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Polymer 47 (2006) 3021–3027

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Synthesis and self-assembly of comb oligomers having rigid racemic or chiral binaphthyl macrocyclic pendant groups

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Received 20 December 2005; received in revised form 1 March 2006; accepted 5 March 2006

Abstract

In this article, we described the synthesis of comb oligomers having rigid racemic or chiral binaphthyl macrocyclic pendant groups via the free radical polymerization. Oligomers obtained were well characterized by MALDI-TOF-MS, ^{1}H NMR, FT-IR, UV, CD and SEC. These comb oligomers having macrocyclic pendant groups showed very good solubility in common organic solvents at room temperature. Furthermore, the oligomers could self-assemble into different morphologies by dropping their THF solutions of different concentrations on the surface of water. At a relatively low concentration, the oligomers self-aggregated into hollow spheres. When the concentration was increased, the aggregates changed into solid spheres. The morphologies of the hollow or solid spheres were observed by TEM and ESEM.

Keywords: Chiral; Comb oligomers; Self-assemble

1. Introduction

Polymeric self-assembled objects with sizes ranging from the nanometer to the micrometer scale have been actively investigated in recent years because of their many potential applications in photonic crystals, templates to synthesize macroporous materials, drug delivery [1,2], controlled storage and release [3], etc. In this connection, colloidal spheres have been extensively studied and applied in many industrial products. Usually, these polymeric colloidal spheres were prepared in two ways as following: (1) direct emulsion polymerization, by which we can obtain various monodispersed polymeric colloidal spheres such as poly (methyl methacrylate) (PMMA) and polystyrene (PS) microspheres [4]; (2) self-assembly method, which has proved to be a versatile way to prepare many different structures of self-aggregates by mixing the solution of polymer and a selective solvent to the polymer. For a long time, block copolymers and grafted copolymers were greatly focused on for their abilities of self-assembly [5,6], but more and more attention was paid to the functional homopolymers that can also form self-assembled structures. Wang et al. recently reported colloidal spheres with photoinduced shape deformation properties prepared from an amphiphilic azo polymer [7]. In Thayumanavan's group, there has been a report about a new class of amphiphilic homopolymers that assemble into micelle in water or inverse micelle in an apolar solvent [8].

Nanoscale macrocyclic molecules with unique properties have been the focus of fundamental and applied research [9]. Cyclic structures with a chiral, rigid molecular backbone contain a functional cavity of well-defined size, which makes these macrocycles remarkable as host molecules capable of chiral recognition [10]. The introduction of the chiral binaphthyl units into these macrocyclic hosts can lead to their enantioselective complexation with chiral guest molecules, which has been applied to the resolution of racemic molecules such as amino acids, amino esters, and other chiral aryl compounds. These macrocyclic molecules have pre-organized cavities based on rigid structures and undergo complexation-induced organization with the guest molecules through weak forces such as π–π stacking, hydrogen bonding, and van der Waals forces [11]. Moreover, the size of the macrocyclic molecular cavities can be adjusted by changing the reaction procedure to cater for guest molecules of different size. For this purpose, a series of comb oligomers having rigid racemic or chiral binaphthyl macrocyclic pendant groups were synthesized and we also wonder if these comb oligomers can

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doi:10.1016/j.polymer.2006.03.018

form some self-assembled structures. Furthermore, since the initial concentration of the polymer during the process of self assembly influenced a lot on the structures of resulting self-aggregates, we also want to investigate how the concentration of the oligomers can affect the self assembled structures.

2. Experimental

2.1. Materials

The chiral compound 1 was synthesized by the method reported in an earlier publication of our group [12]. 3,5-Dihydroxybenzyl alcohol and acryloyl chloride were obtained from Fluka and used without further purification. Tetrahydrofuran (THF) was dried by refluxing over Na metal and distilled just before use. Water used in this experiment was redistilled and deionized. 2,2′-Azoisobutyronitrile (AIBN) was purified by recrystallization from ethanol. *N*,*N*-Dimethylformamide (DMF), toluene, ethanol, dichloromethane (CH_2Cl_2), methanol, ethyl acetate (CH_3OAc) were of analytical grade and used as received.

2.2. Synthesis of racemic and chiral macrocycles (2)

Ring closure to yield the cyclic dimmer (2) was performed by aromatic nucleophilic substitution using 3,5-dihydroxybenzyl alcohol under modified pseudo-high-dilution conditions. In a 3 L round-bottomed flask equipped with a Dean–Stark trap under nitrogen atmosphere, solution of anhydrous K_2CO_3 in a DMF/toluene mixture (2000/100 mL) was brought to a reflux. Over a period of 10 h, a solution of (1) (10 mmol) and 3,5-dihydroxybenzyl alcohol (10 mmol) in DMF (400 mL) was added. The reaction mixture was refluxed for an additional 2 h, cooled to room temperature and then suction filtered to remove solid KF and K_2CO_3. The filtrate was then concentrated to 100 mL and poured into 3% HCl (2400 mL), which yielded a brown precipitate that was suction filtered and washed with copious amounts of water and ethanol. After drying in vacuo at 50 °C for 24 h, the crude (**2**) was purified by column chromatography (silica gel) using a 15:1 mixture of CH_2Cl_2/CH_3OH as the eluent. Analytically pure cyclic dimer (2) obtained was readily soluble in CH_2Cl_2, $CHCl_3$, acetone, and THF.

Characterizations of racemic macrocycles (**2**): yield: 71%: MALDI-TOF-MS: *m*/*z* 782.5 (M^+); ^1H NMR ($CDCl_3$, ppm): $\delta = 7.97$–7.98 (d, 2H), 7.94–7.96 (d, 2H), 7.71–7.73 (d, 4H), 7.51–7.53 (d, 4H), 7.47–7.49 (t, 2H), 7.36–7.39 (t, 2H), 7.33–7.34 (d, 2H), 7.25–7.26 (d, 2H), 7.01–7.03 (d, 4H), 7.00 (s, 2H), 6.61–6.64 (d, 4H), 6.06–6.07 (s, 1H), 4.77 (s, 2H); FT-IR (cm^{-1}): 3440 (–OH), 2923, 2852 (–CH_2–), 1646 (C=O in backbone), 1596 (C=C in benzene), 1247 (C–O–C).

Characterizations of chiral macrocycles (2): yield: 73%; MALDI-TOF-MS: *m*/*z* 783.8 ($M+H^+$); ^1H NMR ($CDCl_3$, ppm): $\delta = 7.97$–7.99 (d, 2H), 7.95–7.97 (d, 2H), 7.72–7.73 (d, 4H), 7.52–7.53 (d, 4H), 7.47–7.51 (t, 2H), 7.37–7.40 (t, 2H), 7.32–7.34 (d, 2H), 7.25–7.27 (d, 2H), 7.02–7.03 (d, 4H), 7.01 (s, 2H), 6.62–6.64 (d, 4H), 6.07 (s, 1H), 4.79 (s, 2H); FT-IR (cm^{-1}): 3448 (–OH), 2923, 2854 (–CH_2–), 1654 (C=O in backbone), 1594 (C=C in benzene), 1246 (C–O–C); specific rotation: $[a]_{589}^{20} = -233.1^{\circ}$ ($c = 0.06$ g/mL, THF).

2.3. Synthesis of racemic and chiral acrylated macrocylic pendants (3)

A polymerizable acrylate group was attached to the hydroxyl terminus of the cyclic dimer (**2**) as follows. To a cooled (0 °C) solution of (**2**) (1.50 g, 1.92 mmol) and triethylamine (NEt_3) (5.6 mL, 40.2 mmol) in 50 mL of anhydrous tetrahydrofuran (THF), was added, over a period of 1 h, a solution of acryloyl chloride (1.5 mL, 18.5 mmol) in 20 mL of anhydrous THF. The reaction mixture was stirred for 5 h at 0–5 °C and suction filtered to remove the $NHEt_3Cl$ salt formed during the reaction. The solvent was stripped by rotary evaporation yielding a dark brown residue that was dried under dynamic vacuum at room temperature for 24 h. Column chromatography (silica-gel) using a 40:1 mixture of CH_2Cl_2/CH_3OAc as the eluent resulted in analytically pure (**3**).

Characterizations of racemic acrylated macrocyclic pendants (**3**): yield: 87%; MALDI-TOF-MS: *m*/*z* 836.9 (M^+); ^1H NMR ($CDCl_3$, ppm): $\delta = 7.97$–7.98 (d, 2H), 7.94–7.96 (d, 2H), 7.72–7.73 (d, 4H), 7.51–7.52 (d, 4H), 7.47–7.49 (t, 2H), 7.36–7.39 (t, 2H), 7.33–734 (d, 2H), 7.25–7.27 (d, 2H), 7.02–7.03 (d, 4H), 6.98–6.99 (s, 2H), 6.61–6.62 (d, 4H), 6.51–6.54 (d, 1H), 6.21–6.26 (m, 1H), 6.07 (s, 1H), 5.91–5.93 (d, 1H), 5.26 (s, 2H); FT-IR (cm^{-1}): 2922, 2852 (–CH_2–), 1716 (C=O in ester), 1656 (C=O in backbone), 1595 (C=C in benzene), 1245 (C–O–C).

Characterizations of chiral acrylated macrocyclic pendants (**3**): yield: 86%; MALDI-TOF-MS: *m*/*z* 837.5 ($M+H^+$); ^1H NMR ($CDCl_3$, ppm): $\delta = 7.97$–7.99 (d, 2H), 7.95–7.97 (d, 2H), 7.71–7.73 (d, 4H), 7.50–7.52 (d, 4H), 7.47–7.49 (t, 2H), 7.37–7.40 (t, H), 7.33–7.34 (d, 2H), 7.26–7.27 (d, 2H), 7.02–7.03 (d, 4H), 6.98–6.99 (s, 2H), 6.61–6.62 (d, 4H), 6.51–6.55 (d, 1H), 6.21–6.26 (m, 1H), 6.07 (s, 1H), 5.92–5.94 (d, 1H), 5.26 (s, 2H); FT-IR (cm^{-1}): 2924, 2855 (–CH_2–), 1728 (C=O in ester), 1655 (C=O in backbone), 1595 (C=C in benzene), 1248 (C–O–C); specific rotation: $[a]_{589}^{20} = -217.1^{\circ}$ ($c = 0.0073$ g/mL, THF).

2.4. Synthesis of racemic and chiral comb oligomers (4)

Polymerization of the acrylated macrocyclic monomer (**3**) was straightforward. A 10 mL flask containing (**3**) (0.1 g), AIBN (0.1 mg), and dry THF (1 mL) was sealed under N_2 and then was subjected to three freeze-pump-thaw cycles. After stirring at 60 °C for 24 h, the mixture was precipitated into MeOH yielding a tan colored precipitate that was suction filtered and dried under dynamic vacuum at room temperature for 24 h. The crude (**4**) obtained was purified by column chromatography (silica-gel) using a 40:1 mixture of CH_2Cl_2/CH_3OAc as the eluent. Analytically pure (**4**) was obtained, which dissolves readily in common solvents such as CH_2Cl_2, $CHCl_3$, THF and DMF.

Characterizations of racemic comb oligomers (4): yield: 82%; MALDI-TOF-MS: *m/z* 2616.5, 3453.7, 4290.0, 5128.0, 5968.4, 6807.6, 7655.6, 8494.5, 9334.1, 10171.9, 11006.7, 11846.7, 12685.3, 13530.7; SEC: $M_w = 6.4 \times 10^3$, $M_n = 5.8 \times 10^3$, PI = 1.10; ^{1}H NMR ($CDCl_3$, ppm): 7.92–7.99 (br, overlap), 7.66–7.73 (br, overlap), 7.47–7.55 (br, overlap), 7.20–7.39 (br, overlap), 6.93–7.05 (br, overlap), 6.56–6.64 (br, 4H), 6.01 (br, 1H), 5.15–5.18 (br, 2H); FT-IR (cm^{-1}): 2924, 2852 ($-CH_2-$), 1735 (C=O in ester), 1654 (C=O in backbone), 1595 (C=C in benzene), 1247 (C–O–C).

Characterizations of chiral comb oligomers (4): yield: 83%; MALDI-TOF-MS: see Fig. 1; SEC: $M_w = 5.8 \times 10^3$, $M_n = 5.5 \times 10^3$, PI = 1.06; ^{1}H NMR ($CDCl_3$, ppm): 7.92–7.96 (br, overlap), 7.65–7.71 (br, overlap), 7.43–7.52 (br, overlap), 7.21–7.38 (br, overlap), 6.93–7.05 (br, overlap), 6.54–6.64 (br, 4H), 6.01 (br, 1H), 5.15–5.18 (br, 2H); FT-IR (cm^{-1}): 2954, 2867 ($-CH_2-$), 1738 (C=O in ester), 1655 (C=O in backbone), 1595 (C=C in benzene), 1248 (C–O–C). Specific rotation: $[a]^{20}_{589} = -204.7^{\circ}$ ($c = 0.0051$ g/mL, THF).

2.5. Self-assembly of racemic and chiral comb oligomers

The self-assembly structures with different sizes and morphologies formed by the comb oligomers spontaneously were studied here. The racemic or chiral oligomers were first dissolved in THF to the desired concentrations. After that, the THF solutions were dropped onto the surface of water. For TEM measurements, a drop of the oligomer solution in THF was dropped onto the surface of distilled water to form a monolayer film. After a few minutes, a carbon-coated copper grid was placed onto the oligomer monolayer on the water surface and then removed and naturally dried in air. For the oligomer solution at low concentration, the monolayer was almost invisible, so a mixture of oligomer and water was dropped onto a carbon-coated copper grid. The sample preparation for ESEM was similar to that for TEM, except that a silicon wafer replaced the carbon-coated grid. The specimens were coated with gold before ESEM observations.

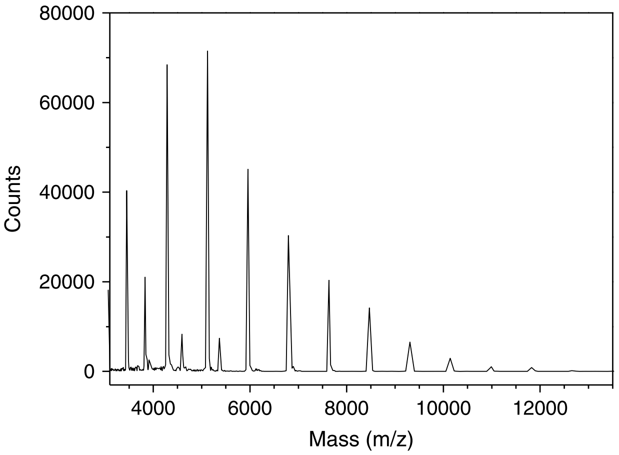


Fig. 1. MALDI-TOF-MS of the chiral comb oligomer containing binaphthyl macrocycles (4).

2.6. Characterizations

IR Spectrum of KBr powder-pressed pellet was recorded on BRUKER VECTOR 22 FT-IR spectrometer. ^{1}H NMR spectra were obtained on a BRUKER AVANCE-500 spectrometer using 5 mm o.d. tubes. Deuterated chloroform ($CDCl_3$) was used as solvent for the NMR analyse, and 1% tetramethylsilane (TMS) was used as an internal reference. Mass spectra were performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT) with 1,8,9-anthracenetriol (dithranol) as matrix. Size exclusion chromatography (SEC) was carried out with a Waters 410 liquid chromatograph and THF was used as solvent. Molecular weights were referred to monodisperse polystyrene standards. Circular dichroism spectra (CD) were recorded on JOBINYVON-SPEX CD6 using 1 cm quartz cell. Optical rotation measurements were performed on a Shanghai Precision and Scientific instrument Co., Ltd WZZ-2S digital automatic polarimeter. Transmission electron microscopy (TEM) observations were performed on a JEM-1200 EX electron microscope at an accelerating voltage of 80 kV. Environment scanning electron microscopy (ESEM) observations were performed on a Philips XL30 electron microscope.

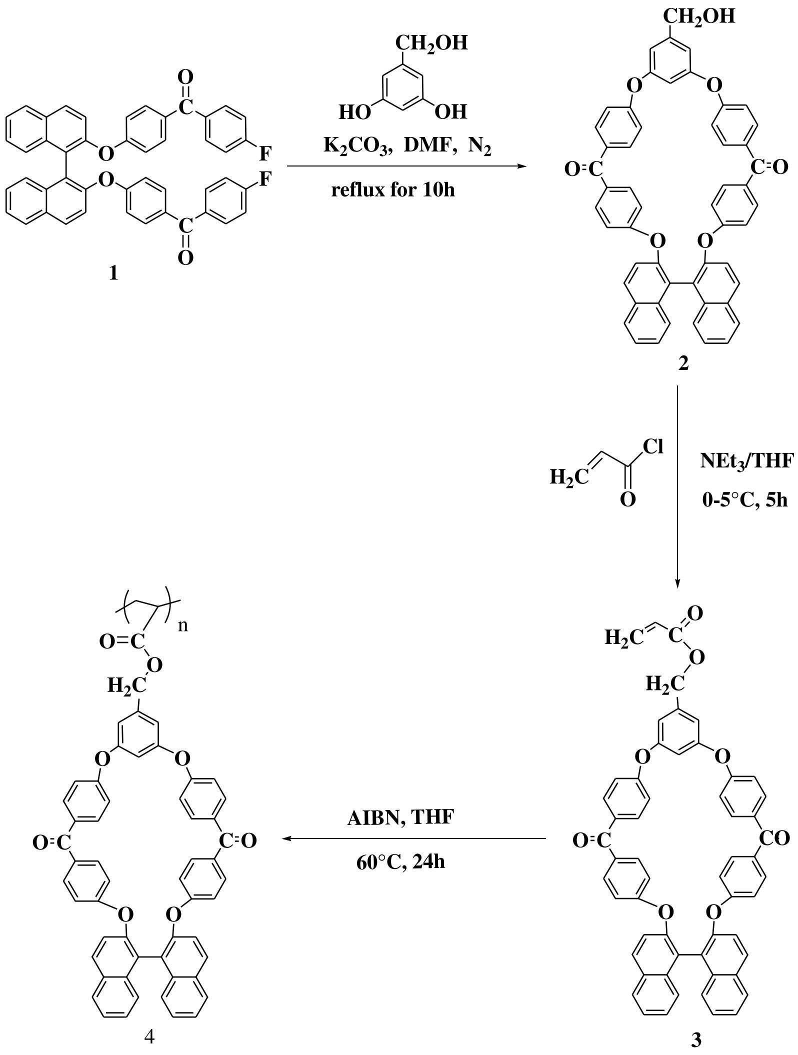
3. Results and discussion

3.1. Synthesis and characterization of racemic and chiral oligomers

Comb oligomers having rigid racemic or chiral binaphthyl macrocyclic pendant groups were synthesized in a route shown in Scheme 1. The coupling of two structural motifs at the molecular level, e.g. a nanometer-size chiral cavity, and a flexible polymeric backbone could lead to new opportunities in molecular recognition and separation. The racemic and chiral macrocycles were first synthesized followed by introduction of the acrylate side-group. Free-radical polymerization yielded low MW racemic and chiral comb oligomers that were characterized.

The prepared chiral oligomer was characterized by MALDI-TOF-MS, as shown in Fig. 1. Oligomer with 4–15 repeating units was well confirmed by a series of equidistant molecular ion peaks. These data present the detail structure of the chiral oligomers prepared by the free radical polymerization method. We can also conclude that the pentamer and hexamer are the predominant composition of the synthesized oligomers with macrocyclic pendants. This is in agreement with the measurement of SEC that affords $M_w = 5791$, $M_n = 5453$, PI = 1.06 versus narrow distribution polystyrene standards. In these oligomers, macrocycles with about 1 nm diameter were confined in repeat units about 0.25 nm and the steric hindrance leads to the formation of relatively low molecular weight oligomers.

The UV and CD spectra of the chiral and racemic oligomers in THF were shown in Fig. 2. In the wavelength range 240–400 nm, the chiral oligomer showed UV absorption at 288.5 nm and very strong CD effects with a negative signal at 308 nm and a positive signal at 284 nm due to the chiral



Scheme 1. Synthesis of the racemic or chiral comb oligomer containing binaphthyl macrocycles (**4**).

binaphthyl units, while the racemic oligomer showed UV absorption at 291.5 nm and no specific Cotton effect.

3.2. Self-assembly behaviors of racemic comb oligomers

The self-assembly behaviors of racemic comb oligomers were investigated by dissolving them in tetrahydrofuran (THF) and then dropping the THF solutions of different concentrations on the surface of water. To gain an insight into the role of concentration of oligomers, we prepared a series of systems with different concentrations to probe the self-assembly behaviors. TEM (Fig. 3) and ESEM (Fig. 4) images showed the aggregates formed by racemic oligomers solutions of different initial concentrations. Clearly, the aggregating morphologies depended strongly on the concentration of oligomers. When the oligomer concentration was 0.1 mg/mL, hollow spheres were formed (Fig. 3(a)). With the polymer concentration increasing to 0.7 and 1.4 mg/mL (Fig. 3(b) and (c)), the morphologies of the aggregates changed into solid spheres and the population of spheres was also enhanced. Spherical aggregates have a narrow size distribution: most of them in the 70–90 nm range for 0.1 mg/mL, 85–140 nm for 0.7 mg/mL and 80–130 nm for 1.4 mg/mL, respectively. A schematic illustration of the self-assembly of the oligomer into hollow and solid spheres was shown in Scheme 2.

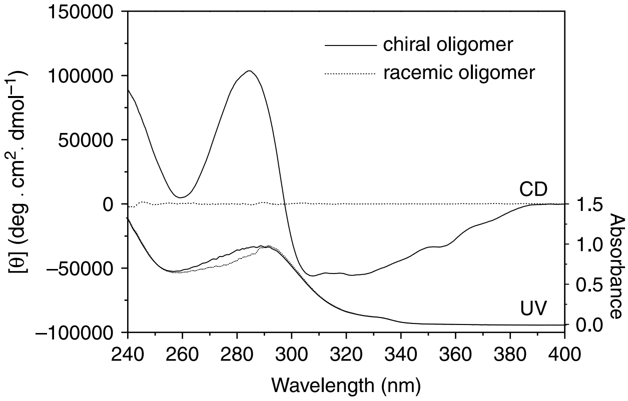


Fig. 2. Absorption spectra (bottom) of the racemic and chiral oligomer with concentration at 2.2×10^{-2} mg/mL in THF and circular dichroism spectra (top) of the racemic and chiral oligomer in THF.

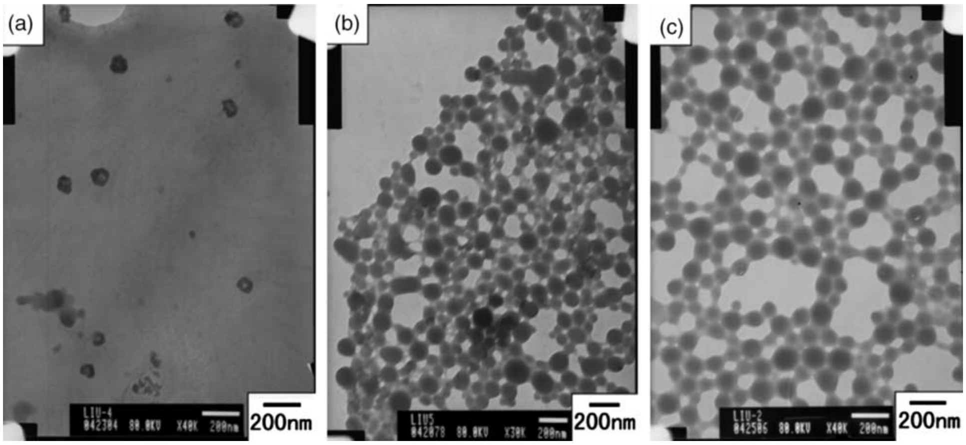


Fig. 3. TEM micrographs of the racemic oligomer at different concentrations on the water surface: (a) 0.1 mg/mL, (b) 0.7 mg/mL, (c) 1.4 mg/mL.

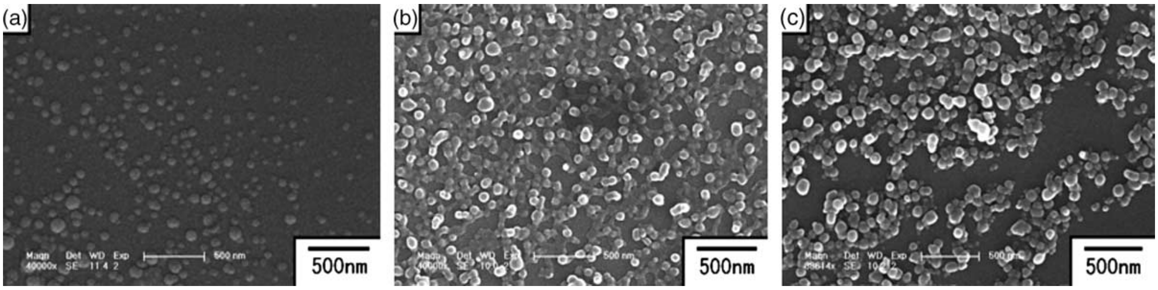
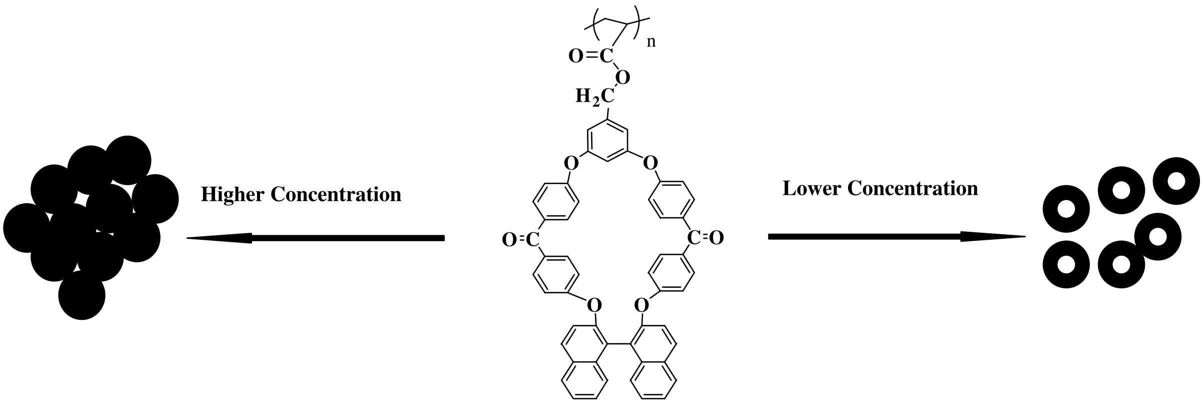


Fig. 4. ESEM micrographs of the racemic oligomer at different concentrations on the water surface: (a) 0.1 mg/mL, (b) 0.7 mg/mL, (c) 1.4 mg/mL.

The fabrication of hollow spheres has been the subject of many recent publications in the field of materials science. Procedures for the fabrication of hollow spheres have been extensively reported. Layer-by-layer (LbL), a simple and facile method has been successfully used to prepare hollow spherical capsules by using polymer or silica beads as templates [13]. Novel polymer hollow spheres can also be prepared through ring-opening cross-metathesis of self-assembled amphiphilic PEG-grafted polyolefins at the oil–water interface [14]. In addition, self-assembly of rod–coil block copolymers in selective solvent or nonselective solvent produced hollow particles [15]. Compared to the existing routes to self-assembled hollow spheres, the process mentioned above seems much simpler and more straightforward.

3.3. Self-assembly behaviors of chiral comb oligomers

The self-assembly behaviors of chiral comb oligomers in THF/H_2O mixture were also investigated. Fig. 5 showed a set of TEM pictures demonstrating various morphologies of the aggregates made by dissolving chiral comb oligomers to THF and dropping the THF solutions of different concentrations on the surface of water. At a low oligomer concentration of 0.1 mg/mL, as shown in Fig. 5(a), a few hollow spheres with



Scheme 2. A schematic illustration of the processes of self-assembly of the racemic or chiral oligomer.

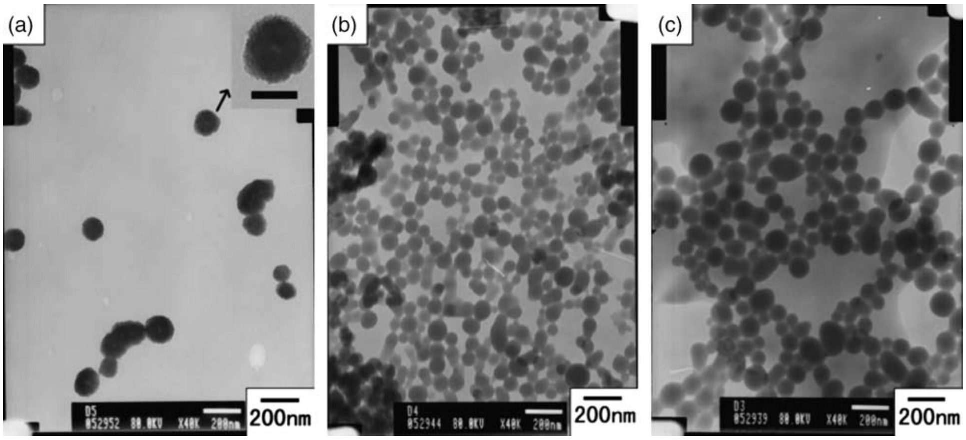


Fig. 5. TEM micrographs of the chiral oligomer at different concentrations on the water surface: (a) 0.1 mg/mL, (b) 0.7 mg/mL, (c) 1.4 mg/mL.

thick shell were formed. As the oligomer concentration increased to 0.7 and 1.4 mg/mL, as shown in Fig. 5(b) and (c), more and more solid spheres formed, which led to the formation of the networks. It was found that most of the hollow spheres possess diameters ranging from 120 to 150 nm from Fig. 5(a) and most of the solid spheres possess diameters ranging from 80 to 125 nm from Fig. 5(b) and (c). Fig. 6 showed the ESEM images of the aggregates, which agreed with the TEM observations very well.

In one of our recent publications, we discussed the possible mechanism of the self-assembly process [16]. Firstly, the steric hindrance caused by large pendants in the single oligomer chain endows the oligomer with a rigid structure in the self-assembly process, which can make the aggregates formed perfect and robust. Secondly, after THF solutions of the oligomer are dropped on the surface of water, the concentration of the solutions gradually increases following the solvent evaporation. The molecular chains of the oligomer become denser, and the affinity among racemic cyclic pendants can make the oligomers form nanometer-scale spheres with minimum free energy. Thirdly, the aggregating morphologies depend strongly on the oligomer concentration. At a higher concentration, the oligomers on the water surface congregate to form the solid spheres, and there are junctions between the spheres. When the concentration is decreased, the amount of oligomer in water falls. Individual hollow spheres can be obtained, because there are no excess oligomer molecules around to infill them after the formation of the hollow spheres.

From the TEM and ESEM images, we can see the hollow spheres from the chiral oligomers are larger than those from the racemic ones, and the shells are also thicker. This can be explained by the different affinities between the chiral macrocycles and the racemic ones according to the previous studies on the crystal structure of the binaphthyl macrocycles [17]. When the distance among the chiral macrocycles reach some critical value, C–H···O=C hydrogen bonding interactions would form. Each O=C group acts as a hydrogen bond acceptor and each –CH$_2$– group acts as a hydrogen bond donor. However, there are multitudinal weak interactions between the racemic macrocycles. Similar to the chiral macrocycles, there are hydrogen bonding interactions between the racemic ones. In addition, two racemic macrocycles can form a stable complex, because the binaphthyl groups are sandwiched between two parallel macrocyclic host cavities. The structure is further stabilized by the C–H···π interactions: the hydrogen atoms of the binaphthyl guest can be directed to the centre of the benzene ring of the macrocyclic host and the hydrogen atoms of the benzene ring can also be directed to the π-stack of the binaphthyl guest.

4. Conclusions

Comb oligomers based on a polyacrylate backbone having rigid, racemic or chiral, C_2 symmetric 1,1′-bi-2-naphthalene macrocyclic side chains, are synthesized. These oligomers can self-assemble into nanometer-scale hollow or solid spheres when their THF solutions are dropped onto water surface. The morphology of the self-assembly is concentration dependent, lower concentrations result in the formation of hollow spheres while higher concentrations favor the formation of solid ones.

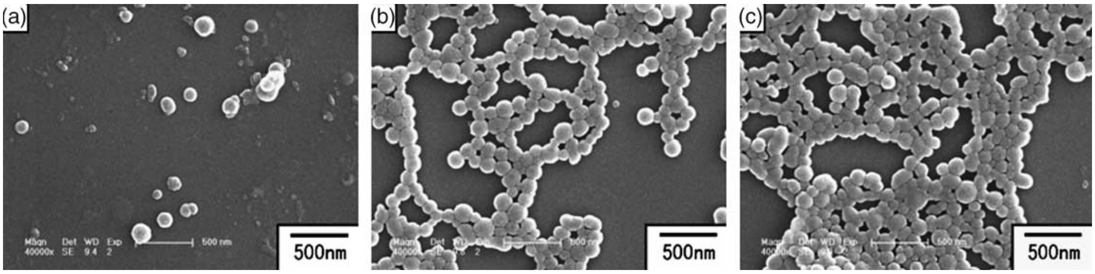


Fig. 6. ESEM micrographs of the chiral oligomer at different concentrations on the water surface: (a) 0.1 mg/mL, (b) 0.7 mg/mL, (c) 1.4 mg/mL.

The hollow spheres from the chiral oligomers are larger than those from the racemic ones, and the shells are also thicker because of the different affinities between the chiral macrocycles and the racemic ones. The self-assembled spheres of the smart oligomers may be of great importance in exploring applications in molecular recognition and separation.

Acknowledgements

We gratefully acknowledge financial support from the National Major Project for Fundamental Research of China (National 973 Program No. G2003CB615604) and the National Natural Science Foundation of China (No. 50473007). We thank Miss Anhua Liu (Peking University, China) for her kindly assistance in CD experiments.

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