# Versatile Fabrication of Nanocomposite Microcapsules with Controlled Shell Thickness and Low Permeability

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Ⓢ *Supporting Information*

ABSTRACT: Novel ethyl phenylacetate (EPA)-loaded nano-composite microcapsules with polyurea (PU) /poly (melamine formaldehyde) (PMF) shells were facilely and fabricated: by using silica nanoparticle-stabilized oil-in-water (o/w) emulsion template and subsequent interfacial reaction and in situ polymerization. SiO_2 nanoparticles absorbed at the interface between oil and water to stabilize the o/w emulsions. The oil droplets containing EPA, isophorone diisocyanate (IPDI) and tolylene 2,4-diisocyanate-terminated poly (propylene glycol) (PPG-TDI) were subsequently reacted with MF prepolymer (pre-MF) dissolved in water phases. The interfacial reaction between pre-MF and IPDI produced interior PU walls. Meanwhile, the in situ polymerization of pre-MF generated exterior PMF walls. It was found that these in/out double walls were compact together. The resulting capsules had spherical shapes and rough exterior surfaces, and could be easily isolated, dried, and redispersed in epoxy resins. The size of the produced microcapsules was dependent on the concentration of SiO_2 nanoparticles. The dynamic thermal gravimetric analysis (TGA) demonstrated that the capsules showed excellent thermal stability with little weight loss when exposed at 150 °C for 2 h. Interestingly, with a double PU/PMF shell, these capsules exhibited an extra-low permeability. Moreover, these microcapsules can also demonstrate exceelent magnetic responsiveness after introducing magnetic nanoparticles inside. We believe our microcapsules could be potential candidates in microcapsule engineering, self-healing composites, and drug-carrying systems.
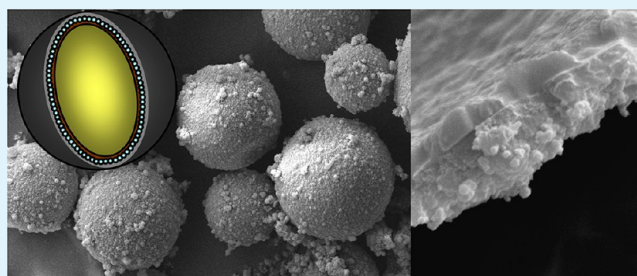
KEYWORDS: *nanocomposite microcapsules, Pickering emulsions, polyurea, poly (melamine formaldehyde), permeability*

1. INTRODUCTION

Microcapsules have attracted much attention, as they are efficient vehicles to deliver active ingredients in catalysis,[1] self-healing materials,[2] drugs,[3] and biorelated chemicals.[4−6] One of the most important characteristics of capsules is their permeability, which can be easily controlled through varying the shell thickness.[7] Generally, capsules can be made of either inorganic or organic compounds. Pure organic capsule allows for controllable permeability, whereas the inorganic capsule exhibits a high permeability to encapsulated compounds, but it would have outstanding mechanical properties. In addition, the inorganic components can also contribute to specific optical,[8] magnetic,[9] and catalytic properties.[1] Hence, hybrid capsules combining the properties both organic and inorganic components could be more promising in practical applications.

A wide variety of protocols of encapsulation are available in the literature, including solvent evaporation technique,[10] coacervation technique,[11] spray-drying method,[12] meltable disperse-phase encapsulation method,[13] and so on. The most versatile preparation of microcapsules would be layer-by-layer (LbL) assembly technique.[14] This method affords microcapsules with the control over their size, stability, loading, and release properties,[15] but some intrinsic disadvantages are unavoidable. First, as the polyelectrolyte multilayer capsule exhibits a high permeability to small molecules, there are considerable challenges in encapsulating and releasing low-molecular-weight molecules from LbL-engineered capsules.[16] Although a pathway to reduce the permeability could be conducted by depositing lipid coatings on the capsules, the lipids are normally unstable under different temperature situation.[17] On the other hand, the numerous processing steps and sacrifice of cores in LbL assembly would strongly limit the large-scale production of capsules.[18] Therefore, considerable efforts should be devoted to exploring an efficient approach that can fabricate capsules allowing the controlled loading and release of small guest molecules based on normal industrial devices.

Water-in-oil (W/O) or oil-in-water (O/W) emulsion templates can provide a facile approach to prepare small molecule-loaded microcapsules.[2,19−21] A double-walled polyurethane-poly (urea formaldehyde) (PU-PUF) microcapsule was recently developed templating from oil-in-water emulsions which were stabilized by ethylene-maleic anhydride copolymer.[21] However, the stabilization of an emulsion presents a challenge in microcapsule formation. Initial work focused on molecular surfactants, such as the sorbitol-based Span series,
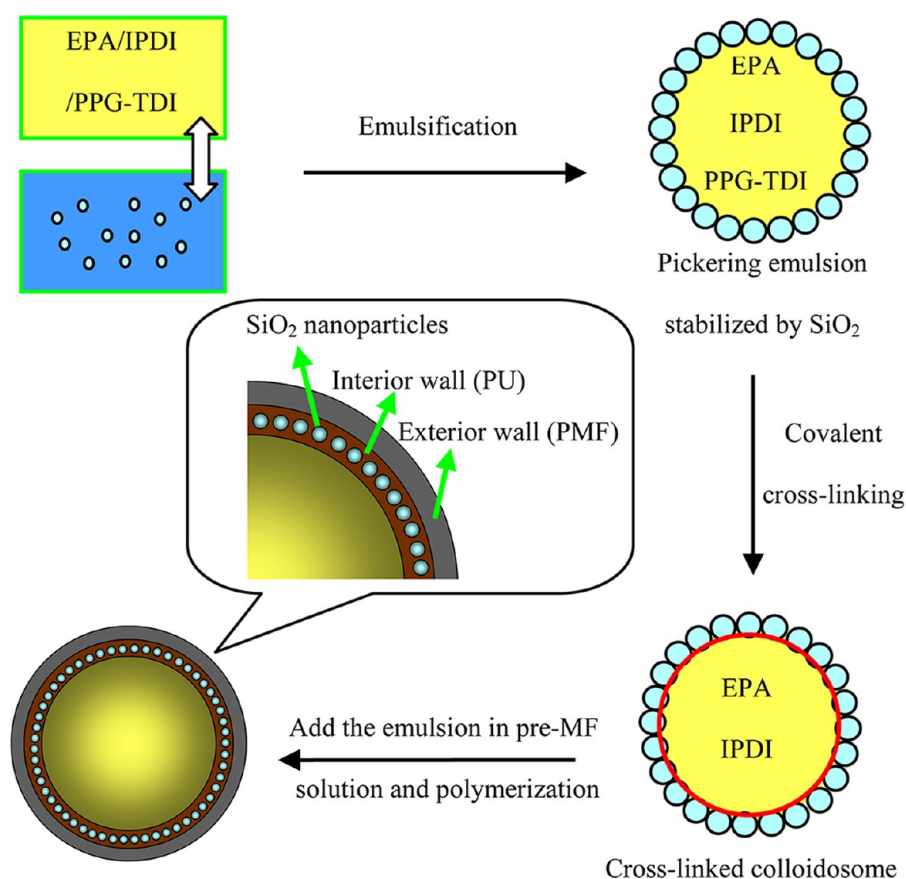
Figure 1. Schematic illustration of the preparation of EPA-loaded organic/inorganic hybrid microcapsules with PU/PMF double-walled shells by polymerization based on SiO$_2$ nanoparticle-stabilized O/W emulsions.

which were unable to provide sufficient stability to prevent the droplets from demulsification during the subsequent capsule shell formation.[20,21] To increase the stability, we adopt solid particles to stabilize the emulsion instead of using molecular surfactants, a so-called Pickering emulsion.[22] In Pickering emulsions, solid particles that are mostly inorganic nano-particles like silica,[23] Fe$_3$O$_4$,[24] laponite,[25] are wetted partially by oil and water, so that they become surface-active and preferentially locate or adsorb at the oil/water interface. Because of the nearly irreversible adsorption of colloid particles with higher attached energy at the oil/water interface, Pickering emulsions exhibit excellent droplet stabilization compared with the conventional molecular surfactant-stabilized emulsions.[26−31] Therefore, the Pickering emulsion templates that are remarkably stable against coalescence can protect the loading materials in the encapsulation process, further optimizing the loading capacity of the obtained capsules. At the same time, the inorganic nanoparticles that are used as Pickering stabilizers can endow the capsule with their own properties. Moreover, Pickering emulsion template technique is a powerful tool to prepare functional organic/inorganic hybrid microcapsules with a hierarchy micro/nanometer struc-tures.[32−38]

In this work, we demonstrate a simple and effective method for the fabrication of double-walled organic/inorganic hybrid microcapsules with controlled shell thickness and extra-low permeability via O/W Pickering emulsion templates. Partic-ularly, as shown in Figure 1, SiO$_2$ nanoparticle stabilized O/W Pickering emulsions were prepared, and the oil phase was composed of isophorone diisocyanate (IPDI), tolylene 2,4-

diisocyanate-terminated poly (propylene glycol) (PPG-TDI) and ethyl phenylacetate (EPA). EPA is a common reactive core material of the microcapsules for self-healing of epoxy resins. Compared with TDI, IPDI is less reactive with amines or alcoholic molecules.[20] A lightly cross-linked polyurethane network membrane was formed through the reaction between −NCO terminal group of the PPG-TDI chains and Si−OH on the surface of SiO$_2$ nanoparticles at the interface of the primary O/W emulsion droplets (see Figure 2C). These membranes make the templates being more stable, ensuring the core materials in different droplets without risk of agglomeration under stirring situation. The polymerization for the capsules includes two parts: one is the interfacial polymerization between IPDI in the inner phase and melamine formaldehyde prepolymer (pre-MF) in the water phase at high temperature to form a highly cross-linked polyurea (PU) shell to encapsulate the core materials; the other reaction is the in situ polymerization of pre-MF on the PU wall surface to generate the PMF wall. With the SiO$_2$ nanoparticles at the oil−water interface, the PU/PMF shell would be an organic/inorganic hybrid mixture. In this study, double-walled organic/inorganic hybrid microcapsules successfully encapsulated small molecules like EPA in a facile pathway, providing large scale applications in chemical encapsulation, storage, and release.

2. EXPERIMENTAL SECTION

2.1. Materials. EPA used as the core material was purchased from Sun Chemical Technology (Shanghai) Co. Ltd., China. The partially hydrophilic modified amorphous fumed silica (N20) acting as Pickering stabilizer was a kindly donated from Wacker Chemie
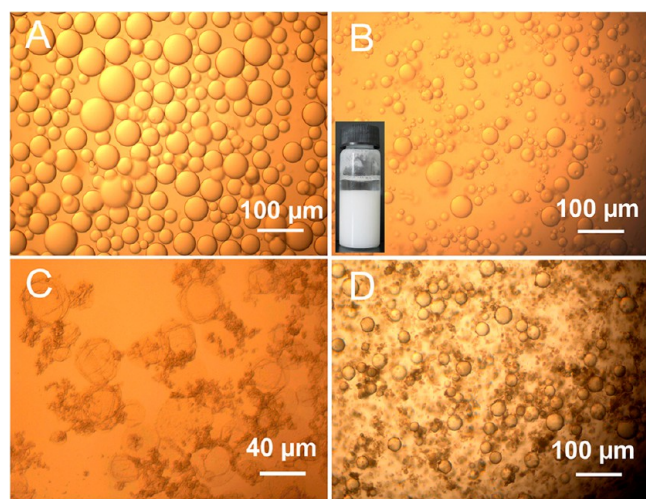
Figure 2. Optical microscopic images of O/W Pickering emulsions stabilized by SiO₂ nanoparticles (A) without PPG-TDI and (B) with PPG-TDI. (C) Dried state of emulsion B. (D) Optical microscopic image of microcapsules that were fabricated templating from emulsion B.

Table 1. Parameters of O/W Pickering Emulsion Templates for EPA-Loaded Microcapsules[a]

	water phase			oil phase			
sample	water (mL)	SiO₂ (wt %)	EPA (mL)	PPG-TDI (wt.%)	IPDI (g)	O/W volume ratio	droplet size (μm)
1	4	0.1	3.6	2.0	0.4	1:1	65 ± 25
2	4	0.5	3.6	2.0	0.4	1:1	44 ± 18
3	4	1.0	3.6	2.0	0.4	1:1	36 ± 10
4	4	1.5	3.6	2.0	0.4	1:1	34 ± 15
5	4	2.0	3.6	2.0	0.4	1:1	36 ± 17
6	4	1.0	3.6	0	0.4	1:1	72 ± 36
7	4	1.0	3.6	4.0	0.4	1:1	36 ± 16
8	4	1.0	3.6	8.0	0.4	1:1	35 ± 14
9	4	1.0	3.6	16.0	0.4	1:1	36 ± 18
10	4	1.0	4.0	2.0	0	1:1	35 ± 15
11	4	1.0	3.85	2.0	0.15	1:1	36 ± 17
12	4	1.0	3.7	2.0	0.3	1:1	34 ± 15
13	4	1.0	3.5	2.0	0.5	1:1	36 ± 16

[a]EPA belongs to the oil phase.

(Burghausen) whose primary particles are approximately spherical of diameter between 5 and 30 nm (see Figure S1 in the Supporting Information). IPDI and PPG-TDI (mean degree of polymerization is 34 according to the supplier) were purchased from Aldrich and used as received. Melamine and 37.0 wt % formaldehyde aqueous solution were obtained from Sinopharm Chemical Reagent Co. Ltd., China, and Guangdong Guanghua Chemical Factory Co. Ltd., China, respectively. Triethanolamine (TEA, Tianjin Fuyu Chemical Reagent Co. Ltd., China) and acetic acid (Jiangsu Qiangsheng Chemical Reagent Co. Ltd., China) were used to control the pH value of solutions. Polyvinyl alcohol (PVA) was supplied by Guangzhou Chemical Reagent Co., China. Diethylenetriamine (DETA) was used as received from Tianjin Fuchen Chemical Factory Co. Ltd., China. Expon CYD 128 (epoxy equivalent is 184−194 g/eq, viscosity at 25 °C is 11 000−14 000 mPa.s according to the supplier) was obtained from Sinopec Group. Other materials were analytical reagents and used as received. Water used in all experiments was purified with a resistivity higher than 18.0 MΩ cm by deionization and filtration with a Millipore purification apparatus.

2.2. Preparation of SiO₂ Nanoparticle-Stabilized Emulsions. Different Pickering emulsions were prepared as listed in Table 1. A typical emulsion of sample 4 was fabricated as follows. To ensure the droplet a standard sphere shape in the other aqueous solution, cross-linker PPG-TDI (0.08 g) was dissolved in 3.6 mL of EPA with 0.4 mL of IPDI. The reaction mixture solution was then mixed with 4.0 mL of 1.0 wt % SiO₂ nanoparticles aqueous disperse solution. Emulsification was performed by vigorous agitation of water and oil phases for 3 min using IKA Ultra Turrax T25 basic instrument at 12 000 rpm. The cross-linking reaction between PPG-TDI and SiO₂ would be conducted at room temperature for the next 20 min to form the lightly cross-linked polyurethane network membrane.

2.3. Synthesis of Pre-MF. The pre-MF was synthesized on the basis of the procedure reported by Zhang et al.:[39] 0.06 mol of melamine, 0.2 mol of formaldehyde, and 10 mL of distilled water were added to a 50 mL two-neck flask. Then, the mixture was adjusted pH 9.0−9.5 with TEA stirred at 70 °C until it became clearly transparent so that prepolymer of melamine and formaldehyde (pre-MF) solution was obtained. The detailed structures of pre-MF is presented in Figure S2 in the Supporting Information.

2.4. Fabrication of EPA-Loaded PU/PMF Hybrid Microcapsules. The above prepolymer solution was added to a 250 mL three-neck flask containing 66.7 mL of PVA aqueous solution, and the pH value was adjusted to 3.8−4.1 with acetic acid. Then, the solution was heated to 50 °C at a heating rate of 10 °C/min. PVA was used to

protect the colloids. Afterward, Pickering emulsion was dropped into the above solution, and the reaction was conducted for 4 h. The products were washed with water to remove the PMF particles suspended in water, and air-dried at room temperature for 24 h. Subsequently, microcapsules were collected. The dried state of these microcapsules came to be a white powder (see Figure S3 in the Supporting Information). Loading capacity of capsules toward substrate and its losses in the process of encapsulation were determined by acetone extraction as follows: First, a Pickering emulsion which was containing W_0 g of EPA was used to fabricate EPA-loaded microcapsules as the above process. All of the obtained microcapsules were weighted as W_1 g, and then the microcapsules were ground with a pestle in a mortar at room temperature. After enough grind, acetone was added into the mortar to wash the leaked EPA. This mixture suspension was centrifuged at 12000 rpm for 3 min, and then the EPA acetone supernatant was decanted from the tubes. This process was repeated for three times. The sediment was dried in a vacuum oven at 70 °C. After cooling in a vacuum desiccator, this sediment was weighed (W_2). Eventually, the loading capacity of these capsules toward the substrate (η_1) and its losses in the process of encapsulation (η_2) were calculated by:

$$\eta_1 = [(W_1 - W_2)/W_1] \times 100\%$$

$$\eta_2 = 1 - [(W_2 - W_1)/W_0] \times 100\%$$

The loading capacity of these capsules toward the substrate (η_1) turned out to be ca. 93 wt %, and its losses in the process of encapsulation (η_2) came to be ca. 4 wt %.

2.5. Embedding the Microcapsules into Epoxy Resins. The microcapsule embedded epoxy resin was prepared by mixing epoxy and DETA with a ratio of 100:12. A vacuum was applied to the resin/hardener mixture for 10 min before adding the EPA-loaded capsules. After capsules were added, a vacuum was reapplied for 5 min. The final mixture was poured into the appropriate mold and cured for 24 h at room temperature followed by 24 h at 35 °C. Part of the samples were frozen in liquid nitrogen and fractured with a razor blade to obtain a smooth fracture plane for scanning electron microscope (SEM) observation.

2.6. Preparation of Magnetic Microcapsules. The magnetic microcapsules were fabricated using Fe₃O₄ nanoparticles as Pickering emulsion stabilizers instead of SiO₂ nanoparticles. The preparation of Fe₃O₄ nanoparticles was as follows:[35] A mixture of 1.01 g of FeCl₃·6H₂O and 0.37 g of FeCl₂·4H₂O dissolved in 10 mL of water was added to a 50 mL three-necked round-bottom flask preimmersed in an oil bath at 343 K and the reaction was allowed to proceed for 2 h after quickly adding dropwise 4 mL 16.5% NH₃·H₂O under vigorous

stirring. The resulting black precipitate was washed and centrifugalized with anhydrous ethanol tree times, then dried at room temperature. Finally, the Fe_3O_4 nanoparticle powder was obtained. The detail data of Fe_3O_4 nanoparticles can be achieved in the Figure S4 in the Supporting Information, including SEM images, sizes distribution, XRD pattern, and zeta potential. The size of Fe_3O_4 nanoparticles appeared to be 142 nm, and the zeta potential came to −22.9 mV.

2.7. Characterizations. Pickering emulsions were observed with a microscope (Carl Zeiss, Germany). The average diameter of the SiO_2 particles stabilized emulsions and the microcapsules were determined with a dynamic light scattering instrument (Malvern mastersizer 2000). Fourier transform infrared (FTIR) spectra of the samples were tested on a German Vector-33 IR instrument, which was recorded using potassium bromide (KBr) pellets for solid samples. The full content of the capsules and thermal stability were determined using thermal gravimetric analysis (TGA). TGA was performed using a NETZSCH TG 209F3 instrument under a nitrogen atmosphere and a heating rate of 10 °C min^{-1} from 30 to 700 °C. For isothermal experiments, the temperature was ramped from 30 to 150 °C (10 °C min^{-1}) and subsequently held at 150 °C for 2 h. Then, the samples were heated from 150 to 700 °C (10 °C min^{-1}). Morphology of the capsules was analyzed using a Zeiss EVO 18 scanning electron microscope (SEM) equipped with a field emission electron gun and energy dispersive spectrometer (EDS). The thickness of shells and walls were calculated by SEM, and each measurement was tested for ten times to improve the accuracy. The direct air-dried or freezing-dried samples were sputter-coated with gold prior to the measurements.

3. RESULTS AND DISCUSSION

Nano/microparticle interfacial self-assembly to form Pickering emulsion droplets has been well documented.[40−42] Herein, liquid oil-loaded microcapsules with inorganic/polymer composite shells were facilely and high effectively fabricated by interfacial and in situ polymerization based on SiO_2 nanoparticle-stabilized Pickering emulsions. The Pickering emulsion templates that are remarkably stable against coalescence can protect the loading materials in the encapsulation process commendably, optimizing the loading capacity of the obtained capsules. Moreover, the inorganic nanoparticles which are used as Pickering stabilizers can endow the capsule with some specific properties. Pre-MF, as it is known, is a water-soluble oligomer.[43] It can self-cross-link to form a PMF resin in an acid solution. With amino and hydroxymethyl groups, pre-MF in the water phase can react with IPDI which is dissolved in the oil phase through an interfacial polymerization to form PU. So we utilized the characteristic of this powerful polymerizability of pre-MF to fabricate liquid oil-loaded microcapsules with inorganic/polymer composite shells. The emulsion templates are illustrated in Figure 2. The EPA, IPDI, and cross-linker PPG-TDI mixture solution was rapidly emulsified in water in the presence of hydrophilic SiO_2 nanoparticles to produce O/W Pickering emulsions by shear agitation, the nanoparticles were then assembled at the liquid−liquid interfaces. Figure 2A shows an O/W Pickering emulsion stabilized by pure SiO_2 nanoparticles without PPG-TDI. Droplets appeared as a typical Pickering emulsion with spherical shape, and the average size devoted to ca. 80 μm. After adding PPG-TDI, membranes with slight cross-linked networks were formed by the reaction between −NCO groups of the PPG-TDI chains and Si−OH groups on the surface of silica nanoparticles (Figure 2C). The membranes dragged the nanoparticles tighter, resulting in much smaller droplets with ca. 36 μm diameter (see Figure 2B). With the nanoparticles assembled at the interface and the cross-linked membranes, these oil droplets are extremely stable in the

procedure of shell-forming to keep the objective microcapsules with clear spherical identity and little size variation (Figure 2D). This indicates that the O/W Pickering emulsions are suitable templates to fabricate inorganic/polymer hybrid microcapsules.

In practical applications, capsules with different size are strongly needed under varied situations. Based on the above discussion, the microcapsules have little size variation compared with the corresponding Pickering emulsion templates. Therefore, we can control the capsule sizes by means of adjusting the emulsion template sizes. Additionaly, the sizes of Pickering emulsion droplets can be tuned by adjusting the volume ratio of oil to water or the concentration of nanoparticles.[42] Both of these two ways have similar effect.[23] Here we investigated the effect of the concentration of SiO_2 nanoparticles on the droplet sizes. From samples 1−4 in Table 1 and Figure 3A, increasing
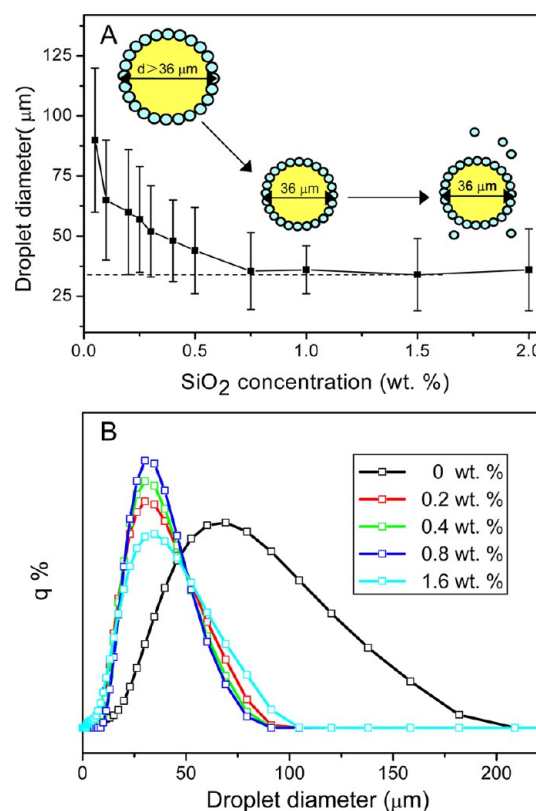

Figure 3. (A) Relationship between SiO_2 concentration and mean droplet diameter for Pickering emulsions. (B) Sistribution graphs of Pickering emulsions with different PPG-TDI contents.

the SiO_2 nanoparticle concentration decreases the mean droplet diameter, and then reaches a plateau about 36 μm. Afterward, higher SiO_2 nanoparticle concentrations do not lead to any further reduction in droplet size but merely excess SiO_2 nanoparticles in solution. This observation is consistent with the previous report.[42] Therefore, polymer/inorganic microcapsules with different sizes can be expediently produced based on the corresponding concentration of SiO_2 nanoparticles to stabilize Pickering emulsion templates.

The cross-linker PPG-TDI also had an obvious effect on the droplet sizes. As is mentioned before, a slight cross-linked network membrane could be formed by reaction of PPG-TDI and SiO_2, resulting in tighter nanoparticle packing and much smaller droplets. However, increasing or decreasing the dosage of PPG-TDI had no effect on the droplet size (Figure 3B). It

can be explained that once the cross-linked network was formed, SiO$_2$ nanoparticle could be dragged into an effectively stable and compact packing, which shows no relation to the PPG-TDI added.

When the EPA-loaded hybrid microcapsules were obtained by the interfacial polymerization between pre-MF and IPDI and the in situ polymerization of pre-MF, they were observed by optical microscopy (Figure 2D) and SEM (Figure 4). Images A
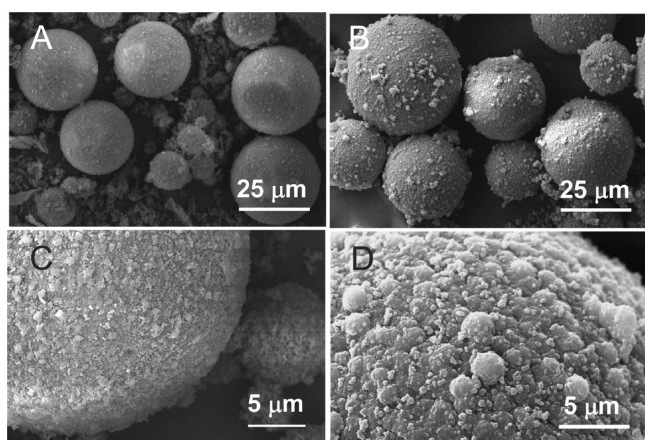

Figure 4. SEM images of EPA-loaded hybrid microcapsules with PU/ PMF double-walled shells: sample 10 in Table 1 observed in (A) low amplification and (C) high amplification; sample 13 in Table 1 observed in (B) low amplification and (D) high amplification.

and C in Figure 4 are SEM images of sample 10 in Table 1 observed in low and high magnification, respectively. Images B and D in Figure 4 are SEM images of sample 13 observed in low and high magnification, respectively. The difference between these two samples is that sample 13 has a higher concentration of IPDI in the oil phase. Although the capsules were under high vacuum in the SEM chamber, all of them stay in their uniform spherical shape without any encapsulated materials leaking, indicating that they have relatively rigid shells. Furthermore, all of the capsules separate with each other and

show rough exterior shell walls. It indicates that the concentration of IPDI has no effect on the capsule surface morphology. Unlike the amino resin walled microcapsules templating from chemical surfactant-stabilized emulsions, which have honeycomb surfaces with many submicropores, these Pickering type template microcapsules possess more compact surfaces with many nano-/sub-microsized mastoids.[2,44] It can be explained that molecular surfactant-stabilized emulsion polymerization is only driven by pre-MF's in situ polymerization. However, multiple interactions are involved in Pickering emulsion polymerization. Besides the in situ polymerization, the electrostatic attraction between the negative charges on the SiO$_2$ nanoparticle surfaces and the positive charges of pre-MF also lead large contributions. Moreover, the capsule shell can germinate based on the nanoparticle seeds.

Ruptured microcapsules were observed by SEM to characterize the morphology of capsule shells. SEM images of shells of microcapsules which were fabricated by different concentrations of IPDI are shown in Figure 5A−D. All of the shells have a compact and double-walled structure. There is clear separation between PU wall and PMF wall (Figure 5D). Moreover, some NaOH-treated PU/PMF microcapsules which were ruptured by a razor blade were observed by SEM (see Figure S5 in the Supporting Information), and the results indicated that the shell of the microcapsules consisted a double-walled structure. With the increasing of IPDI concentration, the thickness of both the inner and the outer walls increases (Figure 6). It indicates that the shell thickness can be tuned by adjusting the concentration of IPDI in the oil phase. Figure 5E shows the EDS result of the double-walled shell. The spectrum shows the silicon peak at 1.75 keV apart from the oxygen peak at 0.5 keV, the nitrogen peak at 0.4 keV and the carbon peak at 0.2 keV. It is well-known that the peak of silicon comes from SiO$_2$ nanoparticles, and the apparent peaks of C, N and O can be attributed to the PU and PMF walls. So the EDS results indicate that the shell of the capsule presents to be an organic/ inorganic hybrid structure. The EDS of the capsule shell after HF aqueous solution treatment turns to be a same spectrum
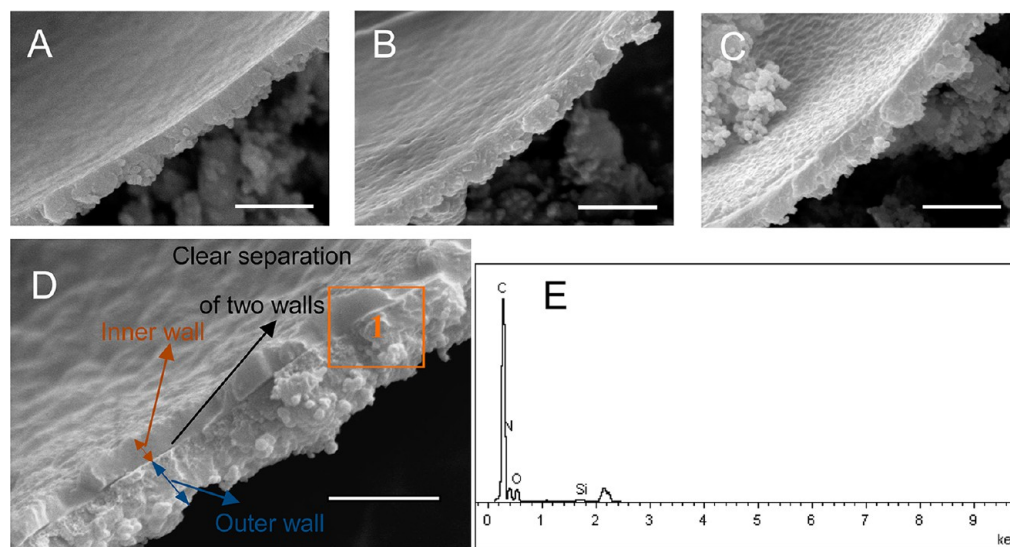

Figure 5. Different microcapsules were ruptured by razor blades. Then use SEM to test the shells of these ruptured microcapsules: (A) sample 10 capsule shell, (B) sample 11 capsule shell, (C) sample 12 capsule shell, (D) sample 13 capsule shell. (E) EDS spectrum of the microcapsule shell area 1 in D. All scale bars are 2 μm.
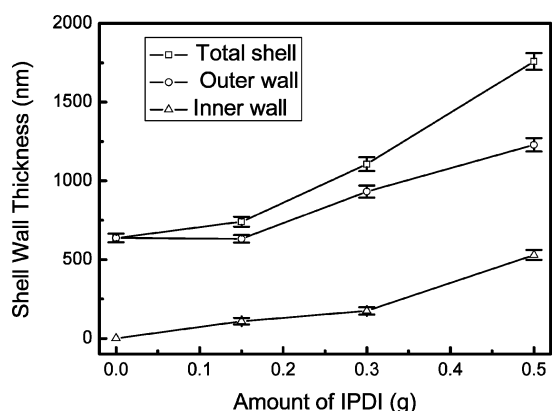
Figure 6. Average thicknesses of PU walls, PMF walls, and total shells as a function of the dosage of IPDI added to the oil phase.

containing Si, C, N, and O peaks, illustrating that the SiO_2 nanoparticles are completely enveloped in the PU/PMF shell.

The FTIR spectra of the shells and capsules are shown in Figure 7. The PMF wall exhibits broad stretching vibration
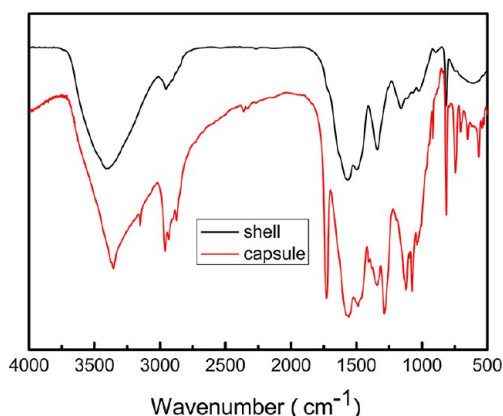

Figure 7. FTIR spectra of the capsule shell and EPA-loaded microcapsules.

peaks of N−H and O−H at about 3360 cm^{-1}, stretching of C−N and C=N at 1366−1556 cm^{-1}, and stretching of the triazine ring at 814 cm^{-1}. The stretch of NH−CO at 1601 cm^{-1} confirms the existence of the PU wall. The EPA-loaded capsule also performs obvious absorbing peak at 1736 cm^{-1}, representing the C=O groups. The absence of stretching of −NCO at 2200−2280 cm^{-1} indicates that there are no IPDI and PPG-TDI residue in the core liquids. Typical strong absorption peaks at 1029 cm^{-1} and 1156 cm^{-1} indicate the existence of silicon−oxygen (−Si-O-) groups. The FTIR spectra of the EPA-loaded microcapsules and their shells without EPA oils manifest that the organic/inorganic shells of PMF/PU with SiO_2 are generated and no free IPDI and PPG-TDI exist in the core liquids.

The mechanism of this novel structure formation can be traced to the shell formation process. First, the PPG-TDI reacts with the Si−OH on the surface of SiO_2 nanoparticles, anchoring the SiO_2 nanoparticles at the oil−water interface. Then, an interfacial polymerization happens between IPDI in the oil phase and pre-MF in the aqueous phase. These two monomers meet each other at the oil−water interface where was the location of the SiO_2 nanoparticles. Some low molecular weight PU polymers deposit on the surface of SiO_2

nanoparticles. With the proceeding of the polymerization, a PU shell that contains SiO_2 nanoparticles is formed. There are many −NH$_2$ and −OH groups on the surface of PU wall. Then, these groups react to pre-MF, anchoring the pre-MF molecules on the PU surface. The residual pre-MF molecules in the water phase polymerize on the seed of the pre-MF modified PU wall, resulting in a compact PMF wall. As the MF reaction proceeding, the rough exterior is produced as colloidal MF particles that self-cross-link in the water phase coalesces depositing along the interface. These PU/PMF shell microcapsules with a rough exterior surface can be dispersed in epoxy resins well without any aggregation (Figure 8A). And the
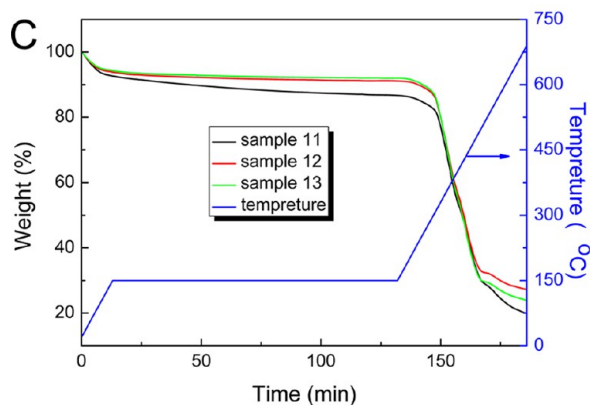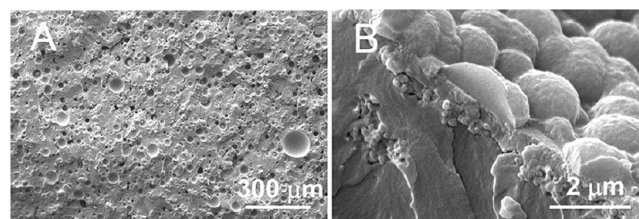

Figure 8. SEM images of a fracture surface of epoxy resins containing EPA-loaded capsules of 10 wt % observed in (A) low amplification and (B) high amplification. (C) Representative isothermal TGA curves for EPA-loaded PU/PMF capsules plotted versus the temperature profile (30 to 150 °C at 10 °C min^{-1}, held at 150 °C for 2 h, and then heated from 150−700 at 10 °C min^{-1}). The capsules in above experiments were samples 11, 12, and 13, respectively.

contact surface between capsules and epoxy resins can be neglected (Figure 8B). The encapsulated material in these capsules is EPA, which is a good solvent for epoxy resins. And these capsules can be well dispersed in epoxy resins. Therefore, these EPA-loaded microcapsules with excellent compatibility with epoxy resins can perform a potential application in solvent-promoted self-healing composite system.[21,45] If we change the oil phase, like replacing it by some pesticides, or degerming agent, these capsules can protect these drugs, leading to broad applications in drug-carrying systems. The addition of pre-MF is far more excess, and the speed of the reaction between IPDI and pre-MF is faster than the in situ polymerization of pre-MF. Increasing the concentration of IPDI leads to the increase of PU wall thickness deservedly. Just as Figure 5 shows, this highly cross-linked PU wall is compact. So pre-MF cannot penetrate into it to form a PU/PMF hybrid wall. The organic component of inner wall can be described as totally PU. Interestingly, increasing the concentration of IPDI leads to an increasing of the thickness of outer PMF wall. It may be explained that increasing the concentration of IPDI

leads to a thicker PU wall, resulting in a broader PU wall surface. The broader PU wall surface possessed more $-NH_2$ and $-OH$ groups, leading to a thicker PMF wall.

As microcontainers of reactive liquid ingredients, the permeability of microcapsules must be low enough to prevent encapsulated materials from leaking. In this work, the permeability of EPA-loaded microcapsules was determined by a dynamic TGA experiment which processed an isothermal protocol in which the temperature was ramped from room temperature to 150 °C and then held constant at 150 °C for 2 h. As shown in Figure 8C, during the 2 h isotherm, the double-walled capsules lost little weight. Although other EPA-loaded single wall capsules lost almost all of their EPA when they were heated in 150 °C.[44] The TGA experiment also indicates that the EPA loading capacity is about 80 wt %. The dramatic improvement in thermal stability can be contributed to the function of PU and SiO_2 nanoparticles. The reaction between IPDI and pre-MF have a tendency to form a compact PU wall because of the Si−OH groups and negative charges on the SiO_2 surfaces. As we knew, PU is a resin of excellent thermal stability. With a compact PU wall encapsulating the EPA core liquid, these capsules lose little active materials until they are exposed to a high enough temperature that can initiate PU thermal degradation. Therefore, compared with the capsules that are prepared by LbL assembly technique,[14,16,17] these microcapsules fabricated via Pickering emulsion templates can load only small molecules, but also have extra-low permeability to efficiently protect the encapsulated materials from leaking.

Microcapsules with some specific properties would have much broader application in many fields. And the versatility can be contributed by the inorganic component in these organic/inorganic microcapsules. For example, magnetic microcapsules can be fabricated by using Fe_3O_4 nanoparticles to replace the SiO_2 nanoparticles (Figure 9). The magnetic microcapsules
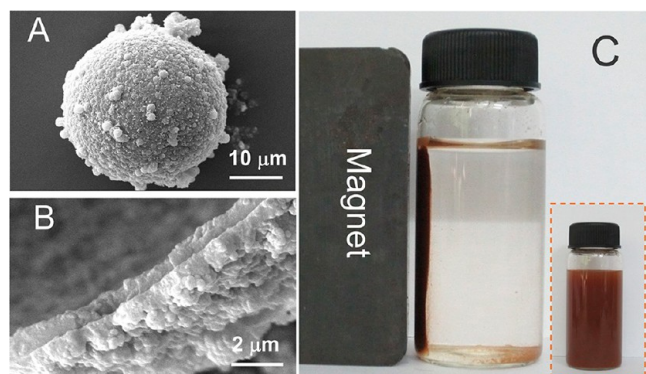

Figure 9. SEM images of (A) magnetic microcapsules, (b) the double-walled shell of one of the ruptured magnetic microcapsules. (C) Photos of the microcapsules in water under an external magnetic field and the inset in (C) shows microcapsules in the water without an external magnetic field.

have a similar surface morphology. And the double-walled structure also appears in the shell. Figure 9C shows microcapsules in water under an external magnetic field. These microcapsules exhibited a clear magnetic response. The magnetic microcapsules can be readily moved and collected using an external magnet.

4. CONCLUSIONS

EPA-loaded organic/inorganic hybrid microcapsules with PU/PMF double-walled shells were prepared by assembly of SiO_2 nanoparticles at the interface of O/W emulsions followed by in situ polymerization of pre-MF and interfacial polymerization between pre-MF and IPDI. Small molecules can be successfully encapsulated in the capsules. The PU/PMF double walled, organic/inorganic hybrid shell structure gives the capsule characteristics of rough exterior surface, an excellent thermal and disperse stability in epoxy resins. The mean diameter of microcapsules can be controlled by adjusting the concentration of SiO_2 nanoparticles. And the thickness of capsule shells is also tunable by varying the IPDI dosage. Moreover, the magnetic double-walled microcapsules can also be developed. Because of these advantages, we hope our hybrid microcapsules can bring up promising applications as guest-molecule carriers.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Characterization of SiO_2, Fe_3O_4, and melamine formaldehyde prepolymer (pre-MF); photograph of the dried microcapsule;s and SEM image of the microcapsule treated by NaOH. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Poe, S. L.; lija, M. K.; McQuade, D. T. *J. Am. Chem. Soc.* **2007**, *129*, 9216−9221.
(2) White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. *Nature* **2001**, *409*, 794−797.
(3) Städler, B.; Price, A. D.; Chandrawati, R.; Hosta-Rigau, L.; Zelikin, A. N.; Caruso, F. *Nanoscale* **2009**, *1*, 68−73.
(4) Chen, T. Y.; Du, B. Y.; Fan, Z. Q. *Langmuir* **2012**, *28*, 11225−11231.
(5) Volodkin, D. V.; Larionova, N. I.; Sukhorukov, G. B. *Biomacromolecules* **2004**, *5*, 1962−1972.
(6) Kim, J.; Lim, H. J.; Hwang, Y. K.; Woo, H.; Kim, J. W.; Char, K. *Langmuir* **2012**, *28*, 11899−11905.
(7) Shchukin, D. G.; Sukhorukov, G. B.; Möhwald, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4472−4475.
(8) Costanzo, P. J.; Beyer, F. L. *Chem. Mater.* **2007**, *19*, 6168−6173.
(9) Yuan, S. M.; Li, J. X.; Yang, L. T.; Su, L. W.; Liu, L.; Zhou, Z. *ACS Appl. Mater. Interfaces* **2011**, *3*, 705−709.
(10) Kim, K. S.; Park, S. J. *Colloids Surf., B* **2012**, *92*, 240−245.
(11) Saihi, D.; Vroman, I.; Giraud, S.; Bourbigot, S. *React. Funct. Polym.* **2005**, *64*, 127−138.
(12) Shi, X. Y.; Tan, T. W. *Biomaterials* **2002**, *23*, 4469−4473.
(13) El-Gibaly, I.; Abdel-Ghaffar, S. K. *Int. J. Pharm.* **2005**, *294*, 33−51.

2501

dx.doi.org/10.1021/am302963d | *ACS Appl. Mater. Interfaces* 2013, 5, 2495−2502

(14) Caruso, F.; Caruso, R. A.; Möhwald, H. *Science* **1998**, *282*, 1111−1114.

(15) Katagiri, K.; Koumoto, K.; Iseya, S.; Sakai, M.; Matsuda, A.; Caruso, F. *Chem. Mater.* **2009**, *21*, 195−197.

(16) Luo, G. F.; Xu, X. D.; Zhang, J.; Yang, J.; Gong, Y. H.; Lei, Q.; Jia, H. Z.; Li, C.; Zhuo, R. X.; Zhang, X. Z. *ACS Appl. Mater. Interfaces* **2012**, *4*, 5317−5324.

(17) Moya, S.; Donath, E.; Sukhorukov, G. B.; Auch, M.; Baumler, H.; Lichtenfeld, H.; Möhwald, H. *Macromolecules* **2000**, *33*, 4538−4544.

(18) Volodkin, D. V.; Delcea, M.; Möhwald, H.; Skirtach, A. G. *ACS Appl. Mater. Interfaces* **2009**, *1* (8), 1705−1710.

(19) Nakato, T.; Ueda, H.; Hashimoto, S.; Terao, R.; Kameyama, M.; Mouri, E. *ACS Appl. Mater. Interfaces* **2012**, *4*, 4338−4347.

(20) McIlroy, D. A.; Blaiszik, B. J.; Caruso, M. M.; White, S. R.; Moore, J. S.; Sottos, N. R. *Macromolecules* **2010**, *43*, 1855−1859.

(21) Caruso, M. M.; Blaiszik, B. J.; Jin, H. H.; Schelkopf, S. R.; Stradley, D. S.; Sottos, N. R.; White, S. R.; Moore, J. S. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1195−1199.

(22) Pickering, S. U. *J. Chem. Soc.* **1907**, *91*, 2001−2021.

(23) Binks, B. P.; Dyab, A. K. F.; Fletcher, P. D. I. *Phys. Chem. Chem. Phys.* **2007**, *9*, 6391−6397.

(24) Zhou, J.; Wang, L. J.; Qiao, X. Y.; Binks, B. P.; Sun, K. *J. Colloid Interface Sci.* **2012**, *367*, 213−224.

(25) Garcia, P. C.; Whitby, C. P. *Soft Matter* **2012**, *8*, 1609−1615.

(26) Chen, T.; Colver, P. J.; Bon, S. A. F. *Adv. Mater.* **2007**, *19*, 2286−2289.

(27) Nie, Z. H.; Park, J. I.; Li, W.; Bon, S. A. F.; Kumacheva, E. *J. Am. Chem. Soc.* **2008**, *130*, 16508−16509.

(28) Bon, S. A. F.; Chen, T. *Langmuir* **2007**, *23*, 9527−9530.

(29) Niu, Z. W.; He, J. B.; Russell, T. P.; Wang, Q. *Angew. Chem., Int. Ed.* **2010**, *49*, 10052−10066.

(30) Kim, J. W.; Nieves, A. F.; Dan, N.; Utada, Marquez, A. S. M.; Weitz, D. A. *Nano Lett.* **2007**, *7*, 2876−2880.

(31) Thompson, K. L.; Armes, S. P.; Howse, J. R.; Ebbens, S.; Ahmad, I.; Zaidi, J. H.; York, D. W.; Burdis, J. A. *Macromolecules* **2010**, *43*, 10466−10474.

(32) Li, Z. F.; Wei, X. L.; Ngai, T. *Chem. Commun.* **2011**, *47*, 331−333.

(33) Li, J.; Hitchcock, A. P.; Stöver, H. D. H. *Langmuir* **2010**, *26*, 17926−17935.

(34) Gao, Q. X.; Wang, C. Y.; Liu, H. X.; Chen, Y. H.; Tong, Z. *Polym. Chem.* **2010**, *1*, 75−77.

(35) Teixeira, R. F. A.; McKenzie, H. S.; Boyd, A. A.; Bon, S. A. F. *Macromolecules* **2011**, *44*, 7415−7422.

(36) Wei, Z. J.; Wang, C. Y.; Zou, S. W.; Liu, H.; Tong, Z. *Polymer* **2012**, *53*, 1229−1235.

(37) Liu, H.; Wang, C. Y.; Zou, S. W.; Wei, Z. J.; Tong, Z. *Langmuir* **2012**, *28*, 11017−11024.

(38) Wei, Z. J.; Yang, Y.; Yang, R.; Wang, C. Y. *Green Chem.* **2012**, *14*, 3230−3237.

(39) Meng, L. M.; Yuan, Y. C.; Rong, M. Z.; Zhang, M. Q. *J. Mater. Chem.* **2010**, *20*, 6030−6038.

(40) Aveyard, R.; Binks, B. P.; Clint, J. H. *Adv. Colloid Interface Sci.* **2003**, *100−102*, 503−546.

(41) Zeng, C.; Bissig, H.; Dinsmore, A. D. *Solid State Commun.* **2006**, *139*, 547−556.

(42) Ning, Y.; Wang, C. Y.; Ngai, T.; Yang, Y.; Tong, Z. *RSC Adv.* **2012**, *2*, 5510−5512.

(43) He, X. D.; Ge, X. W.; Wang, M. Z.; Zhang, Z. C. *Polymer* **2005**, *46*, 7598−7604.

(44) Blaiszik, B. J.; Caruso, M. M.; McIlroy, D. A.; Moore, J. S.; White, S. R.; Sottos, N. R. *Polymer* **2009**, *50*, 990−997.

(45) Caruso, M. M.; Delafuente, D. A.; Ho, V.; Sottos, N. R.; Moore, J. S.; White, S. R. *Macromolecules* **2007**, *40*, 8830−8832.