Carbohydrate Polymers 113 (2014) 353–361

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Preparation of POSS-poly(ε-caprolactone)-β-cyclodextrin/Fe_3O_4 hybrid magnetic micelles for removal of bisphenol A from water

Weizhong Yuan[a,b,*], Jin Shen[a], Lulin Li[a], Xu Liu[a], Hui Zou[a]

[a] Institute of Nano and Bio-Polymeric Materials, School of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China
[b] Key Laboratory of Advanced Civil Materials, Ministry of Education, Shanghai 201804, People's Republic of China

ARTICLE INFO

Article history:
Received 25 April 2014
Received in revised form 27 June 2014
Accepted 15 July 2014
Available online 22 July 2014

Keywords:
Nanocomposites
Magnetic hybrid micelles
β-Cyclodextrin
Host–guest interaction
Bisphenol A

ABSTRACT

A novel amphiphilic star-shaped inorganic–organic hybrid copolymer polyhedral oligomeric silsesquioxane-poly(ε-caprolactone)-β-cyclodextrin (POSS-PCL-β-CD) was synthesized by ring-opening polymerization (ROP) and click chemistry. The amphiphilic copolymer can self-assemble into hybrid micelles with hydrophobic POSS-PCL chain encapsulating Fe_3O_4 nanoparticles as the core and β-CD as the shell after mixing with Fe_3O_4 nanoparticles in solvent and dialysis against water. The chemical structure of POSS-PCL-β-CD was characterized by ^1H NMR and the morphology of the magnetic hybrid micelles was characterized by TEM and DLS. Due to the host–guest interaction of β-CD with bisphenol A (BPA), POSS-PCL-β-CD/Fe_3O_4 hybrid micelles present good adsorption capacity in removal of BPA from aqueous solution. Magnetic measurement reveals that POSS-PCL-β-CD/Fe_3O_4 hybrid micelles still exhibit magnetism for separation by an external magnetic field, indicating that these magnetic hybrid micelles may have potential application in the field of environmental protection.

1. Introduction

With the rapid development of industrialization, considerable attention has been focused on the removal of endocrine disrupting chemicals (EDCs) from water due to the adverse effects of EDCs on humans and animals through interfering with the normal functions of hormonal systems (Basile et al., 2011; Ellis et al., 2010; Jang, Pang, Ma, & Liu, 2012; Lasserre et al., 2009; Yang, Ren, & Xie, 2011; Zhang, Fang, Yang, Zhang, & Wang, 2013). EDCs include compounds formed naturally and man-made chemicals in the environment, among which, bisphenol A (BPA) is an important and well-known chemical with estrogenic activity. And it has been widely used as monomeric substance for the synthesis of polycarbonate, epoxy–phenolic resin, stabilizer and antioxidant for many types of plastics (Besset, Lonnecker, Streff, & Wooley, 2011; Chepelev et al., 2013; Inui et al., 2009; Yu, Su, & Gan, 2009). As a result, it is inevitably released into the aquatic environment through different routes. The potential harmful effects of BPA on human mainly include breast cancer, neurobehavioral problems, type II diabetes and immunodeficiency. Therefore, the removal of BPA from waste water is very essential in the protection of ecological environment and human health. Up to now, various kinds of methods have been used to eliminate BPA in water, such as electrochemical process, chemical oxidation, enzymatic oxidation, photooxidation, solvent extraction, membrane filtration, adsorption, and biodegradation (Chin, Miller, Zeng, Cawley, & Weavers, 2004; Gözmen, Oturan, Oturan, & Erbatur, 2003; Marin, Santos-Juanes, Arques, Amat, & Miranda, 2012; Mitchell & Simpson, 2013; Voutchkova, Osimitz, & Anastas, 2010; Wang, Zhang, Li, & Zhu, 2010; Xu, Wang, & Zhu, 2012; Xuan, Endo, & Fujimoto, 2002). Among these approaches, adsorption is one of the most economically favorable methods and has been extensively employed in waste water treatment. A few materials have been used as sorbents for removal of BPA from aqueous solution, chitosan-bearing β-cyclodextrin, carbon materials, molecularly imprinted polymer, polyethersulfone–organophilic montmorillonite, Fe(III)/Cr(III) hydroxide and so on (Aoki, Nishikawa, & Hattori, 2003; Apodaca, Pernites, Ponnapati, Mundo, & Advincula, 2011; Fuhrer, Herrmann, Athanassiou, Grass, & Stark, 2011; Umar, Roddick, Fan, & Aziz, 2013; Zhang, Li, & Deng, 2012).

β-CD, one of the cyclodextrins, is a kind of cyclic oligosaccharide with seven D-glucose units linked by α-1,4-glucose bonds resulting from the enzymatic degradation of starch. And it is well known to form inclusion compounds with many organic compounds due to the hydrophobicity interior cavities composing of cyclic oligosaccharides (Chen et al., 2013; Xiao, Corvini, Dudal, & Shahgaldian,

---

* Corresponding author at: Institute of Nano and Bio-Polymeric Materials, School of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China. Tel.: +86 21 69580234; fax: +86 21 69584723.
E-mail address: yuanwz@tongji.edu.cn (W. Yuan).

http://dx.doi.org/10.1016/j.carbpol.2014.07.035
0144-8617/© 2014 Elsevier Ltd. All rights reserved.

2013; Yang & Yang, 2013). Therefore, β-CD is promising for applications in the fields of drug carrier systems, nanoreactors, bioactive supramolecular assemblies, molecular recognition, and catalysis (Chang, Li, Wang, He, & Gu, 2013; Deng et al., 2011; Mellet, Femández, & Benito, 2011; Yan et al., 2010; Yuan, Zou, Guo, Wang, & Ren, 2012). Some polymers with the structure of β-CD moiety have been found that they have the potential to remove toxic compounds in water (Cai et al., 2011; Kang, Zhou, Li, & Yuan, 2011). Recently, magnetic nanoparticles (MNPs) have been widely applied in many fields, such as immobilized catalysts, labeling and sorting of biological species, targeted drug or gene delivery, magnetic resonance imaging, and hyperthermia treatment (Cano, Sbargoud, Allard, & Larpent, 2012; Das et al., 2012; Huang, Neoh, Wang, Kang, & Shuter, 2010; Pan, Du, Zhao, & Xu, 2012; Xiong et al., 2012; Yuan, Yuan, Zhou, Wu, & Hong, 2010). MNPs can also be used as removal adsorbents because they can be easily separated by an external magnetic field (Lee et al., 2009). The surface-functionalized magnetic adsorbents by capping agents such as polymers, inorganic metals or oxide, and surfactants have been reported in the elimination of microcystins, heavy metal ions, and dyes in water (Chen, Zhang, Chen, Zhang, & Zhang, 2010; Dai & Nelson, 2010; Deng, Qi, Deng, Zhang, & Zhao, 2008; Vollath, 2010; Zhou, Gao, & Xu, 2010). However, the procedures of preparing magnetic adsorbents via surface-modification are comparatively complicated and inefficient because the magnetic nanoparticles should be modified to be used as the initiator to initiate the polymerization and prepare the hybrid materials. Therefore, it is extremely meaningful to explore novel magnetic adsorbents by facile methods.

Polyhedral oligomeric silsesquioxane (POSS) is a class of unique inorganic component that can be incorporated into polymer matrix to produce novel hybrid polymers with advantageous properties (Li, Chung, & Kuo, 2012; Tanaka & Chujo, 2012). Among them, octasilsesquioxanes ($R_8Si_8O_{12}$) is mostly investigated and it consists of a rigid, cubic silica core with a 0.53 nm side length, where each of the eight corners carries one organic group. The corner group is reactive so it can be used as initiating centers to prepare star-shaped inorganic–organic polymeric materials (Fan, Wang, & Zheng, 2010; Wu & Kuo, 2012; Ye et al., 2012).

In this paper, we have reported the synthesis of a novel amphiphilic star-shaped inorganic–organic hybrid copolymer polyhedral oligomeric silsesquioxane-poly (ε-caprolactone)-β-cyclodextrin (POSS-PCL-β-CD) by ring-opening polymerization (ROP) and click chemistry, as shown in Scheme 1. ^{1}H NMR suggested that the copolymer was synthesized successfully. The hybrid micelles based on the complex of Fe_3O_4 nanoparticles were conveniently prepared by mixing POSS-PCL-β-CD with Fe_3O_4 nanoparticles in solvent and dialysis against water. TEM images showed that Fe_3O_4 nanoparticles were encapsulated into the micelle core consisting of hydrophobic POSS and biodegradable PCL segments. The micelle shell was consisting of mono-functionalized β-CDs. Due to the host–guest interaction of β-CD with BPA, the magnetic hybrid micelles would be used as adsorbents to remove BPA in water (of course, it is a limitation for this micelle system to remove other compounds in polluted water) and then can be easily separated by an external magnetic field, the adsorption behavior of BPA was investigated using UV spectra. The magnetic hybrid micelles have potential application in the field of environmental protection especially in the treatment of polluted water.

2. Materials and methods

2.1. Materials

3-Chloropropyltrimethoxysilane (Acros Organic, USA), sodium azide (NaN_3, Alfa Aesar), dicyclohexylcarbodiimide (DCC; GL Biochem, Shanghai), 4-dimethylaminopyridine (DMAP; Fluka, USA), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, Acros Organic), silver nitrate ($AgNO_3$; Acros Organic), sodium hydroxide (NaOH; Shanghai Chemical Reagent Co., China), iron acetylacetonate ($Fe(acac)_3$; Acros Organic), 1,2-dodecanediol (Aldrich, 90%), oleylamine (Aldrich, 70%), and oleic acid (Aldrich, 90%) were used as received. CuBr was recrystallized and dried under vacuum. CL (Acros Organic, 99%) was purified with CaH_2 by vacuum distillation. Tin 2-ethylhexanoate ($Sn(Oct)_2$, Aldrich) was used without further purification. β-CD (Aldrich) was dried 100 °C for 48 h under vacuum after recrystallization from water before use. Mono-6-deoxy-6-azido-β-CD (β-CD-N_3) was prepared according to the literature (Brady, Lynam, O'Sullivan, Ahern, & Darcy, 2000; Muderawan et al., 2005). Propargyl 3-carboxylic-propanoate was synthesized according to our previous work (Yuan, Zhao, Gu, & Ren, 2010).

2.2. Characterization

Nuclear magnetic resonance (NMR). NMR spectra of samples were obtained from a Bruker DMX 500 NMR spectrometer using $CDCl_3$ as solvent. The chemical shifts were relative to tetramethylsilane.

Gel permeation chromatography (GPC). The molecular weight and molecular weight distribution were measured on a Viscotek TDA 302 gel permeation chromatography equipped with two columns (GMHHR-H, M Mixed Bed). THF was used as eluent at a flow rate of 1 mL min^{-1} at 30 °C.

Dynamic light scattering spectrophotometer (DLS). The hydrodynamic radius (R_h) of copolymer micelles was investigated using DLS techniques. The experiments were performed on a Malven Autosizer 4700 DLS spectrometer. DLS was performed at a scattering angle 90°. The R_h was obtained by a cumulant analysis.

Transmission electron micrographs (TEM). The morphology of nano-assemblies was observed with a JEOL JEM-2010 TEM at an accelerating voltage of 120 kV. The samples for TEM observation were prepared by placing 10 μL of nano-assemblies solution on copper grids coated with thin films and carbon. The samples were stained by 1% phosphotungstic acid.

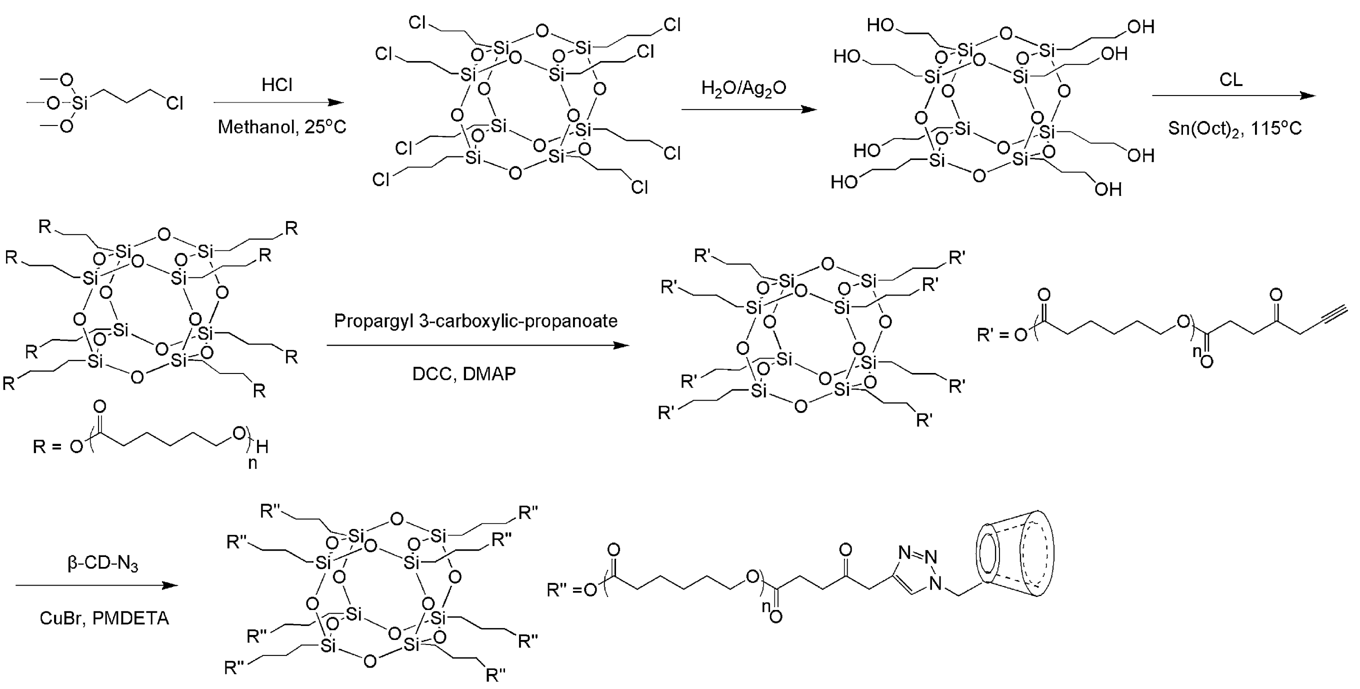
Thermogravimetric analysis (TGA). TGA was carried on a TGA 2050 thermogravimetric analyzer with a heating rate of 20 °C min^{-1} from 20 °C to 800 °C under nitrogen atmosphere.

Magnetic sample magnetometry (VSM). Magnetic measurements were performed on Lakeshore 7307 Vibrating Sample Magnetometer system at room temperature.

Ultraviolet–vis spectroscopy (UV–vis). UV–vis spectroscopy measurements were performed on a UV 2100 UV–vis Spectrophotometer (SHIMADZU, Japan).

2.3. Synthesis of Fe_3O_4 nanoparticles

$Fe(acac)_3$ (706 mg, 2 mmol), 1,2-dodecanediol (2.023 g, 10 mmol), oleic acid (1.695 g, 6 mmol), oleylamine (1.605 g, 6 mmol), and diphenyl ether (20 mL) were mixed and magnetically stirred under a flow of argon. The mixture was heated to 200 °C for 30 min and then heated to 280 °C for another 30 min. The black–brown mixture was cooled to room temperature under argon atmosphere. A black material was precipitated with ethanol and separated via centrifugation. The black product was dissolved in hexane, precipitated with ethanol, centrifuged to remove the solvent, and dispersed into hexane. Fe_3O_4 nanoparticles were obtained after evaporation of hexane at room temperature (yield: 31%).



Scheme 1. Synthesis of POSS-PCL-β-CD star-shaped copolymer by the combination of ROP and click chemistry.

2.4. Synthesis of octa(3-chloropropyl) POSS (POSS-$(Cl)_8$)

Octa(3-chloropropyl) POSS (POSS-$(Cl)_8$) was synthesized according to the literature(Ge, Wang, Zhou, Liu, & Liu, 2009; He, Yang, Zhang, & Zheng, 2006). A typical procedure was as follows. Methanol (1800 mL), 3-chloropropyltri-methoxysilane (79.5 g, 0.4 mol), and concentrated hydrochloric acid (90 mL) were mixed and the hydrolysis and rearrangement reactions were allowed to carry out for 40 days. POSS-$(Cl)_8$ was obtained as a white powder after suction filtration and washing with deionized water (yield: 29%).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.75–0.89 (2H, $SiCH_2CH_2CH_2Cl$), 1.82–1.97 (2H, $SiCH_2CH_2CH_2Cl$), 3.49–3.59 (2H, $SiCH_2CH_2CH_2Cl$). ^{13}C NMR ($CDCl_3$, δ, ppm): 9.5 ($SiCH_2CH_2CH_2Cl$), 26.3 ($SiCH_2CH_2CH_2Cl$), 47.2 ($SiCH_2CH_2CH_2Cl$). ^{29}Si NMR ($CDCl_3$, δ, ppm): −67.1 ($SiCH_2CH_2CH_2Cl$).

2.5. Synthesis of octa(3-hydroxypropyl) POSS (POSS-$(OH)_8$)

POSS-$(OH)_8$ was synthesized by the hydrolysis of POSS-$(Cl)_8$ in the presence of fresh silver oxide (Ag_2O) (He et al., 2006). Ag_2O was prepared as follows. $AgNO_3$ (1.57 g, 9.3 mmol) was dissolved in deionized water (10 mL) and aqueous NaOH (0.37 g, 9.3 mmol) was slowly added to the solution with vigorous stirring. Then Ag_2O precipitates were isolated and washed with deionized water for three times. The typical synthesis procedure of POSS-$(OH)_8$ was as follows. POSS-$(Cl)_8$ (1.0 g, 0.96 mmol), ethanol (25 mL) and THF (25 mL) were added into a round-bottom flask. Then, the above newly prepared Ag_2O together with 1 mL of deionized water was added to the solution. The system was refluxed in the dark with vigorously stirring for 48 h. The insolubilities were filtered out and the solution was subjected to rotary evaporation to obtain white solid (yield: 74%).

^{1}H NMR (DMSO-d_6, δ, ppm): 0.68–0.85 (2H, $SiCH_2CH_2CH_2OH$), 1.69–1.89 (2H, $SiCH_2CH_2CH_2OH$), 3.34 (2H, $SiCH_2CH_2CH_2OH$), 3.62 (2H, $SiCH_2CH_2CH_2OH$).

2.6. Synthesis of star-shaped PCL with POSS core (POSS-PCL)

Star-shaped POSS-PCL was synthesized by ROP of CL using POSS-$(OH)_8$ as the initiator. CL (4.20 g, 36.8 mmol), POSS-$(OH)_8$ (0.20 g, 0.23 mmol) and a catalytic amount of $Sn(Oct)_2$ were added to a fire-dried polymerization tube quickly. The tube was then connected to a Schlenk line, where exhausting–refilling processes were repeated for three times. The tube was put into an oil bath of 115 °C, stirring under argon atmosphere and cooled to room temperature after polymerization for 24 h. The resulting product was dissolved in chloroform and precipitated two times in methanol. The purified POSS-PCL was dried in vacuum at room temperature (yield: 92%).

$M_{n,NMR} = 18{,}200\ g\,mol^{-1}$, $M_{n,GPC} = 16{,}300\ g\,mol^{-1}$, $M_w/M_n = 1.28$. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.79 ($SiCH_2CH_2CH_2$), 1.38 ($OOCCH_2CH_2CH_2CH_2CH_2O$), 1.64 ($OOCCH_2CH_2CH_2CH_2CH_2O$), 1.86 ($SiCH_2CH_2CH_2$), 2.30 ($OOCCH_2CH_2CH_2CH_2CH_2O$), 3.58 ($OOCCH_2CH_2CH_2CH_2CH_2OH$), 4.06 ($OOCCH_2CH_2CH_2CH_2CH_2O$, $SiCH_2CH_2CH_2$).

2.7. Synthesis of star-shaped alkynyl PCL with POSS core (alkynyl POSS-PCL)

POSS-PCL (3.0 g, 165 μmol), propargyl 3-carboxylic-propanoate (827 mg, 5.3 mmol), DCC (1.09 g, 5.3 mmol) and DMAP (323 mg, 2.6 mmol) were dissolved in 40 mL of anhydrous dichloromethane, and the reaction was performed at room temperature for 48 h under argon atmosphere. The reaction byproduct dicyclohexylcarbodiurea was removed by filtration, and the solution was washed with aqueous $NaHCO_3$ solution and deionized water. The organic layer was dried over anhydrous $MgSO_4$ overnight. The purified product was obtained after removing of solvent and precipitating in methanol (yield: 88%).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.88 ($SiCH_2CH_2CH_2$), 1.39 ($OOCCH_2CH_2CH_2CH_2CH_2O$), 1.64 ($OOCCH_2CH_2CH_2CH_2CH_2O$), 1.86 ($SiCH_2CH_2CH_2$), 2.30 ($OOCCH_2CH_2CH_2CH_2CH_2O$), 2.47 ($COOCH_2C{\equiv}CH$), 2.67 ($OOCCH_2CH_2COO$), 4.06 ($OOCCH_2CH_2CH_2CH_2CH_2O$, $SiCH_2CH_2CH_2$), 4.70 ($COOCH_2C{\equiv}CH$).

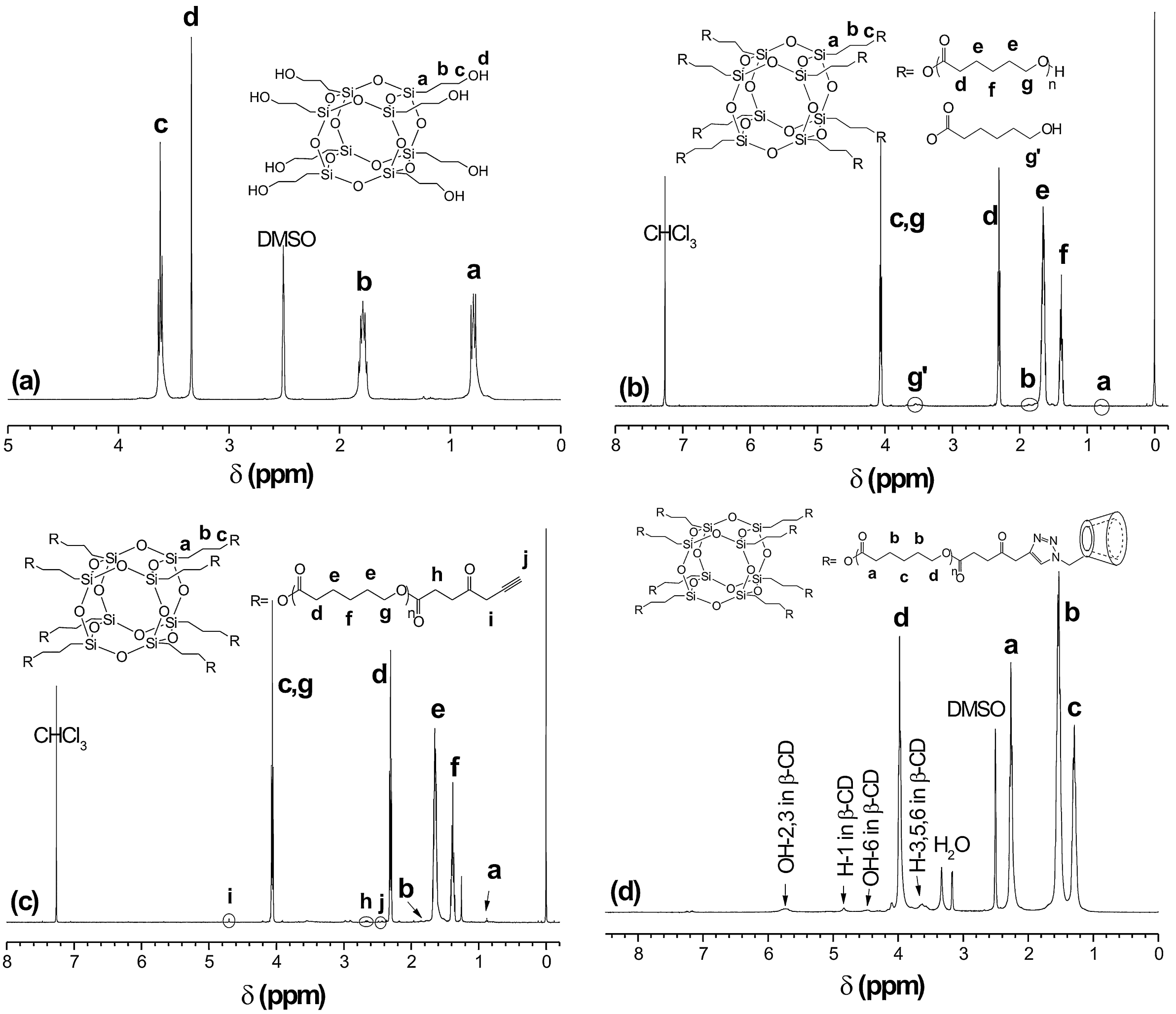


Fig. 1. ^{1}H NMR spectra of (a) POSS-OH, (b) POSS-PCL, (c) alkynyl POSS-PCL, and (d) POSS-PCL-β-CD.

2.8. Synthesis of mono-6-deoxy-6-azido-β-CD (β-CD-N_3)

Mono-6-deoxy-6-(p-tolylsulfonyl)-β-cyclodextrin (TsO-β-CD) was synthesized on the basis of literature (Brady et al., 2000). Firstly, the mixture of mono-6-deoxy-(p-tolylsulfonyl)-β-cyclodextrin (3.0 g, 2.4 mmol) and sodium azide (2.34 g, 36 mmol) was stirred in water at 80 °C for at least 3 days. The reaction solution was then concentrated to half of its initial volume and cooled to room temperature. Acetone (240 mL) was added to precipitate. Obtained white solid was redissolved in water (10 mL) and reprecipitated with acetone (240 mL). And the process was repeated one more time. At last, the white solid was dried under vacuum at 60 °C for at least 2 days (Muderawan et al., 2005) (yield: 78%).

2.9. Synthesis of star-shaped POSS-PCL-β-CD by click chemistry

Alkynyl POSS-PCL (1.93 g, 0.1 mmol) and β-CD-N_3 (1.846 g, 1.6 mmol) were dissolved in 30 mL of anhydrous DMF as the solvent, followed by adding CuBr (114 mg, 0.8 mmol) and PMDETA (167 μL, 0.8 mmol) into the solution. After degassed via three freeze–evacuate–thaw cycles, the reaction was carried out at 45 °C with vigorous stirring for 48 h. Then the mixture was diluted with THF and passed through a neutral alumina column to remove the copper catalyst. The POSS-PCL-β-CD copolymer was further purified by sequential dialysis against DMF and water, to remove the unreacted β-CD-N_3. After dialysis, POSS-PCL-β-CD was obtained by freeze dehydration (yield: 83%).

$M_{n,NMR} = 27{,}700\ \mathrm{g\,mol^{-1}}$, $M_{n,GPC} = 23{,}900\ \mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.42$. The weight content of POSS, PCL and β-CD in POSS-PCL-β-CD: 3.1%, 62.6% and 34.3%. ^{1}H NMR (DMSO-d_6, δ, ppm): 1.30 ($OOCCH_2CH_2C\mathit{H}_2CH_2CH_2O$), 1.54 ($OOCCH_2C\mathit{H}_2CH_2C\mathit{H}_2CH_2O$), 2.27 ($OOCC\mathit{H}_2CH_2CH_2CH_2CH_2O$), 3.62 (H-3,5,6 in β-CD), 3.99 ($OOCCH_2CH_2CH_2CH_2C\mathit{H}_2O$), 4.46 (OH-6, in β-CD), 4.83 (H-1 in β-CD), 5.73 (OH-2,3 in β-CD).

2.10. Preparation of hybrid micelles of POSS-PCL-β-CD/Fe_3O_4 nanoparticles

POSS-PCL-β-CD (100 mg) and Fe_3O_4 nanoparticles (10 mg) were dissolved in DMF (20 mL) and subsequently dialyzed against deionized water for 48 h (dialysis membrane, MW cut: 6000 Da). During the dialysis process, POSS-PCL-β-CD copolymers self-assembled into micelles with POSS-PCL core and β-CD corona. Fe_3O_4 nanoparticles were encapsulated into the micelle cores.

2.11. Removal of bisphenol A (BPA) from water

POSS-PCL-β-CD/Fe_3O_4 hybrid micelles (5 mg, 1.12×10^{-3} mmol of β-CD) were added into 10 mL of solution containing BPA. The solution was stirred for different times and then the hybrid micelles were removed by magnet. The residual aqueous solutions were characterized by UV–vis spectra.

3. Results and discussion

3.1. Synthesis of POSS-PCL-β-CD

Star-shaped POSS-PCL-β-CD amphiphilic copolymer was prepared by click chemistry of alkynyl POSS-PCL and β-CD-N_3. The preparation of alkynyl POSS-PCL underwent four steps. Firstly, POSS-$(Cl)_8$ was easily obtained by the reaction of 3-chloropropyltrimethoxysilane with hydrochloric acid at room temperature. Secondly, POSS-$(OH)_8$ was synthesized by the reaction of POSS-$(Cl)_8$ with Ag_2O. ^1H NMR of POSS-$(OH)_8$ is shown in Fig. 1(a). The protons of methylene groups and the hydroxyl group can be detected. Then, star-shaped PCL with POSS core was prepared by ROP of CL using POSS-$(OH)_8$ as the initiator. ^1H NMR of POSS-PCL is shown in Fig. 1(b). It can be seen that all the peaks of protons of PCL and POSS could be observed. The average number molecular weight $M_{n,NMR}$ (18,200 g mol^{-1}) determined by ^1H NMR spectroscopy was calculated from the integration ratio of the methylene protons in repeat units (g) and the methylene protons in terminal unit (g′). Finally, through the coupling reaction of hydroxyl-terminated POSS-PCL with much excess propargyl 3-carboxylic-propanoate and alkynyl POSS-PCL obtained. ^1H NMR of alkynyl POSS-PCL is shown in Fig. 1(c). Besides the peaks of protons of PCL and POSS, three new peaks can be detected. These signals located at 2.67 ppm (h), 4.70 ppm (i) and 2.47 ppm (j) were attributed to methylene protons next to carbonyl, methylene protons and alkynyl protons of terminal propargyl group, respectively. As for β-CD-N_3, it was prepared through a series of reactions involving the monotosylation of β-CD to give mono-6-deoxy-6-(p-tolysulfonyl)-β-CD, and azide substitution to give β-CD-N_3. The reaction between alkynyl POSS-PCL and excess β-CD-N_3 was completed via Cu(I)-catalyzed click reaction. After purification through dialysis, the resulting POSS-PCL-β-CD was obtained. As shown in Fig. 1(d), the proton peaks of PCL and β-CD can be observed. The coupling reaction efficiency (E%) of click chemistry can be calculated by the ratio of H-1 in β-CD ($I_{H\text{-}1}$) and methylene protons in PCL (a) (I_a) according to Eq. (1):

$$E\% = (2rI_{H\text{-}1}/I_a) \times 100\% \tag{1}$$

Here, r is the average degree of polymerization of each PCL chain and the value is 19.

The E% was about 91%, indicating that click chemistry between POSS-PCL and β-CD is successful. GPC traces were shown in Fig. 2. It can be seen that the traces were monomodal, indicating the pure polymers were obtained.

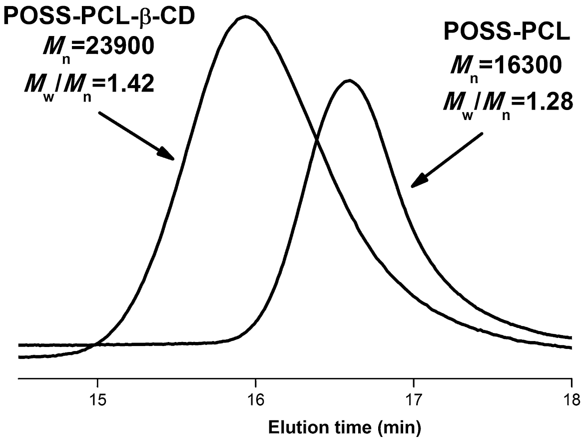


Fig. 2. GPC traces of POSS-PCL and POSS-PCL-β-CD.

3.2. Preparation of POSS-PCL-β-CD/Fe_3O_4 hybrid micelles

The POSS-PCL-β-CD/Fe_3O_4 hybrid micelles were prepared by complexing POSS-PCL-β-CD with Fe_3O_4 nanoparticles and self-assembling in water. POSS-PCL-β-CD was dissolved in DMF; and Fe_3O_4 nanoparticles were also dispersed in DMF. The weight ratio of Fe_3O_4 nanoparticles to POSS-PCL-β-CD was 1:10 in order to ensure the high encapsulation efficiency of Fe_3O_4 and the magnetism

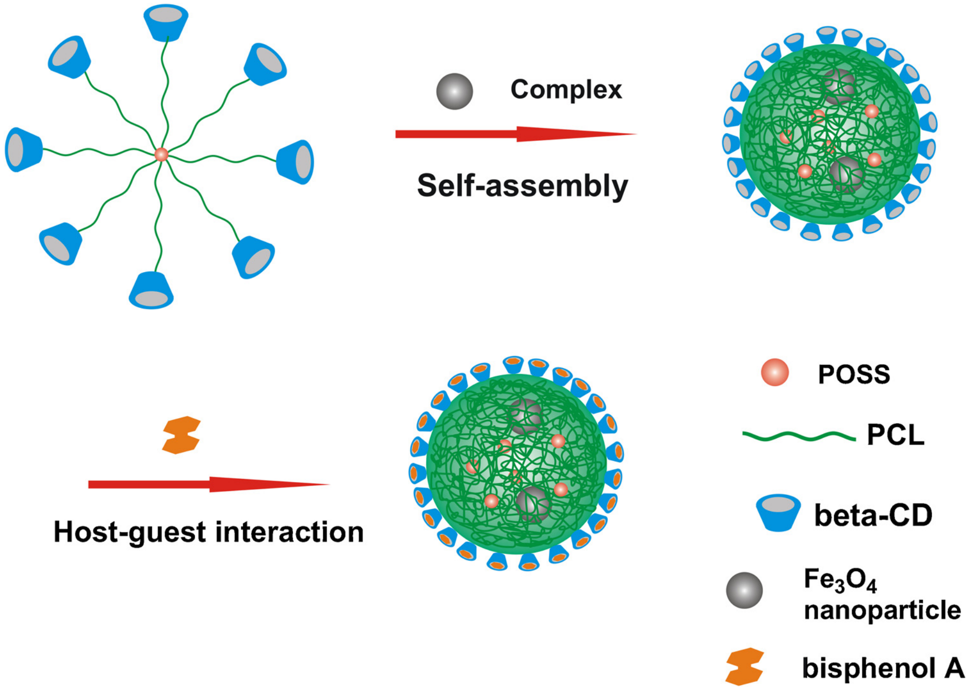


Fig. 3. The schematic representation of the self-assembly of POSS-PCL-β-CD/Fe_3O_4 hybrid micelles and the removal of bisphenol A through host–guest interaction.

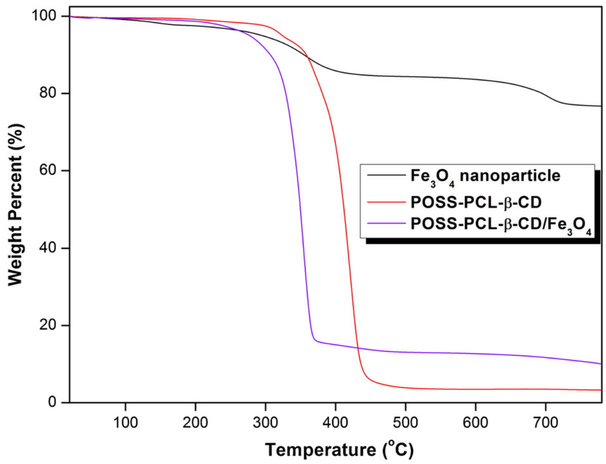


Fig. 4. TGA curves of Fe_3O_4 nanoparticles, POSS-PCL-β-CD and POSS-PCL-β-CD/Fe_3O_4.

of hybrid micelles. During the process of dialysis against water, amphiphilic POSS-PCL-β-CD would self-assemble to micelles. It is reasonable that the hydrophobic POSS-PCL were mainly in the core of the micelles, whereas the hydrophilic β-CD molecules were mainly in the shell of the micelles. Due to the hydrophobicity and size (about 7 nm) of Fe_3O_4 nanoparticles, they were encapsulated into the micelle core. Through host–guest interaction of BPA and β-CD in aqueous solution, BPA will be absorbed by micelles and removed by the magnetic hybrid micelles, as shown in Fig. 3.

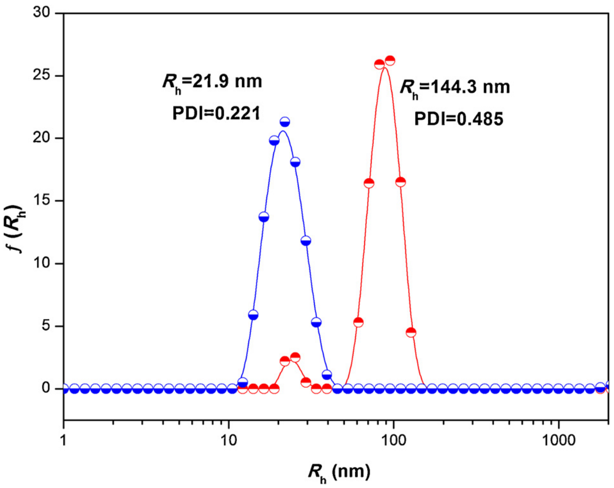


Fig. 5. The radius and size distribution of POSS-PCL-β-CD micelles (blue) and POSS-PCL-β-CD/Fe_3O_4 hybrid micelles (red) in water measured by DLS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4 shows the TGA curves of Fe_3O_4 nanoparticles, POSS-PCL-β-CD and POSS-PCL-β-CD/Fe_3O_4. Fe_3O_4 nanoparticles were coated with oleic acid, which led to a decrease of about 23% by weight at 760 °C. POSS-PCL-β-CD has good thermal stability and a residual of 3% by weight due to the presence of POSS core. For POSS-PCL-β-CD/Fe_3O_4 hybrid micelles, the residual is approximate 11% at 760 °C

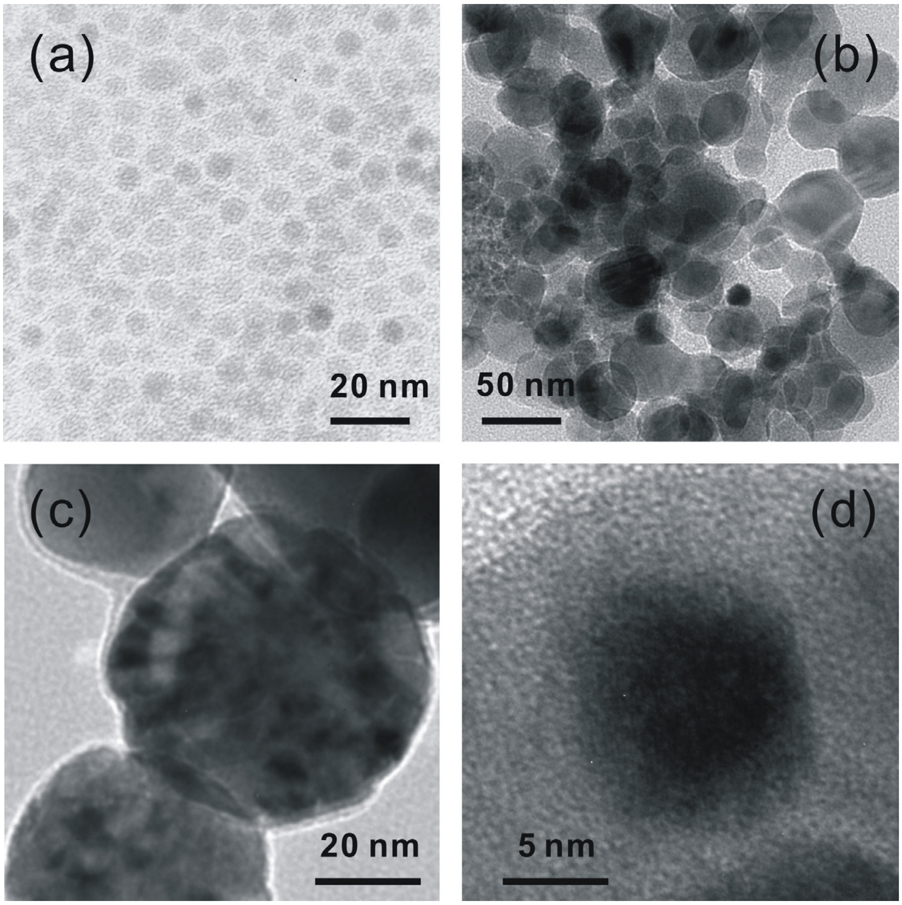


Fig. 6. TEM images of (a) Fe_3O_4 nanoparticles, (b) POSS-PCL-β-CD/Fe_3O_4 hybrid micelles, (c) enlarged POSS-PCL-β-CD/Fe_3O_4 hybrid micelles and (d) Fe_3O_4 nanoparticle encapsulated into the POSS-PCL-β-CD micelle.

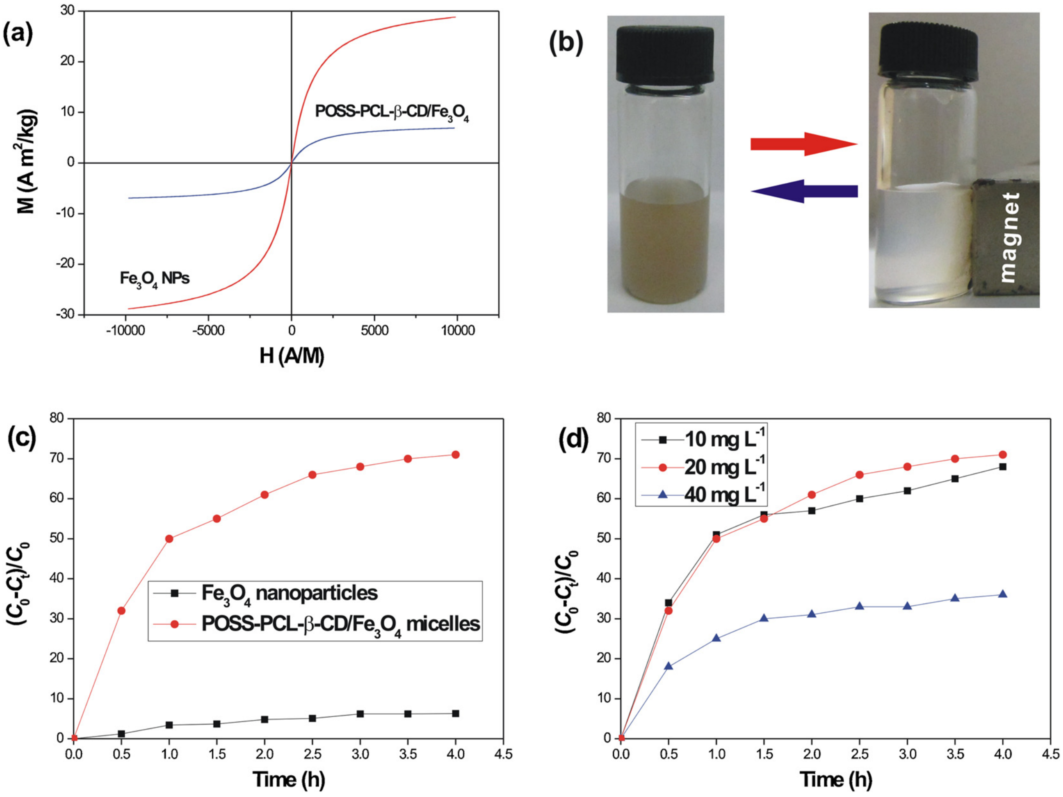


Fig. 7. (a) Magnetic curves of Fe_3O_4 nanoparticles and POSS-PCL-β-CD/Fe_3O_4 hybrid micelles at room temperature, (b) the photograph of the separation and redispersion of POSS-PCL-β-CD/Fe_3O_4 hybrid micelles in deionized water in the absence (left) and presence (right) of an external magnetic field, and bisphenol A removal characterization, (c) effect of time on removal efficiency of Fe_3O_4 nanoparticles or POSS-PCL-β-CD/Fe_3O_4 hybrid micelles (bisphenol A concentration: 20 mg L^{-1}) and (d) effect of concentration of bisphenol A on removal efficiency (bisphenol A concentration: 10 mg L^{-1}, 20 mg L^{-1} and 40 mg L^{-1}).

owing the Fe_3O_4 nanoparticles encapsulated into the POSS-PCL-β-CD micelles.

The sizes of POSS-PCL-β-CD micelles and POSS-PCL-β-CD/Fe_3O_4 hybrid micelles in water were measured by DLS. As shown in Fig. 5, the radius of POSS-PCL-β-CD micelles is 21.9 nm and the PDI is 0.221; however, the radius of POSS-PCL-β-CD/Fe_3O_4 hybrid micelles increased to 144.3 nm and the PDI became wider (PDI = 0.485). POSS-PCL-β-CD can self-assemble into stable micelles in water. After encapsulating Fe_3O_4 nanoparticles into micelle cores, the magnetic hybrid micelles tend to aggregate into compound micelles due to the magnetism. The POSS-PCL-β-CD/Fe_3O_4 hybrid micelles were also stable because no precipitation occurred for three months.

TEM images of Fe_3O_4 nanoparticles and POSS-PCL-β-CD/Fe_3O_4 hybrid micelles are shown in Fig. 6. As shown in Fig. 6(a), the diameter of these monodisperse Fe_3O_4 nanoparticles is about 7 nm. The Fe_3O_4 nanoparticles coated with oleic acid can be well-dispersed in many organic solvents. Fig. 6(b) shows the TEM image of POSS-PCL-β-CD/Fe_3O_4 hybrid micelles. Due to the magnetism of Fe_3O_4 nanoparticles encapsulated into the micelle cores, the hybrid micelles aggregated into compound micelles to some extent. Fig. 6(c) reveals the enlarged POSS-PCL-β-CD/Fe_3O_4 hybrid micelles. It can be found that the Fe_3O_4 nanoparticles existed in the micelles. From Fig. 6(d), Fe_3O_4 nanoparticle can be clearly observed in the polymeric micelle.

The magnetic properties of Fe_3O_4 nanoparticles and POSS-PCL-β-CD/Fe_3O_4 hybrid micelles were investigated in a vibrating sample magnetometer system at room temperature. Fig. 7(a) shows the magnetization curves of Fe_3O_4 nanoparticles and POSS-PCL-β-CD/Fe_3O_4 hybrid micelles. The particles and micelles do not exhibit hysteresis at low magnetic field and room temperature. Moreover, they show superparamagnetism because the diameter of these Fe_3O_4 nanoparticles is much less than the critical particles size of ferromagnetic Fe_3O_4 nanoparticles (25 nm) (Lee, Isobe, & Senna, 1996). The saturation magnetizations of Fe_3O_4 nanoparticles and hybrid micelles are about 28.8 A m^2 kg^{-1} and 6.9 A m^2 kg^{-1}, respectively, indicating that the POSS-PCL-β-CD/Fe_3O_4 hybrid micelles still possesses magnetism for separation by external magnetic field.

Fig. 7(b) shows the photographs of separation and redispersion of POSS-PCL-β-CD/Fe_3O_4 hybrid micelles in deionized water in the absence and presence of an external magnetic field. It can be seen that the homogenous and light-brown color hybrid micelle aqueous solution of POSS-PCL-β-CD/Fe_3O_4 became colorless and transparent solution in the presence of external magnetic field. After removing the external magnetic field, the hybrid micelles form homogenous solution again. Because Fe_3O_4 nanoparticles coated with oleic acid cannot disperse in water alone, the homogenous and light-brown color solution also indicates that the hydrophobic Fe_3O_4 nanoparticles were encapsulated into the micelles and the hybrid micelles are stable in aqueous solution.

3.3. Removal of bisphenol A (BPA) from water

The removal of BPA from water by Fe_3O_4 nanoparticles or POSS-PCL-β-CD/Fe_3O_4 hybrid micelles was shown in Fig. 7(c). C_0 (mg L^{-1}) is the initial concentration of BPA and C_t (mg L^{-1}) is the concentration of BPA after adsorption. $(C_0 - C_t)/C_0$ means the relative amount of BPA that has been removed at any given time. About 71% of BPA in water was removed by POSS-PCL-β-CD/Fe_3O_4 hybrid micelles after 4 h, in comparison with that of only 6.3% removal by Fe_3O_4 nanoparticles. The initial concentration of BPA also affected the removal efficiency of POSS-PCL-β-CD/Fe_3O_4 hybrid micelles. As shown in Fig. 7(d), at low concentrations of 10 mg L^{-1} and 20 mg L^{-1}, 68% and 71% of BPA were removed by POSS-PCL-β-CD/Fe_3O_4 hybrid micelles, in comparison with that of 36% removal efficiency for a high concentration of 40 mg L^{-1}. The results show that the absorption capacity of conjugated β-CD against BPA might be saturated at such conditions with a high concentration of BPA. The saturated absorption capacity of POSS-PCL-β-CD/Fe_3O_4 hybrid micelles could be calculated according to the content of β-CD groups. It could be calculated that the 0.255 mg of BPA would be absorbed for 5 mg of POSS-PCL-β-CD/Fe_3O_4 hybrid micelles. But the actual absorption amount was 0.144 mg at 40 mg L^{-1} of PBA solution. Therefore, the absorption efficiency was about 56.5% in comparison with the saturated absorption capacity. Due to the comparative high absorption capacity for BPA and the convenient separation by external magnetic field, the POSS-PCL-β-CD/Fe_3O_4 hybrid micelles would be expected to remove BPA from the BPA-containing polluted water.

4. Conclusions

A novel POSS-PCL-β-CD star-shaped inorganic–organic hybrid amphiphilic copolymer was synthesized by ring-opening polymerization (ROP) and click chemistry. The hybrid micelles based on the complex of Fe_3O_4 nanoparticle (POSS-PCL-β-CD/Fe_3O_4) were conveniently prepared by mixing POSS-PCL-β-CD with Fe_3O_4 nanoparticles in solvent (DMF) and dialysis against water. The results of TEM, DLS and TGA indicated that Fe_3O_4 nanoparticles were encapsulated into the micelle core consisting of hydrophobic POSS and PCL chains. The corona of the hybrid micelles is composed of hydrophilic β-CD. The hybrid micelles present magnetism for separation by external magnetic field due to the presence of magnetic Fe_3O_4 nanoparticles in the micelles. Through the host–guest interaction of β-CD molecules with BPA, POSS-PCL-β-CD/Fe_3O_4 hybrid micelles present good adsorption capacity in the removal of BPA from aqueous solution in comparison with the adsorption of magnetic nanoparticles. In addition, the hybrid micelles were removed by external magnetic field at last diminishing the usage of organic and inorganic chemicals using other methods to remove BPA. Therefore, these magnetic hybrid micelles may be considered as the potential application in the field of environmental protection.

Acknowledgments

The authors thank the financial supports of the National Basic Research Program of China (973 Program: 2011CB013805), the National Key Technology R&D Program (no. 2012BAI15B06), and the Fundamental Research Funds (20123181) for the Central Universities.

References

Aoki, N., Nishikawa, M., & Hattori, K. (2003). Synthesis of chitosan derivatives bearing cyclodextrin and adsorption of p-nonylphenol and bisphenol A. *Carbohydrate Polymers*, *52*(3), 219–223.

Apodaca, D. C., Pernites, R. B., Ponnapati, R., Mundo, F. R. D., & Advincula, R. C. (2011). Electropolymerized molecularly imprinted polymer film: EIS sensing of bisphenol A. *Macromolecules*, *44*(17), 6669–6682.

Basile, T., Petrella, A., Petrella, M., Boghetich, G., Petruzzelli, V., Colasuonno, S., et al. (2011). Review of endocrine-disrupting-compound removal technologies in water and wastewater treatment plants: An Eu perspective. *Industrial & Engineering Chemistry Research*, *50*(14), 8389–8401.

Besset, C. J., Lonnecker, A. T., Streff, J. M., & Wooley, K. L. (2011). Polycarbonates from the polyhydroxy natural product quinic acid. *Biomacromolecules*, *12*(7), 2512–2517.

Brady, B., Lynam, N., O'Sullivan, T., Ahern, C., & Darcy, R. (2000). 6-O-p-toluenesulfonyl-β-cyclodextrin. *Organic Synthesis*, *77*, 220.

Cai, K.-Y., Li, J.-H., Luo, Z., Hu, Y., Hou, Y.-H., & Ding, X.-W. (2011). β-Cyclodextrin conjugated magnetic nanoparticles for diazepam removal from blood. *Chemical Communications*, *47*(27), 7719–7721.

Cano, M., Sbargoud, K., Allard, E., & Larpent, C. (2012). Magnetic separation of fatty acids with iron oxide nanoparticles and application to extractive deacidification of vegetable oils. *Green Chemistry*, *14*(6), 1786–1795.

Chang, J., Li, Y., Wang, G., He, B., & Gu, Z.-W. (2013). Fabrication of novel coumarin derivative functionalized polypseudorotaxane micelles for drug delivery. *Nanoscale*, *5*(2), 813–820.

Chen, F.-H., Zhang, L.-M., Chen, Q.-T., Zhang, Y., & Zhang, Z.-J. (2010). Synthesis of a novel magnetic drug delivery system composed of doxorubicin-conjugated Fe_3O_4 nanoparticles cores and a PEG-functionalized porous silica shell. *Chemical Communications*, *46*(45), 8633–8635.

Chen, M.-L., Nielsen, S. R., Uyar, T., Zhang, S., Zafar, A., Dong, M.-D., et al. (2013). Electrospun UV-responsive supramolecular nanofibers from a cyclodextrin–azobenzene inclusion complex. *Journal of Materials Chemistry C*, *1*(4), 850–855.

Chepelev, N. L., Enikanolaiye, M. I., Chepelev, L. L., Almohaisen, A., Chen, Q. X., Scoggan, K. A., et al. (2013). Bisphenol A activates the Nrf1/2-antioxidant response element pathway in HEK 293 cells. *Chemical Research in Toxicology*, *26*(3), 498–506.

Chin, Y.-P., Miller, P. L., Zeng, L. K., Cawley, K., & Weavers, L. K. (2004). Photosensitized degradation of bisphenol A by dissolved organic matter. *Environmental Science & Technology*, *38*(22), 5888–5894.

Dai, Q., & Nelson, A. (2010). Magnetically-responsive self assembled composites. *Chemical Society Reviews*, *39*(11), 4057–4066.

Das, M., Bandyopadhyay, D., Singh, R. P., Harde, H., Kumar, S., & Jain, S. (2012). Orthogonal biofunctionalization of magnetic nanoparticles via "clickable" poly(ethylene glycol) silanes: A "universal ligand" strategy to design stealth and target-specific nanocarriers. *Journal of Materials Chemistry*, *22*(47), 24652–24667.

Deng, J.-J., Li, N., Mai, K.-J., Yang, C., Yan, L., & Zhang, L.-M. (2011). Star-shaped polymers consisting of a β-cyclodextrin core and poly(amidoamine) dendron arms: Binding and release studies with methotrexate and siRNA. *Journal of Materials Chemistry*, *21*(14), 5273–5281.

Deng, Y.-H., Qi, D.-W., Deng, C.-H., Zhang, X.-M., & Zhao, D.-Y. (2008). Superparamagnetic high-magnetization microspheres with an Fe_3O_4@SiO_2 core and perpendicularly aligned mesoporous SiO_2 shell for removal of microcystins. *Journal of the American Chemical Society*, *130*(1), 28–29.

Ellis, W. C., Tran, C. T., Roy, R., Rusten, M., Fischer, A., Ryabov, A. D., et al. (2010). Design green oxidation catalysts for purifying environment waters. *Journal of the American Chemical Society*, *132*(28), 9774–9781.

Fan, W.-C., Wang, L., & Zheng, S.-X. (2010). Double reaction-induced microphase separation in epoxy resin containing polystyrene-block-poly(ε-caprolactone)-block-poly(n-butylacrylate) ABC triblock copolymer. *Macromolecules*, *43*(24), 10600–10611.

Fuhrer, R., Herrmann, I. K., Athanassiou, E. K., Grass, R. N., & Stark, W. J. (2011). Immobilized β-cyclodextrin on surface-modified carbon-coated cobalt nanomagnets: Reversible organic contaminated adsorption and enrichment from water. *Langmuir*, *27*(5), 1924–1929.

Ge, Z.-S., Wang, D., Zhou, Y.-M., Liu, H.-W., & Liu, S.-Y. (2009). Synthesis of organic/inorganic hybrid quatrefoil-shaped star-cyclic polymer containing a polyhedral oligomeric silsesquioxane core. *Macromolecules*, *42*(8), 2903–2910.

Gözmen, B., Oturan, M. A., Oturan, N., & Erbatur, O. (2003). Indirect electrochemical treatment of bisphenol A in water via electrochemically generated Fenton's reagent. *Environmental Science & Technology*, *37*(16), 3716–3723.

He, Y.-H., Yang, X.-T., Zhang, W.-A., & Zheng, S.-X. (2006). Star-shaped poly(3-caprolactone) with polyhedral oligomeric silsesquioxane core. *Polymer*, *47*(19), 6814–6825.

Huang, C., Neoh, K. G., Wang, L., Kang, E.-T., & Shuter, B. (2010). Magnetic nanoparticles for magnetic resonance imaging: Modulation of macrophage uptake by controlled PEGylation of the surface coating. *Journal of Materials Chemistry*, *20*(39), 8512–8520.

Inui, H., Takehara, A., Doi, F., Nishi, K., Takai, M., Miyake, S., et al. (2009). A scFv antibody-based immunoaffinity chromatograph column for clean-up of bisphenol A-contaminated water samples. *Journal of Agricultural and Food Chemistry*, *57*(2), 353–358.

Jang, J., Pang, S.-Y., Ma, J., & Liu, H.-L. (2012). Oxidation of phenolic endocrine disrupting chemicals by potassium permanganate in synthetic and real waters. *Environmental Science & Technology*, *46*(3), 1774–1781.

Kang, Y., Zhou, L.-L., Li, X., & Yuan, J.-Y. (2011). β-Cyclodextrin-modified hybrid magnetic nanoparticles for catalysis and adsorption. *Journal of Materials Chemistry*, *21*(11), 3704–3710.

Lasserre, J. P., Fack, F., Revets, D., Planchon, S., Renaut, J., Hoffmann, L., et al. (2009). Effects of the endocrine disruptors atrazine and PCB 153 on the protein expression of MCF-7 human cells. *Journal of Proteome Research*, *8*(12), 5485–5496.

Lee, H. Y., Bae, D. R., Park, J. C., Song, H., Han, W. S., & Jung, J. H. (2009). A selective fluoroionophore based on BODIPY-functionalized magnetic silica nanoparticles: Removal of Pb^{2+} from human blood. *Angewandte Chemie-International Edition*, *48*(7), 1239–1243.

Lee, J., Isobe, T., & Senna, M. J. (1996). Preparation of ultrafine Fe_3O_4 particles by precipitation in the presence of PVA at high pH. *Journal of Colloid and Interface Science*, *177*(2), 490–494.

Li, J.-G., Chung, C.-Y., & Kuo, S.-W. (2012). Transformations and enhanced long-range ordering of mesoporous phenolic resin template by poly(ethylene oxide-b-ε-caprolactone) block copolymers blended with star poly(ethylene oxide)-functionalized silsesquioxane (POSS). *Journal of Materials Chemistry*, *22*(35), 18583–18595.

Marin, M. L., Santos-Juanes, L., Arques, A., Amat, A. M., & Miranda, M. A. (2012). Organic photocatalysts for the oxidation of pollutants and model compounds. *Chemical Reviews*, *112*(3), 1710–1750.

Mellet, C. O., Femández, J. M. G., & Benito, J. M. (2011). Cyclodextrin-based gene delivery systems. *Chemical Society Reviews*, *40*(3), 1586–1608.

Mitchell, P. J., & Simpson, M. J. (2013). High affinity sorption domains in soil are blocked by polar soil organic matter components. *Environmental Science & Technology*, *47*(1), 412–419.

Muderawan, I. W., Ong, T. T., Lee, T. C., Young, D. J., Ching, C. B., & Ng, S. C. (2005). A reliable synthesis of 2- and 6-amino β-cyclodextrin and permethylated β-cyclodextrin. *Tetrahedron Letters*, *46*, 7905–7907.

Pan, Y., Du, X.-W., Zhao, F., & Xu, B. (2012). Magnetic nanoparticles for the manipulation of proteins and cells. *Chemical Society Reviews*, *41*(7), 2912–2942.

Tanaka, K., & Chujo, Y. (2012). Advanced functional materials based on polyhedral oligomeric silsesquioxane (POSS). *Journal of Materials Chemistry*, *22*(5), 1733–1746.

Umar, M., Roddick, F., Fan, L. H., & Aziz, H. A. (2013). Application of ozone for the removal of bisphenol A from water and wastewater – A review. *Chemosphere*, *90*(8), 2197–2207.

Vollath, D. (2010). Bifunctional nanocomposites with magnetic and luminescence properties. *Advanced Materials*, *22*(39), 4410–4415.

Voutchkova, A. M., Osimitz, T. G., & Anastas, P. T. (2010). Toward a comprehensive molecular design framework for reduced hazard. *Chemical Reviews*, *110*(10), 5845–5882.

Wang, C.-Y., Zhang, H., Li, F., & Zhu, L.-Y. (2010). Degradation and mineralization of bisphenol A by mesoporous Bi_2WO_6 under simulated solar light irradiation. *Environmental Science & Technology*, *44*(17), 6843–6848.

Wu, Y.-C., & Kuo, S.-W. (2012). Self-assembly supramolecular structure through complementary multiple hydrogen bonding of heteronucleobase-multifunctionalized polyhedral oligomeric silsesquioxane (POSS) complexes. *Journal of Materials Chemistry*, *22*(7), 2982–2991.

Xiao, P., Corvini, P. F.-X., Dudal, Y., & Shahgaldian, P. (2013). Design and high-throughput synthesis of cyclodextrin-based polyurethanes with enhanced molecular recognition properties. *Polymer Chemistry*, *4*(4), 942–946.

Xiong, Z.-C., Zhao, L., Wang, F.-J., Zhu, J., Qin, H.-Q., Wu, R.-A., et al. (2012). Synthesis of branched PEG brushes hybrid hydrophilic magnetic nanoparticles for the selective enrichment of N-linked glycopeptides. *Chemical Communications*, *48*(65), 8138–8140.

Xu, J., Wang, L., & Zhu, Y.-F. (2012). Decontamination of bisphenol A from aqueous solution by graphene adsorption. *Langmuir*, *28*(22), 8418–8425.

Xuan, Y.-J., Endo, Y., & Fujimoto, K. (2002). Oxidative degradation of bisphenol A by crude enzyme prepared from potato. *Journal of Agricultural and Food Chemistry*, *50*(22), 6575–6578.

Yang, J.-S., Ren, H.-B., & Xie, Y.-J. (2011). Synthesis of amidic alginate derivatives and their application in microencapsulation of λ-cyhalothrin. *Biomacromolecules*, *12*(8), 2982–2987.

Yang, J.-S., & Yang, L. (2013). Preparation and application of cyclodextrin immobilized polysaccharides. *Journal of Materials Chemistry B*, *1*(7), 909–918.

Yan, Q., Yuan, J.-Y., Cai, Z.-N., Xin, Y., Kang, Y., & Yin, Y.-W. (2010). Voltage-responsive vesicles based on orthogonal assembly of two homopolymers. *Journal of the American Chemical Society*, *132*(27), 9268–9270.

Ye, Y.-S., Shen, W.-C., Tseng, C.-Y., Rick, J., Huang, Y.-J., Chang, F.-C., et al. (2012). *Chemical Communications*, *47*(86), 10656–10658.

Yu, Y.-F., Su, H.-H., & Gan, W.-J. (2009). Effects of storage aging on the properties of epoxy prepregs. *Industrial & Engineering Chemistry Research*, *48*(9), 4340–4345.

Yuan, W.-Z., Yuan, J.-Y., Zhou, L.-L., Wu, S.-Z., & Hong, X.-Y. (2010). Fe_3O_4@poly(2-hydroxyethyl methacrylate)-graft-poly(ε-caprolactone) magnetic nanoparticles with branched brush polymeric shell. *Polymer*, *51*(12), 2540–2547.

Yuan, W.-Z., Zhao, Z.-D., Gu, S.-Y., & Ren, J. (2010). Synthesis, characterization, and properties of amphiphilic chitosan copolymers with mixed side chains by click chemistry. *Journal of Polymer Science Part A-Polymer Chemistry*, *48*(15), 3476–3486.

Yuan, W.-Z., Zou, H., Guo, W., Wang, A., & Ren, J. (2012). Supramolecular amphiphilic star-branched copolymer: From LCST–UCST transition to temperature-fluorescence responses. *Journal of Materials Chemistry*, *22*(47), 24783–24791.

Zhang, L., Fang, P., Yang, L.-J., Zhang, J., & Wang, X. (2013). Rapid method for the separation and recovery of endocrine-disrupting compound bisphenol AP from wastewater. *Langmuir*, *29*(12), 3968–3975.

Zhang, X., Li, X.-K., & Deng, N.-S. (2012). Enhanced and selective degradation of pollutants over cyclodextrin/TiO_2 under visible light irradiation. *Industrial & Engineering Chemistry Research*, *51*(2), 704–709.

Zhou, L., Gao, C., & Xu, W.-J. (2010). Magnetic dendritic materials for highly efficient adsorption of dyes and drugs. *ACS Applied Materials & Interfaces*, *2*(5), 1483–1491.