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The mechanism of ^{60}Co γ-ray radiation induced interfacial redox reaction in inverse emulsion and its application in the synthesis of polymer microcapsules

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Abstract

The motivation of this work is to explore the formation mechanism of polymer microcapsules via γ-ray radiation in W/O inverse emulsion system. Utilizing the strong reducing radical (e^-_{aq}, hydrated electron) and oxidant radical ($^{\bullet}OH$, hydroxyl radical) produced in the aqueous phase by the ^{60}Co γ-ray radiation, two interfacial redox initiation systems were proposed and applied to the preparation of polymer microcapsules. In this work, BPO (benzoyl peroxide)–e^-_{aq} and DMA (*N*,*N*-dimethyl aniline)–$^{\bullet}OH$ were used to control the polymerization position at the water–oil interface. Finally, polystyrene (PS) microcapsules were synthesized successfully. From the kinetic curves of monomer conversion, the mechanism of radiation induced interfacial reaction was determined and this method can be extended to synthesize polymer capsules and composite spheres.

Keywords: Microcapsule; Radiation polymerization; Redox initiation

1. Introduction

In recent years, polymer nano/microcapsules have attracted a great deal of interest in the small container for encapsulation process in life science, catalysis, cosmetics, new intracellular delivery systems such as drug delivery and gene therapy [1–6]. Some commonly used approaches in the preparation of polymer microcapsules or hollow polymer spheres include colloidal or liquid-core templating method [7–11], stepwise alkali/acid swelling method (also called osmotic swelling) [12], dynamic swelling method [13], W/O/W emulsion polymerization [14], phase separation of block copolymers [15], lipid/liposome or vesicle templates [16–20], layer-by-layer (LBL) method [21–24], miniemulsion process [25–27], utilizing covalent bonds and hydrogen bonds [28,29] and electrochemical oxidation of pyrrole [30]. In-situ interfacial polymerization has been used to prepare functional polymer [31] or special morphologies, such as microcapsules [32–34], inorganic/organic composite [35] and polyaniline nanoparticles [36]. However, there have been no reports of one-step method to prepare polymer hollow spheres or microcapsules in inverse emulsion system via an interfacial polymerization approach under mild reaction conditions.

Redox interfacial-initiated emulsion polymerization is an efficient way to control the locus of radical formation and monomer polymerization; a redox initiation system usually consists of a hydrophilic reductant and hydrophobic oxidant. By this method, polymer spheres with different morphologies have been prepared, such as polymer hollow spheres [37] and core-shell spheres [38,39]. Generally, in a wide range of redox initiation systems, the hydrophilic reductant includes both inorganic and organic components either wholly or in part, for example ferrous ion (Fe^{2+}), sulfite, bisulfite ion and tetraethylenepentamine (TEPA). But the residues after the reaction remain in the system and are hardly removed thoroughly, so as

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to have the possibility to affect the performance of the final products.

Inverse emulsion was usually applied to the polymerization of hydrophilic monomers, such as acrylamide, acrylic acid, salt of acrylic acid and *N*-isopropylacrylamide. The polymerization can be initiated by using water-soluble initiators (KPS, APS), oil-soluble initiator (BPO) or radiation sources (γ-ray or UV). In our group, the CdS/PS composite hollow spheres were synthesized by inverse microemulsion method in which the polymerization of styrene and the formation of CdS nanoparticles were initiated by γ-ray radiation [40]. The proposed mechanism of the composite hollow spheres originates from the simultaneous synthesis of PS and CdS nanoparticles at the interface of microemulsion droplets.

It's well known that water irradiated by γ-ray can generate active-reducing particles, such as solvated electrons and hydrogen atoms, which can reduce metal ions to metal atoms. In recent years, γ-ray radiation has been extensively used to initiate polymerization of vinyl monomers [41,42] and to prepare nano-crystalline metal, alloys, metal oxide, metal sulfide and composites [40,43–47]. But the hydrated electron has rarely been considered as initiator to conduct the monomer polymerization in radiation chemistry. In addition, peroxides in combination with a reducing agent are a common source of radicals, and the reaction usually involves the electron transfer between reductant and oxidant. Therefore, considering from the viewpoint of the mechanism of redox initiation, the peroxide with hydrated electron may be applied to initiate polymerization.

The motivation of this work is to explore the formation mechanism of polymer microcapsules via γ-ray radiation in W/O inverse emulsion system. For this purpose, it is essential to establish conditions whereby reproducible polymerization position may be obtained using redox initiation. As it is known, redox-initiator system is very easy to produce radical at the water–oil interface. So this model will be addressed in our study. In this work, BPO–e^-_{aq} and DMA–$^{\bullet}OH$ were proposed as initiators to control the polymerization position at the water–oil interface. The mechanism of radiation induced interfacial redox reaction was indirectly characterized by kinetic study, and the morphologies of PS microcapsules approved the hypothesis successfully.

2. Experiment and characterization

2.1. Materials

Styrene (S) and divinyl benzene (DVB) were passed through a basic alumina column before use for removing inhibitors. Benzoyl peroxide (BPO, Shanghai Chemical Reagent Co., China) was recrystallized from methanol and dried at room temperature in vacuum. Isopropanol (AR), acetone (AR) and *N*,*N*-dimethyl aniline (DMA, AR, Shanghai Chemical Reagent Co., China), octyl-phenol polyoxyethylene (*n*) ether ($n = 4$) (OP-4), silicon oil (500 cP/25 °C, Factory of Hangzhou Teacher College), diisooctyl sodium sulfosuccinate (AOT, Wako Pure Chemical Industries Ltd.) were used as received.

2.2. The kinetic study of styrene polymerization initiated by redox reaction

The aim of kinetic study is to confirm the interfacial redox reaction between BPO and hydrated electron (or between DMA and hydroxyl radical). So suspension polymerization recipes were chosen to observe the kinetic study. In kinetic study experiments, 40 mL styrene containing 0.50 g BPO was mixed with 50 mL (1.0 M) NaOH aqueous solution under stirring. The pH value of the system was about 14. The volume ratio of free radical scavenger (isopropanol) and aqueous phase was 1/10. Then, the mixed system was irradiated by ^{60}Co γ-ray at a dose rate of 65 Gy/min and the monomer conversion was measured by weighing method. The conversion can be calculated by the following equation:

$$\text{monomer conversion} = \frac{m_d - m_s}{m_t \times \frac{36}{86.5}} \times 100\%$$

m_t is the total weight before baking, m_d is the weight after drying, m_s is the weight of surfactant and NaOH in the system.

2.3. Preparation of polymer microcapsules

A typical inverse emulsion was prepared by adding 6.0 mL (1.0 M) NaOH aqueous solution into 25.0 mL silicon oil containing 0.50 g AOT and 1.50 g OP-4 under stirring, then 3.6 mL styrene and 0.4 mL DVB containing 0.050 g BPO were added. Polystyrene hollow spheres were synthesized after the inverse emulsion was irradiated by ^{60}Co γ-ray source at a dose rate of 65 Gy/min for a total absorbed dose of 30 kGy. The polymerization was conducted at room temperature (about 20 °C) and the agitation speed was held the same during all the experiments. Finally, kerosene was added into the inverse emulsion to dissolve the silicon oil, and ethanol was used to wash the precipitate for three times.

2.4. Characterization

The morphology of PS spheres was studied by field-emission scanning electron microscopy (FESEM, JEOL JSM-6700) and transmission electron microscopy (TEM, Hitachi H-800). The shell thickness of microcapsules was determined from TEM images by measuring 100 positions (the measurement was made visually through the images).

3. Results and discussion

When pure water or aqueous solution is irradiated by γ-ray, a lot of particles such as the hydrated electrons, hydroxyl radicals, hydrogen atoms, etc. form in the system (see Reaction (1)). Radiation-chemical yield is expressed in terms of the number of converted molecules per 100 eV of energy absorbed, called *G* value. In radiation chemistry, *G* value was introduced to denote the number of molecules changed. The *G* values in aqueous solution of hydroxyl radical, hydrogen atom and hydrated electron are 2.7, 0.55 and 2.7, respectively

(pH = 8–13) [48]. All the three radicals are so active to lead to chemical reactions in the system.

$$H_2O \xrightarrow{\gamma\text{-rays}} {}^{\bullet}OH,\ H^{\bullet},\ e_{aq}^{-},\ H_2,\ H_2O_2,\ H_3O^{+} \quad (1)$$

If we want to discover the role of hydrated electrons in radiolysis, it should inhibit the yield of the other two species to promise the maximum yield of e_{aq}^{-}. Here, two controllable methods are introduced to reach this aim.

One is keeping the aqueous phase in a high pH value (pH > 12). In strong alkaline solution, the conversion of hydrogen atoms to hydrated electrons is significant and the yield of hydrated electrons is slightly enhanced. This fact can be explained by the reaction of hydrogen atoms with hydroxyl ion, according to Reaction (2):

$$H^{\bullet} + OH^{-} \rightarrow e_{aq}^{-} + H_2O \quad (2)$$

At the same time, the reactivity of the $^{\bullet}OH$ radical is markedly depressed in a strong alkaline solution, because of the following reaction:

$$^{\bullet}OH + OH^{-} \rightarrow O^{-\bullet} + H_2O \quad (3)$$

Like the hydroxyl radical, the $O^{-\bullet}$ ion radical is also an oxidizing species, but in the electron transfer reactions, the $O^{-\bullet}$ reacts much slower than $^{\bullet}OH$ does [48].

Another way is that the $^{\bullet}OH$ radical can be effectively captured by isopropanol and turns into a less active radical:

$$RCHOH + {}^{\bullet}OH \rightarrow RCHO^{\bullet} + H_2O \quad (R = (CH_3)_2) \quad (4)$$

In summary, in the presence of a strong alkaline aqueous phase and isopropanol, the effect of hydroxyl radical can be suppressed to the greatest extent, so that the action of hydrated electron and BPO can be studied clearly.

3.1. Mechanism of radiation interfacial redox polymerization

Considering that hydrated electrons generated in water medium by γ-ray radiation possess a very low standard potential ($E^0 = -2.77$ V [48]), the redox reaction is feasible between the oxidant (BPO) and the strong reducing agent (e_{aq}^{-}), in which the electron transfer from e_{aq}^{-} to BPO occurs and the oil-soluble benzoyloxy radical is generated (see the following Reaction (5)). In the conventional polymerization initiated by γ-ray radiation, the hydrated electron would not engage in the initiation of monomer. So the redox reaction between BPO and e_{aq}^{-} is designed to initiate the polymerization at the water–oil interface.

(5)

To examine the validity of the concept of radiation interfacial redox reaction, kinetic study was carried out (Table 1). In the experiments, all the reactions were conducted at room temperature (about 20 °C), so the radical generated from BPO or styrene with temperature can be ignored. Fig. 1 shows that the

Table 1
The recipes of kinetic study of radiation interfacial redox reaction

Recipes	Blank	BPO	Acetone	Blank	DMA
Curves	Fig. 1, A	Fig. 1, B	Fig. 1, C	Fig. 4, A	Fig. 4, B
H_2O/mL	50.0	50.0	50.0	50.0	50.0
NaOH/g	2.00	2.00	2.00	–	–
Isopropanol/mL	4.0	4.0	4.0	–	–
Acetone/mL	–	–	4.0	4.0	4.0
Styrene/mL	40.0	40.0	40.0	40.0	40.0
BPO/g	–	0.50	0.50	–	–
DMA/g	–	–	–	–	0.25

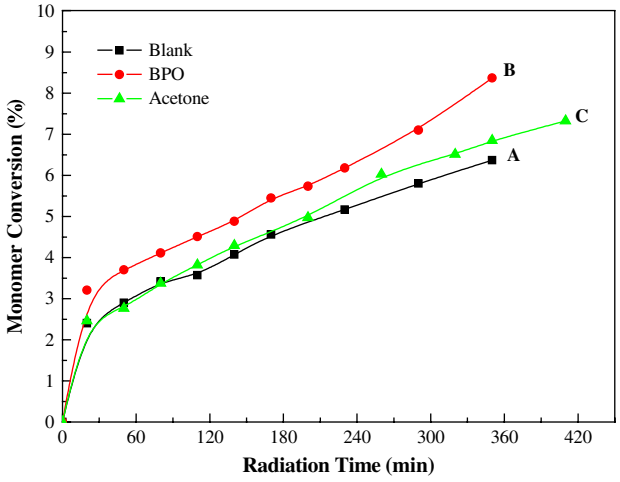


Fig. 1. Monomer conversion vs. radiation time curves for the BPO–e_{aq}^{-} redox initiation system. (For the recipes of curves A–C see Table 1.)

monomer conversion was higher during the existence of BPO than that without BPO (curves B and A). Comparing the recipes of kinetic study, it can be concluded that the higher monomer conversion originates from the higher radical concentration during the suspension polymerization. Without BPO, the polymerization was initiated by the hydroxyl radical or isopropanol radical. Due to those radicals existing in the aqueous phase, it should diffuse to the water–oil interface and initiate the polymerization of styrene subsequently. After adding BPO into the oil phase, the hydrated electron can diffuse to the water–oil interface and reacts with the oxidant to generate benzoyloxy radicals. And this reaction leads to the increase of free radical concentration in the oil phase.

To examine whether the decomposition of BPO takes place by γ-ray radiation or by redox reaction with hydrated electron at the water–oil interface, kinetic study experiment is carried out by scavenging the hydrated electron. Acetone is an effective agent to scavenge hydrated electron. Adding acetone into the aqueous phase, e_{aq}^{-} will combine with acetone and is turned into an inert radical. So the redox reaction (BPO–e_{aq}^{-}) cannot take place at the interface. Fig. 1 shows that the two curves (curves A and C) are almost in superposition. The result confirms that BPO does not decompose by the radiation. These

data provide strong evidence that the interfacial redox reaction (Reaction (5)) plays the important role of increasing the monomer conversion.

In the kinetic study, the experimental condition is different from the synthetic pathway, which gives the PS hollow spheres. It's because the interfacial initiation is only one important factor for the preparation of hollow sphere. There are still other controlling factors, such as the viscosity of emulsion, ratio of water to oil, and the ratio of surfactant to water. To simplify the process, suspension polymerization system was chosen to indirectly prove the interfacial redox reaction.

From the above study, it's confirmed that the redox reaction of BPO–e^-_{aq} can take place at the water–oil interface under γ-ray radiation and prompts the polymerization of monomers in W/O emulsion. Consequently, the radiation induced interfacial redox reaction can be expected to initiate in-situ interfacial polymerization in inverse emulsion.

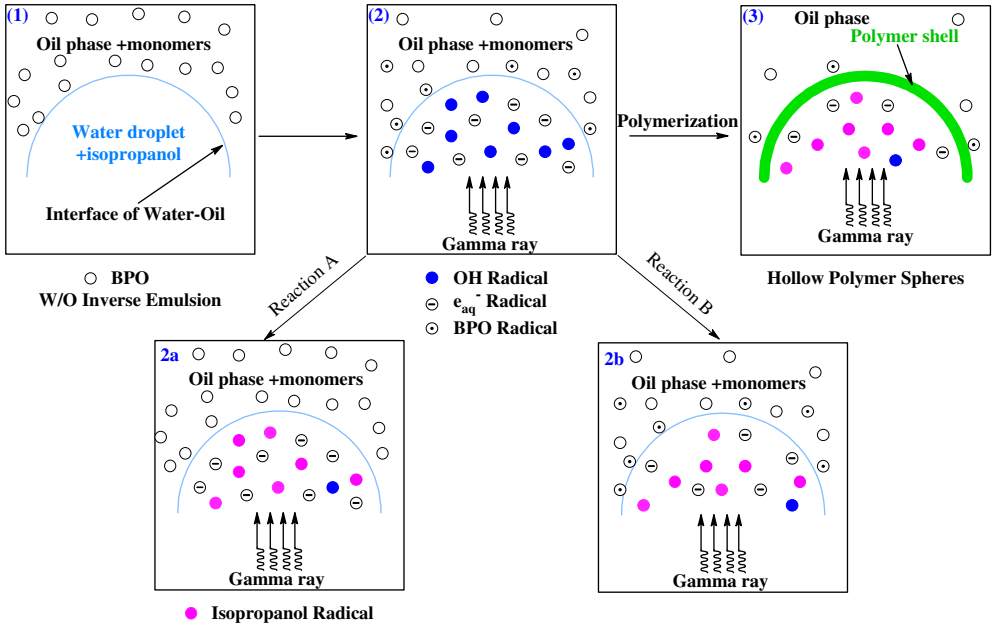
3.2. The preparation of polystyrene microcapsules by BPO–e^-_{aq} initiation system

The process of the preparation of PS microcapsules is illustrated in Scheme 1. As depicted in step 1, the aqueous phase is adding into the oil phase containing styrene and BPO to form W/O inverse emulsion in the presence of surfactants, such as OP-4. In step 2, the inverse emulsion is irradiated by γ-ray. The e^-_{aq} and •OH are generated in the aqueous phase as described in Reaction (1). To eliminate the effect of hydroxyl radical, isopropanol is used as the scavenger of •OH thereby turning into an inert isopropanol radical (Reaction A in Scheme 1). At the same time, the reductant hydrated electron and the oxidant BPO will diffuse to the water–oil interface to generate benzoyloxy radical (Reaction B in Scheme 1). Subsequently (in step 3), the benzoyloxy radicals can initiate styrene to polymerize. Due to the kerosene is the non-solvent of PS, the polymer will deposit at the water–oil interface. Finally, PS microcapsules are synthesized.

The morphology of PS microcapsules was characterized by TEM and FESEM. As shown in Fig. 2, it exhibited a truly hollow structure, with a wall thickness of ca. 100 nm. The cracked or collapsed morphologies and polydispersity of the particle size distribution also could be displayed in Fig. 2. There are two notable facts here: (1) the emulsion stability and water drop size distribution are important for controlling the final product particle size distribution; (2) proper agitation speed is important because the polymer shell formed initially may be destroyed if the speed is too high or else the final product is not strong enough to be a hollow sphere.

Fig. 3 reveals the effect of monomer content on the morphology of microcapsules. With the styrene monomer content varying from 2.0 to 4.0 and to 8.0 mL, the PS shell thickness of the microcapsules increased correspondingly, the values being 52 ± 14, 126 ± 32 and 210 ± 52 nm, respectively.

Another important parameter is the viscosity of the oil phase. It has a large influence on the morphology of polymer spheres (for results see Fig. 4). When kerosene is used as the oil phase, the latex particles are mostly homogeneous solid spheres. It is contributed to the low viscosity of external phase that cannot depress the phase separation and coalescence of polystyrene chains. On the contrary, highly viscous oil phase can reduce the diffusion rate of polymer or polymer radicals, whereas it has a slight effect on the pervasion of monomer molecules. So it's beneficial to keep the polymerization at the interface. At the same time, an increase in the viscosity of external phase reduces the diffusion coefficient of the aqueous droplets i.e., the frequency of collision of the aqueous droplets so that



Scheme 1. In-situ preparation of PS microcapsules via radiation induced interfacial redox reaction: (1) the preparation of W/O inverse emulsion; (2) the generation of benzoyloxy radicals by interfacial redox reaction, (2a) the elimination of hydroxyl radicals by isopropanol, (2b) the redox reaction between BPO and hydrated electron; (3) the formation of polymer microcapsules.

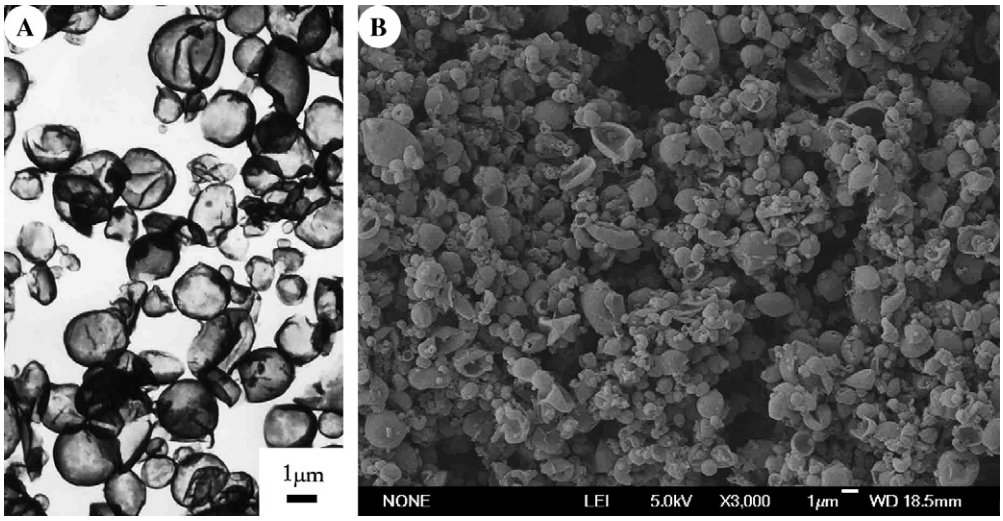


Fig. 2. The morphology of PS microcapsules initiated by BPO–e^-_{aq} in inverse emulsion observed by TEM (A) and FESEM (B): the microcapsules are multi-dispersed and most of them are irregular spheres or cracked.

there is enough time to form the polymer shell at the water–oil interface. In summary, the high viscosity of external phase enhanced the kinetic stability of W/O emulsion and this was beneficial to the fabrication of polymer hollow spheres.

3.3. The DMA–•OH initiation system

In the above study, the redox initiation couple of e^-_{aq} and BPO has been investigated. However, it should be noticed that the hydroxyl radical has the standard potential 2.7 V [48] and has the possibility to be introduced into a redox initiation couple as a strong oxidant. Here DMA was chosen as oil-soluble reductant to compose a redox couple with •OH radical (see Reactions (6) and (7)). It has been admitted that electron transfer is the most frequent mechanism of •OH induced oxidation of inorganic ions while hydrogen atom abstraction and hydroxyl radical addition are the most common types of reaction with organic compounds.

(6)

(7)

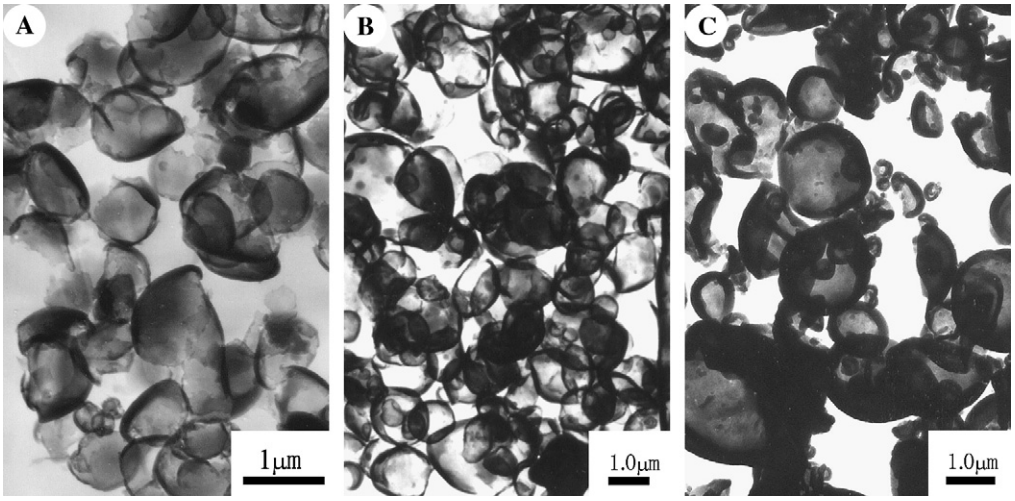


Fig. 3. TEM images of PS microcapsules prepared under different monomer contents: (A) 2.0 mL, (B) 4.0 mL, (C) 8.0 mL (wall thickness increases with the monomer content).

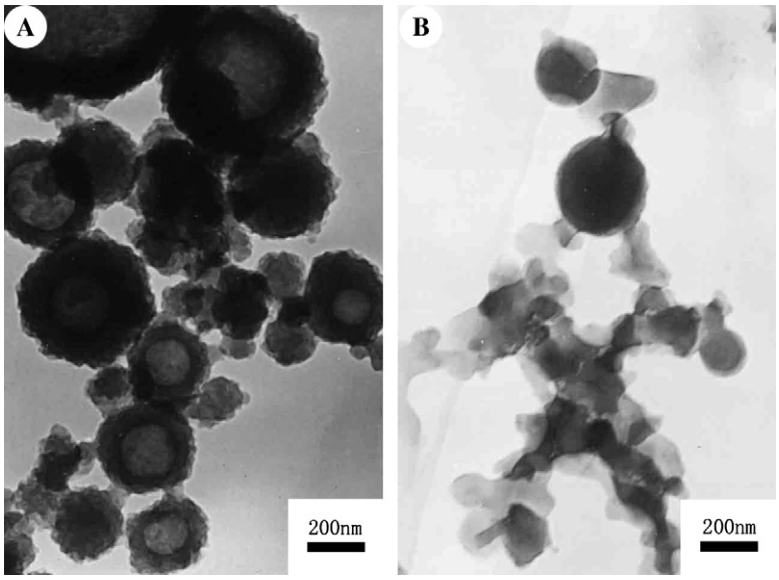


Fig. 4. TEM images of PS particles prepared in different viscous oil phases: (A) high viscosity silicon oil (500 cP/25 °C) and (B) kerosene.

As reported in the BPO/DMA redox couple, it has been suggested that the amine radical cation does not directly involve in initiating chain reaction and the polymerization is mostly initiated by the benzoyloxy radicals [49]. However, Sato et al. [50] have characterized that the aminomethyl radicals could be formed from the radical cation by loss of proton and proposed that these radicals can also initiate polymerization. Therefore, it's accepted that the aminoalkyl radicals are efficient initiators for free radical polymerization [51–54]. In radiation chemistry, the reaction rate of hydrogen atom abstraction is usually slower than that of electron transfer. The Reactions (6) and (7) may proceed at the same time. By transfer of an electron from carbon atom to the nitrogen atom, the amine radical cation turned into aminomethyl radical, which could act as polymerization initiator in the presence of styrene.

The reaction between DMA and hydroxyl radical was indirectly confirmed by the kinetic study (see Fig. 5). After the addition of DMA, the polymerization rate was remarkably slow and this was because the initiating reactivity of DMA radical was lesser than that of hydroxyl radical.

Fig. 6A shows the morphology of PS particles initiated by the redox system of DMA and hydroxyl radical. Hollow structure and solid spheres coexist. The kinetic study has shown that the reactivity of DMA radicals is less comparing with hydroxyl radicals. Hereby, the competition between the DMA radical and hydroxyl radical is obvious during the polymerization. Then the homogeneous nuclei cannot be avoided and solid spheres are obtained finally.

Fig. 6B shows the morphology of PS latex without DMA. The homogeneous solid sphere is according to expectation. The solid spheres were generated by two mechanisms. One, the solubilized monomer in aqueous phase was initiated by hydroxyl radical and became insoluble oligomers. The precipitated species became stabilized by adsorbing surfactants and on subsequent adsorption of monomers, polymerize (homogeneous nuclei). The other, the hydroxyl radical diffused to the water–oil interface to initiate polymerization and the phase separation of polymer from the non-solvent kerosene occurred (sedimentation and aggregation). In the end, only solid PS spheres were observed in the emulsion.

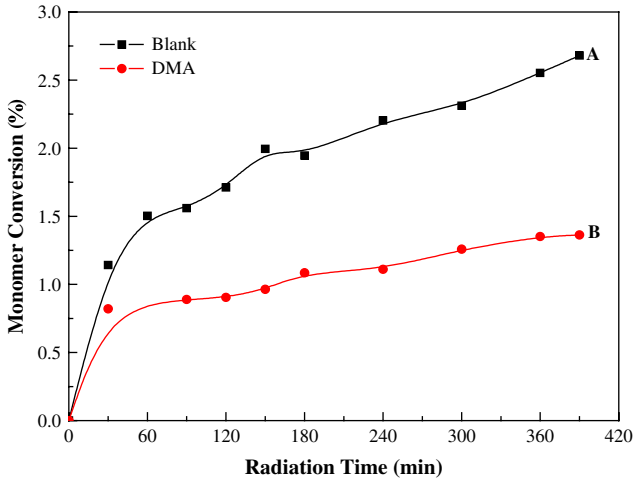


Fig. 5. Monomer conversion vs. radiation time curves in DMA–•OH initiation system: comparing with the BPO–e^-_{aq}, the monomer conversion was obviously low. (For the recipes of curves A and B see Table 1.)

Fig. 6C shows the morphology of PS after adding the scavenger of hydroxyl radical. We have supposed that the initiation was controlled by the redox reaction between DMA and hydroxyl radical. So if the oxidant was consumed by acetone, which turned into an inert radical, the interfacial redox reaction cannot keep going. And the nuclei locus cannot be held at the water–oil interface. Finally, homogeneous solid spheres were prepared instead of hollow spheres.

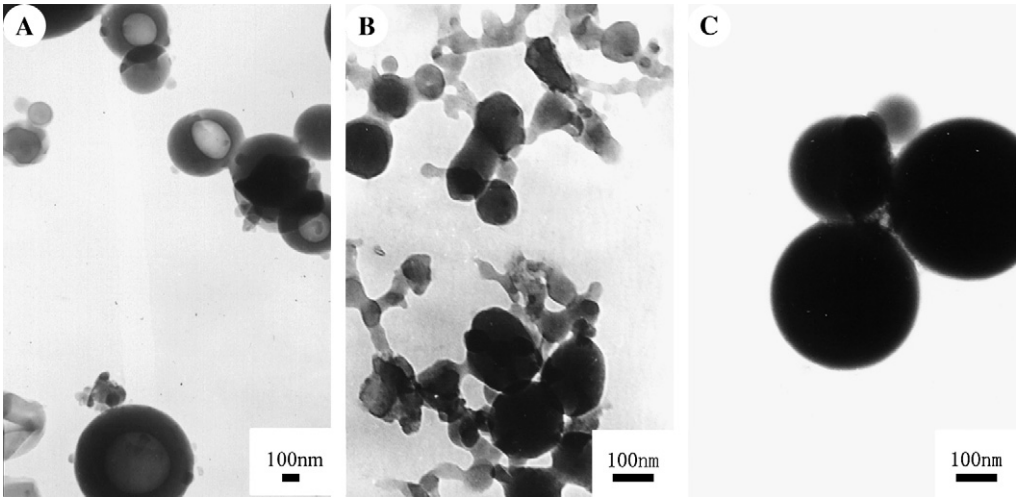


Fig. 6. The morphology of PS latex prepared in W/O emulsion observed by TEM: (A) adding DMA in oil phase; (B) without DMA; (C) with isopropanol in aqueous phase.

4. Conclusion

In conclusion, a novel synthetic strategy to prepare PS microcapsules via ^{60}Co γ-ray radiation interfacial redox reaction at the water–oil interface in an inverse emulsion has been demonstrated. It is based on the radiation chemistry of water and the strong redox capability of free radicals. From the kinetic curves of monomer conversion, two redox systems (BPO–e^-_{aq} and DMA–$^{\bullet}$OH) have been investigated and the validity of the polymerization mechanism has been successfully verified. In the BPO–e^-_{aq} initiating system, the viscosity of oil phase was important for the morphology of PS spheres, and the shell thickness can be controlled by the monomer content in the oil phase. In the DMA–$^{\bullet}$OH system, the aminomethyl radical was confirmed to be an efficient initiator. Because of the multiplicity in choosing oil-soluble monomers and substances being dissolved in the aqueous phase, this approach revealed interests in encapsulation of bioactive materials or drugs.

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