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SYNTHESIS OF THERMO- AND pH-SENSITIVE POLYELECTROLYTE BRUSHES BY COMBINING THERMO-CONTROLLED EMULSION POLYMERIZATION AND PHOTO-EMULSION POLYMERIZATION*

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Abstract Bifunctional spherical polyelectrolyte brushes (SPBs) with tunable thermo- and pH-sensitivity are synthesized by combining thermo-controlled emulsion polymerization and photo-emulsion polymerization. They consist of a spherical polystyrene core and a shell of mixed brushes of poly(*N*-isopropylacrylamide) (PNIPAM) and poly(acrylic acid) (PAA) whose composition can be easily modulated by the dose of monomers. The kinetics of SPB synthesis as well as their size change with temperature and pH is determined by dynamic light scattering (DLS). The scanning electron microscopy (SEM) images show that the bifunctional SPBs have a defined spherical morphology with a narrow size distribution.

Keywords: Spherical polyelectrolyte brush; Thermo-sensitive; pH-responsive.

INTRODUCTION

Synthesis of functional materials which can respond to external stimuli is always of great importance and interest in the field of materials science[1–3]. Due to the unique structure and tunable surface properties, polymer brushes provide an ideal model system for the study on environment-stimuli responsive materials. A particular case of the polymer brushes is the spherical polyelectrolyte brushes (SPBs) which consist of a spherical core particle and a charged polymer shell, whose size strongly depends on the environmental factors such as ionic strength and pH value[4–12]. The synthesis and characterization of mono-component SPB is well documented in review articles[13, 14].

Recently, the mixed polymer brushes with different polymer chains grafted on the same substrate attract extensive attention[15]. Shusharina *et al.* studied theoretically the mixed polyelectrolyte brushes with oppositely charged polymers[16, 17]. Nikolay and *co*-workers synthesized the planar mixed polyelectrolyte brushes of poly(2-vinylpyridine) (PVP) and poly(acrylic acid) (PAA) on a SiO_2 wafer by "grafting to" technique[18, 19]. Husemann *et al.* reported the synthesis of binary poly(*tert*-butyl acrylate) and PAA brushes using surface initiated "living" free radical polymerization[20]. Zhou *et al.* prepared the binary polymer brushes by atom transfer radical polymerization (ATRP)[21] which was frequently employed to synthesize functional polymer brushes[22]. Liu *et al.* synthesized the binary polymer brushes through the combination of the lithography and surface initiated polymerization[23, 24]. The screen technique by using a musk during photo-polymerization is always employed to prepare multi-stimuli response polymer brushes on the planar surface[25, 26] while the multi-functional spherical polymer brushes are always achieved by grafting of different polymers to or grafting from

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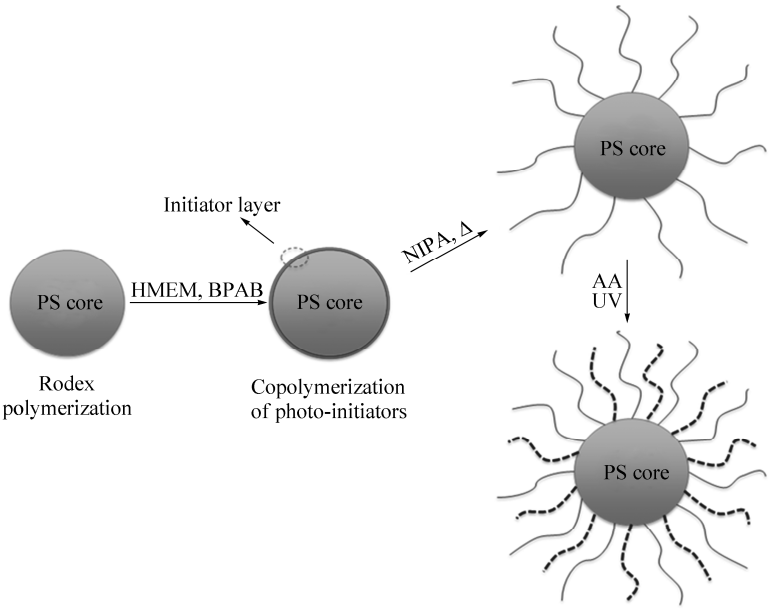
various monomers on the spherical particles[27, 28].

Here, we report a novel method to synthesize SPB with both pH- and thermo-sensitivity by combining thermo-controlled emulsion polymerization and photo-emulsion polymerization. The bifunctional SPB were prepared in three steps (Scheme 1): In the first step, the polystyrene (PS) core particles with a thin layer of copolymer from photo-initiator 2-[*p*-(2-hydroxy-2-methylpropiophenone)]-ethylene glycol-methacrylate (HMEM), thermo-initiator bis-(2-propenyl)-2,2'-azo diisobutyrate (BPAP) and styrene was prepared by a controlled redox emulsion polymerization; In the second step, the thermo-sensitive poly(*N*-isopropylacrylamide) (PNIPAM) brushes were formed by thermo-controlled emulsion polymerization; In the third step, the pH-sensitive PAA chains were grown from the core surface by photo-emulsion polymerization. The advantage of this method is that the thermo- and pH-sensitivities are easily tuned by the ratio of grafted PNIPAM and PAA chains which can be conveniently controlled by the dose of monomers at the combining steps. The prepared bifunctional SPB should be ideal candidates for many potential applications such as biosensors and drug carriers for controlled delivery.



Scheme 1 Schematic representation of the synthesis route of bifunctional spherical polyelectrolyte brush

EXPERIMENTAL

Materials

Styrene and acrylic acid were purchased from Shanghai Reagent Company (SRC) and distilled under a reduced pressure to remove the inhibitor before use. Potassium persulfate (KPS) (from SRC) was recrystallized by water. Sodium hydrogen sulfite (SHS) (from SRC), sodium dodecyl sulfate (SDS, from SRC), *N*-isopropylacrylamide (NIPAM, from Sigma-Aldrich), azodiisobutyronitrile (AIBN, from SRC), ethylene glycol (from SRC), 2-hydroxy-4′-hydroxyethoxy-2-methylpropiophenone (HMP, from Ciba), pyridine (from SRC) and methacryloyl chloride (from TCI) were used without further purification. The water used in all experiments was purified by reverse osmosis (Shanghai RO Micro Q).

Synthesis of Initiators

The thermo-initiator BPAP was synthesized in two steps. In the first step, the intermediate was formed by the reaction between AIBN and ethylene glycol, and then reacted with methacryloyl chloride in the second step by using a Schotten-Baumann reaction[29]. The photo-initiator HMEM was prepared through a Schotten-Baumann

reaction from HMP and methacryloyl chloride[8].

Synthesis of Core Latex

The PS core latex was synthesized *via* a redox emulsion polymerization. In a typical run, 10 g styrene were polymerized in 250 mL H_2O with 0.6 g SDS as surfactant, 6 g KPS and 1.5 g SHS as redox initiator. The well-defined initiator layer was achieved by copolymerizing of two different kinds of initiators BPAP and HMEM with remnant styrene on the particle surfaces under the "starved condition". The as-prepared core latex was purified by extensive serum replacement against pure water.

Grafting of PNIPAM by Thermo-controlled Emulsion Polymerization

Two different kinds of polymer chains were chemically attached by "grafting from" technique on the PS core surface by combining thermo-controlled emulsion polymerization and photo-emulsion polymerization. The PS core latex with initiator layer and a defined amount of monomer *N*-isopropylacrylamide (NIPAM) were added into a three-necked flask. Then the flask was degassed by repeat evacuation and subsequent addition of nitrogen. The amount of NIPAM used in the experiment was from 10 mol% to 100 mol% of the styrene for PS core. The polymerization started when the system temperature reached 60°C. The reaction was lasted for 2 h at 60°C. After polymerization the latex was purified by serum replacement against pure water until the conductivity of outer water was constant.

Grafting of PAA by Photo-emulsion Polymerization

The grafting of PAA chains was carried out in a UV reactor. The purified latex was charged in a UV reactor and diluted to 2.5 wt% by water. The monomer acrylic acid (AA) was added and mixed with latex by vigorous stirring. The whole reactor was degassed by repeated evacuation and subsequent addition of nitrogen at least 5 times. Photo-polymerization was initiated by UV/Vis-radiation at room temperature with the presence of AA. The as-prepared latex was purified by serum replacement until the conductivity of outer water was constant.

Characterization

^{1}H-NMR spectra (Bruker Avance 500 NMR spectrometer) was recorded at room temperature in CD_3COCD_3. Dynamic lighting scattering (DLS) was performed by a Particle Sizing System PSS 380 lighting scattering goniometry. SEM was carried out by using a Zeiss 1530 Gemini instrument equipped with a field-emission cathode. The lateral resolution was approximately 2 nm.

RUSULTS AND DISCUSSION

The kinetics of thermo-controlled emulsion polymerization and photo-emulsion polymerization was studied by monitoring the growth of particles size by DLS. As shown in Fig. 1(a), the diameter of particles has a significant growth after 30 min during the thermo-controlled polymerization of NIPAM. The cleavage temperature of thermo-initiator BPAP ranges from 60°C to 90°C, and the induction time can be observed below 70°C[29]. The decomposition temperature of photo-initiator HMEM is 80°C[30], and HMEM should be safe from cleavage during the thermo-controlled polymerization at 60°C. After the induction period of *ca.* 30 min, the size of PNIPAM brushes increased very fast in 1 h, and reached to a plateau in *ca*. 2 h (Fig. 1a).

The photo emulsion polymerization was carried out under the UV radiation at room temperature. Figure 1(b) showed that the diameter of particles increased significantly during the photo-emulsion polymerization. The increase of brush size is due to the enhancement of grafting density by grafting of PAA chains among the PNIPAM chains on the particle surface. Since the grafting of PNIPAM and PAA chains is performed in two separated steps, their ratio in the final SPB can be easily modulated by the dose ratio of monomers NIPAM and AA.

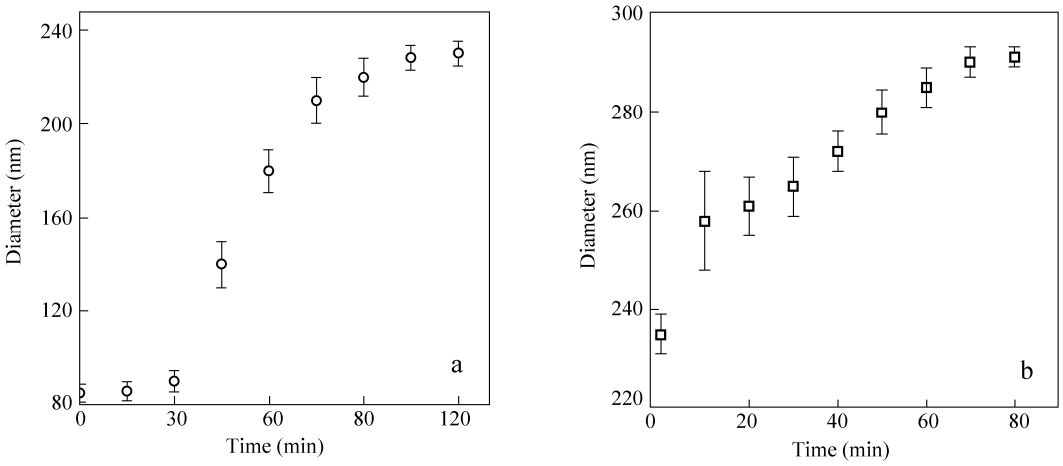


Fig. 1 Kinetics of combined thermo-controlled emulsion polymerization and photo-emulsion polymerization observed by DLS at 20°C: (a) diameter of particles as a function of time during thermo-controlled emulsion polymerization of NIPAM, (b) diameter of particles as a function of time during the photo-emulsion polymerization of AA
The doses of HMEM, BPAP, NIPAM and AA are 1 mol%, 1 mol%, 25 mol% and 25 mol% of styrene for core, respectively.

In Fig. 2, the SEM image revealed that the obtained SPB of mixed PNIPAM and PAA showed a well-defined spherical structure with narrow size-distribution while the brush layer was hardly visible after drying the sample. The size of particles was around 90 nm which was close to the data of PS core determined by DLS.

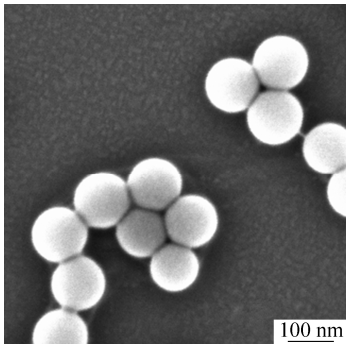


Fig. 2 SEM image of bifunctional SPB
Sample was prepared by 1 mol% BPAP, 1 mol% HMEM, 25 mol% NIPAM and 25 mol% AA of the amount of styrene for core.

Figure 3 demonstrates the comprehensive response of SPB size on both pH and temperature. Upon increasing pH value, the electrostatic repulsion among PAA chains enhanced due to the increase of dissociation degree of carboxylic groups in PAA chains. As a result, PAA chains in the mixed SPB stretched out while the PNIPAM chains either shrank at a high temperate of 50°C or stretched at low temperature of 15°C (Fig. 3a)[8, 10]. PNIPAM is the most widely studied temperature-responsive polymer with the lower critical solution temperature (LCST) of 32°C (see Fig. 3b, pH = 2)[31]. At the temperature below LCST, the PNIPAM chains are water soluble due to the formation of hydrogen bonds between water molecules and amide side groups while the hydrogen bonds will be destroyed upon increasing the temperature over LCST and the PNIPAM chains become water insoluble and shrink[31]. The mixing of PNIPAM and PAA chains in SPB can obtain bifunctional SPB with thermo- and pH-sensitivities whose size can be tunable by changing the temperature, pH value or both of them.

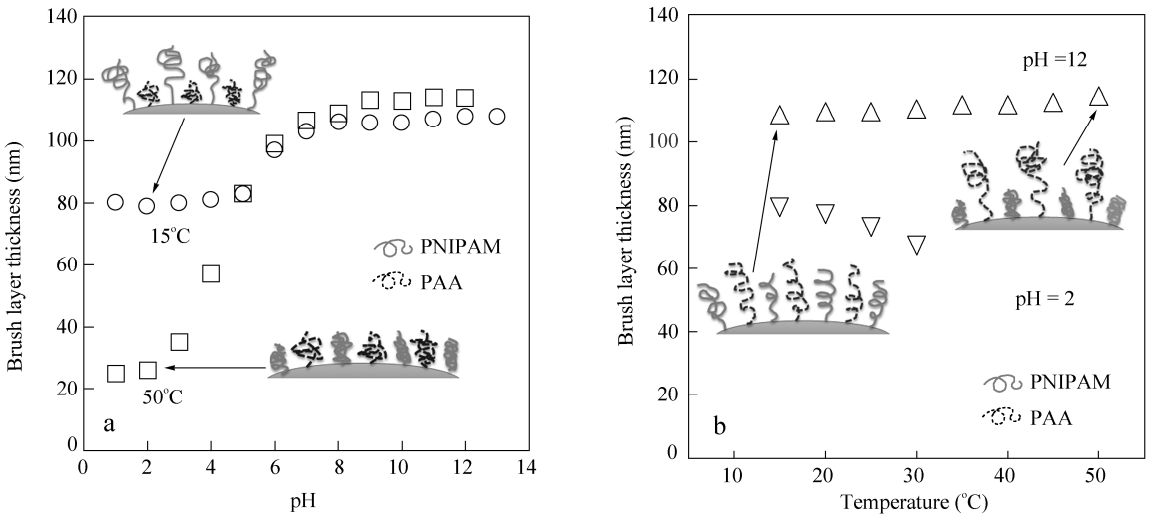


Fig. 3 Thickness change of brush layers as a function of pH and temperature as determined by DLS Sample was prepared by 1 mol% BPAP, 1 mol% HMEM, 25 mol% NIPAM and 25 mol% AA of the amount of styrene for core.

It is interesting that the bifunctional SPBs containing PNIPAM chains can become independent of temperature (Fig. 3b, pH = 12) because the PAA chains are fully stretched and dominated for the total SPB size. Also the SPB containing PAA chains can be insensitive to pH (Fig. 3a, 15°C) when the PNIPAM chains are fully stretched below LCST.

Four typical morphologies of bifunctional SPB were schematically described in Fig. 3. (I) At low temperature (15°C) and low pH value (pH = 2), the PNIPAM chains were fully stretched while the PAA chains shrank (Fig. 3a), and thus the thickness of brush layers was dominated by the PNIPAM chains; (II) In the case of high temperature (50°C) and low pH value, both PAA and PNIPAM chains shrank and the brush layer reached a minimum size (Fig. 3a); (III) At high temperature and high pH value (pH = 12), the PNIPAM chains shrank and the PAA chains became dominated (Fig. 3b); (IV) At low temperature and high pH, both PNIPAM and PAA chains stretched (Fig. 3b), and the longer chains had more contribution on the total size of SPB. Since the polymer chains in SPB obtain more space with the increase of distance out from the spherical surface which is totally different from the case of planar brushes, the impact of the shift of one kind of polymer chains on the total size of SPB seems inconspicuous when the other kind of polymer chains stretch.

At low pH values, effect of molar ratio in the dose of monomers AA and NIPAM on the thermo-sensitivity of bifunctional SPB was observed by DLS. As shown in Fig. 4, the thickness of brush layers with a feed ratio of NIPAM : AA = 9 : 1 displayed a sharp decrease around 32°C (the LCST of PNIPAM) with increasing the temperature. Upon decreasing the dose of NIPAM, the phase transition temperature maintained around 32°C while the transition became more and more vague (Fig. 4). When the molar ratio becomes NIPAM : AA = 3 : 7, no significant transition at 32°C can be determined. In this case, the PAA chains in SPB are dominated, and the temperature response of PNIPAM chains shows less impact on the total size of SPB.

As shown in Fig. 5, the pH sensitivity of bifunctional brushes can be tuned by the molar ratio of AA to NIPAM as determined by DLS at 50°C when the PNIPAM chains shrank. Upon increasing the dose of AA and thus the proportion of PAA chains, the swelling of as-prepared SPB with increasing pH becomes more and more significant. Even for the dose ratio of AA : NIPAM = 1 : 9, the size shift of SPB can reach 50 nm in a pH value range between 2 to 7 (Fig. 5).

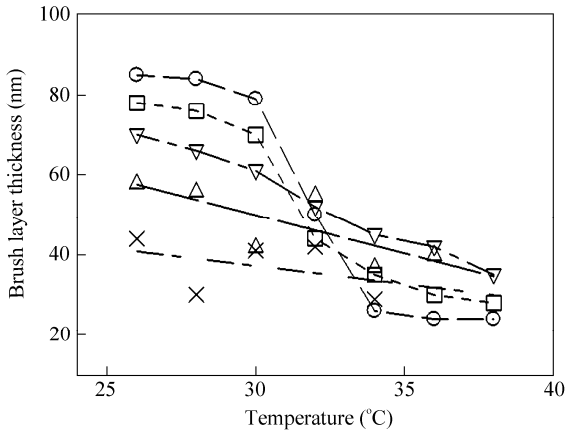


Fig. 4 Effect of monomer ratio on the temperature response of bifunctional SPB at pH = 2: (○) AA:NIPAM = 1:9, (□) AA:NIPAM = 3:7, (▽) AA:NIPAM = 5:5, (△) AA:NIPAM = 7:3 and (×) AA:NIPAM = 9:1

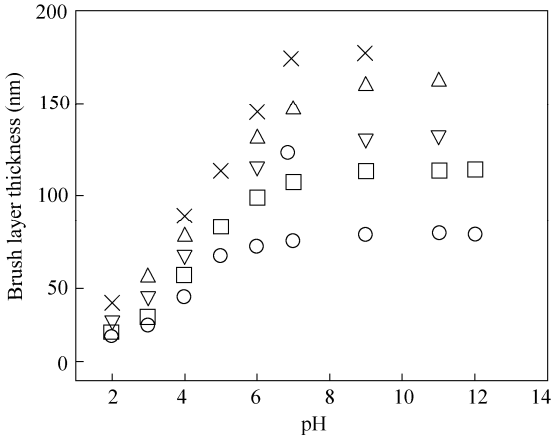


Fig. 5 Effect of monomer ratio on the pH response of bifunctional SPB at 50°C: (○) AA:NIPAM = 1:9, (□) AA:NIPAM = 3:7, (▽) AA:NIPAM = 5:5, (△) AA:NIPAM = 7:3 and (×) AA:NIPAM = 9:1

Obviously, the temperature and pH response of bifunctional SPBs can be tailored by controlling the proportion of PNIPAM and PAA chains in the brushes, while the combination of thermo-controlled emulsion polymerization and photo-emulsion polymerization of two monomers NIPAM and AA is a convenient way to modulate the brush composition by the dose ratio of two monomers.

CONCLUSIONS

Both thermo- and pH-sensitive spherical polyelectrolyte brushes were synthesized by a novel method of combining thermo-controlled emulsion polymerization and photo-emulsion polymerization. The as-prepared SPBs consist of a PS core and a shell of mixed brushes of PAA and PNIPAM chains. The grafting of PNIPAM and PAA chains in SPBs during the thermo-controlled emulsion polymerization and the photo-emulsion polymerization was studied by monitoring the size increase. The bifunctional SPBs show a well-defined spherical structure with narrow size distribution. Their sensitivities to temperature and pH values are increased by increasing the content of PNIPAM and PAA chains in the mixed SPB, respectively, while the ratio of PAA to PNIPAM chains in SPBs can be easily controlled by the dose of NIPAM and AA in two separate polymerization steps. The bifunctional SPB should be ideal candidates for biosensors, smart nano-devices and drug delivery materials.

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