β*-cyclodextrin grafted poly(glycidyl methacrylate) (PGMA-*g*-*β*-CD) with grafting density of 92% has been synthesized via facile "click" reaction and atom transfer radical polymerization. The final polymer complexed with 4'-aminoazobenzene-4-sulfonic acid and 1-naphthylamine in water to be precipitated within one minute. The PGMA-*g*-*β*-CD polymer showed great potential in fast removal of aromatic compounds in water treatment.

Introduction

Cyclodextrins (CDs), which consist of 6 (*α*), 7 (*β*), and 8 (*γ*) glucoses connected by *α*-1,4 linkages, are widely studied in supermolecules for their special molecular recognition. They have wide applications in additives, absorbants as well as controlled release due to their good biocompatibility.[1-3] CD polymers (CDPs), which contain CDs in the polymer, thus show great potential in chiral separation, water treatment, smart materials as well as drug delivery.[4-6] Mayr and coworkers reported that the chiral ferrocene derivatives can be separated by CDPs grafted on the stationary phases.[4] Cationic CDPs were also utilized as chiral selector for open-tubular capillary electrochromatography.[7] The CDPs and CDPs grafted materials were also used to remove organic pollutants, such as phenol, azo-benzene dyes, methylene blue, and naphalene derivatives from water for their inclusion complexation with such organic compounds, which could be easily precipitated from water.[8-11] Supermolecular hydrogels, micelles and nanoparticles were also constructed via the host-guest interactions between CDPs and guest molecules, showing great potential in drug delivery and smart materials.[12-15]

Studies on the preparation of CDPs have gained more attention for the wide applications of CDPs. The preparation methods of CDPs are purposed for the application of such polymers. The CDPs used in separation and water treatment were usually prepared by cross-linking of hydroxyl groups from CDs.[16,17] The resultant CDPs were usually not soluble in solvent, and thus can be removed via filtration or centrifugation. On the other hand, the CDPs used in hydrogels and nanoparticles were non cross-linked.[18] Such CDPs were prepared by polymerization of CD monomers. However, the molecular weight of linear CDPs were usually low by directing polymerization due to the steric hindrance of CDs.[19] CDPs prepared by copolymerization of CD-containing monomers with comonomers often show uncontrolled random structure.[20] Recently, post-modification method was used to prepare linear CDPs. The grafting density of CDs in the polymer can be improved by using high efficiency reactions such as "click" reaction. Furthermore, by post-modification, star and hyperbranched CD polymers were also prepared.[21,22] Nevertheless, some of the polymer main chains might be complexed with CDs to make cross-linked polymer.[23] Although this problem can be avoided by capping polymer main chain ends with steric groups[24], the synthesis step is time consuming. The non cross-linked CDPs were soluble in polar solvent, but could not be used in separation probably because that the complexation between CDPs and guest molecules was difficult to be removed from water for they formed hydrogels or nanoparticles. If the water soluble CDPs complexed with organic compound to form precipitation and can be removed by filtration, thus the CDPs could be used in water treatment. The appearance of the complexation might be related with the structure of CDPs.

In this paper, water soluble linear *β*-CD grafted poly(glycidyl methacrylate) (PGMA-*g*-*β*-CD) with high grafting density as well as controlled main-chain structure is designed and prepared via facile "click" reaction between the azide functionalized PGMA (PGMA-N_3) and the alkyne modified *β*-CD. PGMA was selected as the main chain for its well-controlled structure via atom transfer radical polymerization (ATRP) and the more important is that PGMA main chain will not complexed with *β*-CD, which will fulfill the requirement for linear side-group *β*-CD polymer synthesis. The inclusion complexation between PGMA-*g*-*β*-CD and aromatic compounds such as 4'-aminoazobenzene-4-sulfonic acid (PAABSA) and 1-naphthylamine (NA) were studied to show a great potential in fast removal of aromatic compounds from water for the complexation precipitated from water within one minute.

Experimental

Materials

β-Cyclodextrin (*β*-CD, 99%) was purchased from Tianjin Guang Fu Chemical Reagent Co., Ltd., China, and recrystallized from deionized water twice prior to use. Glycidyl methacrylate (GMA, 97%, Alfa) was distilled under reduced pressure before usage. *p*-Toluenesulfonyl chloride (98%, Beijing Chemical Reagent Co., Ltd., China) was purified by recrystallization from petroleum ether. Propargylamine (94%), epichlorohydrin (EP, 99%), ethyl 2-bromoisobutyrate (EBiB, 99%), and *N,N',N',N'',N''*-

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pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from Aldrich and used without further purification. Sodium azide (NaN_3, 99%), ascorbic acid (Vc), 1-naphthylamine (NA, 98%), ammonium chloride (NH_4Cl, 99%), $CuSO_4$ $5H_2O$ (99%), and 4'-aminoazobenzene-4-sulfonic acid (PAABSA, 98%) were supplied by Beijing Chemical Reagent Co., Ltd., China. All other reagents were commercial available and used as received without further purification.

Materials

All ^1H NMR experiments were performed on a Bruker spectrometer (400 MHz) at ambient temperature. $CDCl_3$, D_2O and DMSO-d_6 were used as solvent. Elemental analysis (EA) was carried out using a Flash 1112 Series EA analyzer with helium as a carrier gas and decomposition temperature at 950 ℃. UV-vis experiments were conducted on a Shimadzu UV-1601 PC spectrophotometer scanning from 200 to 600 nm at room temperature. FTIR spectra were recorded on a Bruker EQUINOX 55. Matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) was performed on Bruker Biflex III using a nitrogen laser (337 nm). Matrix (4-hydroxy-α-cinnamic acid nitrile, CCA) and the samples were dissolved in mixed solvent of acetonitrile and water (1:1 v/v), containing 1% (w/w) of trifluoroacetic acid. The concentration of sample was 1 g/L, and 0.5 μL of the solution was placed on a sample holder. Data were collected by accumulating 100 single scan at an accelerating potential of 19 kV under a forward reflection mode. Size exclusion chromatography (SEC) was performed on a Waters 515 HPLC pump equipped with a Waters 2414 differential refractive index detector. Three Waters Styragel columns (HT2, HT3, and HT4) were used. THF containing 1% (w/w) of triethylamine was used as eluent, and the experiment was run at a flow rate of 1.0 mL/min at 35 ℃. Linear polystyrene standards were used for calibration. Dynamic light scanning (DLS) was performed on an ALV DLS/SLS-5022F laser light-scattering spectrometer, equipped with ALV-5000 multi-τ digital time correlator at a scattering angle of 90 °. Samples were filtered through a membrane (0.45 μm, Millipore) prior to the analysis. The concentration of polymers in DMF or water is 1 mg/mL.

Synthesis of mono-6-deoxy-6-(*p*-toluenesulfonyl)-*β*-CD (6-mono-TsCD)

6-Mono-TsCD was prepared following the procedures reported in literature[25]. ^1H NMR (400MHz, DMSO-d_6): δ 7.73 (d, J = 8.07 Hz, 2H), 7.42 (d, J = 8.02 Hz, 2H), 5.87-5.58 (m, 14H), 4.82 (brs, 4H), 4.76 (br s, 3H), 4.55-4.13 (m, 6H), 3.74-3.43 (m, 28H), 3.42-3.18 (m, overlaps with HOD), 2.42 (s, 3H) ppm. MALDI-TOF MS on CCA matrix, *m/z* calculated: 1311.4 (OTs-CD + Na^+), 1327.4 (OTs-CD + K^+), measured 1311.8, 1327.8.

Synthesis of mono-6-deoxy-6-(alkyne)-*β*-CD (6-mono-alkyne-CD)

6-Mono-TsCD (1.3 g, 1.0 mmol) and propargyl amine (2.0 mL, 29.2 mmol) were charged into a Schlenk flask (25 mL) and dissolved in *N*,*N*-dimethylformamide (DMF, 10 mL). The mixture was stirred at room temperature for 48 h under the protection of N_2. The product was purified by precipitating into excess acetone for three times followed by vacuum drying. The final product was obtained as white solid (1.2 g, yield: 97%). ^1H NMR (400 MHz, DMSO-d_6): δ 5.87-5.58 (m, 14H), 4.82 (br s, 4H), 4.76 (br s, 3H), 4.55-4.13 (m, 6H), 3.74-3.43 (m, 28H), 3.42-3.18 (m, overlaps with HOD), 2.08 (s, 2H) ppm. MALDI-TOF MS on CCA matrix, *m/z* calculated: 1172.4 (6-mono-alkyne-CD + H^+), 1194.4 (6-mono-alkyne-CD + Na^+), 1210.4 (6-mono-alkyne-CD + K^+), measured 1172.6, 1194.7, 1210.6.

Synthesis of poly(glycidyl methacrylate) (PGMA) via ATRP

PGMA was synthesized by ATRP according to procedures reported on literature.[26] A Schlenk flask charged with CuBr (14.5 mg, 0.1 mmol) was degassed by three cycles of pump-thaw, and the deoxygenated EBiB (15.2 μL, 0.1 mmol), GMA (4.3 mL, 30.0 mmol), PMDETA (21.0 μL, 0.1 mmol) and toluene (2 mL) were transferred into the Schlenk flask under the protection of N_2. The polymerization proceeded at 60 ℃ for 3 h under the protection of N_2 while stirring. At the end of the polymerization, 0.1 mL of the solution was taken and mixed with 1 mL $CDCl_3$ for the purpose of conversion study. The residual reactant was diluted with tetrahydrofuran (THF) and passed through an alumina column to remove the catalyst. The sample was purified by precipitating into an excess amount of methanol for three times. PGMA polymers were obtained after vacuum drying (2.2 g, yield: 51.6%, $M_{n,SEC}$ = 13000, M_w/M_n = 1.2). ^1H NMR (400 MHz, $CDCl_3$): δ 4.28 (br s, -COOCH_2CH-), 3.80 (br s, -COOCH^*_2CH-), 3.22 (br s, -CH_2CHCH_2O-), 2.83 (br s, -CHCH_2O-), 2.63 (br s, -CHCH^*_2O-), 1.97 (br s, -CH_2C(CH_3)(COO-)-), 0.93 (br s, -CH_2C(CH_3)(COO-)-). FTIR (KBr, cm^{-1}): 3118-2683 (w, ν_{C-H}), 1726 (s, $\nu_{C=O}$), 1553-1463, 1461-1408, 1406-1310, 1308-1209, 1209-1037, 1037-937 (w, σ_{C-H}, σ_{C-C}), 901, 847 (w, $\sigma_{-CH(O)CH-}$), 566-500.

Synthesis of azide-functionalized PGMA (PGMA-N_3)

In a round-bottom flask, PGMA (2.0 g, 14 mmol of GMA unit), NaN_3 (2.7 g, 42 mmol) and NH_4Cl (2.3 g, 42 mmol) were dissolved in DMF (30 mL) and stirred at 60 ℃ overnight. The mixture was precipitated into excess deionized water for three times to remove residual inorganic salt. The obtained product was dried in a vacuum oven, yielding a white solid (2.5 g, yield: 96%). ^1H NMR (400 MHz, DMSO-d_6): δ 5.53 (br s, -CH_2CH(OH)CH_2-), 3.94 (br s, -COOCH_2CH(OH)-), 3.31 (overlaps with HOD, N_3CH_2-), 1.85 (br s, 2H, -CH_2C(CH_3)(COO-)-), 1.15-0.64 (br, -CH_2C(CH_3)(COO-)-) ppm. FTIR (KBr, cm^{-1}): 3669-3045 (s, broad, $\sigma\nu_{O-H}$), 3037-2774 (w, ν_{C-H}), 2095 (s, ν_{N3}), 1733 (s, $\nu_{C=O}$), 1516-1417, 1381-1326, 1324-1209, 1209-1127, 1125-1001, 1000-973 (w, σ_{C-H}, σ_{C-C}), 964-783, 781-720, 717-621, 566-500. Elementary analysis (EA): C 45.6%, H 6.1% and N 21.4%. Conversion of epoxy group to azido group in the side chain was calculated from the weight percent of N according to EA result. The conversion is 95%.

Synthesis of PGMA-*g*-*β*-CD via "click" chemistry

PGMA-N_3 (37.0 mg, 0.20 mmol of azido group), 6-mono-alkyne-CD (281.0 mg, 0.24 mmol), $CuSO_4$ $5H_2O$ (5.0 mg, 0.02 mmol), ascorbic acid (422.0 mg, 2.40 mmol) and DMF (2 mL) were charged into a Schlenk flask and degassed by three freeze-pump-thaw cycles. The solution was stirred at 80 ℃ for 48 h under the protection of N_2. The reactant was precipitated into excess acetone to remove the unreacted reagents. The crude PGMA-*g*-*β*-CD polymer was purified by dialyzing against water for 7 days (MWCO =3500) and followed by freeze drying (231.0 mg, yield:

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85%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.21-5.27 (br s, 14H, OH-2,3), 5.01 (br s, 7H, H-1), 4.50 (br s, 7H, OH-6), 4.14-2.91 (overlaps with HOD, 35H, H-3,5,6, H-2,4), 1.85 (br s, -CH_2C(CH_3)(COO-)-), 1.15-0.64 (br, -CH_2-C(CH_3)(COO-)-) ppm. FTIR (KBr, cm^{-1}): 3733-3001 (s, broad, ν_{O-H}), 3000-2123 (w, ν_{C-H}), 1860-1498, 1493-1182, 1180-955 (w, σ_{C-H}, σ_{C-C}), 953-892, 891-793, 792-720, 720-666, 612-539. EA: C 43.1%，H 6.2% and N 3.5%. Grafting density of β-CD on to the PGMA-N_3 was calculated from the weight percent of N according to EA result, and the estimated grafting density is 92%.

Preparation of water dispersed cross-linked β-CD polymers (β-CD-EP)

A flask was charged with β-CD (5.0 g, 0.4 mmol) and NaOH solution (8.0 mL, 33% w/w). The reaction mixture was allowed to stir overnight at room temperature. The mixture was heated to 30 ℃, and EP (1.7 mL, 2.2 mmol) was added rapidly. The reaction was stopped after 24 h by the addition of acetone. After decantation, acetone was removed via rotary evaporation, and the crude product was dissolved in water. The pH of the aqueous solution was adjusted to 12 with 6 M HCl aqueous solution. The resultant solution was reacted at 50 ℃ overnight. The crude polymer was purified by dialyzing against water for 7 days (MWCO =14000) and followed by freeze drying (5.3 g, yield: 76%). ^{1}H NMR (400 MHz, D_2O): δ 4.91 (br s, 7H, H-1), 4.16-3.25 (br m, 35H, H-3,5,6, H-2,4), 4.16-3.25 (m, 36.5H, -CH_2CH(OH)-, -CH$_2$CH(OH)-, -CH(OH)CH_2O-) ppm.

Inclusion complexation between aromatic compounds and β-CD polymers in aqueous solution.

The experiments were performed as follows: PGMA-g-β-CD and PAABSA were dissolved in deionized water at the concentration of 2.0 and 0.1 mg/mL, respectively. PGMA-g-β-CD solution (410 μL, 7.2×10^{-4} mmol of CD unit) was mixed with PAABSA solution (2 mL, 7.2×10^{-4} mmol) in a flask. The solution spontaneously became cloudy after shaking without stirring. Light yellow precipitation was obtained at the bottom of the flask within 1 min. The precipitates were removed by centrifugation, and the supernatant was collected and analyzed using the UV-vis with absorption at 385 nm. Compared with the working line of PAABSA at 385 nm, the amount of aromatic compounds removed by PGMA-g-β-CD polymers, Qs (mg/g), was then calculated by Eq. (1):

$$Qs = V \times (C_o - C_e)/ m \quad (1)$$

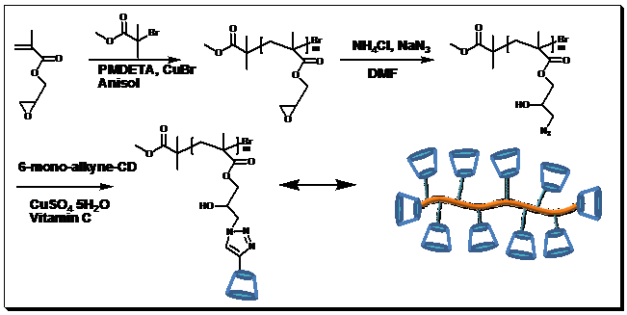
where C_o (mg/mL) is the initial concentration of PAABSA solution, and C_e (mg/mL) is the PAABSA concentration after centrifugation; V (mL) is the volume of solution; and m (g) is the mass of PGMA-g-β-CD polymers used.

The inclusion complexation between PGMA-g-β-CD and NA follows the similar procedures. As a comparison, free β-CD and water dispersed cross-linked β-CD polymer (β-CD-EP) were used to form inclusion complexations with PAABSA and NA at similar conditions.

Results and discussion

Synthesis and characterization of PGM-g-β-CD and β-CD-EP polymers

The synthesis route of linear PGMA-g-β-CD polymers was shown in Scheme 1. Post-modification was chosen in this work because the steric hindrance of CD moiety would prevent homo-polymerization via either free radical polymerization or living polymerization. The "click" reaction was used to provide the high grafting density of the CD units onto the polymer backbone. PGMA precursor was synthesized by ATRP to guarantee the well-defined structure of the polymer backbone. Hence, by this method, linear CD containing polymers with controlled structure and high grafting density can be achieved easily.



Scheme 1. Synthetic routes of β-CD grafted PGMA polymers (PGMA-g-β-CD) via ATRP and "click" reaction.

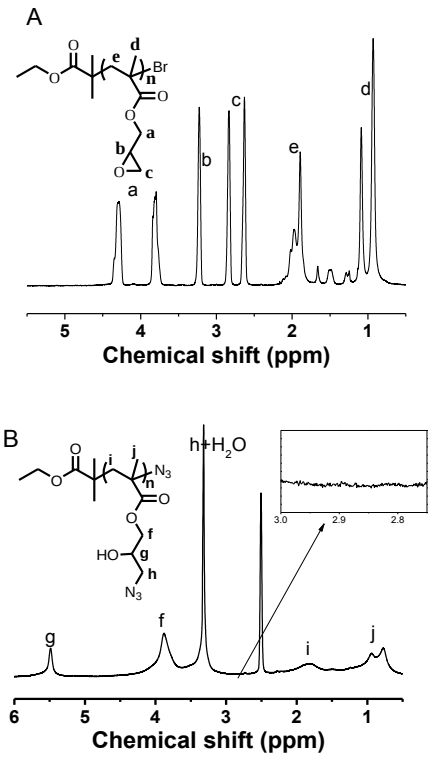


Fig. 1. ^{1}H NMR spectra of PGMA (A) and PGMA-N_3 (B). Inset in Fig. 1B is the magnification from 2.75 to 3.0 ppm. The solvent for A is $CDCl_3$, while DMSO-d_6 for B.

Fig. 1A shows the ^{1}H NMR spectra of PGMA, the peaks were assigned clearly to the corresponding proton signals, and the integration is consistent with the theoretical value respectively. The average polymerization degree (DP) of PGMA is 156 estimated from monomer conversion determined from ^{1}H NMR. When PGMA reacted with sodium azide in the presence of NH_4Cl, azido group was incorporated into the side-group. Similar

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to reported results,[27, 28] the signals of methylene groups in side chain changed from double peaks to broad mono peaks. The chemical shift of one methylene (-COOCH_2-) shifted from 4.05 to 3.90 ppm, and the other methylene from epoxy group down shifted from 2.82 to 3.30 ppm (Fig. 1). The methenyl group shifted from 3.2 ppm to 5.4 ppm due to the ring opening of epoxy group. All these chemical shifts clearly demonstrated the 100% conversion from epoxy to azido group in the side chain of PGMA. However, the conversion obtained from ^{1}H NMR is not so accurate for polymers because of the limited accuracy of ^{1}H NMR. EA was used to study the conversion of epoxy group in addition. By calculating from the weight percentage of nitrogen (N) in PGMA-N_3, the conversion was shown to be more than 95%, which is consistent with the ^{1}H NMR result.

The "click" reaction between 6-mono-alkyne-CD and PGMA-N_3 was conducted under a mild condition in DMF under the catalysis of copper (I) to produce a linear PGMA-*g*-*β*-CD polymer with a high grafting density of *β*-CD. FTIR was used to characterize PGMA, PGMA-N_3, and PGMA-*g*-*β*-CD polymers qualitatively. In Fig. 2, two typical absorption bands at 800-900 cm^{-1} are assigned to signals from epoxy group of PGMA. The peaks at ca. 2900 cm^{-1} are assigned to the C-H vibration from the PGMA main chain, and the signal at 1620 cm^{-1} is corresponding to the ester group. After reacting with NaN_3, the peaks at 800-900 cm^{-1} corresponding to epoxy group in PGMA were disappeared, and a new peak at 2100 cm^{-1} was generated for the presence of azido group. The signal at 3300 cm^{-1} represents the formation of hydroxyl group. All the other peaks remain the same as PGMA. This demonstrates that the reaction of epoxy group and the generation of azido group in PGMA-N_3. For the PGMA-*g*-*β*-CD polymer, the signals became broader after the grafting of *β*-CDs, probably because of the intermolecular and intermolecular hydrogen bonding in the polymers. The signal at 2100 cm^{-1} was completely disappeared as a result of the "click" reaction between PGMA-N_3 and 6-mono-alkyne-CD. The results clearly demonstrated that almost 100% conversion was achieved after the "click" reaction.

In addition, ^{1}H NMR was used to study the conversion of "click" reaction quantitatively. As depicted in Fig. 3A, the ^{1}H NMR of PGMA-*g*-*β*-CD showed signals from *β*-CDs. Since the PGMA-*g*-*β*-CD was purified by dialysis against water to remove free *β*-CDs, the presence of signals from *β*-CDs demonstrating the successfully grafting of *β*-CDs onto the polymer backbone. The weak signal from the PGMA backbone at ca. 0.95 ppm might be related with the high weight percent of *β*-CDs grafting onto the polymer backbone. However, grafting density is difficult to be calculated via ^{1}H NMR analyses. EA analysis was utilized to calculate the grafting density of *β*-CDs by comparing the weight percent of N and C in PGMA-*g*-*β*-CD, which gives a result of 92% grafting density. Hence, by FTIR, ^{1}H NMR and EA analyses, side-group linear *β*-CD grafted polymer with 92% grafting density was prepared successfully.

In order to study the chain structures of CD containing polymer on the molecular recognition properties of the corresponding polymers, water dispersed *β*-CD polymers (*β*-CD-EP) were prepared easily with low cross-linking density according to literature.[29] As shown in Fig. 3B, the signal ascribed to methylene and methenyl groups (five hydrogen atoms) for 2-hydroxypropyl ether segment from one EP molecule was shifted below the two broad peaks between 3.0 and 4.0 ppm, which are assigned to be signals from *β*-CD (H-2, 3, 4, 5, 6). The substitution degree of *β*-CD-EP polymer is 7.3 and the *β*-CD content in polymer is 73.2%, as determined by the ratio of peak integration between H-1 of *β*-CD and two broad peaks between 3.0 and 4.0 ppm.

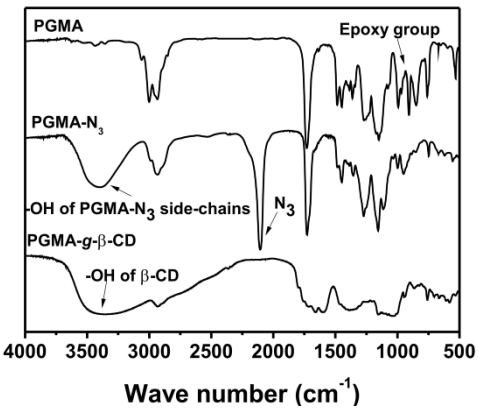

Fig. 2. FTIR spectra of PGMA, PGMA-N_3 and PGMA-*g*-*β*-CD.

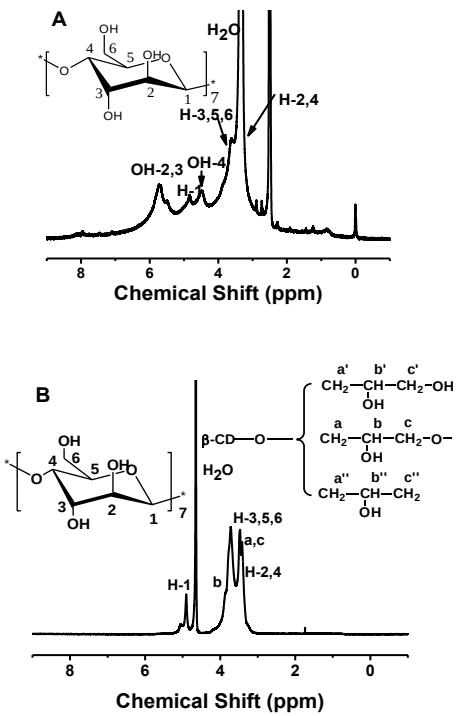

Fig. 3. ^{1}H NMR spectra of PGMA-*g*-*β*-CD (A) and *β*-CD-EP (B). The solvent for A is DMSO-d_6, while D_2O for B.

DLS characterization of *β*-CD polymers

In order to demonstrate the solution behaviour and the linear grafting structure of *β*-CD polymers prepared in this work, DLS measurement was carried out in DMF and water. Linear polymer precursor (PGMA-N_3) and PGMA-*g*-*β*-CD were studied by DLS in DMF at a concentration of 1 mg/mL. As shown in Fig. 4A, the intensity-average hydrodynamic radius (R_h) of PGMA-N_3 is ca. 8 nm. However, the peak is widespread, ranging from 1 to 100 nm, which might be the aggregation of PGMA-N_3 for the poor

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compatibility of the azido group in DMF. With a 92% grafting density of *β*-CDs, R_h value of PGMA-*g*-*β*-CD in DMF increased dramatically to 100 nm as shown in Fig. 4A. According to literature, the complexation between *β*-CD and the main chain will be cross-linked in the system to form hydrogels, while the linear *β*-CD grafted polymers dissolve very well in solution.[23,24] The DLS result indicated that the *β*-CDs were grafted onto the side chain to form linear *β*-CD polymers, and there were no complexation between *β*-CDs and the PGMA main chain as proposed. A uniform peak was obtained with a polydispersity index (PDI) of ca. 0.27, which is resulted from the good control of ATRP manipulation on PGMA polymer precursors. DLS measurement of PGMA-*g*-*β*-CD was also carried out in water since *β*-CD is water soluble. As shown in Fig. 4B, a symmetrical and narrow peak was obtained with the R_h value of 120 nm and the PDI of 0.20, similar to the results obtained when using DMF as a solvent. By grafting *β*-CDs onto the backbone of PGMA, the solubility of the grafted polymer in water substantially increased, probably because of the increase in the hydrophilicity from the *β*-CDs. Hence, water well soluble and well controlled CD grafting linear polymers can be obtained by a post-modification of PGMA via a "click" reaction at a high grafting density.

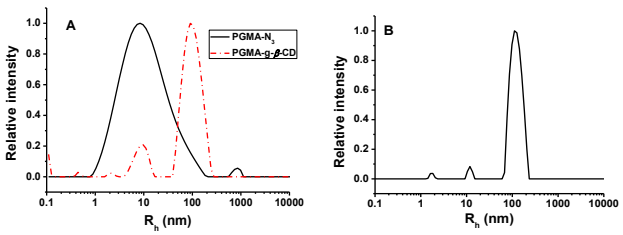

Fig. 4. Hydrodynamic radius distributions of PGMA-N_3 and PGMA-*g*-*β*-CD in DMF at the concentration of 1 mg/mL (A), and PGMA-*g*-*β*-CD in aqueous solution at the concentration of 1 mg/mL (B).

The DLS study of the water soluble/dispersed *β*-CD-EP polymer in DMF and water was carried out at the same condition as PGMA-*g*-*β*-CD. However, in the sample preparation, the solution can not be filtered by the filter membrane, which means the particle size of *β*-CD-EP is bigger than 450 nm, the upper pore size limitation of the membrane.

Inclusion complexation between aromatic compounds and *β*-CD polymers

As is well known, CD polymers have a great affinity with aromatic compounds, and have been used to trap aromatic compounds from waste water.[9] In this work, the inclusion complexation between CD polymers and aromatic compounds were studied. PAABSA and NA were selected as model aromatic compounds using in dye industry to represent well water soluble (PAABSA) and poor water soluble (NA) aromatic compounds. As reported, azobenzene and naphthylamine derivatives formed 1:1 inclusion complexation with *β*-CD.[29,30]

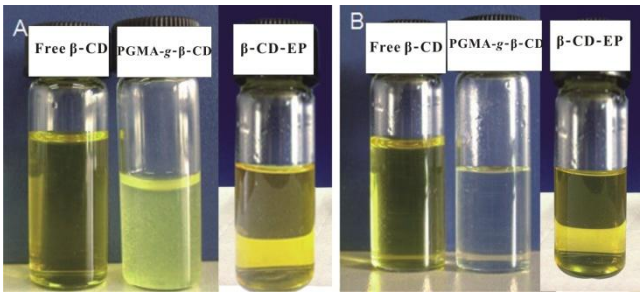

Fig. 5. Optical photos of 4'-aminoazobenzene-4-sulfonic acid aqueous solutions mixed with free *β*-CD, PGMA-*g*-*β*-CD and *β*-CD-EP at 1 minute before (A) and after (B) centrifugation.

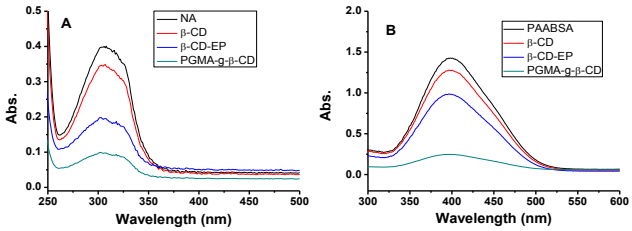

Fig. 6. UV-vis spectra of (A) initial NA aqueous solution (black), *β*-CD and 1-NA solution after 48 h (red), *β*-CD-EP and 1-NA solution after 48 h (blue), and PGMA-*g*-*β*-CD and 1-NA solution after centrifugation (cyan), and (B) initial PAABSA aqueous solution (black), *β*-CD and PAABSA solution after 48 h (red), *β*-CD-EP and PAABSA solution after 48 h (blue), and PGMA-*g*-β-CD and PAABSA solution after centrifugation (cyan).

As shown in Fig. 5A, when mixing PAABSA solution with PGMA-*g*-*β*-CD solution at molar ratio of ca. 1:1 (PAABSA: *β*-CD unit), the yellow solution turned cloudy immediately because of the formation of inclusion complexation between CDPs and PAABSA. Precipitation was evident within 1 minute. The phenomena is different from the water soluble CDPs reported elsewhere,[12] as the inclusion complexation formed hydrogels or nanoparticles. This is might be related with the high grafting density and controlled structure of PGMA-*g*-*β*-CD. When one PAABSA molecule form a complex with a *β*-CD unit at one side-group end, the polymer with residual free *β*-CD units is still dispersed in water very well, and can complex with more PAABSA molecules until the amount of inclusion complexation is much enough for the precipitation to be occurred. After removing of precipitant from the mixture by centrifugation, the solution became colourless (Fig. 5B). Since PAABSA has a yellow colour, this result demonstrates a successful removal of PAABSA from the mixture by PGMA-*g*-*β*-CD. UV-vis analysis was used to characterize the absorption capacity (R and Q_s) of PGMA-*g*-*β*-CD in PAABSA solution. Calculated from Fig. 6B, the absorption capacity is 230 mg/g, suggesting that 90% of the PAABSA has been removed. Compared with the materials made by CD grafting onto the matrixes, which has absorption capacity of 46 mg/g to aromatic compounds,[31] the absorption capacity of PGMA-*g*-*β*-CD is significantly higher.

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Table 1. Adsorption capacity of PGMA-*g*-*β*-CD compared with free CD and *β*-CD-EP polymer for PAABSA and NA in aqueous solution.

Sample	R (%) [a]		Q_s (mg/g) [b]	
	PAABSA	NA	PAABSA	NA
free *β*-CD	23	10	13.1	7.5
PGMA-*g*-*β*-CD	90	80	230	200
β-CD-EP	47	40	37.8	26.3

[a] Obtained from this formula: R (%) =(C_o-C_e)/C_o ×100, where C_o (mg/mL) is the initial concentration of PAABSA or NA aqueous solution and C_e (mg/mL) is the residual concentration of solutions; [b] Obtained from this formula: $Q_s = V(C_o\text{-}C_e)/m$, where V (mL) is the volume of solution and m (g) is the mass of β-CD polymers used.

The absorption of NA by PGMA-*g*-*β*-CD was studied at a similar condition as described above, and similar results were obtained. By calculated from the UV-vis analysis (Fig 6A), the absorption capacity of NA by PGMA-*g*-*β*-CD is 200 mg/g. The absorption capacity results were listed in Table 1.

As well-known, cross-linked CDPs are usually used in water treatment. In order to compare the absorption capacity of PGMA-*g*-*β*-CD polymer between cross-linked CDPs, free *β*-CD and water dispersed *β*-CD polymers prepared via cross-linking (*β*-CD-EP) were employed as control studies. As shown in Fig. 5A and 5B, the sample containing free *β*-CD and *β*-CD-EP were clear, and still remained as it is even after one month storage. However, the absorption capacity of PAABSA and NA is much lower than that of PGMA-*g*-*β*-CD as shown in Table 1. For *β*-CD-EP system, it is likely due to the disordered alignment of *β*-CD unit while most of *β*-CDs are embedded in the polymer without a chance to complexed with PAABSA or NA. For free *β*-CD system, it is difficult for a complexation to form aggregation or precipitation because the long distance between *β*-CD molecules in dilute aqueous solution. Hence, the solutions are transparent, and the absorption efficiency is low. However, in single PGMA-*g*-*β*-CD chain, the polymer backbone shortened the distance between the inclusion complexations in the side-group end via a covalent bonding in main chain while maintaining a certain movement by the short side-group linker between *β*-CD and the backbone. On the other hand, the intermolecular interactions between PGMA-*g*-*β*-CD polymers make the inclusion complexation aggregated in increasing size. Hence, the inclusion complexations are much easier to aggregate and finally precipitate from the solution. The PGMA-*g*-*β*-CD polymers have great potential in fast removal of aromatic compounds from water.

Conclusions

In summary, water soluble side-group PGMA-*g*-*β*-CD polymer with 92% grafting density was successfully prepared via "click" reaction between PGMA-N_3 and 6-mono-alkyne-CD. The PGMA-*g*-*β*-CD polymer exhibited a well inclusion complexation with aromatic compounds such as PAABSA and NA in dilute aqueous solution. Compared with the free CD and water dispersed cross-linked *β*-CD-EP, PGMA-*g*-*β*-CD showed a significantly higher absorption capacity to PAABSA and NA. The inclusion complexation between PGMA-*g*-*β*-CD and aromatic compounds leads to a precipitation which can be readily removed from the system. As PGMA-*g*-*β*-CD is fairly easy to prepare, nontoxic, and soluble in water, it can serve as a promising candidate for a treatment of polluted water.

Notes and references

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