

Miniemulsion Cross-linking: A Convenient Route to Hollow Polymeric Nanocapsule with a Liquid Core*

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Abstract Miniemulsion stabilized by poly(2-(dimethylamino) ethyl methacrylate)-block-poly(butyl methacrylate) (PDMAEMA-*b*-PBMA) diblock copolymers has been used as liquid templates for the synthesis of polymer nanocapsules *via* quaternization cross-linking of PDMAEMA segments of the copolymer by 1,2-bis(2-iodoethoxy)ethane (BIEE) crosslinkers. PDMAEMA-*b*-PBMA here as a stabilizer in miniemulsion with different molecular weights led to a size variation in diameters of nanocapsules, demonstrating the capsules have potential design capability of this technique. The solution behavior of the capsules has been also investigated in this paper.

Keywords: Cross-linking; Miniemulsion; Nanocapsule; Block copolymer.

INTRODUCTION

Polymeric nanocapsules have received considerable attention over past decades because of their wide applications, such as in drug/gene delivery, carrier and cosmetics^[1–4]. The various synthetic methods to design nanocapsules can be categorized into three different approaches: sacrificial template approaches, self-assembly, and emulsion (miniemulsion)-based techniques. Increased emphasis has been placed on developing more robust synthetic pathways enabling one to tune the particle size and the shell thickness as well as incorporate different functionalities.

The sacrificial template pathway to produce hollow polymeric nanoparticles has gained significant interest^[5–7]. The sacrificing hard core could be silica, gold nanoparticles (nanocrystals) or polymer particles due to their properties of solvent dissolution or thermolysis behavior. However, the theses *via* sacrificial templates are often tedious. Polymeric micelles are often obtained by self-assembly of amphiphilic copolymers. These micelles can subsequently undergo a cross-linking reaction to result in polymeric nanocapsules (nanocage)^[8–12]. For instance, Armes and co-workers^[13] developed 1,2-bis(2-iodoethoxy)ethane (BIEE) quaternization technique for fixing the core-shell structure of the micelles in water or alcohol. Sugihara *et al.*^[14] prepared cross-linked micellar capsules using BIEE for cross-linking the dimethylamine(ethylmethacrylate) (PDMAEMA) segments of the PEO-*b*-PDMA-*b*-PMPC triblock copolymers micelles. After BIEE quaternization, the cross-linked micelles in alcohol/water were dialyzed against pure water. Consequently, the nanocapsules were obtained by the swelling of PMPC segments of micelles in pure water. However, micelles usually have small

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cores which prevented the shell cross-linking techniques from being used for the preparation of capsules with large cavity. This limitation has been addressed by using emulsion/(inverse) miniemulsion based techniques, which offers a number of advantages over previous synthesis techniques including, 1) liquid core can be easily removed; 2) the size of the cavity can be readily varied in a range between 50 nm to 500 nm; 3) efficient encapsulation of functional species into the liquid core is possible. For instance, Luo and co-workers^[15] prepared nanocapsules using miniemulsion interfacially confined reversible addition fragmentation chain transfer (RAFT) polymerization. The amphiphilic RAFT agent molecules (ammonolyzed styrene/maleic acid adduct of phenyldithioacetate, denoted SMA-RAFT) and surface active oligoradicals (primary radical added several monomers) could anchor on the interface of miniemulsion droplets confining the most polymerization period in the interface of miniemulsion to form the shell structure. Wang and co-workers^[16, 17] developed a miniemulsion periphery polymerization (MEPP) technique for the preparation of the metal coordination polymer nanoshells. Stenzel and coworkers^[18, 19] reported the synthesis of polymeric nanocapsules using the inverse miniemulsion periphery (RAFT) polymerization (IMEPP) process. However, one of the drawbacks of these miniemulsion polymerization techniques is that the formation of unwanted solid is difficult to avoid^[20]. To overcome these limitations, we describe a novel technology that addresses those above-described challenges.

Herein, for the nanocapsule synthesis we combine miniemulsion periphery polymerization (MEPP) with BIEE induced micelle shell cross-linking techniques. Amphiphilic block copolymers of poly(*N,N*-dimethylaminoethyl methacrylate)-block-poly(butyl methacrylate) (PDMAEMA-*b*-PBMA) were prepared by RAFT and used as stabilizers for the preparation of miniemulsion. Upon BIEE quaternization of the tertiary amine groups on the DMAEMA blocks, the miniemulsion droplets were stabilized. The removal of the liquid core (toluene and hexadecane) produced nanocapsules directly with large hollow space.

EXPERIMENTAL

Materials

N,N-dimethylaminoethyl methacrylate (DMAEMA) (99%, ACROS) and butyl methacrylate (BMA) (99%, Sigma-Aldrich) were passed through alumina column to remove inhibitor before use. 1,2-Bis-(2-iodoethoxy) ethane (BIEE, Sigma-Aldrich), hexadecane (HD, Alfa Aesar), toluene (anhydrous; Sigma-Aldrich), *N,N*-dimethylformamide (DMF; reagent grade; Sigma-Aldrich) and tetrahydrofuran (THF; HPLC grade; Sigma-Aldrich) were purchased from Aldrich and used without further purification. 4-Cyanopentanoic acid dithiobenzoate (4-CPDB) was synthesized according to the literature method^[21].

Characterization

¹H-NMR (500 MHz) spectra were recorded using a Bruker 400 UltraShield spectrometer at ambient temperature (about 20 °C) in CDCl₃ or DMSO-*d*₆. The number average weight (*M_n*) and polydispersity index (PDI) was determined using size exclusion chromatography (SEC) equipped with a LC1120 HPLC pump (polymer laboratories, UK), a differential refractive index (DRI) detector (Shodex, RI-101), a 5.0 μm bead-sized guard column (50 mm × φ7.5 mm), and two PLgel 5.0 μm MIXED-C columns (300 mm × φ7.5 mm) in series (Polymer laboratories, UK). Tetrahydrofuran (THF) with trimethylamine (TEA) (5%) and 2,6-di-*tert*-butyl-4-methylphenol (0.2 g) was used as the eluent at a flow rate of 1 mL·min⁻¹ at ambient temperature, and toluene was used as a flow marker. The SEC system was calibrated with poly(methyl methacrylate) (ranging from 1020 to 1944000 g·mol⁻¹). Dynamic light scattering (DLS) was performed at room temperature on a Brookhaven's light scattering system (BI-200SM Laser Light Scattering Goniometer) with a BI-APD detector using a He-Ne laser at 633 nm. The detector angle was set at 90°. For DLS samples preparation, the non-cross-linked miniemulsion (0.2 g) was diluted into methanol or water (10 g) directly for DLS measurements. For the cross-linked miniemulsion, DLS samples were prepared by adding 0.2 g of miniemulsion into a dialysis tube (Standard Regenerated Cellulose (RC) Membrane (Dry Spectra/Por®, MWCO 12–14 kD, SpectrumLabs)). The tube was equilibrated with the solvent (4 × 500 mL) for 48 h. The resulting samples were diluted into 10 g solvent for DLS analysis. The thermogravimetric analysis (TGA) curves were recorded using a TGA instrument (TGA-2900

model) thermo-balanced in a temperature range of 25–550 °C at a heating rate of 10 K·min⁻¹ under nitrogen. A transmission electron microscope (TEM; Philips CM-10) with an acceleration voltage of 80 kV was used to take low magnification TEM images. TEM samples were prepared by dropping miniemulsion of water dilution or methanol dilution onto a carbon-coated copper grid under ambient conditions. The specimens were observed with negative staining by using uranyl acetate. Scanning electron microscopy (SEM) was obtained by using an FEI QUANTA 200F Gemini FEGSEM apparatus. SEM specimens were coated with a gold/platinum alloy thin film prior to observation.

Synthesis of Poly(*N,N*-(dimethylamino) ethylmethacrylate) Chain Transfer Agent (PDMAEMA-CTA)

The PDMAEMA-CTA with a targeted polymerization degree of 150 were prepared as the following description: DMAEMA (16.88 g, 0.107 mol), 4-CPDB (0.20 g, 0.72 mmol) and AIBN (0.02 g, 0.12 mmol), were dissolved in 2 mL of toluene. The mixture was purged with nitrogen for 30 min and then heated at 60 °C for 24 h. The reaction was quenched by rapid cooling with ice-water. After the removal of toluene using a rotary evaporator, the mixture was dissolved in THF and precipitated in hexane. The polymer was filtered and dried under vacuum at room temperature overnight yielding final product of 10.63 g (62%). The molecular weight ($M_n = 12100 \text{ g} \cdot \text{mol}^{-1}$) and molecular weight distribution (PDI = 1.12) of the product were determined by SEC with PMMA standards.

Synthesis of Poly(2-(dimethylamino) ethyl methacrylate)-block-poly(butyl methacrylate) (PDMAEMA-*b*-PBMA)

BMA (1.97 g, 1.39×10^{-2} mol), PDMAEMA₉₀-CTA (5.0 g, 0.35 mmol) and AIBN (0.013 g, 7.92×10^{-2} mmol) were dissolved in toluene (12 mL). The mixture was purged with nitrogen for 30 min, and then heated at 60 °C for 24 h. The polymerization was quenched by cooling the reaction vessel in water-ice bath. The resulting polymers were dissolved in THF and precipitated in hexane. The cycle of the dissolution and precipitation were repeated three times. The polymer was filtered and dried under vacuum at room temperature yielding final product of 3.95 g (79%). The molecular weight ($M_n = 16400 \text{ g} \cdot \text{mol}^{-1}$) and molecular weight distribution (PDI = 1.23) were determined by SEC with PMMA standards.

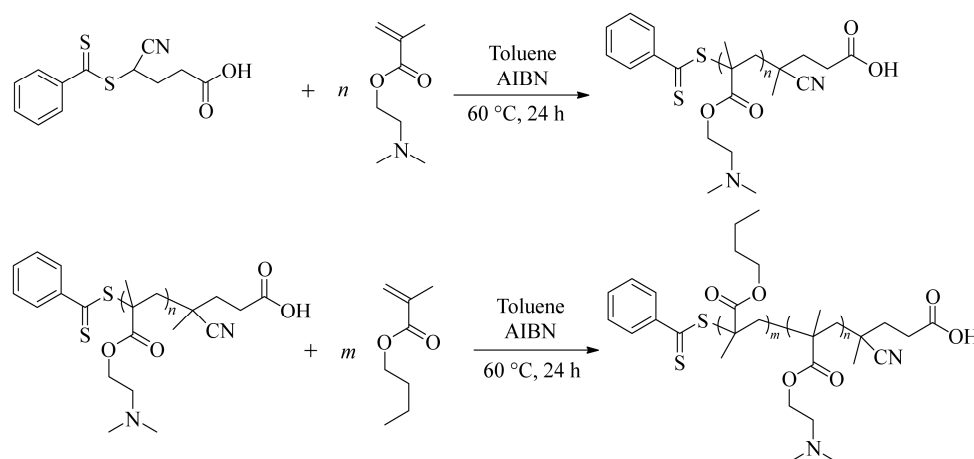
Preparation of Cross-linked Miniemulsion

In a typical experiment, 20 mg of hexadecane (HD) and 50 mg of PDMAEMA₉₀-*b*-PBMA₂₈ were first dissolved in toluene (0.5 g). This organic phase was then added to distilled water (9.43 g) under vigorous stirring. After 45 min of pre-emulsification by magnetic stirring, the resulting mixture was sonicated at the power of 120 W (Bandelin Sonopuls HD2200) for 15 min in water-ice bath. Upon the sonication, opaque solution with white colour was obtained, suggesting the formation of oil droplets. The resultant miniemulsion was stable for 4 days. To prepare cross-linked miniemulsion, 1,2-bis-(2-iodoethoxy) ethane (BIEE) (0.10 g) was added to above miniemulsion to induce quaternization reaction of PDMAEMA. The mixture was then stirred for 120 h at room temperature.

RESULTS AND DISCUSSION

4-Cyanopentanoic acid dithiobenzoate (4-CPDB) was used as a reversible addition fragmentation chain transfer agent (CTA) for the controlled polymerization of *N,N*-dimethylaminoethyl methacrylate (DMAEMA). The resulting well-defined PDMAEMA-CTA was subsequently used as macro-chain transfer agent for further polymerization of BMA, leading to the formation of diblock copolymers of PDMAEMA-*b*-PBMA (Scheme 1). The molecular weight, polydispersity and repeat units of PDMAEMA-CTA and PDMAEMA-*b*-PBMA were characterized by size exclusion chromatography (SEC) and ¹H-NMR (Fig. 1 and Fig. 2), respectively. The molecular weights, molecular weight distributions and the monomer conversion of the resultant polymers are summarized in Table 1. As shown in Table 1, the chain extension is evidenced by the molecular weight increase from homopolymers to block copolymers. In addition, both PDMAEMA-CTA and block copolymers have narrow PDIs (< 1.23), suggesting well defined block copolymers were obtained as designed. Comparison of the

apparent molecular weight of the polymer with the molecular weight obtained from NMR determination by comparison the signal of the end group with that of the repeat units, showed that the SEC analysis provided underestimated molecular weight values. It is because PMMA standards were used for the homopolymers and block copolymers molecular weight calculation. Such use might not be truly appropriate. Moreover, the theoretical molecular weight of PDMAEMA₁₉₀-CTA could not be obtained by NMR analysis due to the indiscernible weak signal of the end group. These block copolymers were used as stabilizers in miniemulsion preparation for the synthesis of nanocapsules *via* cross-linking reaction.



Scheme 1 Synthetic scheme for the preparation of PDMAEMA-CTA and PDMAEMA-*b*-PBMA block copolymers

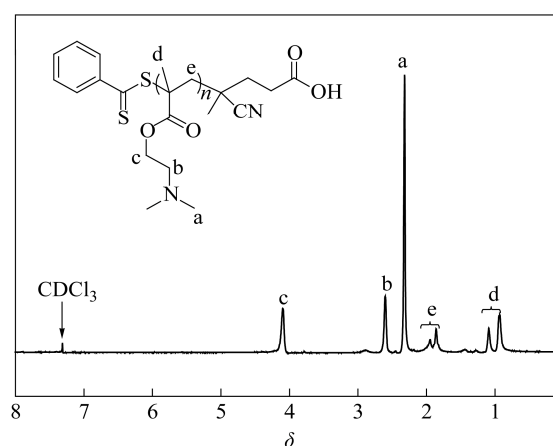


Fig. 1 Typical ¹H-NMR spectrum of poly(*N,N*-(dimethylamino) ethylmethacrylate) macro chain transfer agent (PDMAEMA₉₀-CTA) in CDCl₃

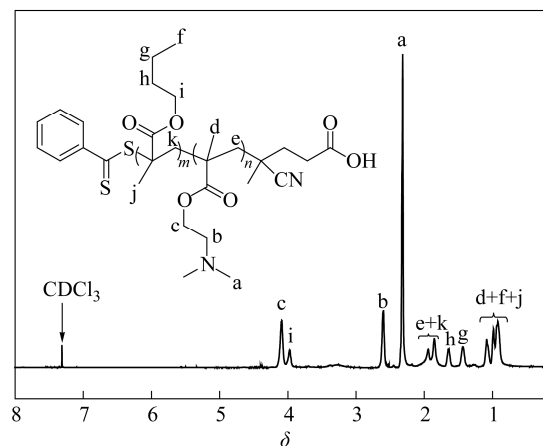


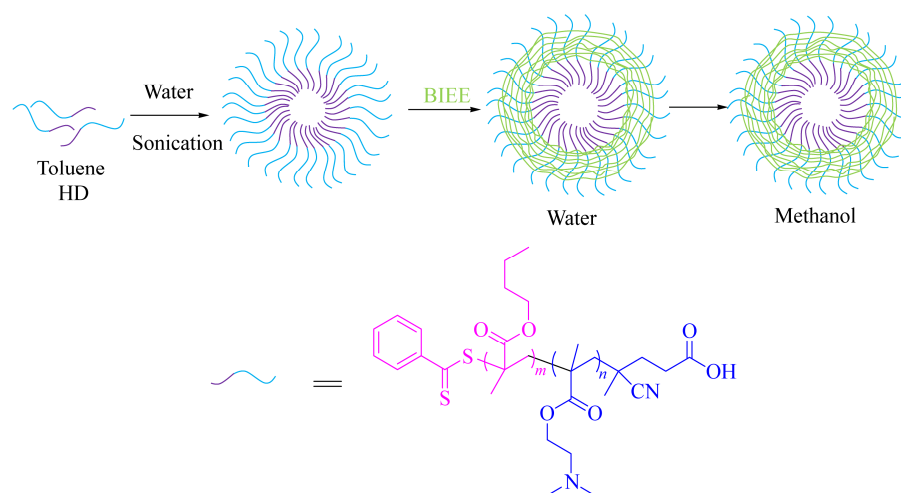
Fig. 2 Typical ¹H-NMR spectrum of poly(2-(dimethylamino) ethyl methacrylate)-block-poly(butyl methacrylate) (PDMAEMA₉₀-*b*-PBMA₂₈) in CDCl₃

Table 1. Characteristics of the PDMAEMA-CTA and PDMAEMA-*b*-PBMA block copolymers

Polymer ^a	M_{theo} (g·mol ⁻¹)	M_n^c (g·mol ⁻¹)	PDI ^c
PDMAEMA ₁₉₀ -CTA	—	23600	1.11
PDMAEMA ₁₉₀ - <i>b</i> -PBMA ₃₉	—	30500	1.15
PDMAEMA ₉₀ -CTA	14478 ^b	12100	1.12
PDMAEMA ₉₀ - <i>b</i> -PBMA ₂₈	18454	16400	1.23

^a The subscript number denotes the degree of polymerization (DP); ^b Determined by comparison of the intensity of the end group (phenyl group protons) resonating at $\delta = 7.4$ to 8.0 to the intensity of the resonance from $\delta = 2.2$ to 2.4 from PDMAEMA in the ¹H-NMR spectra; ^c Molecular weight and polydispersities (PDI) of polymers were determined by SEC. The SEC system was calibrated with poly(methyl methacrylate) PMMA standards.

As shown in Scheme 2, the miniemulsion was prepared from a mixture of water, PDMAEMA₉₀-*b*-PBMA₂₈, toluene and hexadecane (94.3:0.5:5:0.2 *W/W*), in which the block copolymers acted as stabilizers. The resulting miniemulsion is stable for at least 3 days, but phase separation with toluene floating on the top layer of the solution was observed in the fourth day. This suggests PDMAEMA₉₀-*b*-PBMA₂₈ miniemulsion can be prepared, but have a limited stability. To cross-link the miniemulsion (Scheme 2), BIEE (1 equivalent amount of BIEE with respect to tertiary amine group in the PDMAEMA block) was added to a freshly prepared miniemulsion for quaternization reaction. We noticed that the BIEE initially dispersed as yellow droplets in the miniemulsion due to its relatively low solubility in water. After stirring at room temperature overnight, these yellow droplets disappeared probably because BIEE diffused into the oil phase (toluene and HD). In contrast to colloidal instability of PDMAEMA-*b*-PBMA miniemulsion, the addition of BIEE substantially improved the stability of the colloids and no phase separation was observed for one month. This colloidal behavior suggests that the attempted cross-linking reaction occurred. In addition, the quaternization may also lead to an increase in the hydrophilic character of PDMAEMA chains and enhance the stability of cross-linked structures^[22]. We also introduced 5 amount of BIEE with respect to tertiary amine group of PDMAEMA segments into the freshly prepared miniemulsions under same experiment conditions. The cross-linking process was monitored by DLS. Interestingly, 5 equivalent amount of BIEE did not contribute to speed up the reaction rate. Four days reaction was necessary to fix the particles structure. It may be caused by a slow diffusion process of BIEE from water phase into miniemulsion oil phase to quaternize the PDMAEMA segments of the stabilizers at the oil/water interface.



Scheme 2 Schematic illustration for the preparation of cross-linked miniemulsion *via* BIEE quaternization of stabilizers (PDMAEMA-*b*-PBMA)

After four days of reaction, BIEE cross-linked miniemulsion (ME-BIEE) was transferred to pure water or other organic solvents *via* a dialysis process. The diameters and polydispersities of the ME-BIEE in these solvents were characterized by using DLS. The results are present in Fig. 3. As shown in Fig. 3(a), the diameter and polydispersity of the ME-BIEE in water are 235 nm and 0.144, respectively. These values keep constant over time. In a contrast, the DLS measurement indicated that the diameter of a diluted uncross-linked miniemulsion in water increased from 190 nm to 300 nm within 30 min. This comparison suggested that the cross-linking reaction occurred, which stabilized the colloids of the miniemulsion in water. The colloidal stability of the cross-linked miniemulsion was further confirmed by DLS experiments of the samples in methanol. No light scattering signal could be detected when non-cross-linked miniemulsion colloids were diluted in methanol as expected, while ME-BIEE shows a diameter of 218 nm with PDI of 1.45 (Fig 3b), which is comparable to their size in water. DMF is a good solvent for both quaternized PDMAEMA and PBMA blocks,

in which the colloids are expected to swell. As shown in Fig. 3(c), comparing with those in water and methanol, a substantial increase in size of the cross-linked colloids (~ 280 nm) are indeed observed. This increase is accompanied by a polydispersity index increasing from 0.144 in water to 0.280 in DMF. Such swelling behavior of ME-BIEE in DMF is instrumental in designing nanocapsules for controlled releasing applications. It is interesting to note that the ME-BIEE precipitated during the dialysis process against THF. Although THF is a good solvent for both PDMAEMA and PBMA, quaternized PDMAEMA is insoluble in THF and responsible for the observed precipitation. This result implies that the cross-linking reaction was indeed achieved *via* the quaternization between BIEE and tertiary amine group.

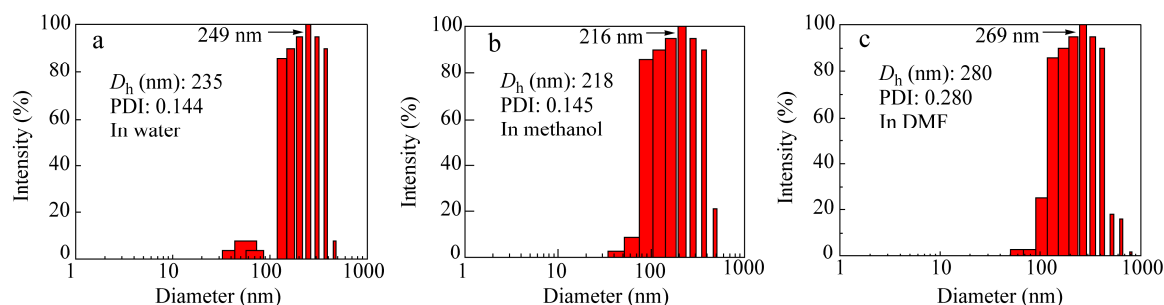


Fig. 3 Diameter and polydispersities of BIEE cross-linked miniemulsion (ME-BIEE) in water (a), methanol (b) and DMF (c)

Miniemulsion formulation: PDMAEMA₉₀-*b*-PBMA₂₈ 0.05 g, toluene 0.5 g, HD 20 mg and DI water 9.43 g. 1 equivalent of BIEE with respect to tertiary amine group in the PDMAEMA block was added to the above miniemulsion. The reaction was kept at room temperature for 4 days, followed by a dialyzing process to transfer the cross-linked miniemulsion to various solvents.

To prove it, $^1\text{H-NMR}$ analysis was performed. NMR samples were prepared by firstly dialyzing the cross-linked miniemulsion against $(\text{CH}_3)_2\text{SO}$ to remove water, toluene and unreacted BIEE. An aliquot of the DMSO was then subsequently mixed with 2 equivalents of cross-linked emulsion $(\text{CH}_3)_2\text{SO}$ solution for the NMR characterization. As shown in Fig. 4(a), the NMR spectrum of the cross-linked miniemulsion shows signals at

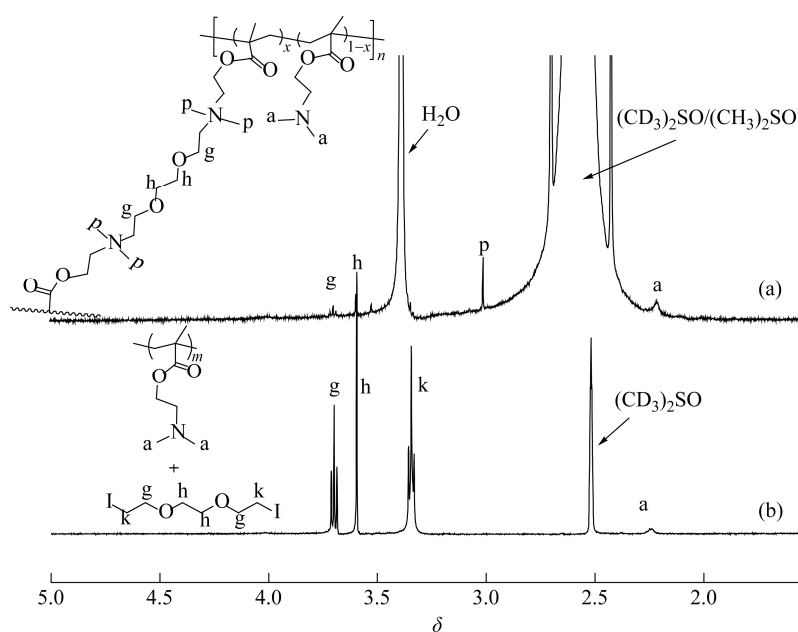


Fig. 4 $^1\text{H-NMR}$ spectra of BIEE and PDMAEMA mixture in $(\text{CD}_3)_2\text{SO}$: after cross-linking (a) and without cross-linking (b)

$\delta = 3.7$ (peak g) and $\delta = 3.6$ (peak h) corresponding to the linking fragment between the PDMAEMA chains. In addition, the signal at $\delta = 3.0$ (peak p) (Fig. 4a), which is absent in the NMR spectrum of the BIEE and PDMAEMA mixture without cross-linking (Fig. 4b, note: the NMR sample was prepared by dissolving a small amount of PDMAEMA-*b*-PBMA copolymers in BIEE followed by the addition of $(\text{CD}_3)_2\text{SO}$ deuterated solvent. The sample was then measured by NMR immediately.) This new signal corresponds to the methyl group attached to the quaternized nitrogen in PDMAEMA residue, confirming the occurrence of quaternization between BIEE and tertiary amine groups of PDMAEMA. However, the actual degree of shell cross-linking is somewhat low; a significant proportion of the cross-linking agent probably remains unreacted due to the reaction only occurred at the interface of the oil/water droplets.

Thermogravimetric analyses (TGA) of the solid samples prepared from cross-linked and non-cross-linked miniemulsions were also performed and used as an evidence to prove the occurrence of quaternization cross-linking reaction. As illustrated in Fig. 5, a lower thermal degradation temperature for BIEE cross-linked samples is observed that is caused by the easy loss of anion and ammonium groups of quaternized PDMAEMA (Hofmann elimination)^[23]. All the above results including DLS, NMR and TGA suggest that the quaternization cross-linking occurred in ME-BIEE *via* quaternization leading to enhanced colloid stability of the capsules.

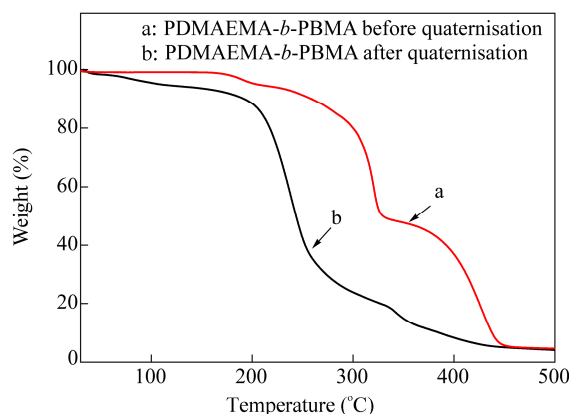


Fig. 5 TGA thermograms of PDMAEMA₉₀-*b*-PBMA₂₈ block copolymer before (a) and after (b) quaternization with BIEE

Figure 6 displays the TEM and SEM images for the cross-linked particles (Figs. 6a, 6b, 6c and 6d) and non-cross-linked sample (Fig. 6e). The samples were prepared from water (Figs. 6a and 6c) and methanol (Figs. 6b and 6e) solutions using PDMAEMA₉₀-*b*-PBMA₂₈ as stabilizers respectively. TEM samples were stained by using uranyl acetate. As shown in Figs. 6(a) and 6(b), spherical particles are observed. In contrast, no particles are observed in Fig. 6(e). If cross-linking was unsuccessful, no particles should exist in pure methanol (Fig. 6e), since toluene is a methanol-miscible solvent and miniemulsion dissociation would inevitably occur. This observation suggests that the particles remain in methanol (Fig. 6b) owing to their relatively high degree of cross-linking. The size of the particles estimated from the images is in the range between 50 nm and 140 nm in diameters, which is much smaller than the diameter of 218 nm determined by DLS (Fig. 3b), suggesting the large degree of shrinkage of the capsules upon drying of the samples^[24]. Probably because of this large degree of shrinkage, the TEM images do not show typical nanocapsules morphologies, such as dimples or ring-link structure. Nevertheless, as shown in the SEM image, the particle clusters with the deformed or indented morphologies due to the collapse of the shells were observed (Fig. 6c), which provides evidence supporting the formation of hollow particles.

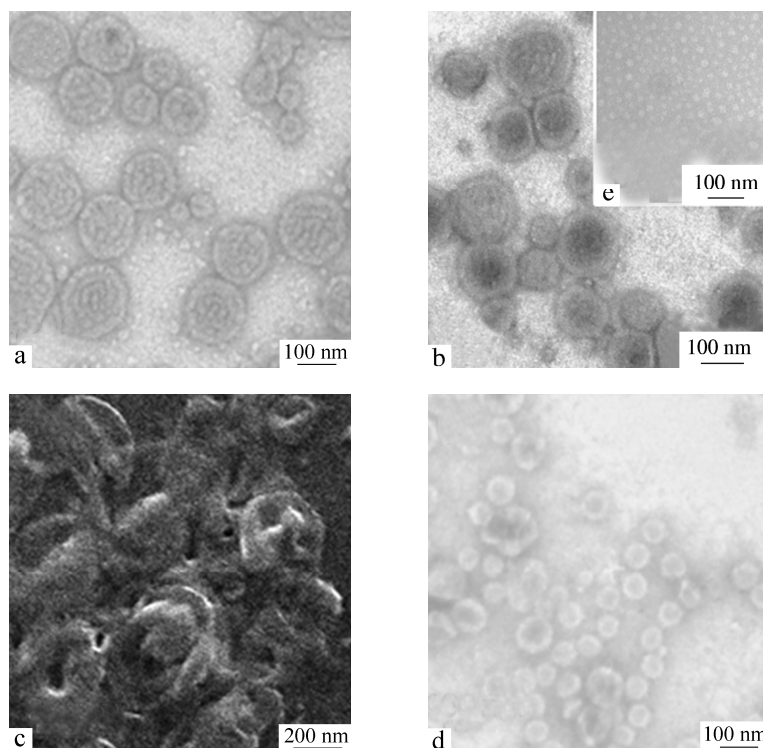


Fig. 6 TEM images of cross-linked miniemulsion prepared using PDMAEMA₉₀-*b*-PBMA₂₈ as stabilizers from water (a), and from methanol (b), and SEM image prepared from water (c); TEM image of cross-linked miniemulsion prepared using PDMAEMA₁₉₀-*b*-PBMA₃₉ as stabilizers from methanol (d) and TEM image of non-cross-linked miniemulsion prepared from methanol using PDMAEMA₉₀-*b*-PBMA₂₈ as stabilizers (e)

We also prepared cross-linked miniemulsion using the same technique, but replacing PDMAEMA₉₀-*b*-PBMA₂₈ with the same amount of PDMAEMA₁₉₀-*b*-PBMA₃₉. The success of the cross-linking reaction was proven by the DLS experiment, which showed a hydrodynamic diameter of about 185 nm in water. The TEM image (Fig. 6d) of the sample prepared from methanol solution confirms the formation of the capsules but with much smaller size as compared to those in Figs. 6(a), 6(b) and 6(c). This experiment indicated that the cavity size can be readily varied *via* the miniemulsion cross-linking technique. Moreover, it can be anticipated that, using designed amphiphilic block copolymers with varied block ratios, the swelling property and functionality of the cross-linked miniemulsion nanocapsules can be rationally designed.

CONCLUSIONS

Polymeric nanocapsules were prepared from PDMAEMA-*b*-PBMA miniemulsion *via* BIEE quaternization cross-linking reaction. The particles size can be varied by using block copolymers with different molecular weight. The cross-linked capsules were able to swell in DMF due to its good solubility for both PBMA and partially quaternized PDMAEMA. This new technique of miniemulsion cross-linking is a desired complement to currently available nanocapsule synthesis techniques and will be potentially useful for the design and preparation of encapsulation and releasing nanomaterials.

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