Colloidosomes Constructed by Seamless Connection of Nanoparticles: A Mobile and Recyclable Strategy to Intelligent Capsules

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Materials:

Maleic anhydride (MA), polyethylene glycol 600 (PEG-600), polyethylene glycol 1500 (PEG-1000) and polyethylene glycol 2000 (PEG-2000) were obtained from Shanghai Chemical Reagent Industry. Methylbenzene *p*-toluene sulphonic acid (TSA) and octadecyl alcohol (OA) were purchased from Aldrich.

Synthesis

2-butenedioic acid (Z)-, monooctadecyl ester (O-Be) 13.5 g of Maleic anhydride (0.05 mol) and 4.9 g of octadecyl alcohol (0.05 mol) were dissolved in methylbenzene (0.5 mol, 53 ml). The reaction mixture was refluxed 4 h, the disappearance of peaks at 1850 and 1780 cm⁻¹ (C=O stretch vibration of Maleic anhydride) in IR spectrum indicated that the reaction was carried out completely. After evaporating methylbenzene by rotary evaporator, O-Be was obtained (18.1 g , 98%).

O-B-EG600 7.5 g of PEG-600 (0.0125 mol) and *p*-toluene sulphonic acid (0.172g, 1 mmol) was dissolved in methylbenzene (0.3 mol, 31.8 ml), and 4.6 g of O-Be (0.0125 mol) was dissolved in 21.2 ml of methylbenzene (0.2 mol). O-Be solution was dropwised into PEG-600 solution under a stirring condition, the reaction mixture was refluxed 6h, and a water segregator was used to remove the generated water. Then methylbenzene was evaporated by rotary evaporator. The product was dialyzed in water using a dialytic-bag (molecular weight cutoff 3500) to remove unreacted materials (O-B-EG can form micelles in water and can not pass though the dialytic-bag). Final product (O-B-EG) was obtained after drying at a temperature of 60 ^oC for several days (9.6 g, 79%). O-B-EG15000 and O-B-EG2000 were synthesized via the same route using PEG-1500 and PEG-2000 as materials, respectively.

Characterization

The ¹H NMR spectra of the resultant products were measured on a Bruker ARX 400MHz spectrometer with 1000 scans at a relaxation time of 2 s.

Thermal property of core-shell structural NPs was determined by differential scanning calorimetry (DSC) (Netzsch DSC 204). Dry samples were placed in individual hermetic sample pans and then sealed. The thermal analysis of the samples was performed at a heating rate of 5 $^{\circ}$ C/ min in the temperature range of 0–120 $^{\circ}$ C under a nitrogen flow rate of 40 ml/min.

Supplementary Material (ESI) for Soft Matter To measure the fluorescence eminiparties the poyens date Strangues solution, pyrene in benzene solution

(0.2 ml, 3.0 mmol/L) was added into a conical flask. After the benzene was evaporated completely, 5.0 ml CSNP aqueous solution (0.1%) was added to the conical flask. Then the fluorescence emission spectra were measured by fluorescence spectrophotometry on HITACHI F-7000 at predetermined temperatures. The fluorescence emission spectra of pyrene in water were tested using the same method.



Figure 1S. ¹H NMR spectra of O-B-EG600 (a), O-B-EG1500 (b) and O-B-EG2000 (c) in CDCl₃.



Figure 2S. ¹H NMR spectra of non-cross-linked P(St-co-O-B-EG600) (A-a), P(St-co-O-B-EG1500) (A-b) and P(St-co-O-B-EG2000) (A-c) NPs in CDCl₃; ¹H NMR spectrum of non-cross-linked P(St-co-O-B-EG600) in D₂O.



Figure 3S. DSC curves of P(St-co-O-B-EG600) (a), P(St-co-O-B-EG1500) (b) and P(St-co-O-B-EG2000) (c). Peaks are attributed to the melting of NPs shell constructed by P(O-B-EG). As the NP cores based on PSt were highly cross-linked, Tg of PSt can not be observed.



Figure 4S. Photos of core-shell structural NPs (a) and colloidosomes (b) in aqueous solution.

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Figure 5S. TEM images of P(St-co-O-B-EG1500) (a) and P(St-co-O-B-EG2000) (b) core-shell structural NPs; SEM images of colloidosomes constructed by P(St-co-O-B-EG1500) (c) and P(St-co-O-B-EG2000) (d) core-shell structural NPs, respectively.



Figure 6S. TEM image of P(MMA-co-O-B-EG) CSNPs (a) and SEM image of colloidosomes based on P(MMA-co-O-B-EG) CSNPs (b).



Figure 7S. Diameter distribution of P(St-co-O-B-EG600) CSNPs in oil-in-water system before heating (A), after heating 10 min (B) and 20 min (C).



Figure 8S. SEM image of P(St-co-O-B-EG600) colloidosomes self-assembled in 0.5 vol% benzene/ water system while the dosage of P(St-co-O-B-EG600) CSNPs is 0.05 g (non-tightly structure is clear).



Figure 9S. SEM images of colloidosomes made from P(St-co-O-B-EG600) with dosages about 0.01 g (a) and 0.2 g (b), while keeping the content of benzene at 2.0 vol%.



Figure 10S. Influence of temperature on fluorescence emission spectra of pyrene encapsulated in colloidosomes based on P(St-co-O-B-EG600) (A), P(St-co-O-B-EG1500) (B) and P(St-co-O-B-EG2000) (C) CSNPs, respectively.



Figure 11S. Fluorescence emission spectra of pyrene encapsulated in P(St-co-O-B-EG600) colloidosomes, when turning down the temperatures from 54 to 26 O C (a). (b) and (c) are the fluorescence emission spectra of pyrene at different temperatures in water and in P(St-co-O-B-EG600) CSNP aqueous solution, respectively. (d) represents the effect of temperature on the intensity of I_{M} (peak at 373 nm) when turning down the temperatures. (e) and (f) display the influence of temperature on the intensity of I_{M} in water and in P(St-co-O-B-EG600) CSNP aqueous solution, respectively.