Research Article

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Innovative and high performance synthesis of microcapsules containing methyl anthranilate by microsuspension iodine transfer polymerization

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Abstract

In this research, preparations of polymer microcapsule encapsulated methyl anthranilate (MA) as an essential oil model by both microsuspension conventional radical polymerization (*ms* CRP) and microsuspension iodine transfer polymerization (*ms* ITP) using methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) copolymer as the polymer shell were studied. In the case of *ms* CRP, a large amount of free polymer particles nucleated in aqueous medium were obtained. Using *ms* ITP, the free polymer particle formation was significantly depressed. Iodoform (CHI_3) as a chain transfer agent with 0.8 wt% relative to the monomer, such a phenomenon was not observed. Various emulsifiers (oleic acid, Span 80 and PEG 30 dipolyhydroxystearate (DPHS)) with low hydrophile–lipophile balance value were used to retain MA in the monomer droplets or polymerizing particles. DPHS is the most effective emulsifier to retain MA in microcapsules giving 58% encapsulation at 20 wt% of DPHS relative to MA. In addition, from the controlled release study, only 55 wt% of the encapsulated MA was released by 90 days. Polymer microcapsule encapsulated MA using an MMA-EGDMA copolymer shell with a high percentage of encapsulation and without free polymer particles was successfully prepared for the first time. Based on slow release of the encapsulated MA, the prepared microcapsules could be used in various applications.

Keywords: microsuspension iodine transfer polymerization; methyl anthranilate; microcapsule

INTRODUCTION

An essential oil is normally a liquid containing various aroma compounds produced by different parts of plants[1] such as flowers, leaves, stems and roots. Methyl anthranilate (MA) is one of the main aroma components, and is extensively used in perfumery[2,3] and applied in many industries such as textiles,[4,5] food[6] and cosmetics.[7,8] The main disadvantages of the direct use of essential oils are that they easily become volatile[9] and quickly oxidize[10] which results in loss of their beneficial properties. To overcome these drawbacks, encapsulation within a polymer shell may depress such phenomena.[11] Microencapsulation of essential oils has been reported using various techniques with different polymer shells. For example, the interfacial polymerization of polyurea microcapsules containing essential oils,[12] phase inversion precipitation of polysulfone microcapsule encapsulated vanillin microcapsules[13,14] and *in situ* polymerization of melamine resin microcapsules containing fragrant oil[15] have been reported. One of the most famous techniques for microcapsule preparation is an environmentally friendly technique – suspension polymerization.[16,17] The core–shell particles obtained could be prepared via an internal phase separation mechanism. In our previous papers, polydivinyl benzene (PDVB) microcapsules encapsulated in a commercial wax such as rubitherm 27[16,18] and octadecane[17,19,20] were successfully prepared by microsuspension polymerization with high encapsulation efficiency. Spherical microcapsules with high shell strength were obtained. Because of the high water solubility of MA, a hydrophilic polymer shell should be more suitable than a hydrophobic shell to encapsulate MA with high encapsulation efficiency. However, a lot of free polymer particles as byproduct were formed during the microsuspension conventional radical polymerization (*ms* CRP) of polar monomers for microcapsule preparation.[16] Byproduct particles of polar monomers such as methyl methacrylate, methyl acrylate and ethyl acrylate were produced by emulsion polymerization via homogeneous nucleation in aqueous media competition to droplet nucleation.[21] In the early stage of polymerization, oligomeric radicals at first initiated into the monomer droplet and then exited into the aqueous medium to form particles by self-assembly of a polymer chain. To depress such phenomena, a hydrophobic chain transfer agent such as iodoform was

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used in microsuspension iodine transfer polymerization (*ms* ITP). Iodine radicals having a high activity to capture the oligomeric radicals can significantly reduce the radicals exiting from the monomer droplet/polymerizing particle by acting as an end-capping agent of the oligomeric chain. Therefore, byproduct particles of poly(methyl methacrylate) (PMMA)[21] and microcapsule encapsulated wax[22] were significantly suppressed using *ms* ITP compared with *ms* CRP. However, it is difficult to obtain a high encapsulation efficiency of a polar molecule such as MA with only a hydrophilic polymer shell. It is well known that a polar molecule such as water can be smoothly dispersed in the oil or hydrophobic phase as a water-in-oil emulsion system without coalescence using an emulsifier having a low hydrophile–lipophile balance (HLB) value. Then, utilization of such an emulsifier in the monomer droplet (phase) may retain MA in the microcapsule and improve the encapsulation efficiency.

Therefore, in this research, *ms* ITP was used to prepare PMMA-based microcapsule encapsulated MA (PMMA-based/MA) to depress the formation of free polymer particles. In addition, the influence of MMA:MA ratios and emulsifier (with low HLB value) kinds and amounts on encapsulation efficiency was studied.

EXPERIMENTAL

Materials and methods

MMA (Aldrich, Wisconsin, USA; purity 99%) and ethyleneglycol dimethacrylate (EGDMA) (Aldrich, Beloit, WI, USA; purity 99%) were purified by passing through a column packed with basic aluminium oxide. MA (Aldrich; purity 98%) was used as an essential oil model. 2,2′-azobis (4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako Pure Chemicals, Osaka, Japan) and iodoform (CHI_3) (Aldrich; purity 99%) were used as an initiator and a chain transfer agent, respectively. Poly(vinyl alcohol) (PVA) (Aldrich; degree of saponification 87% – 90% and molecular weight $(3-7) \times 10^4$ g mol^{-1}), oleic acid (Aldrich), Span 80 (Aldrich) and PEG 30 dipolyhydroxystearate (DPHS) (Croda Inc., New Jersey, USA) were used as received.

Synthesis of polymer microcapsules

Polymer microcapsule encapsulated MA was prepared by *ms* CRP under the conditions listed in Table 1. First, MMA, MA and V-70 (1 wt% relative to monomer) were homogeneously mixed as an oil phase. This was then poured into a PVA aqueous solution (1 wt%) and homogenized at 5000 rpm for 5 min to form an oil-in-water emulsion. Second, the emulsion was subsequently transferred to a round bottom flask, sealed with a silicone rubber septum and purged with a vacuum/N_2 cycle five times (finally in N_2). It was finally polymerized at 40 °C for 4 h at a stirring rate of 500 rpm. In the case of *ms* ITP, the conditions were the same as for *ms* CRP except for the addition of CHI_3 as the chain transfer agent in the oil phase. In addition, to increase encapsulation efficiency, emulsifiers having a low HLB value such as Span 80, oleic acid and DPHS were also added in the oil phase.

Characterization

The prepared microcapsules were observed with an optical microscope (SK-100 EB and SK-100 ET, Seek Inter Corporation Ltd, Thailand) and a scanning electron microscope (JSM-6510, JEOL Ltd, Japan) to investigate the inner structure of the microcapsules and the morphology of the surface, respectively. For SEM observations, one drop of each polymer dispersion was placed on a nickel SEM stub and dried before being coated with Au. Conversion and the amount of free polymer particles were measured by gravimetry. Suspension samples (*ca* 2.0 g) taken from the reactor were transferred directly into an aluminium cup and weighed. Several drops of hydroquinone solution (1 wt%) were added therein before the free liquid was evaporated in an oven at 70 °C. The sample was dried until a constant weight of the dried polymer was obtained. Monomer conversion was obtained by comparing the weight of dried polymer with that of the original monomer. The partition ratio of MA between monomer and aqueous phases with the same composition as in the polymerization recipe (without initiator and PVA in the monomer and aqueous phases, respectively) was measured as follows. The oil phase containing monomers, emulsifier and MA was mixed with water and then stirred at 40 °C for 2 h. Thereafter, 0.50 g of water phase was withdrawn and the amount of MA in the aqueous phase was determined by spectrophotometry. Weight- and number-average molecular weights (M_w and M_n, respectively) were measured by gel permeation chromatography (GPC) (Waters 2414, Waters, USA) with two poly(styrene/divinylbenzene) gel columns (Phenogel 5×10^3 and 5×10^5 Å (pores), 7.8 mm (internal diameter) × 30 cm (length), Phenomenex, USA) connected in series and using tetrahydrofuran as eluent. The flow rate of the eluent was maintained at 1.0 mL min^{-1} with a column temperature of 40 °C and the elution was monitored with a refractive index detector (RI 2414/Waters). The columns were calibrated with six standard polystyrene (PS) samples (2.5×10^3 to 6.0×10^5, $M_w/M_n = 1.05 - 1.15$).

The MA content in the polymer microcapsules was determined with a thermogravimetric analyzer (TGA 4000, Perkin-Elmer, USA) at a heating rate of 5 °C min^{-1}. For TGA measurement, approximately 10 mg of the dried microcapsules before and after washing with hot water was placed into the TGA pan. The encapsulation efficiency was calculated using

$$\%L_{th} = \frac{W_{MA}}{W_{MA} + \left[\left(\%Conv - \%F_P\right)/100\right] \times W_M} \times 100 \quad (1)$$

Table 1. Reagent amounts for the preparation of PMMA/MA and P(MMA-*co*-EDGMA)/MA microcapsules by microsuspension polymerization[a]

Entry	MMA (g)	EDGMA (g)	MA (g)	CHI_3 (g)	V-70 (g)	Emulsifier (g)	1 wt% PVA solution (g)
1	5.00	–	5.00	–	0.05	–	90
2	5.00	–	5.00	0.01	0.05	–	90
3	5.00	–	5.00	0.02	0.05	–	90
4	5.00	–	5.00	0.04	0.05	–	90
5	10.00	–	–	0.04	0.05	–	90
6	7.00	–	3.00	0.04	0.05	–	90
7	3.00	–	7.00	0.04	0.05	–	90
8	4.50	0.50	5.00	0.04	0.05	–	90
9	3.50	1.50	5.00	0.04	0.05	–	90
10	2.50	2.50	5.00	0.04	0.05	–	90
11	1.50	3.50	5.00	0.04	0.05	–	90
12	2.50	2.50	5.00	0.04	0.05	0.50[b]	90
13	2.50	2.50	5.00	0.04	0.05	1.00[c]	90
14	2.50	2.50	5.00	0.04	0.05	1.50[b]	90

[a] Temperature 40 °C, homogenized at 5000 rpm for 5 min and polymerization time 4 h.
[b] DPHS.
[c] DPHS, oleic acid and Span 80.

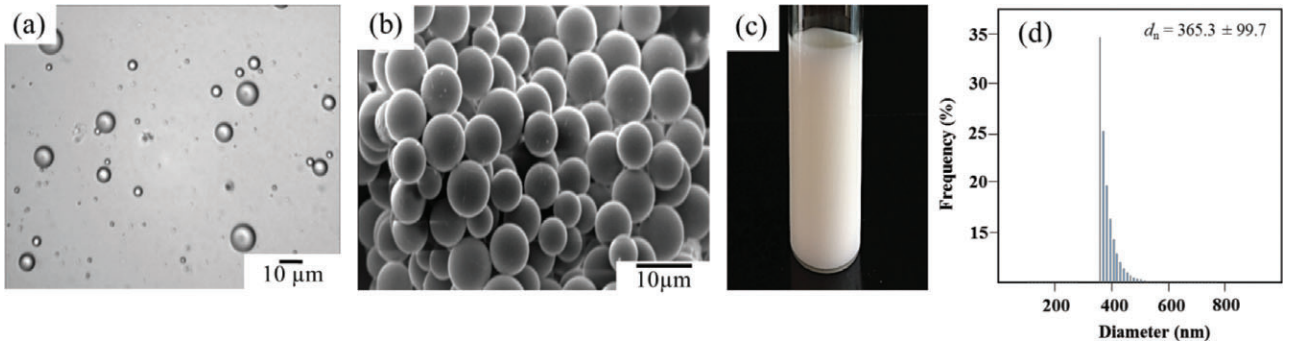

Figure 1. (a) Optical and (b) SEM micrographs and (c) suspension photograph of PMMA/MA microcapsules prepared by *ms* CRP (entry 1); (d) dynamic light scattering histogram of the number-average diameter (d_n) of polymer particles in aqueous phase after centrifugation at 8000 rpm.

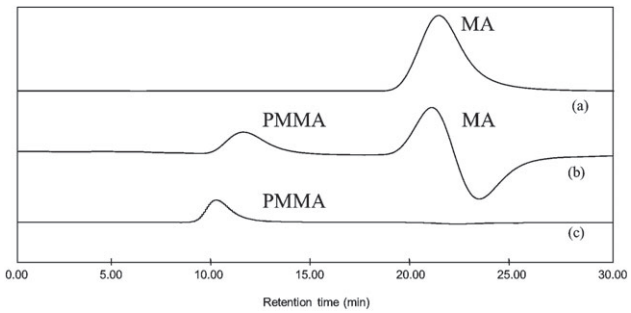

Figure 2. GPC chromatograms of MA (curve (a)), PMMA/MA microcapsules (lower layer) (curve (b)) and aqueous dispersion (upper layer) (curve (c)) prepared by *ms* CRP (entry 1).

$$\%E = \frac{\%L_E}{\%L_{th}} \times 100 \quad (2)$$

where W_{MA} and W_M are, respectively, the weights of MA and monomer from the recipe, %Conv and $\%F_P$ are the percentage monomer conversion and the free polymer particles, respectively, $\%E$ is the percentage encapsulation, $\%L_E$ is the loading (wt%) obtained from TGA and $\%L_{th}$ is the theoretical percentage loading (wt%) calculated using Eqn (1).

Controlled release study

Approximately 0.1 g of dried microcapsules were separately immersed in 10 mL of water in each bottle and kept at 50 °C. During the study, each bottle had water added to it to maintain the water amount at 10 mL. Triplicate 2 ml samples of each bottle (using seven bottles for 2 months) were then withdrawn. The microcapsules were filtered and dried in a vacuum oven. The amount of MA inside the microcapsules was measured by TGA and that released from the microcapsules to water was calculated by subtraction of the remaining MA from the original MA.

RESULTS AND DISCUSSION

In general, polymer or polymer capsule particles of micrometer size prepared by microsuspension polymerization are formed by droplet nucleation where the monomer droplets are generated by a high shear rate with the homogenizer before being polymerized. If the monomer droplet maintains colloidal stability during the polymerization, the particle size of the polymer particle obtained should be similar to that of a monomer droplet. Optical and SEM micrographs of PMMA/MA microcapsules prepared by *ms* CRP are shown in Figs 1(a) and 1(b), respectively. The PMMA/MA microcapsules obtained were spherical in shape with a smooth outer surface. Because a core – shell morphology was not observed, the encapsulated MA seemed homogeneously distributed throughout the particles. In addition, turbidity of the aqueous phase of the suspension after centrifugation was observed (Fig. 1(c)) where all microcapsules were precipitated. This indicated that byproducts (approximately 40%) as free PMMA particles with a particle size of 365 nm (Fig. 1(d)) were formed in an aqueous medium. This accorded well with the previous work where a large amount of free PMMA particles were found in microsuspension polymerization of PMMA/RT27 microcapsules.[22] This seems to be a general phenomenon in suspension polymerization of hydrophilic

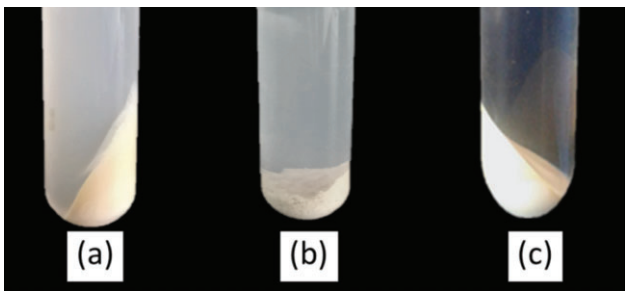

Figure 3. Photographs of aqueous dispersions after centrifugation of samples prepared by *ms* ITP at various CHI_3 concentrations (wt% of monomer): (a) 0.2 (entry 2); (b) 0.4 (entry 3); (c) 0.8 (entry 4).

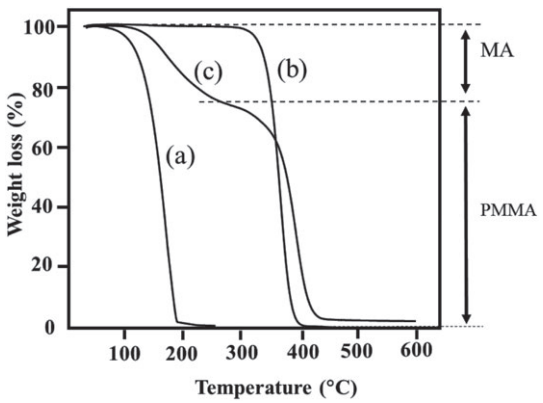

Figure 4. TGA thermograms (scanning rate 5 °C min^{-1}) of MA (curve (a)), PMMA particles (curve (b), entry 5) and PMMA/MA microcapsules (curve (c), entry 4) prepared by *ms* ITP. The dashed lines are a guide only to estimate the two steps of weight loss of PMMA/MA microcapsules.

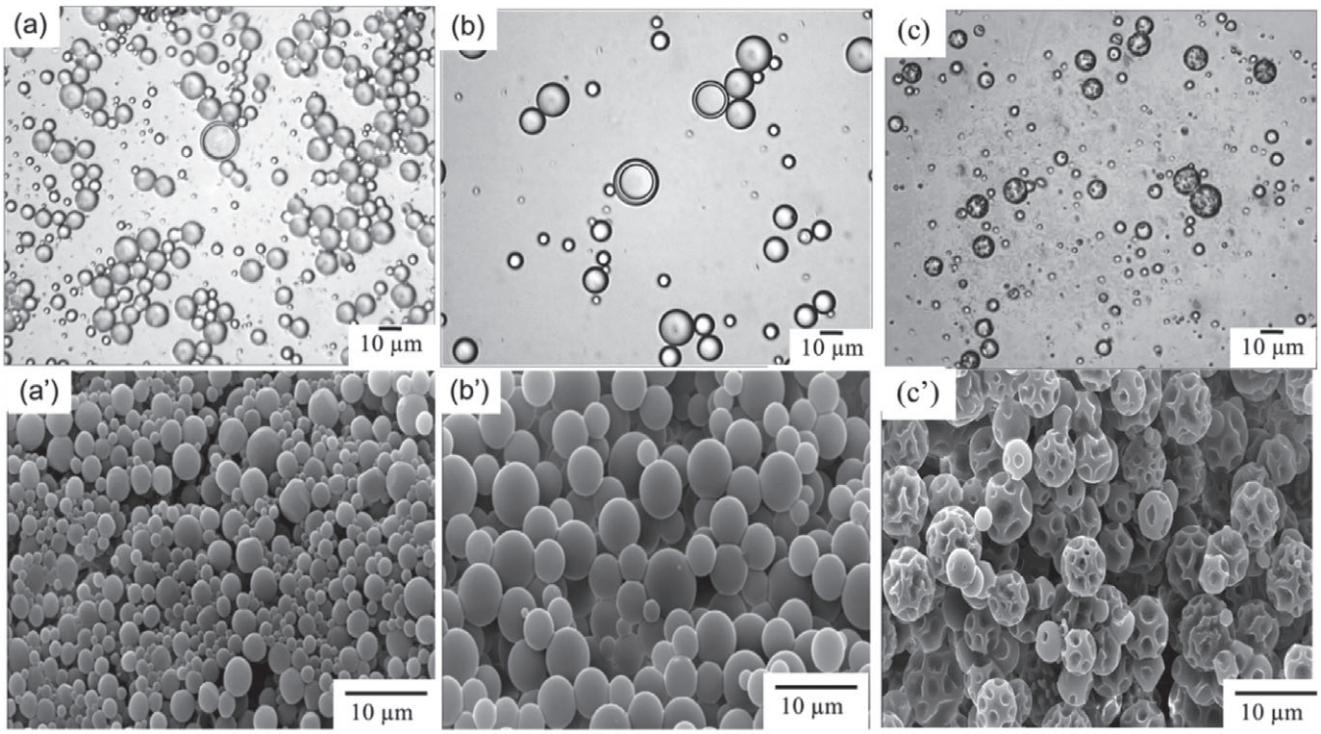

Figure 5. Optical (a) – (c) and SEM (a') – (c') micrographs of P(MMA-*co*-EGDMA)/MA prepared by *ms* ITP with 20 wt% of various kinds of emulsifiers relative to MA: (a), (a') Span 80; (b), (b') oleic acid; (c), (c') DPHS.

monomer.[21] Due to byproduct formation, the polymer shell thickness will decrease which may result in a decrease of the percentage encapsulation of MA. The free PMMA particles were formed by emulsion polymerization via homogeneous nucleation where MMA which was soluble in aqueous medium reacted with the radicals exiting from the monomer droplet or polymerizing particles. When the growing polymer chains are long enough and no longer soluble in the water, free PMMA particles of sub-micrometer-size are then formed by self-assembly. To clarify the formation of free PMMA particles in an aqueous medium of *ms* CRP, its M_n was measured by GPC and compared with that of PMMA microcapsules.

Before GPC measurement, the suspension of *ms* CRP was centrifuged to obtain free PMMA particles as an upper layer and PMMA/MA microcapsules precipitated on the bottom. Both free PMMA particles and PMMA/MA microcapsules were washed with hot water and dried overnight prior to GPC measurement. GPC chromatograms of standard MA, PMMA/MA microcapsules and free PMMA particles prepared by *ms* CRP are shown in Fig. 2, curves (a), (b) and (c), respectively. The retention volumes are the volume of eluent (product of the eluent flow rate and the retention time) used to elute the analytes in the GPC column; they were mainly dependent on size or molecular weight of the analytes. Small molecules were retained in the column longer while larger ones quickly passed out from the column. In the case of the PMMA/MA microcapsule chromatogram, two peaks at retention times of 13 and 21 min were observed. As the second peak agreed with the retention time of the MA standard peak (Fig. 2, curve (a)), the first peak was the PMMA polymer shell with M_n about 104 000 g mol^{-1} compared with the PS standard curve (molecular weight *versus* retention volume). In the case of free PMMA particles, the chromatogram showed one peak at a retention time of 11 min. It might be free PMMA particles because the M_n obtained (*ca* 428 000 g mol^{-1}) was much higher than that of the PMMA microcapsule shell. Based on the compartmentalization effect, this can confirm our idea that smaller particles were formed as free PMMA particles by emulsion polymerization. This clearly indicates that both droplet and homogeneous nucleations had taken place during *ms* CRP.

The formation of large amounts of free PMMA particles is a drawback of microcapsule preparation for application in industry. In previous work on PMMA/RT27 microcapsules,[21,22] free PMMA particle formation was successfully depressed by *ms* ITP. Therefore, in this work, *ms* ITP with various concentrations of the chain transfer agent CHI_3 was first implemented on a prepared PMMA microcapsule containing essential oils such as MA. The suspension photos after centrifugation of the prepared PMMA/MA microcapsule at different concentrations of CHI_3 are shown in Fig. 3. It was found that the formation of free PMMA particles was significantly reduced from 40 to 4 wt% with 0.2 wt% (relative to monomer) of CHI_3. The amount of free PMMA particles decreased with increase in CHI_3 and disappeared at 0.8 wt% of CHI_3. The results are clearly shown in Fig. 3(c) where a transparent aqueous medium was observed in the case of *ms* ITP.

To measure the percentage encapsulation of MA in the microcapsules based on Eqn (2), the amount of MA in the microcapsules was first measured by TGA. Figure 4, curve (c), shows the TGA curve of dried PMMA/MA microcapsules representing two steps of weight loss, which are encapsulated MA (80 – 250 °C) and PMMA shell (250 – 450 °C), compared to those of the MA standard (Fig. 4, curve (a)) and PMMA particles (Fig. 4, curve (b)) prepared by *ms* ITP (entry 5), respectively. The percentage loading experiment (%L_E) can be obtained from the percentage weight loss of MA in PMMA/MA microcapsules while the percentage encapsulation (%*E*) was calculated using Eqn (2). It was found that before washing the microcapsule %*E* (97%) was quite high. However, after washing the microcapsule with hot water, it was significantly decreased

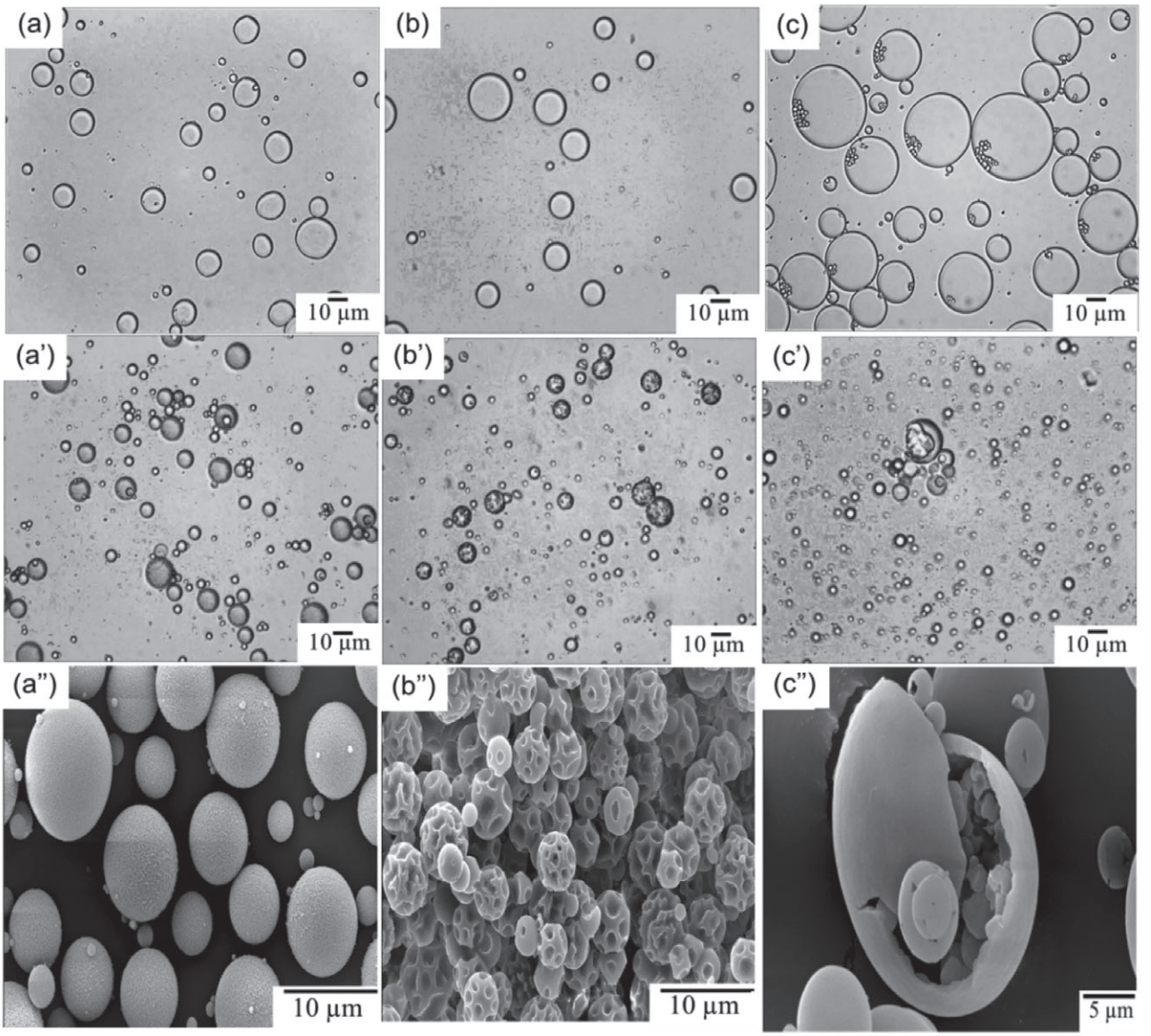

Figure 6. Optical micrographs of monomer droplets (a) – (c) and P(MMA-*co*-EGDMA)/MA microcapsules (a′) – (c′) and SEM micrographs of P(MMA-*co*-EGDMA)/MA microcapsules (a″) – (c″) prepared by *ms* ITP at various concentrations of DPHS (wt% relative to MA): (a), (a′), (a″) 10 (entry 12); (b), (b′), (b″) 20 (entry 13); (c), (c′), (c″) 30 (entry 14).

as only 37% remained in the microcapsule. The decrease of %*E* is due to the removal of MA absorbed on or near the microcapsule surface which suggests that most of the MA is distributed near the surface. This may be due to the high polarity of MA which makes it difficult to retain inside the microcapsule core. The encapsulation efficiency was not significantly improved (33% – 40%) using various MMA:MA ratios (50:50, 70:30 and 30:70 (entries 4, 6 and 7, respectively)) and copolymerization of MMA with various amounts of EGDMA (10, 30, 50 and 70 wt% of EDGMA based on MMA (entries 8 – 11)). However, because the chemical and thermal stabilities of the crosslinked microcapsule shell are practical in a wide range of applications, the P(MMA-*co*-EGDMA)/MA microcapsule with 50 wt% EGDMA (entry 10) giving a %*E* of 40% was the best and was selected for further study.

It is well known that emulsifiers with a low HLB value are used as the emulsifier to stabilize water dispersed in an oil phase to form a water-in-oil emulsion. Based on this idea, it might be possible to retain a polar molecule such as MA dispersed inside a monomer droplet or microcapsule in order to increase %*E*. Therefore, various kinds of emulsifiers such as Span 80, oleic acid and DPHS were used. Figure 5 shows optical and SEM micrographs of P(MMA-*co*-EGDMA)/MA at 20 wt% relative to the MA of the three emulsifiers. Spherical microcapsules with a smooth surface were obtained by using Span 80 (Figs 5(a) and 5(a′)) and oleic acid (Figs 5(b) and 5(b′)) while microcapsules that were non-spherical in shape with multiple dents on the surface were obtained by using DPHS (Figs 5(c) and 5(c′)). It seems that, owing to the higher HLB value (5.5) of DPHS than those of Span 80 (4.3) and oleic acid (1.0), the P(MMA-*co*-EGDMA) chains formed during polymerization might not adsorb uniformly to the monomer droplet or polymerizing particle/water interface because the hydrophilic part of some DPHS chains adsorbed there. This then resulted in non-uniform shell thickness. This phenomenon has been ascribed to the adsorption of sodium dodecyl sulfate on PDVB, PS/PDVB

and PS/PEGDMA particle surfaces to produce hole and multiple hole particles.[23–25] The multiple dents in the polymer shell were thus formed because the thinner shell part having low shell strength might be insufficient to withstand the external pressure. For encapsulation efficiency, the highest %*E* of MA was obtained with DPHS (58%) while the other emulsifiers were about 40%. It seems that DPHS which contains two to three chains in a molecule represents higher affinity to retain MA in monomer droplets or polymerizing particles than the other emulsifiers. The partitioning study showed that the MA concentration in an aqueous phase with DPHS was about 0.013 wt%, which was lower than those of Span 80 (0.116 wt%) and oleic acid (0.072 wt%). In addition, it was about half that (0.025 wt%) without an emulsifier.

To clarify the influence of the emulsifier, various amounts of DPHS were also studied. Figure 6 shows optical micrographs of monomer droplets and P(MMA-*co*-EGDMA)/MA microcapsules and SEM micrographs of P(MMA-*co*-EGDMA)/MA microcapsules with various DPHS amounts. It was found that the microcapsule shape changed with DPHS concentration. At a low concentration of DPHS such as 10 wt% (Figs 6(a), 6(a′) and 6(a″)), spherical microcapsules with a smooth surface were observed. At higher concentrations of DPHS, non-spherical microcapsules with multiple dents and multiple holes were obtained for 20 wt% (Figs 6(b), 6(b′) and 6(b″)) and 30 wt% (Figs 6(c), 6(c′) and 6(c″)) of DPHS, although spherical monomer droplets (Figs 6(b) and 6(c)) were formed before polymerization. There is competition between DPHS molecules and P(MMA-*co*-EGDMA) chains to adsorb at the polymerizing particle/water interface. At low DPHS, large amounts of P(MMA-*co*-EGDMA) might adsorb at the interface as P(MMA-*co*-EGDMA)-rich spherical microcapsules. As mentioned above, for 20 wt% DPHS, some parts of the microcapsule shell were DPHS-rich and have low shell strength resulting in a microcapsule with multiple dents. At 30 wt% DPHS, broken or multiple hole microcapsules were observed. High dense DPHS domains were formed at the droplet/water interface before polymerization (Fig. 6(c)) due to incomplete miscibility of DPHS in the monomer droplets. Thereafter, during polymerization, P(MMA-*co*-EGDMA) chains could not adsorb there leading to the formation of holes. In addition, it seemed that an increase in DPHS increased the %*E* of MA to 42 and 58 wt% for 10 and 20 wt% DPHS, respectively. However, the %*E* (33 wt%) decreased at 30 wt% of DPHS because the microcapsules contained multiple holes. Therefore, 20 wt% DPHS was the optimal condition to improve the encapsulation efficiency.

From the viewpoint of applications, a controlled release study of the encapsulated MA in the prepared microcapsules for optimal conditions (entry 13) was implemented by *in vitro* testing. From Fig. 7, it was found that the amounts of MA (*ca* 13 wt% relative to the original encapsulated MA) released from the microcapsules to water were fast in the first week. This may be due to the release of MA adsorbed at or near the microcapsule surface. Thereafter, the encapsulated MA was released gradually and reached 55 wt% by 90 days because of the MA distributed inside the microcapsules. These results show that P(MMA-*co*-EGDMA) effectively encapsulated MA and controlled the release of encapsulated MA which could be potentially applied in various applications.

CONCLUSIONS

P(MMA-*co*-EGDMA) microcapsules containing MA without free polymer particles was successfully prepared by *ms* ITP for the first time. At 0.8 wt% CHI_3, the formation of free polymer particles in the aqueous phase had completely disappeared. For encapsulation efficiency, the variation of the monomer and MA ratio had less influence on the %*E* of MA. In contrast, DPHS dispersed in the oil phase showed high efficiency for retaining MA inside microcapsules and the %*E* increased to 58 wt% at 20 wt% of DPHS relative to MA. In addition, the prepared microcapsules showed a high performance for encapsulating and controlling the release of the encapsulated MA as only 55% MA was released by 90 days of an *in vitro* release study.

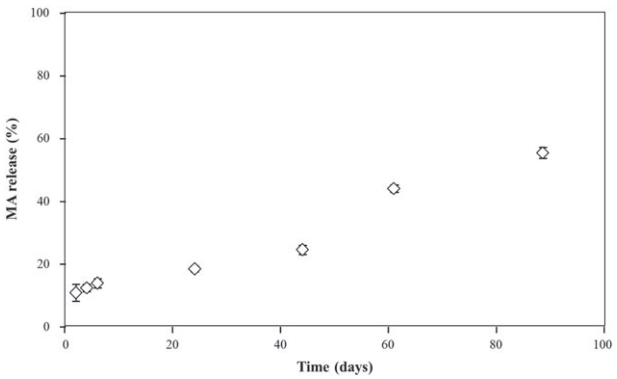

Figure 7. *In vitro* release of the encapsulated MA in P(MMA-*co*-EGDMA) microcapsules prepared by *ms* ITP (entry 13).

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