

J.-W. Kim
Y.-G. Joe
K.-D. Suh

Poly(methyl methacrylate) hollow particles by water-in-oil-in-water emulsion polymerization

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Abstract Poly(methyl methacrylate) particles having hollow structures were produced by water-in-oil-in-water (W/O/W) emulsion polymerization where sorbitan monooleate (Span80) was used as a primary surfactant and sodium laurylsulfate and Glucopen (APG, polypeptide derivative) were used as secondary surfactants. Urethane acrylate having a molecular structure with a hard segment in the molecular backbone, a long soft segment in the middle, and vinyl groups at both ends was employed as a reactive viscosity enhancer. At low concentration of urethane acrylate, only a few particles contained a void in the polymer phase. However, as the concentration of urethane acrylate increased, the number of the particles containing the void increased. This was because urethane acrylate increased

the viscosity of the monomer mixture and helped to form the stable W/O/W emulsion droplets, which possibly restricted droplet coalescence during emulsion polymerization. Moreover, at high concentration of urethane acrylate (above 7 wt%), multi-hollow-structured particles were obtained. It is believed that the increase in the lyophilicity of the monomer mixture caused by urethane acrylate led to stronger interfacial activity of the primary surfactant (Span80) and finally resulted in many internal aqueous droplets.

Key words Hollow structure – Reactive viscosity enhancer – Stable water-in-oil-in-water emulsion droplets – Multi-hollow-structured particles – Lyophilicity increase

J.-W. Kim · Y.-G. Joe · K.-D. Suh (✉)
Division of Chemical Engineering
College of Engineering
Hanyang University
Seoul 133-791, Korea

Introduction

Polymer particles having voids in the polymer phase (hollow particles) have gained considerable interest in the fields of cosmetics, coatings, inks, and in the paper industry, due to their ability to protect against ultraviolet radiation and to control the difference in the refractive index between the polymer and air.

Conventional hollow particles have been achieved by the alkali swelling procedure [1], the dynamic swelling method [2], and water-in-oil-in-water (W/O/W) emulsion polymerization [3, 4]. Especially, the hollow particles produced by W/O/W emulsion polymerization have comparatively large sizes (tens of microns). Above all, in

the cosmetics industry these hollow particles have been used as screening filters of ultraviolet rays, because they can attach to the skin evenly and can protect the skin from ultraviolet rays because of their hollow structure. Moreover, when the polymer phase is porous, the hollow particles display compatibility with, and adhesion to, the skin by means of their airing and water-absorbing properties. However, in all applications of these hollow particles produced by W/O/W emulsion polymerization, the inherently unstable W/O/W emulsion droplets readily coalesce to form agglomerates during emulsion polymerization.

In this study, in order to improve the stability of the W/O/W emulsion droplets, we incorporated urethane

acrylate (UA) as a reactive viscosity enhancer into the monomer mixture. This UA is composed of a long polyether soft segment, a hard segment, and reactive vinyl groups, which eventually crosslink during polymerization. The effect of the concentration of UA on the morphology of the hollow particles was studied.

Experimental

Materials

Isophorone diisocyanate (IPDI, Tokyo Chemical Industry Co.) was vacuum distilled before use. Polytetramethylene glycol (PTMG, $M_w = 1.0 \times 10^3 \text{ g mol}^{-1}$, Hyosung BASF), butanediol (BD, Aldrich), ethylene glycol dimethacrylate (EGDMA, Tokyo Chemical Industry Co.), sodium metaphosphate $[(\text{NaPO}_3)_6]$, Aldrich], sorbitan monooleate (Span80, Yakuri Pure Chemical Co.), Glucopen215 (APG, activity 64–65%, $\text{C}_8:\text{C}_{10} = 55:45$, LG Chemicals), and sodium laurylsulfate (SLS, Aldrich) were used as received.

Synthesis of UA

UA was synthesized by the stepwise reaction procedure [5]. The schematic molecular structure is represented in Scheme 1. In the first step, 2 mol IPDI was poured into the glass reactor and nitrogen gas was inlet for 10 min to

eliminate residual moisture. After dissolving 1 wt% dibutyltindilaurate (DBTDL), 1 mol BD dissolved in tetrahydrofuran (THF) was reacted with IPDI at 80 °C for 4 h, resulting in a molecular structure having a hard segment in the middle and isocyanates at both ends. The change in NCO value during the reaction was determined using the dibutylamine back-titration method to find out the end point of the reaction. In the second step, 0.5 mol PTMG was reacted to incorporate the soft segment in the middle of the molecules with the same method as the first step. In the last step, after dissolving 1 wt% DBTDL in the reactor, 2 mol 2-hydroxyethyl methacrylate was reacted with the residual NCO groups at 45 °C for 12 h, capping the molecular ends with reactive vinyl groups. Lastly, after evaporating the THF, a gum-like UA resin was obtained.

W/O/W emulsion polymerization

The ingredients for the production of poly(methyl methacrylate) (PMMA) hollow particles are listed in Table 1. All ingredients of mixture A were dissolved in a round-bottomed reaction kettle equipped with a mechanical stirrer, a reflux condenser, thermocouples and a nitrogen gas inlet system. The water-in-oil emulsion prepared by sonification (5 min) of mixture B

Scheme 1 Schematic reaction procedure and molecular structure of urethane acrylate

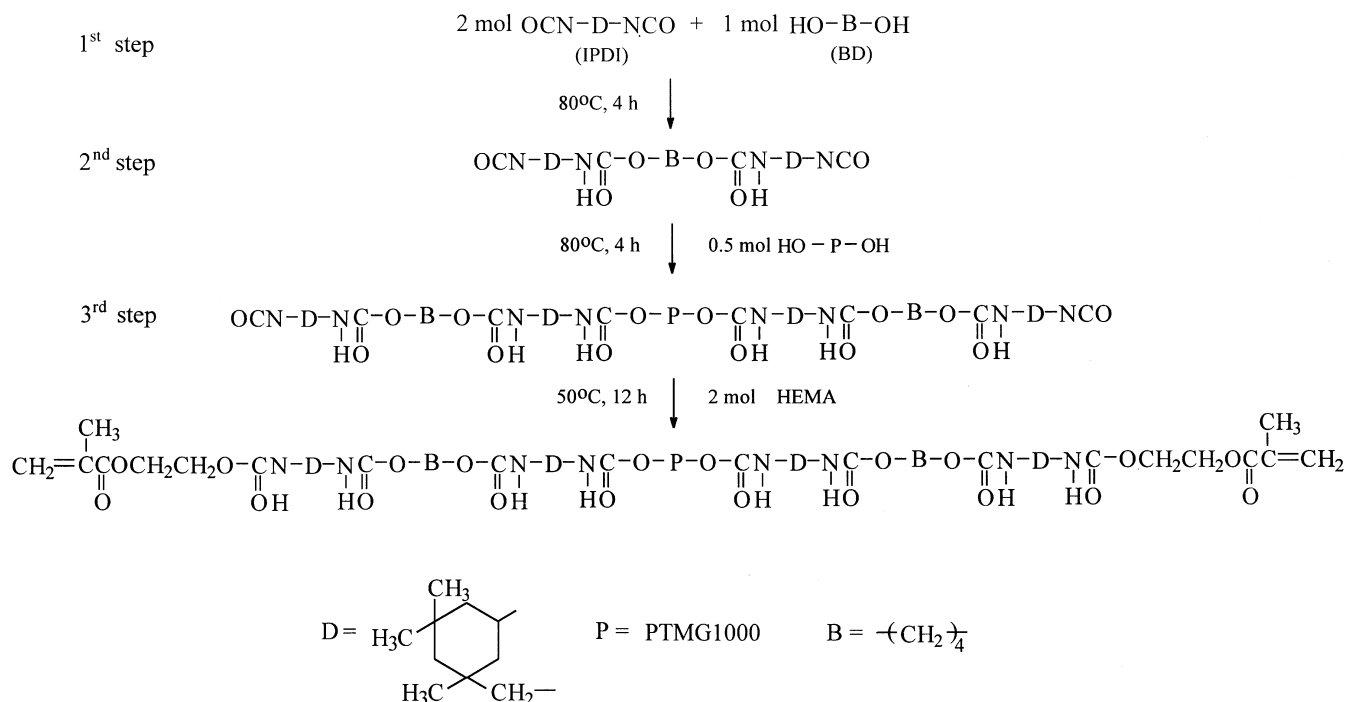


Table 1 The ingredients for the preparation of water-in-oil-in-water emulsion polymerization^a

Mixture	Ingredients	Weight (g)
A	SLS	0.50
	(NaPO ₃) ₆	1.20
	APG ^b	2.00
	Water	220
B	MMA	9.50
	EGDMA	4.00
	UA ^c	1.01 ^{variable}
	AIBN	0.14
	Span80	3.50
	Water ^d	1.00

^a 60 °C; 4 h^b APG was added as a cosurfactant to stabilize the interface between the oil phase and the outer water continuous phase^c The concentration of UA was varied against the total monomer weight (7 wt% on this sample)^d Water in mixture B was added to prepare the water-in-oil emulsion first

was dropped slowly into the reaction kettle containing mixture A at a rotation speed of 100 rpm; thus the W/O/W emulsion was prepared. Then, emulsion polymerization was carried out at 60 °C for 4 h. The supernatant was then decanted and the remaining precipitate was washed repeatedly with butyl alcohol, and dried at ambient temperature overnight in vacuo.

Measurements

The molecular weight of the UA synthesized was measure with a model 410 GPC. The molecular weight and the polydispersity index obtained were $M_w = 8.5 \times 10^3 \text{ g mol}^{-1}$ and 1.3, respectively. The specific viscosity was measured as a function of the UA concentration in the monomer mixture with a standard Ubbelohde viscometer in a thermostated bath at $25 \pm 0.1 \text{ °C}$. The hollow structure of the particles obtained was observed with an optical microscope (OM, Nikon Microphot Fax). In order to verify the hollow structure, the particles were placed onto a cover glass and diluted with a drop of toluene ($n = 1.4967$) the refractive index of which is almost similar to that of PMMA ($n = 1.4893$).

Results and discussion

A schematic representation of the W/O/W emulsion droplets is shown in Fig. 1a and an OM photograph is shown in Fig. 1b. Span80 was used as a primary surfactant (lyophilic surfactant) and SLS and APG (polypeptide derivative) were used as secondary surfactants (hydrophilic surfactant). When the W/O/W emulsion formed, the internal and external aqueous phases

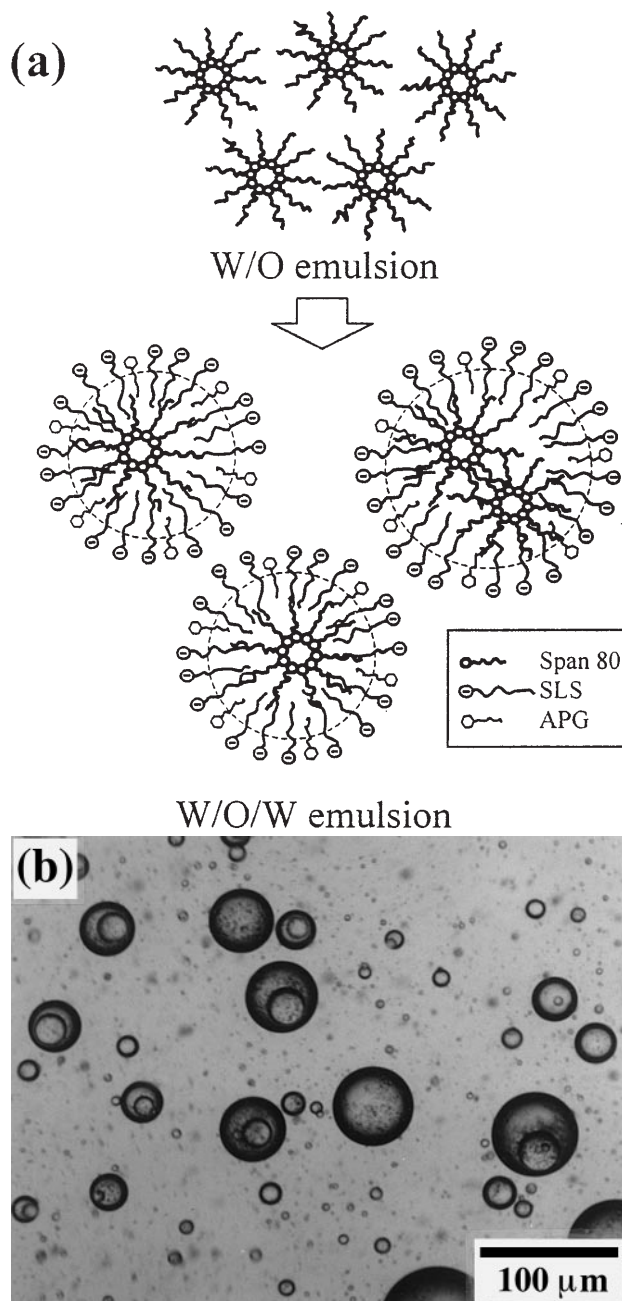


Fig. 1 **a** Schematic representation of water-in-oil-in-water (W/O/W) emulsion droplets containing 7 wt% urethane acrylate (UA), based on the total monomer weight, and **b** their optical microscope (OM) photograph

were separated by an oil layer (MMA, EGDMA, and UA). The two dispersed phases can be clearly seen in Fig. 1b. The small internal aqueous droplets, surrounded by a primary surfactant-stabilizing layer, were dispersed in the oil phase which, in turn, was dispersed in the external aqueous phase and was also surrounded by a secondary surfactant layer. Especially, in the

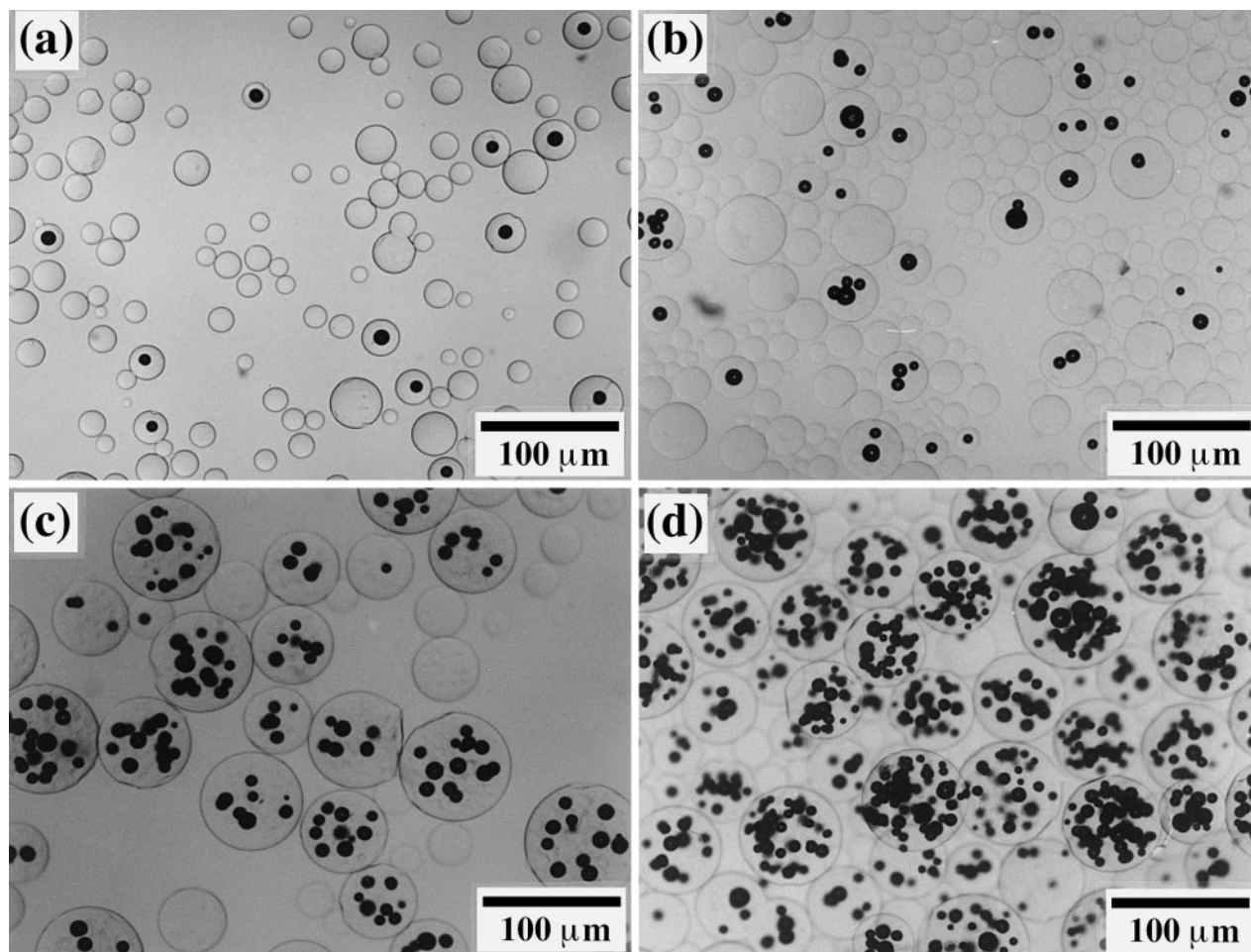


Fig. 2a-d OM photographs of Poly(methyl methacrylate) (PMMA) hollow particles with different concentrations of UA, based on the total monomer weight. **a** 5 wt%, **b** 7 wt%, **c** 10 wt%, and **d** 15 wt%

mixture of the secondary surfactants, APG acting as a cosurfactant increased the efficiency of the interfacial activity between the oil and the external aqueous phase [6]. Therefore, the secondary surfactant layer seemed to be well oriented and packed by SLS and APG, as shown in Fig. 1a.

The OM photographs of the hollow particles produced on changing the concentration of UA are shown in Fig. 2. In this study, in order to confirm the hollow structure, the particles were redispersed in toluene. Because the refractive index of the PMMA is similar to that of toluene, the inner voids filled with air display different contrast from the PMMA polymer phase. In all the OM photographs shown in Fig. 2, high contrast regions were observed. From this result, we could say that the particles produced had a hollow structure. However, the high contrast region disappeared with time. This was because the voids were refilled with toluene.

The number of hollow particles increased with increasing UA concentration. This result can be explained by considering the viscosity properties of the monomer mixture. At low viscosity of the oil phase, the internal aqueous droplets have the tendency to move toward the external aqueous phase, because the internal aqueous droplets have an inherent thermodynamic instability in W/O/W emulsion systems [3]. Therefore, macroscopic particle coalescence was a common observation during polymerization. The viscosity change of the monomer mixture with UA concentration is shown in Fig. 3. A shear viscosity increase of the monomer mixture was observed as the concentration of UA increased. This increased viscosity of the monomer mixture enhanced the stability of the internal aqueous droplets. So, the internal aqueous droplets could not readily move toward the external aqueous phase. From this result, the coalescence caused by the thermodynamic instability of the W/O/W emulsion system could be considerably prevented, which resulted in the particles having more voids in the polymer phase.

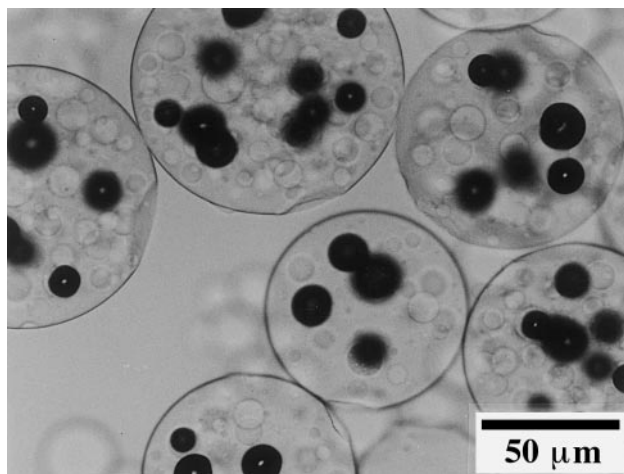


Fig. 3 Specific viscosity change of the monomer mixture (methyl methacrylate, ethylene glycol dimethacrylate, and UA) with UA concentration

It was interesting to observe that when a high concentration of UA was added, above 7 wt%, the particles contained many internal voids (Fig. 2c, d). This appeared to be attributed to the enhanced lyophilicity of the monomer mixture with higher concentrations of UA [7]. Therefore, the interfacial activity of the lyophilic primary surfactant (Span80) became stronger, which eventually resulted in many smaller internal aqueous droplets. So, when polymerization was carried out,

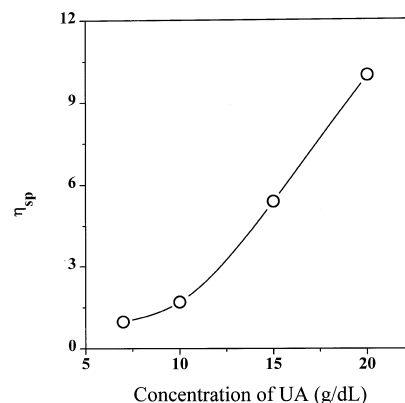


Fig. 4 OM photograph of PMMA hollow particles at high magnification. The concentration of UA was 15 wt%, based on the total monomer weight

hollow particles containing many voids, multi-hollow particles, were produced. The OM photograph of the multi-hollow particles in Fig. 2d at high magnification is shown in Fig. 4. It could be easily found that each particle had a large number of internal voids.

From this study, it was concluded that in the production of PMMA hollow particles by W/O/W emulsion polymerization, the increase in the viscosity and the lyophilicity of the monomer mixture caused by UA prevented droplet coalescence during polymerization and helped to form a multi-hollow particle.

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