

Preparation of block copolymer particles by two-step atom transfer radical polymerization in aqueous media and its unique morphology[☆]

Yasuyuki Kagawa^a, Hideto Minami^b, Masayoshi Okubo^{a,b,*}, Jian Zhou^a

^aGraduate School of Science and Technology, Kobe University, Kobe 657-8501, Japan

^bDepartment of Chemical Science and Engineering, Faculty of Engineering, Kobe University, Kobe 657-8501, Japan

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Abstract

Submicron-sized poly(*i*-butyl methacrylate)-*block*-polystyrene particles were successfully prepared by two-step atom transfer radical polymerization (ATRP) in aqueous media: ATRP in miniemulsion (miniemulsion-ATRP) followed by ATRP in seeded emulsion polymerization (seeded-ATRP). When PiBMA particles, which were prepared by the miniemulsion-ATRP process with polyoxyethylene sorbitan monooleate (Tween 80, nonionic emulsifier) of 6–10 wt % based on *i*BMA, were used as seed in the seeded-ATRP of styrene, the block copolymer particles having narrow molecular weight distribution and pre-determined molecular weight were prepared at high conversion. Some block copolymer particles had an ‘onion-like’ multilayered structure. In this way, controlled/living free radical polymerization can be employed to obtain unique particle morphologies that may not be easily accessible using conventional free radical polymerization.

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1. Introduction

Atom transfer radical polymerization (ATRP) [1,2] has emerged as a powerful method for the synthesis of well-defined vinyl polymers of controlled molecular weight and narrow molecular weight distribution. Its success is due to the effective minimization of termination and chain transfer reactions. The kinetics of ATRP have been investigated in detail by many research groups [3]. Syntheses of block copolymers by solution, emulsion, and miniemulsion ATRP in aqueous media have also been reported [4–16]. In most of the papers describing the synthesis of block copolymer by miniemulsion-ATRP, the first block was prepared by solution- or bulk-ATRP, and after purification of macroinitiator (first block), the miniemulsion-ATRP was conducted. In a previous paper, poly(*i*-butyl methacrylate)-*block*-polystyrene (PiBMA-*b*-PS) was prepared in aqueous media by two-step ATRP, employing the ethyl 2-bromoisobutyrate/CuBr/4,4′-dinonyl-

2,2′-dipyridyl (dNdp) initiator system [16]. The first and second steps were, respectively, carried out in miniemulsion polymerization (miniemulsion-ATRP) of *i*-butyl methacrylate (*i*BMA) and in seeded emulsion polymerization (seeded-ATRP) of styrene. The purification of macroinitiator was not required, and the synthesis of block copolymer was smoothly and easily conducted. However, the polymerization rate of styrene in the second step at 70 °C was low and the conversion was only taken to approximately 40% for 96 h.

In this article, further optimization of the experimental conditions for the preparation of PiBMA-*b*-PS polymer particles having narrow molecular weight distribution at high conversion by the two-step ATRP and its unique particle morphology will be reported.

2. Experimental

2.1. Materials

Styrene and *i*BMA were purified by distillation under reduced pressure in a nitrogen atmosphere. Deionized water

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* Corresponding author. Tel./fax: +81 78 803 6161.

E-mail address: okubo@kobe-u.ac.jp (M. Okubo).

with a specific resistance of $5 \times 10^6 \Omega \text{ cm}$ was distilled prior to use. Ethyl 2-bromoisobutyrate (EBiB) (Tokyo Kasei Kogyo Co. Ltd, Tokyo, Japan) as initiator, 4,4'-dinonyl-2,2'-dipyridyl (dNdp) (Aldrich Chem Co. Ltd) as ligand, CuBr (Nacalai tesque Inc., Kyoto, Japan) as catalyst and polyoxyethylene sorbitan monooleate (Tween 80) (Nacalai tesque Inc., Kyoto, Japan) as nonionic emulsifier were used as received.

2.2. Preparation of PiBMA macroinitiator by miniemulsion-ATRP

PiBMA macroinitiator (PiBMA-Br) was prepared by miniemulsion-ATRP under the conditions listed in Table 1 according to the polymerization procedure described previously [16]. Firstly, CuBr, a part of *i*BMA, and dNdp were mixed and heated in a sealed glass tube under nitrogen atmosphere at 70 °C until the mixture became a homogeneous solution. The solution to which the remains of *i*BMA and EBiB were added was immediately poured into various concentrations of Tween 80 aqueous solution, and subsequently ultrasonicated for 2 min in an ice-water bath. After emulsification, the miniemulsion was immediately transferred to a glass tube, where nitrogen was filled. Miniemulsion polymerization was conducted in the sealed glass tube at 40 °C for 48 h under nitrogen atmosphere. The hydrodynamic diameters of the polymer particles were measured using dynamic light scattering (DLS) (DLS-700, Otsuka Electronics Co., Ltd, Kyoto, Japan) at the light-scattering angle of 90° at room temperature after the emulsions were diluted to 10 ppm with distilled water. The conversion of monomer was calculated from consumption of monomer measured with a gas chromatography (GC-18A, Shimadzu Co., Kyoto, Japan).

2.3. Preparation of PiBMA-*b*-PS particles by seeded-ATRP of styrene with PiBMA-Br emulsion

Seeded-ATRPs with the macroinitiator PiBMA-Br seed particles were conducted in sealed glass tubes under the conditions listed in Table 2 following the previously

Table 1
Preparation of PiBMA-Br particles by miniemulsion-ATRP

Ingredients		
<i>i</i> BMA (g)	1.5	(110×10^{-4} mol)
EBiB (mg)	10	(0.5×10^{-4} mol)
CuBr (mg)	16	(1.1×10^{-4} mol)
dNdp (mg)	86	(2.1×10^{-4} mol)
Tween 80 (mg)	15–450 ^a	
Water (g)	15	

Abbreviations: *i*BMA, *i*-butyl methacrylate; EBiB, ethyl 2-bromoisobutyrate; dNdp, 4,4'-dinonyl-2,2'-dipyridyl; Tween 80, polyoxyethylene sorbitan monooleate. Miniemulsion: prepared with an ultrasonic homogenizer in an ice-water bath for 2 min. ATRP: in sealed glass tubes: N₂; 40 °C; 48 h.

^a 1–30 wt % based on *i*BMA.

Table 2
Preparation of PiBMA-*b*-PS particles by seeded-ATRP of styrene with PiBMA-Br seed particles

Ingredients	
PiBMA-Br emulsion ^a (g)	11
PiBMA-Br seed particles (g)	1
Monomer emulsion ^b	
Styrene (g)	1
Tween 80 (mg)	14
Water (g)	4.5

ATRP: in sealed glass tubes: N₂; 70 °C; 96 h; shaking rate, 60 cycles/min.

^a Prepared by miniemulsion-ATRP.

^b Monomer emulsion was prepared with the ultrasonic homogenizer for 10 min in the ice-water bath before mixing with the seed.

reported procedure [16]. After the miniemulsion-ATRP, the PiBMA-Br emulsion was mixed to a styrene emulsion that was prepared by ultrasonication of a mixture of Tween 80 aqueous solution and styrene for 10 min in an ice-water bath, and then the polymerization was conducted at 70 °C for 96 h under nitrogen atmosphere.

2.4. Molecular weight measurements

Number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution were measured by gel permeation chromatography (GPC) with two styrene/divinylbenzene gel columns (TOSOH Corporation, TSKgel GMH_{HR}-H, 7.8 mm i.d. \times 30 cm) using THF as eluent at 40 °C at a flow rate of 1.0 mL/min employing refractive index (TOSOH RI-8020/21) and ultraviolet detectors (TOYO SODA UV-8II). The columns were calibrated with six standard PS samples (1.05×10^3 – 5.48×10^6 , $M_w/M_n = 1.01$ – 1.15). Theoretical molecular weight (M_{th}) was calculated by following equation;

$$M_{th} = \alpha[M]_0 M_M / [I]_0$$

where α is the conversion of monomer, $[M]_0$ and $[I]_0$ are the initial concentration of monomer and initiator, respectively, and M_M is the molecular weight of monomer.

2.5. Morphology observation

The morphology of the PiBMA-*b*-PS particles was examined by observation of their ultrathin cross sections using a transmission electron microscope (H-7500, Hitachi High-Technologies Co., Tokyo, Japan). The cross sections were prepared by staining the dried PiBMA-*b*-PS particles with RuO₄ vapor at room temperature for 30 min in the presence of 1% RuO₄ aqueous solution, and subsequent dispersed in an epoxy matrix, cured at room temperature for 24 h, and finally microtomed.

3. Results and discussion

3.1. Effect of emulsifier concentration

PiBMA-Br seed particles were prepared by miniemulsion-ATRP at various concentrations of Tween 80 (1–30 wt % based on *i*BMA) as emulsifier at 40 °C for 48 h. The data at 30 wt % concentration of Tween 80 were obtained in the previous paper [16]. As shown in Table 3, the *i*BMA conversions were above 93% in all cases. The experimental M_n values agreed relatively well with the theoretical values. The polydispersities (M_w/M_n) were above 1.6 for 6, 10 and 20 wt % emulsifiers, but approximately 1.4 at 1, 3 and 30 wt %. Coagulation was observed at the emulsifier concentrations of 1 and 3 wt %, and therefore the particles size could not be accurately measured by DLS in these cases. Slight coagulation was observed in the emulsifier concentration range of 6–20 wt %, but none at 30 wt %. The particle size decreased with an increase in the emulsifier concentration, but it was still large even at higher emulsifier concentration (10–30 wt %). The reason may be due to the partition of the nonionic emulsifier in monomer droplets [17] and polymer particles [18] during emulsion polymerization. The surface tensions of all PiBMA emulsions prepared by the miniemulsion-ATRP of *i*BMA were higher than that of Tween 80 aqueous solution at the critical micelle concentration, which indicates no free micelle. Moreover, since this ATRP system is the direct ATRP using Cu(I)Br, which is sensitive to oxygen, the ultrasonication for preparation of *i*BMA emulsion was carried out for a short time to avoid the hindrance due to oxygen. This may be also one of the reasons for the preparation of such large particles even at higher emulsifier concentrations.

Table 3 also shows that in all seeded-ATRPs, PiBMA-*b*-PSs were successfully prepared in a controlled manner at high conversion, in particular at 3, 6, and 10 wt % of the emulsifier concentrations in the first-step polymerization. Unexpectedly, as the emulsifier concentration increased, the styrene conversion went through a maximum. Only intermediate conversions were achieved at 1 and 30 wt %, whereas higher conversions were obtained at 6 and 10 wt %. In this way, there was an optimum range of the emulsifier concentration in the first-step ATRP (miniemulsion-ATRP) to carry out the second-step ATRP (seeded-ATRP) smoothly. The reason for the low conversion at the lowest emulsifier concentration (1 wt %) may be based on that the absorption rate of styrene into the seed particles was low because of the coagulation during the miniemulsion polymerization. On the other hand, the low conversion at the highest emulsifier concentration (30 wt %) may be due to a marked escape of Cu(II)/dNdpy complexes from the polymerizing particles to the aqueous medium because of its large total interfacial area. Matyjaszewski and Charleux et al. reported that the escape of Cu(II)/ligand complexes from polymerizing particles to the aqueous medium occur with

Table 3
Preparations of PiBMA-Br particles by miniemulsion-ATRP at various concentrations of Tween 80 as emulsifier and of PiBMA-*b*-PS particles by seeded-ATRP with the PiBMA seed particles

Miniemulsion-ATRP		Seeded-ATRP					
Emulsifier conc. (wt %) ^a	Conv. (%) ^b	$M_n \times 10^4$	M_w/M_n^c	D_h^d (nm)	Conv. (%) ^b	$M_n \times 10^4$	M_w/M_n^c
1	97	2.8	1.43	> 572 ^e	52	4.4	1.39
3	94	2.7	1.42	> 411 ^e	81	5.3	1.25
6	97	2.8	1.90	280	90	5.1	1.26
10	93	2.6	1.69	255	96	5.1	1.40
20	100	2.8	1.67	263	79	5.3	1.51
30	99	2.8	1.43	201	40	3.6	1.28

Miniemulsion: prepared with the ultrasonic homogenizer in the ice-water bath for 2 min. Miniemulsion-ATRP: in sealed glass tubes; N₂; 40 °C; 48 h; shaking rate, 60 cycles/min. Seeded-ATRP: in sealed glass tubes; N₂; 70 °C; 96 h; shaking rate, 60 cycles/min.

^a Concentration of Tween 80 based on *i*BMA.

^b Measured with gas chromatography.

^c Measured with gel permeation chromatography.

^d Measured with dynamic light scattering.

^e Coagulation was observed.

not only hydrophilic ligand but also hydrophobic ligand such 4,4'-di-(5-nonyl)-4,4'-bipyridine [7,8]. Since the similar ligand was used in our polymerization systems, the escape of Cu(II)/ligand complexes to the aqueous medium could be considered as the reason for the low rate of polymerization in the case of small particles, that is, the large surface area.

Fig. 1 shows molecular weight distributions of the *PiBMA-Br* and *PiBMA-*b*-PS* (a–c) prepared by miniemulsion-ATRP at 1, 10, and 30 wt % of Tween 80 concentrations and seeded-ATRP with those *PiBMA* seed particles, respectively, and molecular weight distributions of *PiBMA-*b*-PS* (a'–c') prepared by seeded-ATRP, employing RI and UV detectors. As shown in Fig. 1(a–c), the molecular weight distributions of all *PiBMA-Br* had tailing at both high and low molecular ends. These phenomena were not generally observed in homogeneous systems [3]. Compared with the peaks of *PiBMA-Br*, those of the *PiBMA-*b*-PS* shifted to higher molecular weight with maintaining narrow molecular weight distributions ($M_w/M_n=1.26$ – 1.51). However, the molecular weight distributions had a small shoulder at the low molecular weight end corresponding to the *PiBMA* seed. These results show that a small amount of dead *PiBMA* existed after the miniemulsion-ATRP of *iBMA*. As illustrated in Fig. 1(a'–c'), the molecular weight distributions of *PiBMA-*b*-PS* detected with RI and UV corresponded well at all Tween 80 concentrations. These results show that almost all polymers were *PiBMA-*b*-PS*.

3.2. Morphology

Fig. 2 shows TEM photographs of ultrathin sections of RuO₄-stained *PiBMA-*b*-PS* particles, which were prepared by the seeded-ATRPs with *PiBMA-Br* particles prepared at 3 and 6 wt % of the emulsifiers. The *PiBMA-*b*-PS* (1/1, w/w) had narrow molecular weight distributions ($M_w/M_n=1.25$ – 1.26). Interestingly, 'onion-like' multilayered morphology, of which thickness of one layer was ca. 19 nm, was observed without solvent absorbing/releasing method (SARM), explained below. In a previous article, we reported that micron-sized, monodisperse poly(methyl methacrylate) (PMMA)/PS composite particles consisting of a PMMA core and a PS shell were prepared by seeded dispersion polymerization of styrene, though the morphology was thermodynamically unstable in an ethanol/water medium [19]. Furthermore, absorption of toluene followed by release and slowly evaporation, which was named 'solvent absorbing/releasing method (SARM)' [20], resulted in a drastic change in the morphology of the PMMA/PS (1/1, w/w) composite particles, from the core-shell structure to an 'onion-like' alternating multilayered structure [21]. It was found that the formation of such a unique morphology was affected by the PMMA-*b*-PS and/or PMMA-*g*-PS prepared during the seeded dispersion polymerization [22]. Moreover, PMMA-*b*-PS particles, which were prepared by evaporation of toluene from the commercial PMMA-*b*-PS/toluene droplets dispersed in sodium dodecyl sulfate aqueous solution, had the onion-like alternating

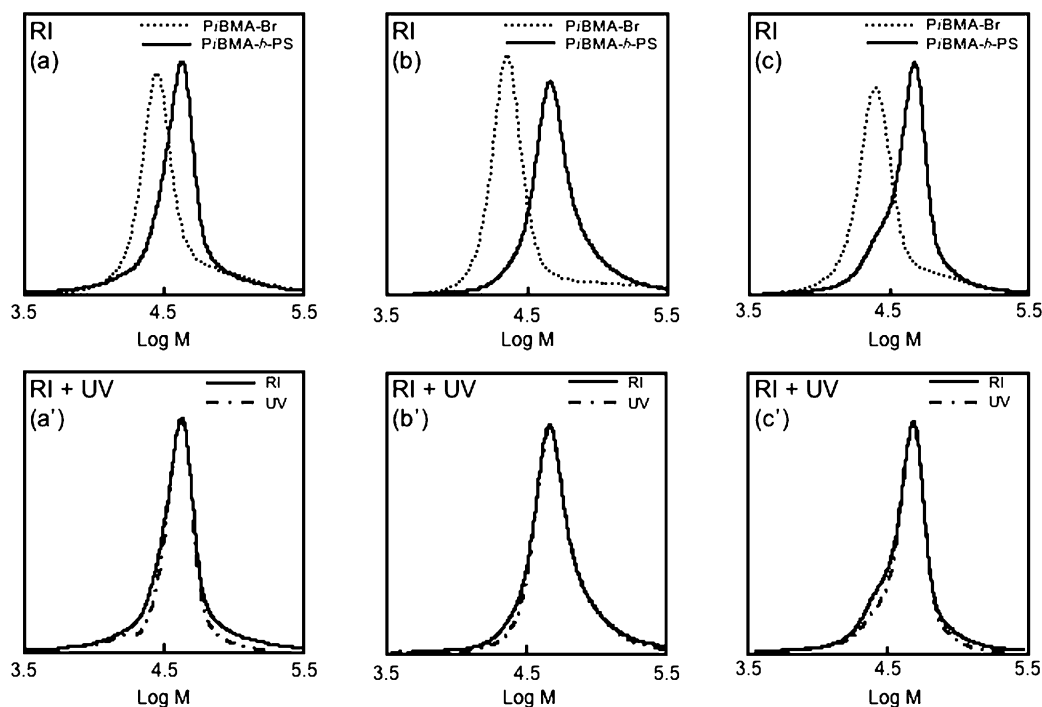


Fig. 1. Molecular weight distributions of *PiBMA-Br* and *PiBMA-*b*-PS* (a–c) prepared by miniemulsion-ATRP at various Tween 80 concentrations (wt % based on *iBMA*): (a) 1; (b) 10; (c) 30 and seeded-ATRP, respectively, and molecular weight distributions of *PiBMA-*b*-PS* (a'–c') prepared by seeded-ATRP with these *PiBMA-Br* seed particles. *PiBMA-Br* (RI), - - -; *PiBMA-*b*-PS* (RI), —; *PiBMA-*b*-PS* (UV) - - - -.

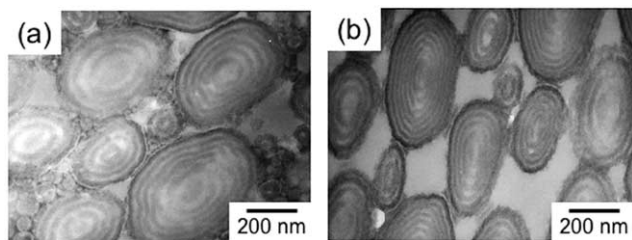


Fig. 2. Transmission electron microscope photographs of ultrathin cross sections of *PiBMA-b-PS* particles, stained RuO_4 with vapor for 30 min, prepared by seeded-ATRP with *PiBMA-Br* particles prepared by the miniemulsion-ATRP at Tween 80 concentrations of 3 (a) and 6 (b) wt % based on *iBMA*.

multilayered morphology [23]. The formation of ‘onion-like’ particles was based on that the PMMA or PS was alternately laminated from the particle/water interphase toward the center of particle during the evaporation of toluene and the most outside (first) layer, which contacted with the aqueous medium, consisted of PMMA. Such an ‘onion-like’ morphology should be thermodynamically stable. PMMA-*b*-PS and/or PMMA-*g*-PS prepared during the seeded dispersion polymerization would play the role of compatibilizer at the PMMA/PS interphases [24]. In the present paper, such a particle morphology was directly prepared during the seeded-ATRP in the aqueous medium. In future work, the effects of monomer composition, kind of monomers, and molecular weight of each block segment on the formation of the ‘onion-like’ particles will be investigated.

From the above results, it is clarified that there was an optimum range of the emulsifier concentration (6–10 wt % based on monomer) in the first-step ATRP (miniemulsion-ATRP) to prepare the block copolymer particles having narrow molecular weight distribution and pre-determined molecular weight at high conversion in the second-step ATRP (seeded-ATRP). In this paper, the effect of particle size on polymerization rate was discussed. Up to now, there is no investigation about the effect of particle size on polymerization rate at second-step ATRP for preparation of block copolymer in aqueous medium. Furthermore, it was found that the *PiBMA-b-PS* particles had the ‘onion-like’ alternating multilayered morphology. To our knowledge, there has been no report dealing with the direct preparation of polymer particles having such a unique morphology. In this way, controlled/living radical polymerization can be employed to obtain unique particle morphologies that may

not be prepared easily by using conventional radical polymerization in aqueous medium.

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