

# Self-Assembly of pH-Responsive Acrylate Latex Particles at Emulsion Droplets Interface

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**ABSTRACT:** The self-assembly of pH-responsive poly(methyl methacrylate-co-acrylic acid) latex particles at emulsion droplet interfaces was achieved. Raising pH increases the hydrophilicity of the latex particles *in situ* and the latex particle acts as an efficient particulate emulsifier self-assembling at emulsion droplet interface at around pH 10–11 but exhibits no emulsifier activity at higher pH. This effect can be reversibly induced simply by varying the aqueous phase pH and thus the latex emulsifier can be reassembled. The effect factors, including the aqueous phase pH, the surface carboxyl content,  $\zeta$ -Potential of the latex particles and oil phase solvent have been investigated. Using monomer as

oil phase, the latex particles could stabilize emulsion droplets during polymerization and cage-like polymer microspheres with hollow core/porous shell structure were obtained after polymerization. The mechanism of the latex particles self-assembly was discussed. The morphologies of emulsion and microspheres were characterized by optical microscopy, scanning electron microscopy, and transmission electron microscopy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1018–1024, 2007

**Key words:** colloids; surfactants; interfaces; self-assembly; emulsion polymerization

## INTRODUCTION

The development of fabrication methods for advanced colloid materials is an important area in science and technology. The synthesis of hollow spheres in the range from nanometer to millimeter has attracted much interest in recent years, since efficient encapsulation of active ingredients such as drugs, proteins, vitamins, flavors, gas bubbles, or even living cells is becoming increasingly important for a wide variety of applications and technologies, such as functional foods, drug delivery, biomedical applications, etc.<sup>1–8</sup>

Increasingly sophisticated techniques are being developed to create hollow structures that can meet the demanding requirements of these applications. As one direction it might be of interest to obtain ordered aggregates of defined size and shape out of self-assembled colloids at interfaces. For example, Caruso et al.<sup>9,10</sup> used layer-by-layer assembly of charged SiO<sub>2</sub> particles and polymers on the surface of charged polystyrene latex particles. Subsequent dissolution of the core template transformed these core-shell composite particles into hollow microspheres. The ability of monodisperse latex particles to pack regu-

larly has contributed to the electrostatic attraction between the underlying oppositely charged aggregate layers, which leads to a compact and mechanically stable composite aggregate. It is not surprising that the size and shape uniformity of these particles has been attracting the attention of a wider cross section of materials chemists interested in trying to create other novel highly ordered structures.

Recently, there has been increased interest in using self-assembled colloids at emulsion droplet interface to form microcapsules for controlled delivery applications. In the method, emulsion droplets are used as 3D colloidal “templates” whose size and shape determine the morphology of the obtained particle aggregates. For example, Velev et al. reported the multistep ionic assembly of negatively charged (sulfate) or positively charged (amidine) PS latex particles at the oil–water interface, resulting in capsular structures without the need for a sacrificial core.<sup>11–13</sup> Croll et al. have used crosslinked poly(divinylbenzene-*alt*-maleic anhydride) microspheres and microgels self-assemble at the oil–water interface, followed by being covalently fixed with polyamines to form capsules.<sup>14</sup> Dinsmore et al. have coined the phrase ‘colloidosome’ to describe the micrometersized particle aggregates that can be prepared by sintering the particulate emulsifiers around the droplet phase, and a number of controlled-release applications have been suggested for such systems.<sup>15</sup> We also reported a submicron scale polystyrene/melamine–formaldehyde hollow microsphere composite prepared by self-assembling of sul-

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fonated polystyrene latex particles at the interface of emulsion droplets and following fixed in place, using a hard melamine–formaldehyde composite layer.<sup>16</sup> The method presents a flexible approach for the preparation of hollow and elastic capsules, with sizes ranging from micrometers to millimeters and with easily adjustable and controlled permeability and elasticity. The reportorial materials of the method are all concerned with various types of charge-stabilized polystyrene latex. The other colloid types employed were very few studied. It is well known that acrylate materials are widely used in the latex industry, the pharmaceutical field, e.g., in capsules, aerosols, and parenteral emulsions, and in cosmetics, e.g., those in skin care, decorative, and sunscreen products. It is of interest to investigate whether acrylate latex particles could self-assemble at acrylate emulsion droplet interfaces and surfactant-free emulsions stabilized by such latex particles could be polymerized into stable emulsions. If it is possible, the obtained acrylate emulsion can be used directly without needing to remove the particulate emulsifier.

In this article, self-assembling of poly(methyl methacrylate-*co*-acrylic acid) [P(MMA-AA)] latex particles at the emulsion droplet interface was studied. By adjusting aqueous phase pH with NH<sub>3</sub>·H<sub>2</sub>O, the latex particle could act as a pH-responsive particulate emulsifier self-assembling at emulsion droplet interface and the system could form a pH buffer solution. In wide addition scope of NH<sub>3</sub>·H<sub>2</sub>O, the latex particles all could stably self-assemble at oil–water interface and then the polymerization of stabilized emulsion is easily carry out without strict limit. It is very convenient for industrial application. The effect factors, including the aqueous phase pH, the surface carboxyl content,  $\zeta$ -Potential of the latex particles and oil phase solvent were considered. Using monomer as oil phase, the latex particles could stabilize emulsion droplets during polymerization and cage-like polymer microspheres with hollow core/porous shell structure were obtained after polymerization. The microspheres have potential applications in drug storage and controlled release, selective separation, catalytic supports, electronics, optics, chromatography, and so on.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA), acrylic acid (AA), *n*-butyl acetate (nBA), vinyl acetate, butyl methacrylate, and ethyl acetate were all obtained from Shanghai Chemical Reagents (China) and used without further purification. Tetrachloromethane (CCl<sub>4</sub>) was purchased from Bengbu Chemical Reagents (Anhui, China). Methanol (MeOH) was purchased from

**TABLE I**  
**Recipe for the Synthesis of P(MMA-AA) Latex Particles**

No	Constituents (g)				
	MMA	AA	PVP	MeOH	H <sub>2</sub> O
A1	10	0.05	0.5	19.8	2
A2	10	0.1	0.5	19.8	2
A3	10	0.25	0.5	19.8	2
A4	10	0.5	0.5	19.8	2

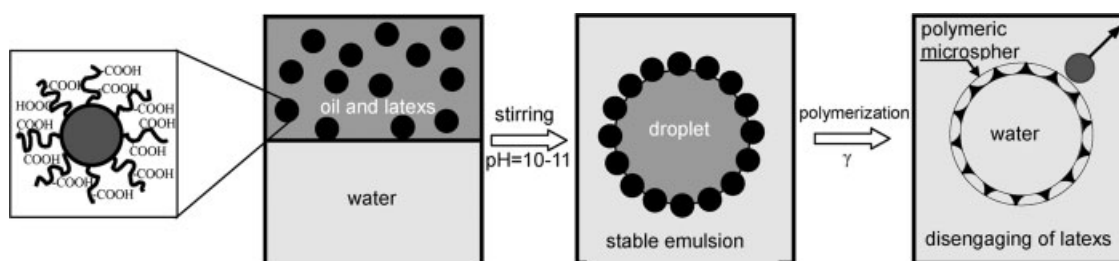
Zhenxing Chemical (Shanghai, China). Ethyl chloride, aqueous ammonia (NH<sub>3</sub>·H<sub>2</sub>O) and poly(vinylpyrrolidone) (PVP) were all purchased from Shanghai Chemical Reagents. All the solvents were analytical grade and were used as received. Deionized water (resistivity > 18.2 M $\Omega$  cm<sup>-1</sup>) prepared by Milli-Q 185 system (Millipore, USA) was used for all experiments.

### Preparation of P(MMA-AA) latex particles

P(MMA-AA) latex particles were prepared by dispersion polymerization and the recipe was shown in Table I. In the recipe, the addition of MeOH makes MMA could dissolve in the cosolvent but PMMA couldn't. PVP was used as stabilizer of polymeric particles. MMA, AA, and PVP were added into the mixed solvent of MeOH and deionized water in beaker. Then the mixture was stirred continuously for 20 min to form a homogeneous system. After bubbled by purified nitrogen for about 20 min to remove the oxygen solvated in the system, the system was sealed and irradiated in a field of  $2.59 \times 10^{15}$  Bq <sup>60</sup>Co  $\gamma$ -ray source at a dose rate of 80 Gy min<sup>-1</sup> with an absorbed dose of 14.4 kGy. The product was repeatedly centrifuged and washed with distilled water and ethanol, followed by vacuum drying at room temperature for 10 h. The obtained particles have linearly molecular with an average diameter of 2.75  $\mu$ m.

### Preparation and polymerization of P(MMA-AA) stabilized emulsion

P(MMA-AA) latex particles 0.03 g were dispersed into 2 mL nBA (or MMA if need to polymerize), using a high-intensity ultrasonic vibracell processor operating at 20 kHz for 2 min to form homogeneous systems. Then 7.5 mL of deionized water was introduced and stirred continuously using a magnetic stirrer operating at 500 rpm. Aqueous ammonia (0.0075 N mL<sup>-1</sup>) was dropped into the system to adjust pH. The mixture changed from turbid into creamy-white in appearance gradually. The emulsification took about 5 min to complete. For polymerization, the obtained MMA emulsion was bubbled through with purified nitrogen for about 20 min to remove the oxygen solvated in the system and then the system was sealed



**Scheme 1** The schematic illustration of preparation and polymerization of P(MMA-AA) stabilized emulsion.

and irradiated at a dose rate of  $80 \text{ Gy min}^{-1}$  with an absorbed dose of 9.6 kGy. The product was obtained by centrifugation and washing the deposit repeatedly with distilled water and ethanol, followed by vacuum drying at room temperature for 5 h (Scheme 1).

### Characterization

The spherical morphology and size of microspheres were observed by a Nicolet X-65 scanning electron microscopy (SEM) and a Hitachi Model H-800 transmission electron microscope (TEM) at an accelerating voltage of 200 keV. The emulsions were examined by OLYMPUS BX41 optical microscopy (OM) equipped with a Nikon COOLPIX4500 high-resolution digital CCD camera and the average droplet diameters were measured from at least 100 droplets on the OM photos. The milliequivalents of surface carboxyl per gram of P(MMA-AA) latex particles were measured by titration, referring to the method reported by Hen.<sup>17</sup> The measurements of electrophoretic mobility were carried out using a Zetasizer Nano ZS  $\zeta$ -potential analyzer. The  $\zeta$ -potentials are calculated from the obtained electrophoretic mobility, using the Smoluchowski equation. After homogenization, the conduc-

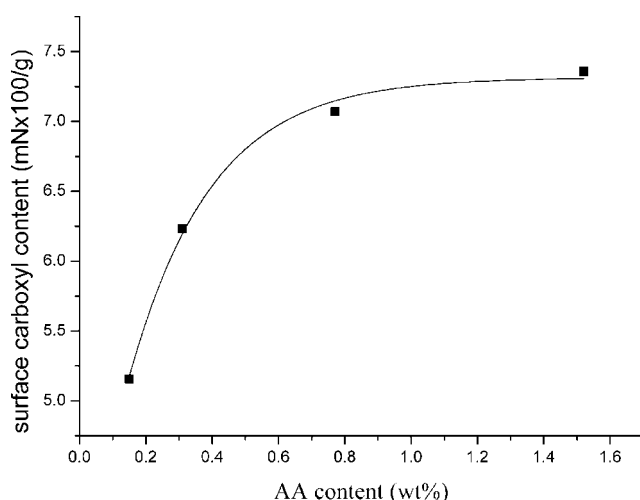
tivity of the emulsions was immediately determined using a DDS-11D digital conductivity meter with Pt/Pt black electrodes. Emulsion stability at 25°C was evaluated in graduated vessels by monitoring the movement of the oil-emulsion and emulsion-water interfaces with time. The solution pH was monitored using a pH meter.

## RESULTS AND DISCUSSION

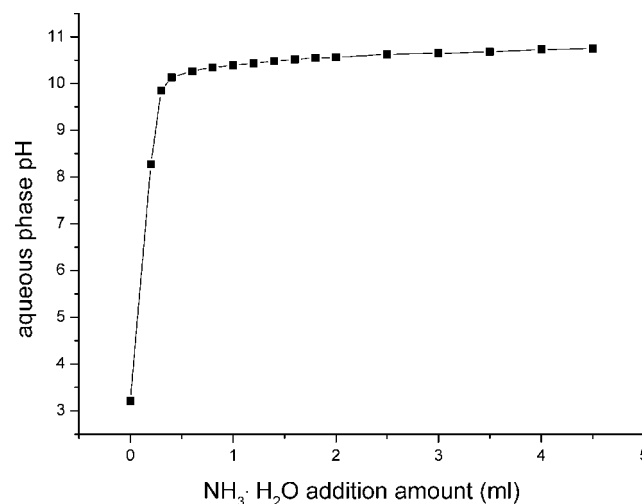
### The content of carboxyl on P(MMA-AA) latex particles surface

The hydrophilicity of latex particles is analogous to the hydrophile-lipophile balance number of surfactant molecules that determine on emulsion type and stability. The hydrophilicity of PMMA particles was adjusted by copolymerizing certain AA, therefore, the density of hydrophilic carboxyl on the particle surfaces. The milliequivalent of surface carboxyl per gram of P(MMA-AA) latex particles varies with different content of AA in recipe was shown in Figure 1.

With the increase of AA content, the surface content of carboxyl first increased promptly, and then



**Figure 1** The surface carboxyl content of P(MMA-AA) latex particles varies with different content of acrylic acid.



**Figure 2** The aqueous phase pH varied with the addition of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  with P(MMA-AA) latex particles of No A3 dispersed in oil phase.

**TABLE II**  
**Stability of MMA-in-Water Emulsions at Different Aqueous Phase pH Stabilized by P(MMA-AA) Latex Particles of No A3 at 25°C**

Aqueous phase pH	Conductivity ( $\mu\text{S}/\text{cm}$ )	Emulsion stability after 12 h
5.5	156	100% Coalescence
7	193	40% Coalescence
7.5	212	12% Coalescence; cream
8	229	4% Coalescence; cream
9.5	247	2% Coalescence; cream
10	424	Creaming only
11	583	Creaming only
11.5	649	12% Coalescence; cream
12	830	33% Coalescence; cream

leveled off. Usually, the carboxylic acid-functionalized polymer mostly distributes on the surface layer of the latex particles and reaches a balance value (about  $6.9 \times 10^{-8} \text{ mol m}^{-2}$ ).<sup>18</sup> So the further increase of AA content in recipe would no longer improve the density of carboxyl on the particle surfaces.

#### Effect of aqueous phase pH on the latex particles self-assembly

The P(MMA-AA) latex particles in their original state cannot be adsorbed at the oil–water interface, because carboxyl is weakly hydrophilic and has a finite density on the particles surface, which made it not enough to stabilize the latex particles. Therefore, it is necessary to further modify latex surface properties (i.e., electrostatic charge and hydrophilicity). The ideal modification of the latex surfaces should not cause the flocculation of the particles in the suspension and 2D coagulation after the particles were adsorbed to the interface.

The hydrophilic character of the P(MMA-AA) latex particles can be adjusted by controlling the solution pH. At initial pH, the surface carboxyls are in their weakly-protonated form and are only weakly hydrophilic. In alkalic solution the carboxyl are fully protonated. Surface weakly-protonated P(MMA-AA) latex particle is dispersible in a wide range of weakly-polar solvents, including nBA and pentyl acetate, whereas surface protonated latex particle is only dispersible in aqueous solution. Thus adsorption of the P(MMA-AA) latex particles at the oil–water interface is expected to be pH dependent. The pH of the aqueous phase was raised progressively from its initial value by addition of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and the pH varied with the addition of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was shown in Figure 2.

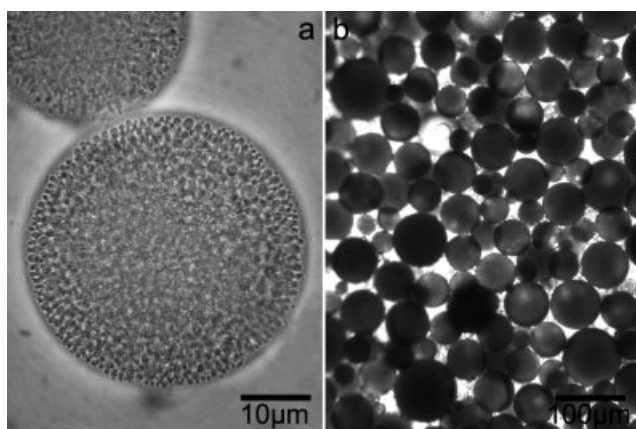
During the addition scope of 0.5–4.5 mL, the system pH didn't obviously change, hinting the formation of pH buffer solution, which is a remarkable advantage by using  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . In the wide scope of adding  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , the latex particles, which were dispersed in oil phase firstly, all could self-assemble at oil–water interface and form a compact pack-density at emul-

sion droplet interface as shown later. So the formation of stable emulsion is in a wide scope, which is very convenient for further application. Contrastively, the pH will rapidly rise in the system of using NaOH and few latex particles could self-assemble at emulsion droplet interface as observed in experiment.

The effect of aqueous phase pH on the stability of the MMA-water emulsions was summarized in Table II. At low pH, the PAA-based stabilizer chains were weakly-ionic, which made the particles weakly hydrated by water on one side of the oil–water interface and strongly solvated by oil on the other. As a result the particles would easily stay in oil phase and emulsion was unstable. Between pH 10 and 11, the protonated PAA-based stabilizer chains enabled the latex particles to adsorb strongly at the oil–water interface, leading to the formation of stable emulsions. The obtained emulsions were of the oil-in-water (O/W) type and were completely stable to coalescence but creamed slowly with time. The emulsion droplets were polydisperse with an average diameter of approximately 50  $\mu\text{m}$ . If the pH further increased from 11 to 12, the PAA-based stabilizer chains became fully protonated, leading to the particles strongly hydrated by water on one side of the oil–water interface and weakly solvated by oil on the other and hence the P(MMA-AA) latex particles no longer adsorbable at oil–water interface. Coalescence of the oil droplets occurred, followed by macroscopic phase

**TABLE III**  
 **$\zeta$ -Potentials of the P(MMA-AA) Latex Particles of No A3 at Different pH at 25°C (0.4 wt % Aqueous Latex And Conductivity  $\kappa = 420 \text{ S}/\text{cm}$ )**

pH	$\zeta$ -Potential (mV)
5.5	–6.08
7	–8.36
7.5	–10.68
8.5	–16.66
9.5	–22.5
10.5	–23.15
11.5	–27.63
12.5	–31.74



**Figure 3** The OM images of MMA-in-water emulsion droplets stabilized by P(MMA-AA) latex particles of No A3 at the aqueous phase pH 10.5 (a) high magnification, (b) low magnification.

separation. This observation of demulsification is consistent with earlier work by Binks and Clint, which showed that if the particles were either too hydrophilic or too hydrophobic they tended to remain dispersed in either the aqueous or oil phase, respectively, giving rise to very unstable emulsions.<sup>19,20</sup>

The  $\zeta$ -potential at different pH obtained for a 0.4 wt % aqueous dispersion of the P(MMA-AA) latex particles of No A3 was shown in Table III. At low pH, the PAA-based stabilizer chains were weakly-ionic and weakly charged. With the increase of pH, the particles were rendered negatively charged to their higher extent because of the ionization of surface carboxyl. When pH is between 10 and 11, the surface charges of the latex particle were about  $-23$  mV and the ideal P(MMA-AA) latex particles packed emulsion was obtained as shown in Figure 3. It was observed that the surfaces of emulsion droplets were covered with dense, P(MMA-AA) particle monolayer and each particle had a Brownian motion itself. Velev et al. ever estimated the homocoagulation threshold of the lysine hydrochloride modified sulfate latex particle to be about  $-20$  mV.<sup>11</sup> In a previous article, we also described stable self-assembly of sulfonated PS latex particles with a particle surface  $\zeta$ -potential of  $-26$  mV.<sup>16</sup> It can be seen that different latex particles have an approximately same potential threshold to stably self-assemble at emulsion droplet interfaces. As further raising the pH, the surface charge in-

creased markedly as the PAA become fully protonated at around pH 11. Under these conditions the PAA-based stabilizer chains are highly anionic and strong electrostatic repulsion between the particles results in unstable self-assembly of the latex particles at droplet interface. The strongly charged latex particles would diffuse into aqueous phase. This pH-modulated surface charge was fully reversible, which reflects the adsorption/desorption of the latex particles at the emulsion droplets interface being pH-dependent.

### Effect of oil phase solvent on the latex particles self-assembly

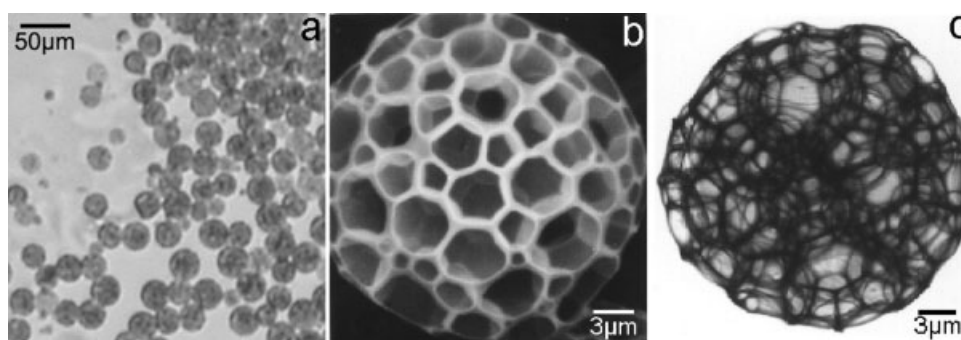
The oil phase solvent also affect self-assembly of latex particles at droplet interface. The increase of the oil polarity will lead to the decrease of interfacial tension.<sup>20</sup> So the oil phase with different polarity will affect the wettability of a single particle surface of given hydrophilicity. Several kinds of solvent were chosen to study. The relevant properties<sup>21</sup> and the adsorption of the particles at the droplet interface were summarized in Table IV. Clearly, the appropriate conditions for particle adsorption are of the solubility parameter  $\delta$  around  $8.7\text{--}8.2$  ( $\text{cal cm}^{-3}$ )<sup>1/2</sup> and polarity  $0.052\text{--}0.167$ .

### The mechanism of P(MMA-AA) latex particles self-assembly

The P(MMA-AA) latex particles is basically hydrophobic and could only be dispersed in oil phase. After the addition of  $\text{NH}_3\text{-H}_2\text{O}$  in aqueous phase, the surface carboxyls of P(MMA-AA) latex particles will be protonated once the particles diffusing into oil-water interface under stirring. The protonation made the hydrophilicity and surface charges of the latex particle increased, which results in stable self-assembly of latex particles at oil-water interface. Due to the consecutive diffusion of particles to oil-water interface and subsequently neutralized by ammonia, the system comes into a stable period of pH. When oil drops were adequately packed, optimal stability of emulsion was obtained. Adding ammonia further, the surface carboxyls of self-assembled latex particles will be fully protonated, which made the hydrophilicity and surface charges of the latex particle further increased.

**TABLE IV**  
Properties of Oil Phase Solvents and the Adsorption of the P(MMA-AA) Latex Particles of No A3 at the Oil-in-Water Droplet Interfaces (the Aqueous Phase pH = 10.5)

Solvent	EA	nBA	MMA	VA	BMA	$\text{CCl}_4$	EC
Hildebrand $\delta$ ( $\text{cal/cm}^3$ ) <sup>1/2</sup>	9.1	8.55	8.7	8.7	8.2	8.6	8.5
Polarity	0.167	0.167	0.149	0.052	0.096	0	0.319
Particles adsorption	Poor	Good	Good	Good	Good	Poor	No



**Figure 4** (a) OM, (b) SEM, and (c) TEM, images of PMMA microsphere fabricated by  $\gamma$ -rays induced polymerization of MMA droplets, which were stabilized by P(MMA-AA) latex particles of No A3 at the aqueous phase pH 10.5, with an absorbed dose of 9.6 kGy at a dose rate of 80 Gy min<sup>-1</sup>.

As a result the particles were strongly hydrated by water on one side of the oil–water interface and weakly solvated by oil on the other. At the same time the increase of surface charges and electrostatic repulsion also lead to the P(MMA-AA) latex particles no long stably self-assembling at oil–water interface. So the particles will enter aqueous phase and macroscopic phase separation occurred.

#### Interface polymerization of P(MMA-AA) latex particles stabilized emulsion

In view of it was stable for MMA-in-water emulsion stabilized by P(MMA-AA) latex particles of No A3 at the aqueous phase pH 10.5, we then polymerized the monomer emulsion by  $\gamma$ -ray irradiation with an absorbed dose of 9.6 kGy at a dose rate of 80 Gy min<sup>-1</sup>. The OM image of the polymeric emulsion droplets was showed in Figure 4(a). It was founded that the obtained emulsion droplets still kept spherical morphology, which suggest that the P(MMA-AA) latex particles could stabilize the emulsion droplets during polymerization. After polymerization, if the P(MMA-AA) latex particles could integrate with polymeric microspheres, strawberry-like core-shell structure will be obtained. However, the SEM image showed that the microsphere possessed porous shell structure [Fig. 4(b)]. The average pore size of polymeric shell is similar to that of P(MMA-AA) latex particles, suggesting that the disengagement of the latex particles leads to the formation of the holes. The TEM image in Figure 4(c) showed that the polymer microsphere had hollow core/porous shell structure. The polymerization of MMA was mainly initiated by the radicals R produced from the radiolysis of water via  $\gamma$ -irradiation. Therefore, the polymerization would occur at the interface of the droplet. Finally, hollow structure was obtained. The formation mechanism of cage-like polymer microspheres with hollow core/porous shell structure was ever discussed in our former study.<sup>22</sup>

#### CONCLUSIONS

We have achieved the self-assembly of pH-responsive P(MMA-AA) latex particles at emulsion droplet interfaces. Raising the aqueous phase pH increased the hydrophilicity of the latex particles *in situ*. A closely packed layer of the latex particles was formed at the droplet interface by adjusting the solution pH from 10 to 11. However, at higher pH, strong electrostatic repulsion between the particles leads to desorption of the latex particles from the oil–water interface and results in rapid demulsification. This effect is reversible and thus the latex emulsifier can be reassembled. The oil phase solvents were selected. The appropriate conditions for latex particles self-assembly are of the solubility parameter  $\delta$  around 8.7–8.2 (cal cm<sup>-3</sup>)<sup>1/2</sup> and polarity 0.052–0.167. Using MMA monomer as oil phase to form P(MMA-AA) latex particles packed emulsion, the latex particles could stabilize emulsion droplets during polymerization and cage-like polymer microspheres with hollow core/porous shell structure were obtained after polymerization. The obtained microspheres may find potential applications in controlled release systems and catalytic supports.

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