Colloid Polym Sci (2004) 282: 747–752
DOI 10.1007/s00396-003-1010-2

ORIGINAL CONTRIBUTION

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Preparation of block copolymer by atom transfer radical seeded emulsion polymerization

Received: 10 April 2003
Accepted: 22 September 2003

Part CCXLVIII of the series "Studies on Suspension and Emulsion"

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Abstract Poly(*i*-butyl methacrylate)-polystyrene block copolymer was successfully prepared in an aqueous medium by two-step atom transfer radical polymerization (ATRP), mini-emulsion- and seeded-ATRP, in which ethyl 2-bromoisobutyrate/CuBr/4,4'-dinonyl-2,2'-dipyridyl initiator system was used. The block copolymer had narrow molecular weight distribution ($Mw/Mn=1.1$) and the number-average molecular weight measured by gel permeation chromatography agreed with the calculated value.

Keywords Atom transfer radical polymerization (ATRP) · Mini-emulsion polymerization · Seeded polymerization · Living radical polymerization · Block polymer

Introduction

Living radical polymerization leads to a well-defined polymer having controllable molecular weight and narrow molecular weight distribution, due to absence of termination and chain transfer reactions. Since the first paper reporting living radical polymerization by Otsu et al. [1] in 1982, many research groups have begun to pay attention to this area. Several techniques such as nitroxide-mediated living polymerization [2] (NMLP), degenerative transfer [3, 4] (DT), atom transfer radical polymerization [5, 6] (ATRP), and reversible addition-fragmentation chain transfer polymerization [7] (RAFT) have been explored for living radical polymerization. These techniques are applicable to various monomers and the most distinguishable advantage is tolerance to aqueous systems, which are environmentally favorable systems, as compared with living ionic polymerization.

Recently, there have been papers dealing with living radical polymerization in an aqueous medium. Water-soluble α-methoxypolyethylene oxide methacrylate macromonomer was successfully polymerized by ATRP in an aqueous solution [8]. Polystyrene (PS) with narrow molecular weight distribution was prepared by NMLP [9, 10] and DT [11] methods in mini-emulsion systems. ATRP of *n*-butyl methacrylate was also successfully carried out in a mini-emulsion system [12]. Emulsion polymerization by the RAFT process led to a stable poly(4-acetoxystyrene) emulsion with a molecular weight distribution of 1.61 [13].

Moreover, some papers [13, 14, 15, 16, 17] reported preparation of block copolymers by using the above living radical polymerization processes. Poly(4-acetoxystyrene)-*b*-PS was prepared by RAFT in bulk and solution polymerizations [13]. Poly(methyl acrylate)-*b*-PS was prepared by ATRP in an organic solution [14]. Preparation of block copolymer by ATRP in supercritical carbon dioxide, in which fluoroalkyl-substituted 2,2'-bipyridine was used as a ligand, has been reported [15]. Matyjaszewski and coworkers also prepared polybuthylacrylate (PBA)-*b*-PS in an aqueous medium [16], with PBA-Br macro-initiator that was prepared by ATRP in bulk system. Sawamoto and coworkers also prepared PBA-*b*-PS in a suspension system, in which the organic phase contained toluene [17]. In these ways, as far as we know, preparation of hydrophobic block copolymer in a complete aqueous system has not been reported, though water-soluble poly(ethylene oxide)-*b*-poly(2-hydroxyethyl methacrylate) has been prepared by ATRP in an aqueous solution [18].

This article describes the preparation of poly(*i*-butyl methacrylate) (P*i*-BMA)-*b*-PS in a complete aqueous system by a two-step ATRP, i.e., mini-emulsion-ATRP and seeded-ATRP.

Experimental

Materials

Styrene and iso-butyl methacrylate (*i*-BMA) were purified by distillation under reduced pressure in a nitrogen atmosphere. Deionized water with a specific resistance of 5×10^{6} Ω cm was distilled. Ethyl 2-bromoisobutyrate (EB*i*B) as initiator (Tokyo Kasei Kogyo, Tokyo, Japan), 4,4'-dinonyl-2,2'-dipyridyl (DNdpy) as ligand (Aldrich.), CuBr as catalyst (Nacalai tesque, Kyoto, Japan) and the emulsifier, polyoxyethylene sorbitan monooleate (Tween 80) (Nacalai tesque, Kyoto, Japan) were used without any further purification.

Preparation of P*i*-BMA macro-initiator by ATRP in a mini-emulsion system

P*i*-BMA macro-initiator (P*i*-BMA-Br) was prepared by ATRP in a mini-emulsion system (mini-emulsion-ATRP) under the conditions listed in Table 1. Firstly, CuBr was added to the glass tube with a rubber septum and the tube was degassed with nitrogen to remove oxygen. DNdpy dissolved in a part of the *i*-BMA was added into the tube by syringe, and then the tube was closed and put into a shaking water bath at 70 °C for 20 min in order to dissolve the CuBr, which became dark brown. Remains of *i*-BMA monomer and EB*i*B were added to the tube in a glove-box under nitrogen atmosphere. The homogeneous solution was mixed with 3 wt% Tween 80 aqueous solution and ultrasonicated for 10 min at 0 °C. Mini-emulsion-ATRP was carried out at 40 °C for 48 h under a nitrogen atmosphere in sealed glass tubes.

Preparation of P*i*-BMA-b-PS by ATRP in the P*i*-BMA-Br seed emulsion

Atom transfer living radical seeded emulsion polymerization (seeded-ATRP) was carried out in a sealed glass tube under the conditions listed in Table 2. Styrene was emulsified in Tween 80 aqueous solution by ultrasonication for 10 min at 0 °C and the styrene emulsion was mixed with the P*i*-BMA-Br emulsion in the glove-box under a nitrogen atmosphere. Seeded-ATRP was carried out in a shaking water bath at 70 °C under a nitrogen atmosphere. The particles were observed with an optical microscope (Microphot-FXA, Nikon, Japan) and a scanning electron microscope (SEM) (S-2460N, HITACHI, Japan).

Table 1 Preparation of P*i*-BMA-Br by bulk[a]- and mini-emulsion[b]-ATRP[c]

Ingredients		No. 1[a]	No. 2[a]	No. 3[c]
i-BMA	(g)	1	2	1.5
EB*i*B	(mg)	10	10	10
CuBr	(mg)	8	8	16
DNdpy	(mg)	39	39	86
Tween 80	(g)	-	-	0.45
Water	(g)	-	-	15
Conversion[d]	(%)	97	86	99

i-BMA *i*-butyl methacrylate, *EBiB*2-bromoisobutyrate, *DNdpy* 4,4'-dinonyl-2,2'-dipyridyl, *Tween 80* polyoxyethylene sorbitan monooleate

[a] N$_2$, 30 °C, 12 h

[b] Prepared using an ultrasonic homogenizer for 10 min

[c] N$_2$, 40 °C, 48 h

[d] Conversion was measured by gas chromatography

Particle diameter measurement

The hydrodynamic particle-size distributions of monomer and polymer emulsions were measured by dynamic light scattering (DLS) (DLS-700, Otsuka Electronics, Osaka, Japan) at the light-scattering angle of 90° at room temperature, after the emulsion had been diluted to 10 ppm with styrene-saturated water, dissolving Tween 80 to avoid the elution of monomer and desorption of Tween 80 from the monomer droplets into the aqueous medium.

Molecular weight measurement

Number-average molecular weight (*Mn*), weight-average molecular weight (*Mw*), and the 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.×30 cm) using THF as an eluate at 40 °C and a flow rate of 1.0 mL/min. The column was connected with a refractive detector and an ultraviolet detector (Toyo Soda UV-8II). The column was calibrated against five standard PS samples (1.05×10^{3}–5.48×10^{6}, $Mw/Mn = 1.01$–1.15).

Table 2 Preparation of block copolymer (P*i*-BMA-*b*-PS) by seeded-ATRP[a] of styrene with P*i*-BMA-Br seed particles

Ingredients				Conversion[d] (%)
P*i*-BMA-Br emulsion[b] (mL)	Monomer emulsion[c]			
	Styrene (g)	Tween 80 (mg)	Water (g)	
11[b]	1	14	4.5	40

Tween 80 polyoxyethylene sorbitan monooleate

[a] N$_2$, 70 °C, 96 h

[b] Prepared by mini-emulsion-ATRP under the conditions of No. 3 listed in Table 1 ; 1 g of Pi-BMA-Br particles (Dh = 203 nm) were dispersed

[c] Monomer emulsion was prepared using an ultrasonic homogenizer before mixing with the seed emulsion

[d] Conversion was measured by gas chromatography

NMR measurement

The composition of polymers was confirmed by ^{1}H-NMR with a Bruker DPX250 MHz spectrometer at room temperature in deuterated pyridine including 0.1 wt% tetramethylsilane as an internal standard.

Thin-layer chromatography

Thin-layer chromatography (TLC) plates, (Merck, Germany) coated with a silica gel layer of thickness 0.25 mm, were used. The silica gel phase was activated by heating the TLC plates at 110 °C for 1 h immediately before use. Choloroform solutions of P*i*-BMA-Br, PS and P*i*BMA-*b*-PS were prepared by dissolving the corresponding samples in chloroform at a concentration of 100 g/L and then dropping them onto the TLC plates with a microsyringe. After elution with various developing solvents, the TLC plates were dried and the separation was visualized with iodine vapor.

Results and discussions

Preliminarily, ATRP in bulk systems (bulk-ATRP) were carried out in sealed glass tubes under the conditions of Nos. 1 and 2 listed in Table 1 to confirm whether the EB*i*B/CuBr/DNdpy initiator system would be applicable to the ATRP or not, before the initiator system was applied to an aqueous system. After oxygen was carefully removed, the sealed glass tube was closed and horizontally shaken in a water bath. The two polymerizations were almost completed in 12 h.

Figure 1 shows GPC curves of the two P*i*-BMA-Br prepared by the bulk-ATRP. Both polymers had narrow molecular weight distributions ($Mw/Mn = 1.3$ and 1.2) and the number-average molecular weights ($Mn = 21{,}800$ and 34,100, respectively) agreed with the calculated values ($M_{\mathrm{cal}} = 19{,}000$ and 33,500, respectively). These results indicated that the initiator system was applicable to ATRP.

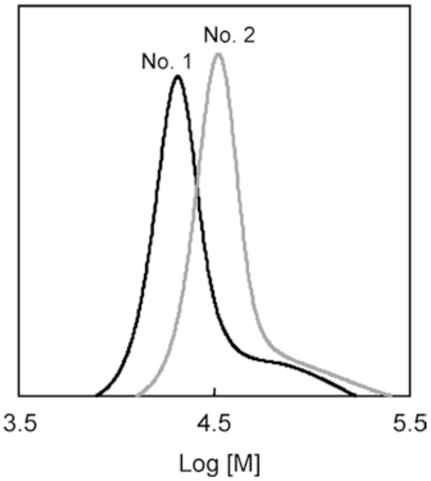


Fig. 1 GPC charts of P*i*-BMA-Br prepared by bulk-ATRP under the conditions of *Nos. 1* and *2* listed in Table 1

The conditions of No. 3 listed in Table 1 show the recipe for preparation of P*i*-BMA-Br particles by mini-emlsion-ATRP. $CuBr_2$ oxidized from CuBr was easily soluble in water and the CuBr concentration in monomer droplets decreased, which led to an uncontrolled reaction. In order to keep a well-controlled reaction, the quantity of CuBr was increased, though excessive CuBr would cause the aggregation of mini-emulsion. A low reaction temperature and a highly hydrophobic ligand were chosen in order to avoid the loss of CuBr from monomer droplets. The conversion after 48 h at 40 °C was 99%, which indicated that the polymerization was completed.

Figure 2 shows the hydrodynamic particle size and size distributions of the monomer and polymer emulsions before (a) and after (b) the mini-emulsion-ATRP, measured by DLS. There was no change in the diameters before and after the mini-emulsion-ATRP, which indicates that the mini-emulsion polymerization successfully proceeded without aggregation and no by-product particle.

Table 2 shows the conditions of preparation of P*i*-BMA-*b*-PS by seeded-ATRP with the P*i*-BMA-Br seed emulsion as macro-initiator. As the rate of ATRP of styrene was much slower than that of *i*-BMA, the seeded-ATRP was carried out at 70 °C for 96 h, though the solubility of $CuBr_2$ in water was increased by elevating the temperature. The conversion was 40%. Though the conversion was not high, the result suggests the P*i*-BMA-Br worked as macro-initiator. SEM photographs of the P*i*-BMA-Br (a) and the P*i*-BMA-*b*-PS (b) particles are shown in Fig. 3. Both particles were submicron-size and no coagulant was observed.

Figure 4 shows ^{1}H-NMR charts of the P*i*-BMA-Br (a) and the P*i*-BMA-b-PS (b). In the spectrum of P*i*-BMA-Br, the peaks appeared at around 4 and 0.5–2.7 ppm, which correspond to the protons just beside the oxygen of the butyl of P*i*-BMA units and the other alkyl protons, respectively. The peaks of pyridine were also observed at 7.2, 7.6, and 8.7 ppm. On the other hand, in the spectrum of the P*i*-BMA-*b*-PS, not only the P*i*-BMA peaks but also the PS peaks at 6.5–7.5 ppm, which correspond to phenyl protons, were observed. The molar ratio of styrene to *i*-BMA was 0.54, which was calculated from the area of the exclusive resonance peaks of *b* and *s*. This accorded with the calculated value of 0.55.

Figure 5 shows GPC charts of the P*i*-BMA-Br and the P*i*-BMA-b-PS. In the chart of the P*i*-BMA-Br with a RI detector, the molecular weight distribution was narrow ($Mw/Mn = 1.2$) and the molecular weight ($Mn = 23{,}100$) agreed with the calculated value ($M_{\mathrm{cal}} = 28{,}900$). These indicate that the mini-emulsion-ATRP was well controlled. In the charts of the P*i*-BMA-Br detected with a UV detector, at a wavelength of 260 nm at which absorbance was strong for styrene but very weak for *i*-BMA, a very small peak was observed at the same molecular

Fig. 2a,b Hydrodynamic particle-size (Dh) distributions of monomer (**a**) and polymer (**b**) emulsions before (**a**) and after (**b**) mini-emulsion-ATRP measured by dynamic light scattering

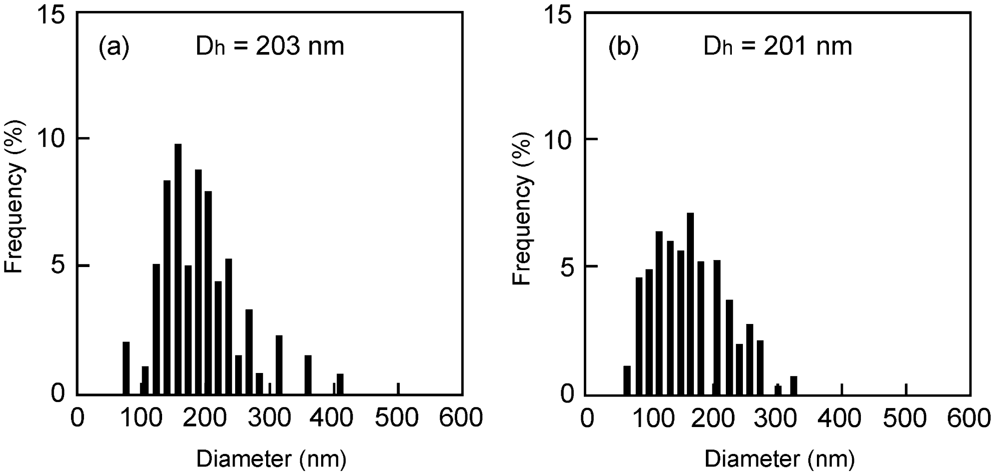


Fig. 3a,b SEM photographs of P*i*-BMA-Br particles (**a**) and P*i*-BMA-*b*-PS particles (**b**) prepared, respectively, by mini-emulsion- and seeded-ATRP under the conditions listed in Tables 1 and 2

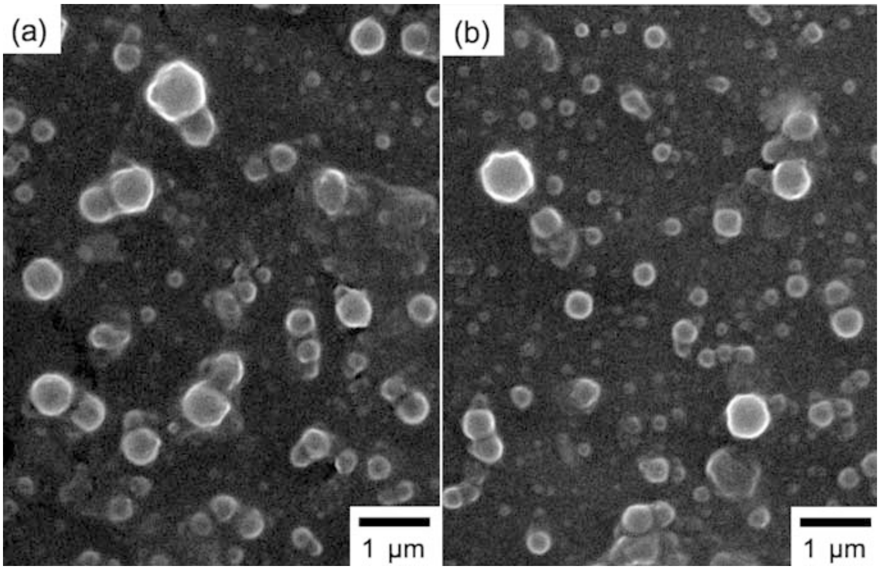
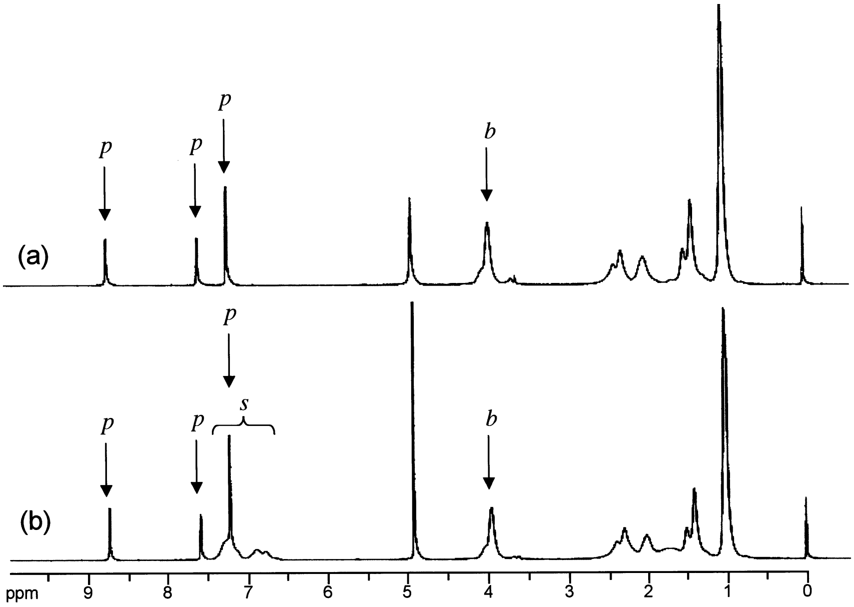


Fig. 4a,b ^{1}H-NMR charts of P*i*-BMA-Br (**a**) and P*i*-BMA-*b*-PS (**b**) prepared by mini-emulsion- and seeded-ATRP under the conditions listed in Tables 1 and 2, respectively



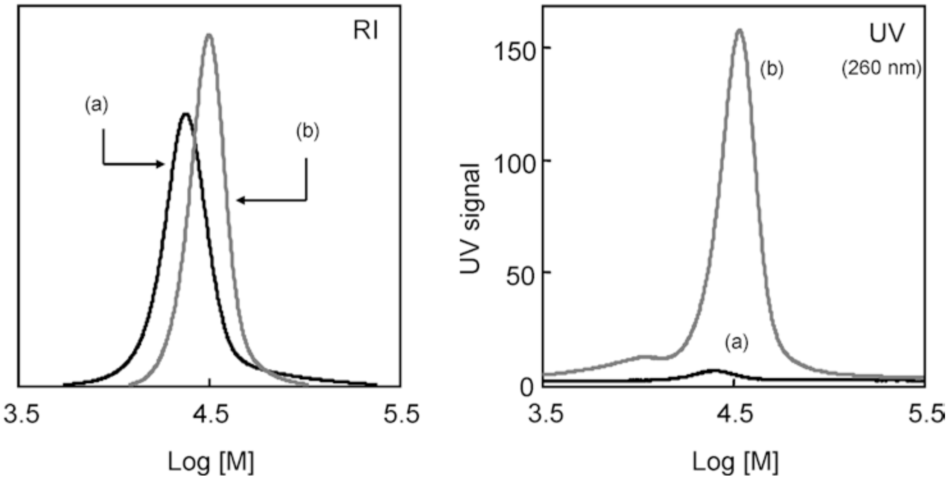


Fig. 5a,b GPC charts of P*i*-BMA-Br (**a**) and P*i*-BMA-*b*-PS (**b**) prepared by mini-emulsion and seeded-ATRP under the conditions listed in Tables 1 and 2, respectively

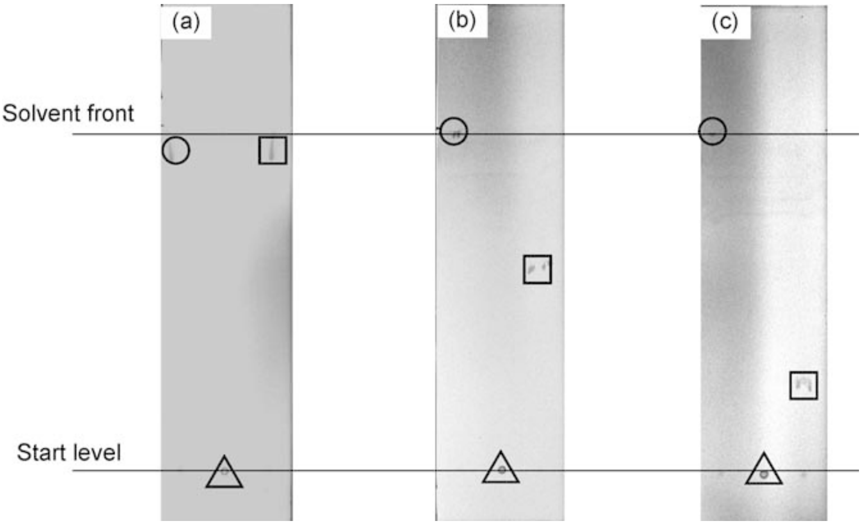


Fig. 6 Photographs of thin-layer chromatograms of P*i*-BMA-Br (○), PS (△), and P*i*-BMA-*b*-PS (□) developed with the different solvents: acetone (*a*), acetone/methanol (60/40 v/v) (*b*), and acetone/methanol (40/60 v/v) (*c*)

weight. On the other hand, the peak of the P*i*-BMA-*b*-PS shifted to higher molecular weight, keeping the narrow molecular weight distribution ($Mw/Mn = 1.1$). The molecular weight ($Mn = 30{,}100$) agreed with the calculated value ($M_{\mathrm{cal}} = 32{,}000$). In the UV chart, strong absorbance was observed at the same molecular weight and the shape of the curve was also almost the same as that of RI. These indicate that P*i*-BMA-*b*-PS block copolymer was prepared by all the P*i*-BMA-Br macro-initiator.

Figure 6 shows thin-layer chromatograms of the P*i*-BMA-Br, PS prepared by solution polymerization, and the P*i*-BMA-*b*-PS with acetone and acetone/methanol mixtures as developing solvents. Acetone was a good solvent for P*i*-BMA but a poor solvent for PS, and methanol was a poor solvent for both PS and P*i*-BMA. In case of acetone, the P*i*-BMA-Br and the P*i*-BMA-*b*-PS were developed to the solvent front, but the PS remained at the start level. In cases of acetone/methanol mixtures of 60/40 and 40/60 (v/v), the locations of the PS and the P*i*-BMA-Br were the same as those in the case of acetone. On the other hand, in each acetone/methanol mixture only one small spot due to the P*i*-BMA-*b*-PS was observed at an intermediate develop distance between the PS and the P*i*-BMA-Br. The develop distance became shorter with an increase in methanol content. These indicate that P*i*-BMA and PS homopolymers were not contained in the P*i*-BMA-*b*-PS. Small spots observed in the TLC may indicate that the P*i*-BMA-*b*-PS had a comparatively sharp composition though Inagaki and Tanaka reported that the block copolymer prepared by anionic living polymerization cannot be homogeneous in composition [19].

From the above results, it is concluded that P*i*-BMA-*b*-PS block copolymer having narrow molecular weight distribution ($Mw/Mn = 1.1$) was successfully synthesized in an aqueous medium by two-step ATRP, i.e., mini-emulsion-ATRP and seeded-ATRP.

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