

Poly(methyl methacrylate) Multihollow Particles by Water in Oil in Water Emulsion Polymerization

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ABSTRACT: Multihollow-structured poly(methyl methacrylate) (PMMA) particles were produced employing the water in oil in water (W/O/W) emulsion polymerization technique where sorbitan monooleate was used as a primary surfactant and sodium laurylsulfate and Glucopen, a polypeptide derivative, were used as secondary surfactants. Vinyl acetate was copolymerized to improve the wettability of the particles. The agitation speed and concentration of the urethane acrylate employed as a reactive viscosity enhancer played a crucial role in determining the morphology and average size of the PMMA multihollow particles. In high agitation speed the multihollow particles displayed a small size and narrow size distribution resulting from efficient droplet breakup. Especially when the urethane acrylate was incorporated, PMMA multihollow particles with a smooth and clear surface were achieved. This was believed to be because the urethane acrylate increased the viscosity of the monomer mixture and helped to form the stable W/O/W emulsion droplets that restricted droplet coalescence during polymerization. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 38–44, 2000

Key words: poly(methyl methacrylate); multihollow structure; agitation speed; urethane acrylate; reactive viscosity enhancer; stable water in oil in water emulsion droplet

INTRODUCTION

Hollow particles have many applications in the coatings, ink, cosmetics, and paper industries, mainly because of their potential ability to protect against ultraviolet radiation and to manipulate the difference in the refractive index between the polymer and air.¹ Conventional hollow particles have been produced by the alkali swelling procedure (ASP),^{2–4} dynamic swelling method (DSM),^{5–7} and water in oil in water (W/O/W) emulsion polymerization.^{8–11}

Below 10 μm in size relatively monosized hollow particles are produced by ASP and DSM with

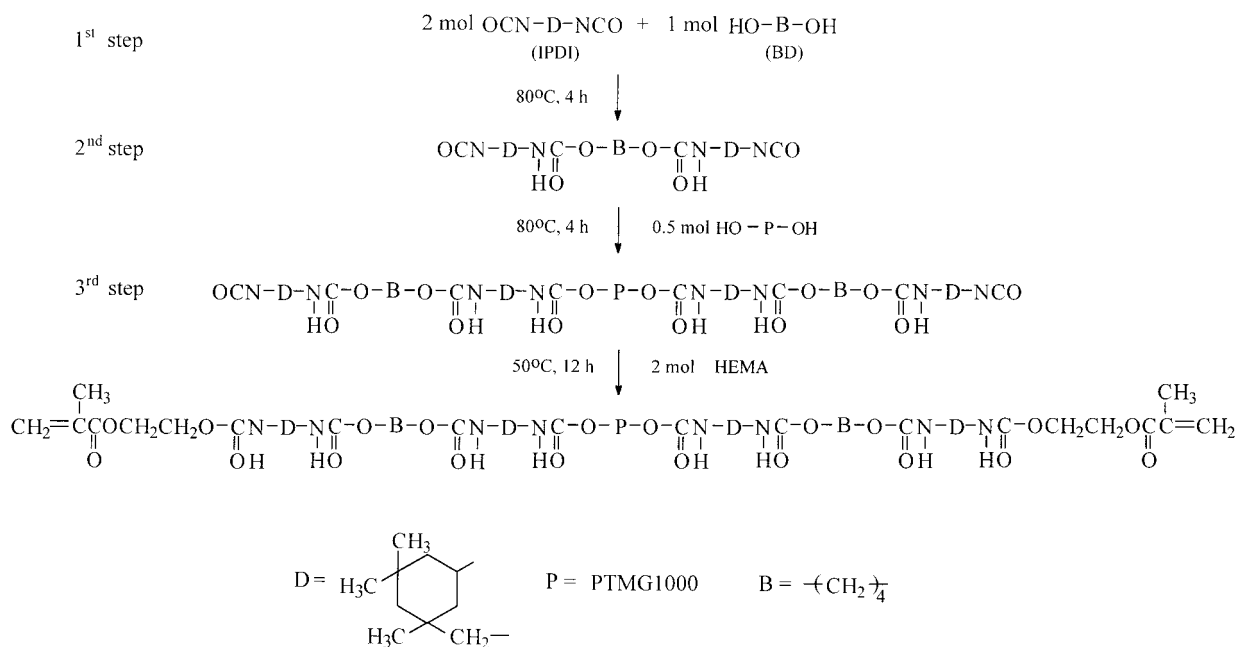
the intention of substituting them for the expensive opacifier titanium dioxide and/or applying them to the medical field. However, they commonly need a complex production process and consume a considerably long time to produce. Therefore, although a monodisperse size distribution could not be expected, the hollow particles produced by W/O/W emulsion polymerization were favored. Besides, because of their excellent ability to screen ultraviolet rays and to adhere to the skin, they found real application in the cosmetic industries. In spite of the above-mentioned advantages, before or during the emulsion polymerization the W/O/W emulsion droplets initially formed have a tendency toward coalescing to form agglomerates because of their inherent thermodynamic instability. Therefore, this instability of W/O/W emulsion droplets needs to be improved.

In our previous work¹¹ we prepared stable W/O/W emulsion droplets by treating the viscos-

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Scheme 1 A schematic reaction procedure and the molecular structure of the urethane acrylate.

ity of the monomer mixtures and obtained hollow-structured poly(methyl methacrylate) (PMMA) particles. As a reactive viscosity enhancer, a urethane acrylate (UA) was synthesized with a long poly(tetramethylene oxide) in the molecular backbone and two acryl groups at both ends. By enhancing the viscosity of the monomer mixture, stable W/O/W emulsions were prepared from the initial stage of the emulsion droplet formation, consequently helping to keep the spherical shape throughout the polymerization. However, the final size of the PMMA hollow particles was somewhat large (to about 100 μm) and there was a broad size distribution.

The ultimate goal of this study was to meet the size requirement by producing smaller PMMA hollow particles by W/O/W emulsion polymerization. The effect of the reaction condition and monomer composition on the morphology and particle size of the PMMA hollow particles was investigated.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI, Tokyo Chemical Industry Co., Ltd.) was vacuum distilled before use. Poly(tetramethylene glycol) (PTMG, M_w

= $1.0 \times 10^3 \text{ g mol}^{-1}$, Hyosung BASF), butane diol (BD, Aldrich), ethylene glycol dimethacrylate (EGDMA, Tokyo Chemical Industry Co., Ltd.), sodium *meta*-phosphate [$(\text{NaPO}_3)_6$, Aldrich], sorbitan monooleate (Span 80, Yakuri Pure Chemical Co. Ltd.), Glucopen 215 (APG, activity 64–65%, $\text{C}_8:\text{C}_{10}$ = 55:45, LG Chemicals), sodium laurylsulfate (SLS, Aldrich), vinyl acetate (VAc, Junsei Chemical Co.), and poly(vinyl alcohol) (PVA, M_w = $8.8\text{--}9.2 \times 10^4 \text{ g mol}^{-1}$, saponificating value, ca. 88%, Aldrich) were used as received.

Synthesis of UA

The UA was synthesized by the stepwise reaction procedure.^{11,12} The schematic molecular structure is represented in Scheme 1. In the first step 2 mol of IPDI were poured into the glass reactor and treated with nitrogen gas for 10 min to eliminate the residual moisture. After dissolving 1 wt % of dibutyltindilaurate (DBTDL), 1 mol of BD dissolved in tetrahydrofuran (THF) was reacted with IPDI at 80°C for 4 h, resulting in the molecular structure with the hard segment in the middle and isocyanates on both ends. The change of the NCO value during the reaction was determined using dibutylamine backtitration method to find the end point of the reaction. In the second step 0.5 mol of PTMG was reacted with the same method as the first step to incorporate the soft

Table I Composition for Preparation of W/O/W Emulsion Polymerization at 60°C for 4 h

Composition	Ingredient	Weight (g)
A	SLS	1.00
	(NaPO ₃) ₆	2.40
	APG ^a	4.00
	Water	440
B	MMA	19.00
	VAc ^b	2.00 ^{variable}
	EGDMA	8.00
	UA ^c	3.22 ^{variable}
	AIBN	0.48
	Span 80	7.00
	Water ^d	2.00

^a APG was added as a cosurfactant to stabilize the interface between the oil phase and outer water phase.

^b Vinyl acetate (VAc) was added as a component to improve the wettability.

^c The concentration of the urethane acrylate (UA) was varied against the total monomer weight (15 wt % in this sample).

^d The water in composition B was added to prepare the W/O emulsion.

segment in the middle of the molecules. In the last step, after dissolving 1 wt % of DBTDL into the reactor again, 2 mol of HEMA were reacted with the residual NCO groups at 45°C for 12 h, which capped the molecular ends with the reactive vinyl groups. After evaporating the THF solvent, a gumlike UA resin was obtained.

W/O/W Emulsion Polymerization

The composition for the production of PMMA hollow particles is listed in Table I. All ingredients of composition A were dissolved in the round-bottomed reaction kettle equipped with a mechanical stirrer, a reflux condenser, thermocouples, and an N₂ inlet system. The W/O emulsion prepared by 5-min sonification of composition B was dropped slowly into the reaction kettle of composition A at a given agitation speed. Then 1 wt % of PVA aqueous solution (40 g) was poured into the reaction kettle. Thus, the W/O/W emulsion was prepared. The polymerization was carried out continuously at 60°C for 4 h. The supernatant was then decanted and the remaining precipitate was washed with butyl alcohol repeatedly and dried at ambient temperature overnight *in vacuo*.

For the preparation of hydroxy group containing hollow particles, the PMMA particles copolymerized with VAc were saponified in 1% NaOH aqueous solution for 24 h at ambient temperature.

Measurements

The molecular weight of the synthesized UA was measured using a model 410 GPC. The molecular weight and the polydispersity index obtained were 8.5×10^3 g mol⁻¹ and 1.3, respectively.

The saponification procedure was confirmed by using IR spectroscopy (Nicolet, Magna IR-550).

The viscosity for the monomer mixture was measured with a standard Ubbelohde viscometer in a thermostated bath at $25 \pm 0.1^\circ\text{C}$. All measurements were with done with an average of 10 runs.

The hollow structure of the produced PMMA particles was observed with an optical microscope (OM, Nikon Microphot Fax). In order to verify the hollow structure, the particles were placed onto a coverglass and diluted with a drop of toluene ($n = 1.4967$), which has similar refractive index to that of PMMA ($n = 1.4893$).

The particle size of PMMA multihollow particles was determined from the OM photographs. The surface properties of the particles were observed with a field-emission scanning electron microscope (JSM-6340F, Jeol).

RESULTS AND DISCUSSION

Morphology of PMMA Hollow Particles

In our previous work¹¹ we produced PMMA hollow particles by incorporating a W/O/W emulsion polymerization technique. Span 80 was used as a primary surfactant (lyophilic surfactant) and SLS and APG as secondary surfactants (hydrophilic surfactant). When the emulsion formed, the internal and external aqueous phases were distinctly separated: the small internal aqueous droplets surrounded by a primary surfactant-stabilizing layer were dispersed in the oil phase that was in turn dispersed in the external aqueous phase and was also surrounded by a secondary surfactant layer.

Based on the preliminarily surfactant composition determined in this study, we tried to prepare smaller sized PMMA hollow particles with improved wettability. The morphology of PMMA hollow particles with changing the concentration of VAc is shown in Figure 1. The morphology of the particle inner phase could be confirmed by redispersing the dried particles in toluene.¹¹ Because the refractive index of the PMMA is similar to that of toluene, the inner voids filled with air display a different contrast from the PMMA poly-

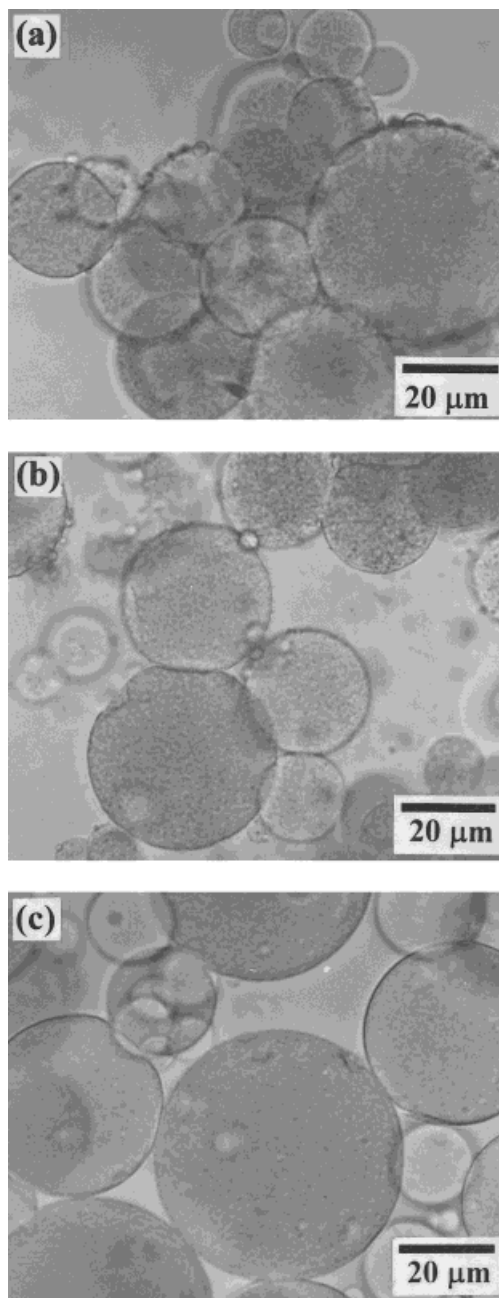


Figure 1 An OM photograph of PMMA multihollow particles varying with the concentration of VAc based on the total monomer weight (wt %) of (a) 0, (b) 13.5, and (c) 30 at 130 rpm.

mer phase. But the high contrast region became gradually evanescent. This is because the voids were replenished with toluene. All PMMA particles shown in Figure 1 contained a large number of high contrast inner voids. This turned out to be that the PMMA particles had a multihollow structure. Unlike previous work that usually displayed

single hollow particles,¹¹ the particles produced in this study showed a multihollow structure. This multihollow structure can be accounted for by considering each interface area of the W/O/W emulsion droplets. When smaller sized W/O/W emulsion droplets were formed, the total interface area between the oil and outer water phase is enhanced. Then the interface area between the inner water and oil phase should also have larger surface area. This trend can be shown by the many small sized inner water droplets. Moreover, the size of the inner voids observed from the OM photographs was around 200–400 nm. This size range is well known to be effective in adjusting the refractive properties between the polymer and air. Figure 2 shows the average particle size of PMMA multihollow particles with the concentration of VAc. The average diameter of the particles was negligibly changed with the concentration of VAc. This appeared to be closely related to the fact that the solubility of VAc [$\delta = 9.0$ (cal/cm³)^{1/2}] was similar to that of MMA [$\delta = 8.8$ (cal/cm³)^{1/2}]. Therefore, the solution properties of the monomer mixture were nearly independent of the concentration of VAc.

In order to improve the wettability of the PMMA multihollow particles, the produced particles were saponified. Figure 3 shows the IR spectra before and after saponification for the PMMA multihollow particles containing 30% VAc. An infinitesimal hydroxy peak was detected before saponification, which was attributed to the remnant PVA used as a stabilizer. On the contrary, after

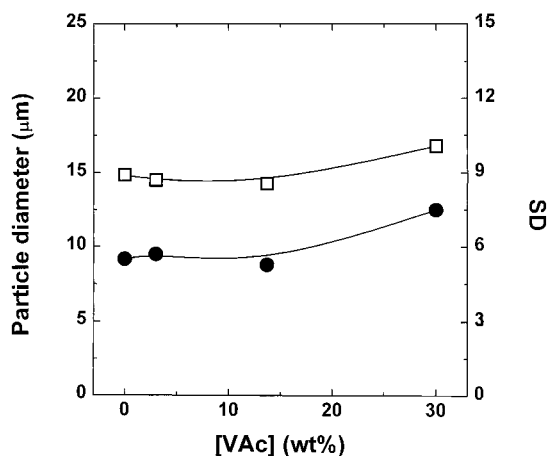


Figure 2 The particle diameter change of PMMA multihollow particles with the concentration of VAc. (□) Particle diameter and (●) standard deviation; 130-rpm agitation speed.

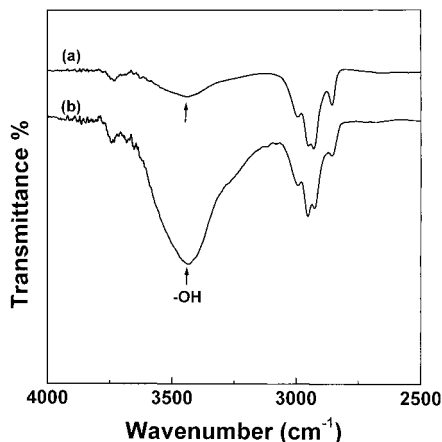


Figure 3 IR spectroscopy (a) before and (b) after saponification of PMMA multihollow particles copolymerizing 30% VAc.

saponification the hydroxy peak was significantly sharpened. This result explains that the acetate groups in the PMMA particles were changed into hydroxy groups through hydrolysis, imparting the wettability to the particles. In addition, even after the saponification the multihollow structure of the PMMA particles remained constant.

Effect of Agitation Speed

Figure 4 shows the average particle size of the PMMA multihollow particles produced by changing the agitation speed. One can easily find that the particle size of the PMMA multihollow particles had a strong dependency on the agitation speed. The emulsion droplets are deformed by the normal and tangential strains on the interfaces between the internal and external phases. Especially at higher agitation speed, the fluctuating velocities on the surface and the associated variation in the pressure distribution exert stresses on the droplet, causing them to break up.¹³ At around a 300-rpm agitation speed especially, the appropriate particle sizes (below 10 μm) for the size requirement in the applications were obtained. However, at high agitation speed (above 300 rpm) a number of submicron-sized small particles were observed, which seems to have stemmed from the conventional emulsion polymerization: that is, the radical reentry of the oil soluble initiator (AIBN) was readily generated from the aqueous phase at harsh shear fluid.¹⁴

Effect of UA Viscosity Enhancer

Figure 5 shows the OM photographs of PMMA multihollow particles produced by changing the

concentration of UA based on the total monomer weight. The figure shows that all particles had a multihollow structure regardless of the concentration of UA. It was noticeable in the hollow structure that large inner voids started to appear at a high concentration of UA. These large inner voids were possibly generated by the enhanced hydrophobicity of the monomer mixtures. The UA has strong hydrophobicity in terms of its long hydrophobic molecular chain.¹⁵ Therefore, the interfacial activity of Span 80 became weak, which eventually resulted in large inner water droplets during emulsion droplet formation. Besides, the enhanced hydrophobicity of the monomer mixture makes the interfacial activity of the secondary surfactants (SLS and APG) lower, so the final W/O/W emulsion droplets also had larger sizes. Figure 6 shows that the final size of the PMMA multihollow particles increased with the increase of UA concentration.

One of characteristics for the PMMA multihollow particles in Figure 5 is that incorporating UA into the particles caused the surface of the final particles to become very smooth and clear. This result can be illustrated from the aspect of the viscosity of the monomer mixture. At low viscosity of the dispersed oil phase, the force to maintain the W/O/W emulsion structure is debilitated because of the inherent thermodynamic instability of the internal aqueous droplets.¹⁰ Therefore, the internal aqueous droplets are inclined to deviate to an external aqueous phase during polymerization. Figure 7 shows the viscosity change of the

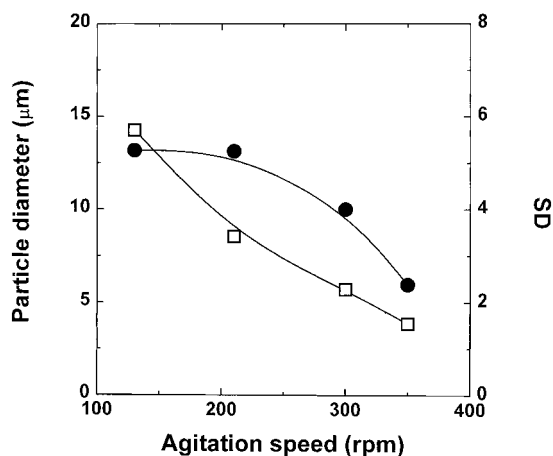


Figure 4 The particle diameter change of PMMA multihollow particles with the agitation speed. (\square) Particle diameter and (\bullet) standard deviation; 13.5% VAc content.

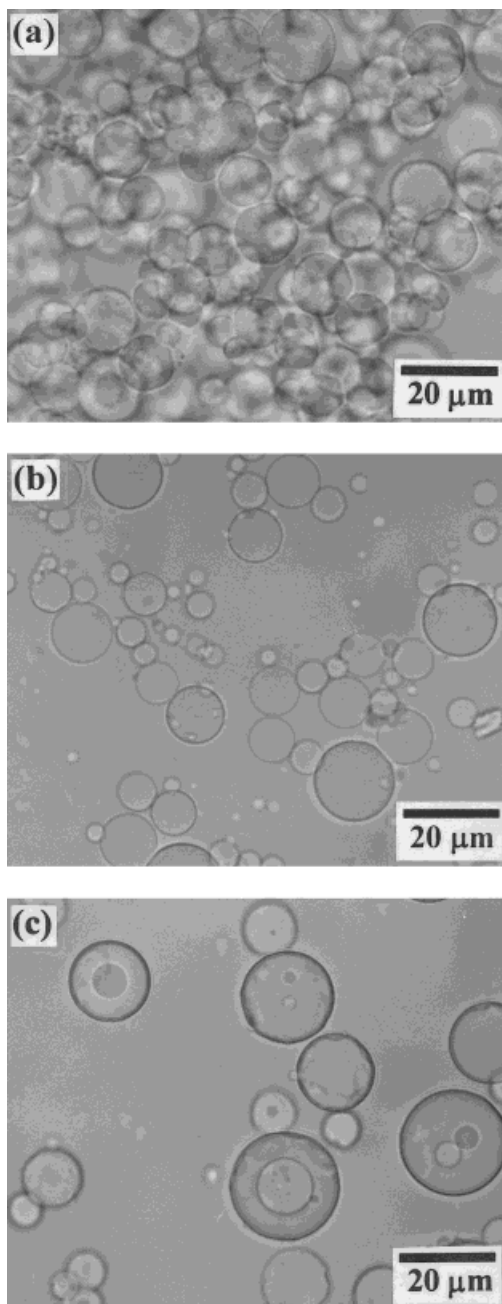


Figure 5 OM photographs of PMMA multihollow particles varying with the concentration of UA, based on the total monomer weight (wt %) of (a) 0, (b) 10, and (c) 15.

monomer mixture with the concentration of UA. As shown, the viscosity of the monomer mixture increased as the concentration of UA in the monomer mixture increased. This increased viscosity of the monomer mixture gave rise to the steric restriction of the mobility of the internal aqueous droplets. Therefore, the internal aqueous droplets

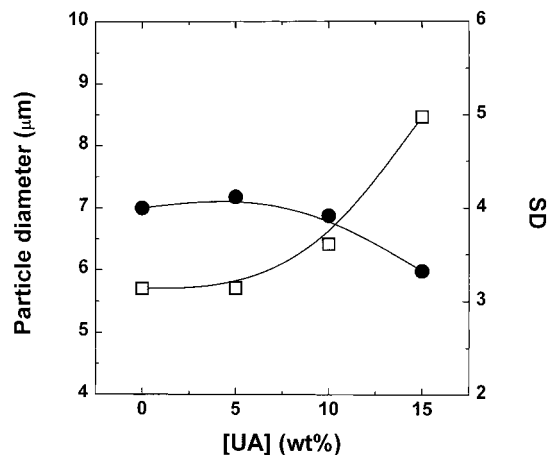


Figure 6 The particle diameter change of PMMA multihollow particles with the concentration of UA. (□) Particle diameter and (●) standard deviation; 300-rpm agitation speed.

could not easily migrate to the external aqueous phase during polymerization. From this result the aggregation caused by the thermodynamic instability of the W/O/W emulsion system could be prevented. Figure 8 shows SEM photograph of PMMA multihollow particles containing 10 wt % UA. The particle surface was very smooth and clear unlike the ones not containing UA in Figure 1. This result strongly supports the idea that the UA in the monomer mixture enhanced the stability of the W/O/W emulsion during polymerization.

CONCLUSIONS

PMMA multihollow particles were produced by W/O/W emulsion polymerization by varying the

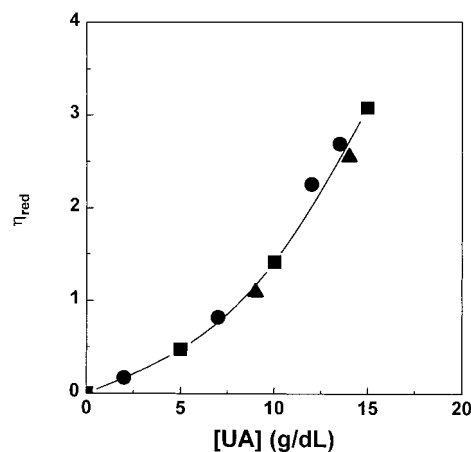


Figure 7 The viscosity change of the monomer mixture (MMA, EGDMA, VAc, and UA) with the concentration of UA: (■) 0 wt % VAc, (●) 6.9 wt % VAc, and (▲) 13.8 wt % VAc.

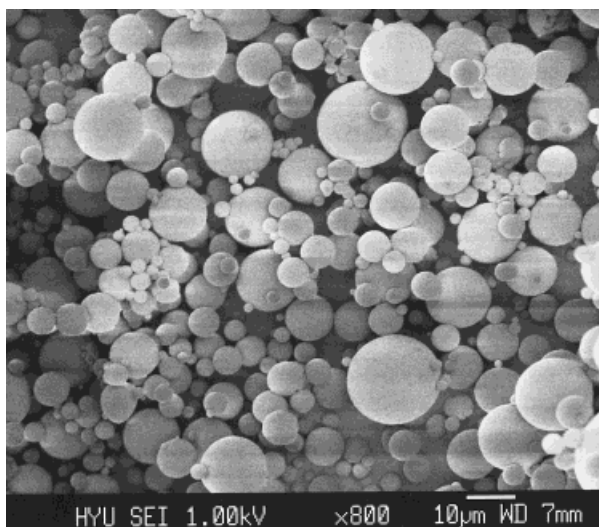


Figure 8 An SEM photograph of PMMA multihollow particles with 10 wt % UA and 3.5 wt % VAc; 300-rpm agitation speed.

agitation speed and concentration of the UA. All the prepared particles had a multihollow structure and a small particle size. The agitation speed had a great influence on determining the final particle size by the droplet breakup process. The UA especially had an effect on producing stable W/O/W emulsion droplets and on obtaining the clear surface of the final PMMA multihollow particles by controlling the hydrophilic and hydrophobic properties and the viscosity of the monomer mixture. A further study will be conducted

because an interesting application of these PMMA multihollow particles is expected to be found in the field of the cosmetic and coating industries.

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