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Production of micron-sized hollow microspheres by suspension polymerization of St-DEGDA (diethylene glycol diacrylate) with petroleum ether (90−120 °C)

Qi Liu, Chi Huang, Shi Luo, Zonghui Liu*, Bailing Liu*

Department of Polymer Chemistry and Physics, Chengdu Institute of Organic Chemistry, The Graduate School of CAS,
Chinese Academy of Sciences, Chengdu 610041, PR China

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Abstract

Suspension polymerization for the droplets of the mixture with monomers, solvent, initiator in water phase with a dispersant PVA was carried out. During the polymerization the molecular weight increasing resulted in the phase separation in the droplets, and a hollow structure was formed. The influence of the hollow structure of the content of the crosslinking agent (DEGDA) and the solvent was discussed. The hollow microspheres prepared in the present study were characterized by optical microscopy (OM), scanning electron microscopy (SEM), particle size analyzer and differential scanning calorimeter (DSC).

Keywords: Suspension polymerization; Micron-sized; Hollow microspheres

1. Introduction

Recently, control of morphology of polymer microspheres has become an intensive area in research of polymer science. The synthesis of microdomain, interpenetrating network, core−shell, and hollow microspheres is now possible. The porous and hollow microspheres are more widely used because they can be used as toners, inks, cosmetics, coatings, supports for medical assays, enzyme immobilization carrier, chromatographic packing, and sound damping and absorption materials [1]. Hollow microspheres also offer a number of advantages due to their relatively low density and consumption [2]. The mechanism for hollow microspheres' fabrication is mainly classified by Murthy et al. into (1) sacrificial core method and (2) interfacial synthesis [3]. In the former method, inorganic or organic shells are formed around cores which are called "template" [4−7]. This method involves many steps or severe conditions in shell forming and template removing. Comparatively, the latter method is more simple because liquid cores are often used practically. Many approaches have been reported to prepare hollow microspheres. Okubo [8−10] prepared submicrometer-sized multihollow particles via ASP (alkali swelling procedure) and DSM (dynamic swelling method). Schlarb et al. [11] used copolymer with −COOH group as an emulsifier for the second-step emulsion polymerization in the presence of organic solvents. After removing the solvents, the pore formation is finished. Omi et al. [12] produced hollow microspheres by suspension polymerization using SPG (a Shirasu porous glass) membrane. Above all, those methods also bring some drawbacks: complex treatment procedures and industrial waste, which leads to much time wasting and consumption.

Just as the fabrication of the microcapsules, the interfacial polymerization is also adopted to fabricate hollow microspheres with encapsulation of nonsolvent [13] based on the differences of interfacial tension and phase separation process. Because of the existence of polymer/hydrocarbon or water/polymer interface, several configurations of particles can be

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* Corresponding authors. Tel.: +86 28 85229123.
E-mail address: zonghuiliu@hotmail.com (Z. Liu).

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obtained under different synthesis conditions [14]. In this suspension system, it has been published that many kinds of hydrocarbon solvents have been introduced such as benzene, toluene, hydrocarbon with chlorine or fluorine and so on which are poisonous and environment polluting. Here we choose petroleum ether (90−120 °C) as a friendly agent comparatively due to its main components heptane and octane. For obtaining a better hollow morphology, a crosslinking structure should be introduced within the microspheres [15]. In such researches, many crosslinking agents have been introduced, such as DVB (divinylbenzene) [16] and EGDMA (ethylene glycol dimethacrylate) [17], but DEGDA (diethylene glycol diacrylate) has been less reported in the similar system, due to its long chain with more vinyl groups than EGDMA, and higher reactivity than DVB in lower reacting temperature within the same time.

2. Experimental

2.1. Materials

Styrene (St), benzoyl peroxide (BPO), poly(vinyl alcohol) (PVA), petroleum ether (90−120 °C) were purchased from Kelong Chemical (China). St was purified by distillation under reduced pressure in a nitrogen atmosphere. PVA (PVA-1788: degree of polymerization, 1700; degree of saponification, 88%) was used without further purification. Reagent-grade BPO, petroleum ether and DEGDA (diethylene glycol diacrylate, Tianjiao Chemical Co., Ltd) were used as received without any purification.

2.2. Suspension polymerization

Homogeneous solutions of St, DEGDA, petroleum ether and BPO were dispersed into 3.33% PVA aqueous solution under a high-speed shearing condition, until the droplets were emulsified to the micron-sized object about 20−30 μm. Suspension polymerization reactions were performed in a glass 250 ml four-necked flask fitting with a mechanical stirrer, reflex condenser and nitrogen inlet. After removing air with nitrogen gas for 30 min, suspension polymerizations were carried out at 80 °C for 8 h under the conditions listed in Tables 1 and 2.

Table 1
Recipes for the production of P(St-DEGDA) hollow microspheres by suspension polymerization with different DEGDA amount

Ingredient	No. 1	No. 2	No. 3
St (g)	20.8	20	19.2
DEGDA (g)	0.8	1.6	2.4
BPO (mg)	250	250	250
Petroleum ether (g)	30	30	30
PVA (g)	2	2	2
Water (g)	58	58	58

Table 2
Recipes for the production of P(St-DEGDA) hollow microspheres by suspension polymerization with different petroleum ether amount

Ingredient	No. 4	No. 2	No. 5
St (g)	20	20	20
DEGDA (g)	1.6	1.6	1.6
BPO (mg)	250	250	250
Petroleum ether (g)	20	30	40
PVA (g)	1.61	2	2.39
Water (g)	46.76	58	69.24

O/W ratio remains at 51.6/60; PVA%, 3.33% (by water); 80 °C, N_2, 8 h.

2.3. Characterization of the hollow microspheres

The resulting microspheres were washed, sequentially, with water and ethanol to remove the dispersant, residual solvent (petroleum ether) and any unreacted monomers. The morphology of the hollow microspheres was observed with a JNOEC-MICROPHOT-XSP24N optical microscopy (OM) and a Hitachi S-2500 scanning electron microscopy (SEM), and each sample was dropped onto a glass plate. Differential scanning calorimeter (DSC) showed us the microspheres' T_g alternation under the condition of crosslinking.

3. Results and discussions

In order to keep the interface intension on a similar value for forming a uniform droplets size, the O/W ratio was remained at a fixed value in this suspension system. Due to the changing of the O/W ratio, the content of PVA% should be verified consequently. The addition of PVA would be helpful to decrease interfacial energy, resulting in smaller droplets corresponding to an overall larger surface area in this system.

3.1. Effect of amount of DEGDA

These series of experiments were based on the fixed value of petroleum ether (150%, wt% by St).

The microspheres prepared from No. 1 recipe are shown in Fig. 1a and b by SEM. It was indicated that the surface of the microspheres was not glossy and clean and the OM photograph Fig. 1c showed us that the microvoids had not been obvious. The phenomena of microphase separation were still not visible.

The microspheres prepared from No. 2 recipe are shown in Fig. 2a by OM. This time, the particle surface was much glossy and clean than No. 1, the hollow morphology had been formed successfully and the inner boundary between the polymer and air was obvious. The microspheres prepared from No. 2 recipe are shown in Fig. 2b by SEM. From this micrograph, the hollow structure formation was proved by the broken part of the microspheres, the surface was glossy and the shape was kept without little transformation and collapsing almost.

The microspheres prepared from No. 3 recipe are shown in Fig. 3a by OM. From this figure, the particle shape had been transformed into some collapsing and irregular types. The

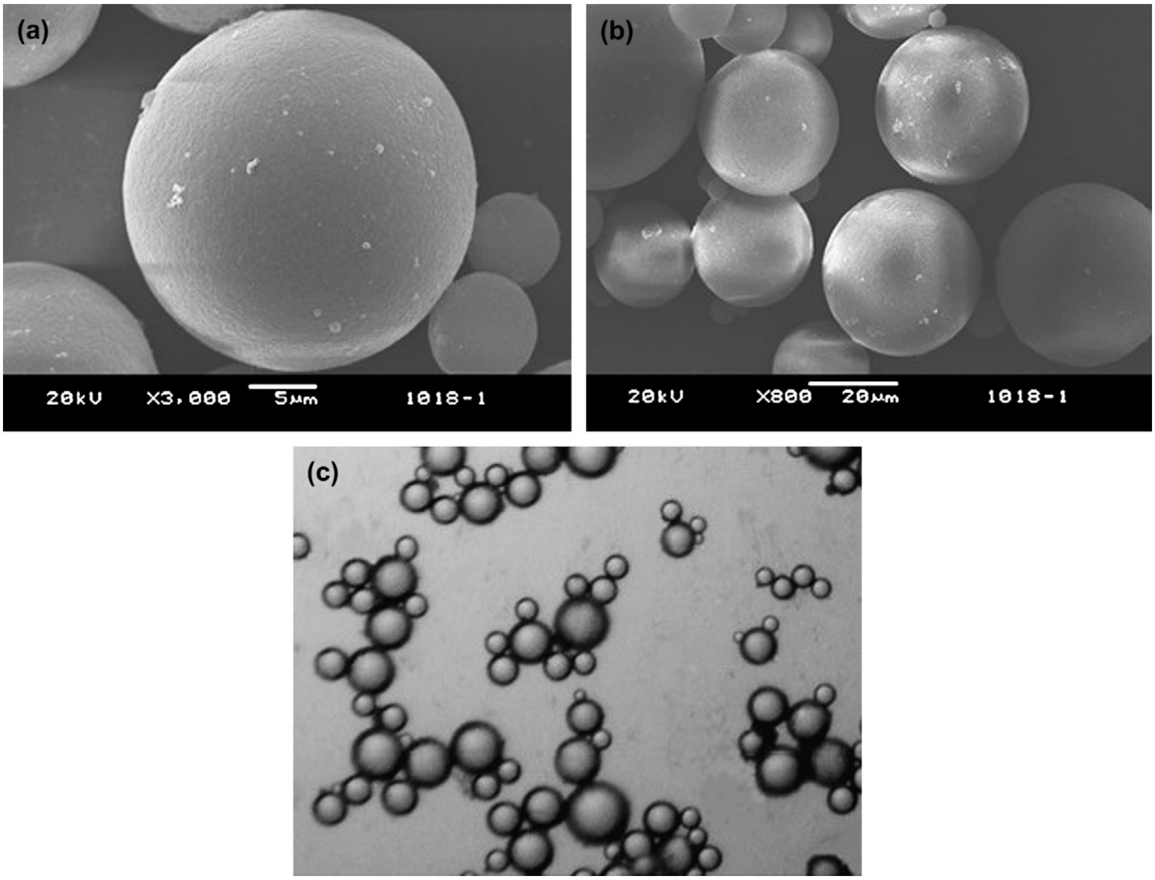

Fig. 1. (a and b) SEM micrographs and (c) OM micrograph of recipe No. 1.

SEM micrographs Fig. 3b–d showed us the same phenomena. From these micrographs, we can see there were many little particles grew inside and outside of the shell.

Fig. 4 is the DSC curve of the sample Nos. 1–3 under the same acceleration rate of 10 °C/min.

Comparing between Nos. 1, 2 and 3, with increasing the amount of DEGDA in the suspension polymerization, the phase separation in the microsphere changed obviously. When the crosslinking agent amount increasing to 7.4% (wt% by monomers), the hollow structure has been obtained. After reaching to 11.1%, the aimed structure was not obtained instead of the collapsing morphology. Generally with the crosslinking degree increasing the crosslinking network of the particle body will become tighter, which effect not only contributes to the phase combination of microdomain, but also inhibits the diffusion of it. The above opinion had been discussed by Michael Schulz [18]. The microvoids' coalescence and combination in the center part resulted in the formation of big voids and hollow structure further, while the outer part microvoids which cannot diffuse into the center in time,

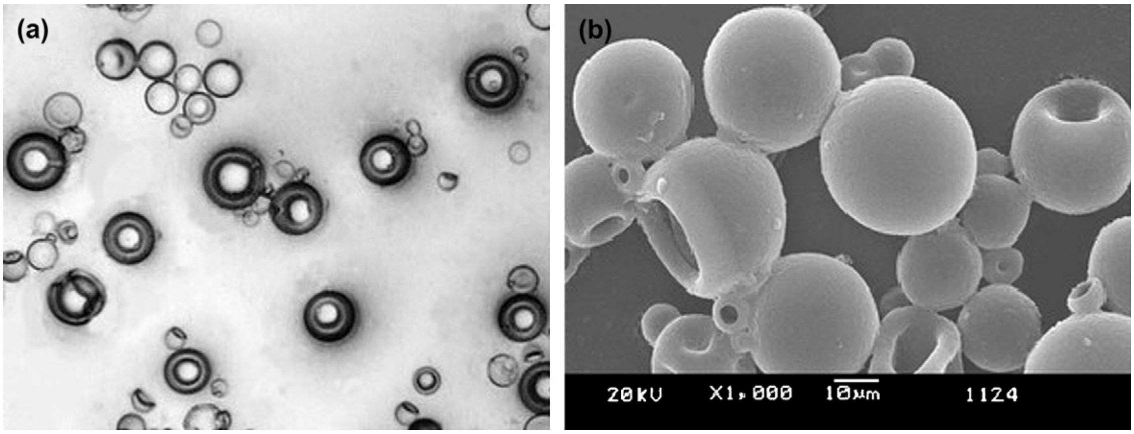

Fig. 2. (a) OM micrograph and (b) SEM micrograph of recipe No. 2.

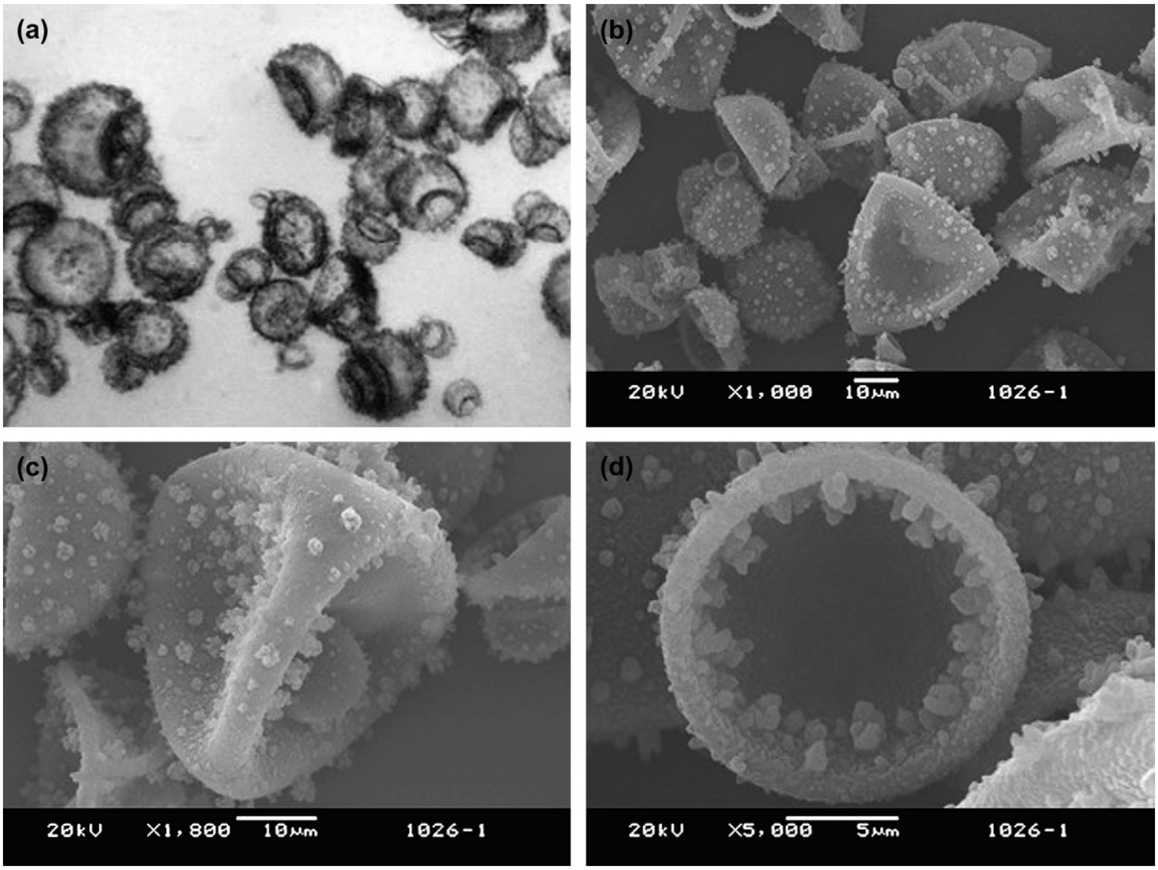

Fig. 3. (a) OM micrograph and (b–d) SEM micrographs of recipe No. 3.

combined with each other in the surface domain. Furthermore, as a crosslinking agent DEGDA had high reactivity with other acrylates by which polymerization can be carried out fast and completely, help the phase combination and diffusion mostly. With its amount increasing the homo-polymerization part become much more, in the end those factors resulted in the little particles grown on the surface under the condition of higher amount of DEGDA. From Fig. 4 the difference between Nos. 1, 2 and 3 was not obviously observed. That is because the crosslinking degree of these series of experiments was not too much to make a remarkable change of T_g. But there was a different point in No. 3's DSC curve which was worthy to be noted. The lower T_g of 51.86 °C should be attributed to the copolymer (St-DEGDA) with much more DEGDA units under the corresponding condition of higher dosage of crosslinking agent. The hypothesis above could be proved accessorily by SEM of No. 3 shown in Fig. 3. There were many little particles grew inside and outside of the shell. And the collapsing of the particles could also be attributed to the "Soft" crosslinking units of the copolymer.

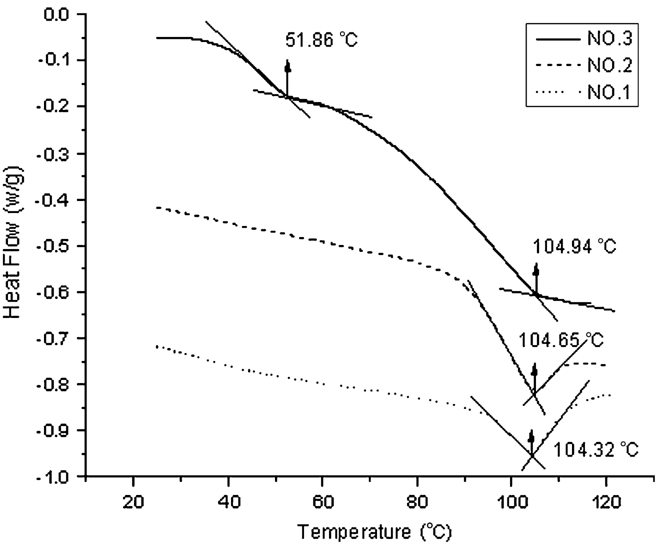

Fig. 4. DSC of recipe Nos.1–3.

3.2. Effect of amount of solvent (petroleum ether 90–120 °C)

These series of experiments were based on the fixed value of DEGDA (7.4%, wt% by monomers).

The microspheres prepared from No. 4 recipe are shown in Fig. 5a and b by SEM and OM. When petroleum ether was 100% (wt% by St), the microspheres were not hollow and transparent instead of dark body without much light to transmit. It could be considered that many super microvoids of phase separation had been formed, due to less solvent dissolved in the droplets of the monomers and made them polymerize on their own sites which were small but stable.

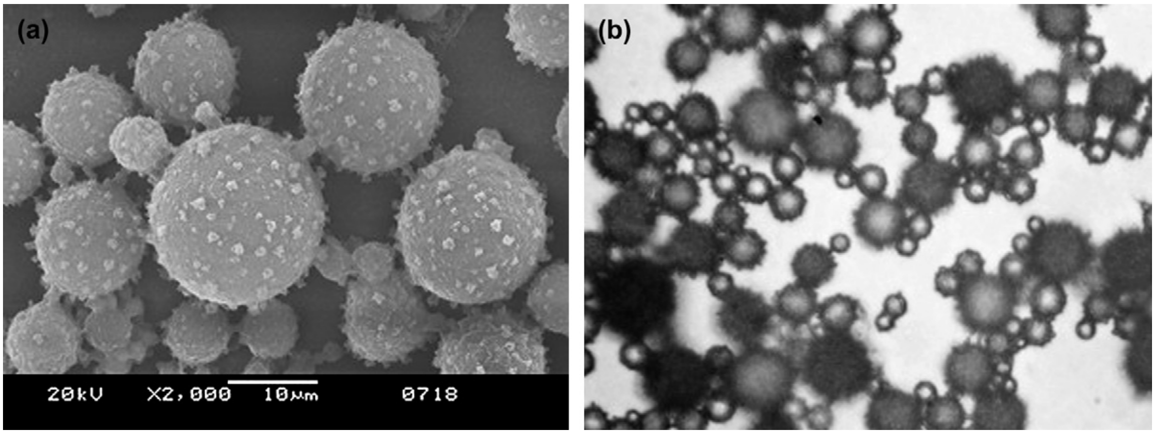

Fig. 5. (a) SEM micrograph and (b) OM micrograph of recipe No. 4.

Therefore, the formed microdomain would not be combined with each other, which also resulted in the formation of the micropolymer unit anchored on the particles' surfaces.

The microspheres prepared from No. 5 recipe are shown in Fig. 6a–c by SEM and OM. The amount of solvent was up to 200% (wt% by St). Although the hollow structure was obvious, the thinner wall of the particles made the bodies collapse. Especially the coalescence of the microsphere existed before washing by water and ethanol. When dispersing into water, there were some oil droplets floating on the surface. Its component should be mainly the solvent (petroleum ether), because there were not any similar phenomena in the former samples (before the solvent amount reaching to 150%) and the reaction was always performed well with less residues.

Comparing between Nos. 2, 4 and 5, with the amount of solvent increasing in the suspension polymerization, the phase separation in the microsphere also changed obviously. As we know in this system, the monomers are dispersed into the

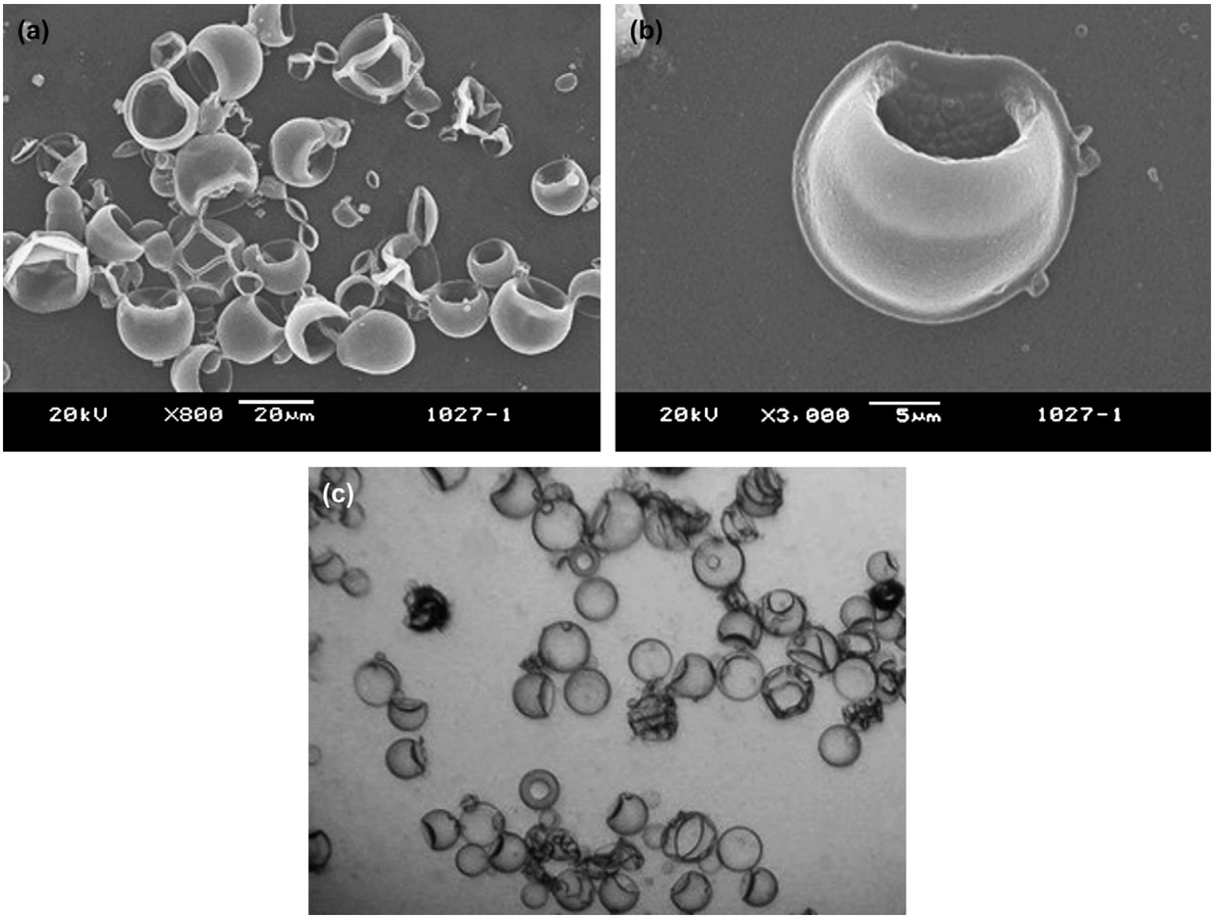

Fig. 6. (a and b) SEM micrographs and (c) OM micrograph of recipe No. 5.

water phase in the form of little oil droplets with other oil–solvent substance, with the molecular weight enlarging the phase separation between the solid (polymer) and liquid (monomers and solvent) begin. Because of the difference between petroleum ether and polymer and the similarity between petroleum ether and monomers, it was mostly possible for the solvent to absorb the monomers in the oil phase without further diffusion into the water phase, and at the same time it had accelerated the reaction rate [19] and made the polymerization fast and completely, which conduced to the formation of the thinner wall. As the amount of solvent increasing, this cooperation effect extends much more obviously. Due to the different interface tension of monomers/water, solvent/water, monomers/polymer and solvent/polymer, with the solvent amount increasing and the crosslinking network forming rapidly, it was difficult that the outer solvent diffused into the polymer phase as usual. So, there were always some residue oil droplets floating on the water surface.

4. Conclusions

The micron-sized hollow microspheres had been obtained by suspension polymerization under the conditions of the proper amount of DEGDA and solvent petroleum ether (90–120 °C). The microspheres' morphology was controlled by the crosslinking degree and porogenous solvent amount. The morphology of these particles could be seen from OM and SEM micrographs. The crosslinking degree had contributed to the phase separation and diffusion of the polymer particles inside and outside, more or less should not be advisable. The same as the porogenous solvent importing, it had contributed to the controlling of the pore size and the thickness of the shell and activating the monomers diffusing into the oil droplets so as to accelerate the polymerization rate. As the auxiliary characterization, the DSC results had interpreted the crosslinking agent (DEGDA) negative effect during the formation of the hollow structure. The mechanism of hollow morphology formation was that, rapid phase separation between solvent and crosslinked polymer, due to the diffusion of a lot of monomers into the water phase, was responsible for the formation of the hollow structure.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2007.01.034.

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