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Synthetic Route to Ultra-High Molecular Weight Polystyrene (>10^6) with Narrow Molecular Weight Distribution by Emulsifier-Free, Emulsion Organotellurium-Mediated Living Radical Polymerization (Emulsion TERP)

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Abstract

We propose a route to synthesizing ultra-high molecular weight (> 10^6) polystyrene (PS) having a narrow molecular weight distribution by controlled/living radical polymerization. The process is an emulsifier-free, emulsion organotellurium-mediated living radical polymerization (emulsion TERP) using poly(methacrylic acid)-methyltellanyl as a macro-chain transfer agent with a degenerative chain transfer (DT) mechanism. Under the polymerization conditions that PS particles were formed by a self-assembly nucleation of polymerizing macro-chain transfer agents, very stable PS particles were successfully obtained. The segregation effect in the emulsion polymerization system can suppress the radical termination reaction, resulting in an ultra-high number-average molecular weight (M_n) PS in almost 24 h under 1 atm. The final M_n value was able to be controlled by changing the initial monomer loading (solids contents of styrene), then PS having M_n: ~1.2 × 10^6 with a low polydispersity index (~1.3) was successfully obtained.

Keywords: particle, organotellurium-mediated living radical polymerization (TERP), controlled/living radical polymerization, emulsion polymerization, ultra-high molecular weight, self-assembly, styrene

Introduction

Controlled/living radical polymerization (CLRP) has opened a new era in the world of radical polymerizations as a powerful method for synthesizing a wide range of vinyl polymers having narrow molecular weight distribution (MWD) and complex molecular architectures (block, gradient and star polymers).[1-10] Until now, one of the most serious limitations of CLRP was the synthesis of ultra-high molecular weight (MW) polymers having well-controlled MWD. The upper limit of MW of synthetic polymers is decided by the side reactions (mainly by the termination reaction). Some successful approaches have been reported for the synthesis of ultra-high MW methacrylic and acrylic polymers by CLRP in homogeneous systems, where the methacrylic and acrylic monomers have high k_p values. In 2002, Agarwal et al. synthesized a moderately-high MW (number-average molecular weight (M_n) ~ 3.67×10^5) poly(methyl methacrylate) (PMMA) by atom transfer radical polymerization (ATRP).[11] Using ATRP, ultra-high MW poly(2-dimethylaminoethyl methacrylate) ($M_n \sim 1.1 \times 10^6$) was synthesized by Gan et al.[12] Percec et al. reported the synthesis of ultra-high MW poly(methyl acrylate) ($M_n \sim 1.5 \times 10^6$) and poly(2-hydroxyethyl methacrylate) ($M_n \sim 1.0 \times 10^6$) by single electron transfer living radical polymerization (SET-LRP).[13-15] Poly(acrylamide) and its derivatives with ultra-high MW ($M_n \sim 1.0 \times 10^6$) were successfully synthesized using a

reversible addition-fragmentation chain transfer (RAFT)/macromolecular design via interchange of the xanthate (MADIX) system.[16] Matyjaszewski et al. proposed an activator regenerated by electron transfer (ARGET) ATRP,[17] in which a pseudo-halide initiator decreased the side reaction between the radical species and the copper catalyst and improved the livingness of the polymer chains, resulting in an ultra-high MW (M_n ~ 1.17×10^6) PMMA with narrow MWD (polydispersity index (PDI) = weight-average molecular weight (M_w)/M_n ~ 1.2).[18]

However, in the case of styrene with a low k_p value, an ultra-high MW polystyrene (PS) with narrow MWD could not be prepared in the same way as the methacrylic and acrylic monomers could be prepared by CLRP techniques. For example, the M_n for PS was 2.5×10^5 at most in the ARGET ATRP with a pseudo-halide initiator, and this technique raised another problem of the need for a long polymerization time (~ 120 h) due to the low catalyst concentration. Only under high pressure (600 MPa) could an ultra-high MW PS (M_n ~ 1.0×10^6) be synthesized by ATRP in 30 h, during which the k_t value decreased but k_p increased.[19] However, the formulation of a high-pressure reactor is not easy in industrial applications.

Recently, the application of CLRP techniques to aqueous dispersed systems such as emulsion polymerization has been aggressively pursued from the aspects of

environmental and industrial concerns.[20-22] Recent research has been introduced in a review by the Zetterlund et. al..[23] Cunningham et al. successfully synthesized well-controlled PMMA and poly(butyl methacrylate) (PBMA) with M_n ranging from 3.0×10^5 to 1.0×10^6 by reverse ATRP in miniemulsion systems with a redox initiation system in a short time (~8 h) under ordinary pressure,[24] but they mentioned that the origin of the ultra-high MW is currently unknown. Thus, a universal technique for the synthesis of ultra-high MW PS having controlled MWD by CLRP under ordinary pressure is still a challenging prospective.

Organotellurium-mediated living radical polymerization (TERP) is one of the well-established CLRP techniques using organotellurium compounds such as ethyl 2-methyltellanyl-2-methylpropionate (EMA-TeMe) as a control agent under mild temperatures.[25-27] The possible reversible activation processes of TERP are degenerative chain transfer (DT) and thermal dissociation (TD) mechanisms, in which the TD can be negligible below 100°C (Scheme 1). A chain transfer reaction between the initiator radical species and the organotellurium compounds occurred with a high frequency ($k_{ex}/k_p = C_{ex} = 17$).[28] In our previous work, TERP was successfully applied to an emulsifier-free emulsion polymerization system (emulsion TERP) with poly(methacrylic acid)-methyltellanyl (degree of polymerization of PMAA: 30)

(PMAA$_{30}$-TeMe), with the synthesis of well-controlled homopolymers and block copolymers via the DT mechanism.[29-38] Styrene, acrylates, and methacrylates were used in the emulsion TERP to prepare these polymer particles bearing narrow MWD. In addition, the effect of the stirring rate and monomer hydrophilicity were also discussed for this system. Very recently, emulsion TERP was performed using a low MW TERP agent, ethyl-2-butyltellanyl-2-methyl propionate, at 90°C in the absence of a conventional radical initiator with surfactants.[39]

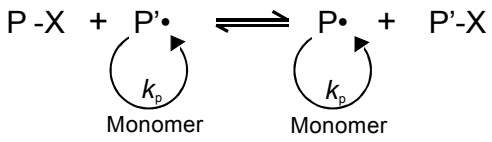
Emulsion polymerization is an especially attractive technique for the production of ultra-high MW polymers, in which the termination reaction between radical species existing in different particles is inhibited due to isolation of the radical species (segregation effect).[40] The segregation effect physically decreases the radical termination rate, resulting in extension of the lifetime of the radical species compared with homogeneous systems. Therefore, the emulsion polymerization system allows simple and rapid synthesis of ultra-high MW polymers. Moreover, the segregation effect is strengthened as the number of particles increases (i.e. the particle size decreases) because the probability of termination reactions decreases. For example, if the particle size is decreased by half, the upper limit of the molecular weight theoretically increases eight-fold in case II of the Smith-Ewart theory.[41] We have

clarified that particles obtained by emulsion TERP had a nanometer-sized diameter (~20 nm) because the PMAA block works as an effective protective hairy layer on the polymer particles, and the probability of termination reactions should be quite low in the system. For this reason, the emulsion TERP should have a great potential for synthesizing ultra-high MW PS. Very recently, Davis and coworkers successfully synthesized ultra-high MW (M_n ~1.0 × 10^6) PS having a low PDI (~1.39) by applying RAFT polymerization of styrene in an emulsion system (emulsion RAFT).[42]

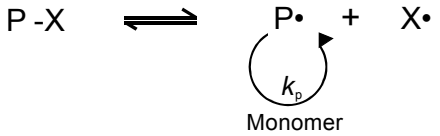
In this paper, we present a versatile route to the synthesis of ultra-high MW (> 10^6) PS having a narrow MWD under ordinary pressure using the emulsion TERP system with a conventional thermal initiator. The key point is physically reducing the probability of a termination reaction by the segregation effect.

Scheme 1. Reversible activation processes in TERP (X = TeMe in this work)

(a) Degenerative Chain Transfer (DT)



(b) Thermal Dissociation (TD)



Experimental part

Materials

Styrene (Nacalai Tesque, Japan) was purified by distillation under reduced pressure in a nitrogen atmosphere. Deionized water used in all experiments was prepared with an Elix® UV (Millipore Japan) purification system that had a resistivity of 18.2 $M\Omega \cdot cm^{-1}$. 4,4'-Azobis(4-cyanovaleric acid) (V-501, Wako Pure Chemicals, Japan) and 2,2'-azobis(isobutyronitrile) (AIBN, Wako Pure Chemicals, Japan) were purified by recrystallization. EMA-TeMe and $PMAA_{30}$-TeMe (degree of polymerization of PMAA: 30, M_w/M_n: approximately 1.3) were supplied by Otsuka Chemical Co., Ltd., Osaka, Japan. Trimethylsilyldiazomethane (TMSD, Nacalai Tesque) and tetrahydrofuran (THF, Nacalai Tesque) were used as received.

Bulk TERP of Styrene

In the typical procedure, styrene (5.67 g (54.5 mmol)), deoxygenated by nitrogen bubbling, and AIBN (6.3 mg (37.8 μmol) or 12 mg (75.6 μmol)) were added to a round-bottom Schlenk flask, sealed off with a silicon rubber septum, followed by degassing with several N_2/vacuum cycles. EMA-TeMe (2 μL (11 μmol) or 4 μL (5.7 μmol) for the theoretical number-average molecular weight ($M_{n,th}$): 0.5×10^6 or 1.0×10^6,

respectively) was injected into the system via a syringe. The flask was then placed in a water bath at 60°C (considered to be the start of the polymerization, t = 0). In all polymerizations, the stirring rate of the magnetic stirrer was fixed at 1000 rpm.

Preparation of High Molecular Weight PS by Emulsion TERP

In the typical procedure, water and styrene were first deoxygenized by nitrogen bubbling. Subsequently, NaOH aqueous solution (45 g) and V-501 (10.5 mg (37.8 μmol)) were added to a round-bottom Schlenk flask, sealed off with a silicon rubber septum, followed by degassing with several N_2/vacuum cycles, where the amount of NaOH was the same as that of the carboxyl groups of V-501. $PMAA_{30}$-TeMe (500 μL, 22.8 mM aqueous solution neutralized by NaOH (11.3 μmol)) was injected into the system via a syringe. After styrene (5.67 g (54.5 mmol), 11.34 g (109 mmol) or 17.01 g (164 mmol)), for different targeted molecular weights) had been injected via the syringe, the flask was placed in a water bath at 60°C (considered to be the start of the polymerization, t = 0). In all polymerizations, the stirring rate of the magnetic stirrer was fixed at 1000 rpm, where most of the styrene dispersed as droplets in the aqueous phase. The pH value during the polymerization was > 9.0, leading to neutralization of the carboxyl groups of the PMAA chain.

Characterization

Conversion was measured by gravimetry. M_w, M_n and MWD were measured by gel permeation chromatography (GPC) using two poly(styrene/divinylbenzene) gel columns (TOSOH Corporation, TSKgel GMHHR-H, 7.8 mm i.d x 30 cm) and THF as an eluent at 40°C at a flow rate of 1.0 mL/min employing refractive index (RI) (TOSOH RI-8020/21) and ultraviolet (UV) 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). $M_{n,th}$ was calculated with the following equation:

$$M_{n,th} = MW_{PMAA30-TeMe} + \left(\frac{[M]_0 \cdot MW_M \cdot \alpha}{[PMAA - TeMe]_0} \right)$$

where α is the conversion of monomer, $MW_{PMAA30\text{-}TeMe}$ and MW_M are the molecular weights of $PMAA_{30}$-TeMe and styrene, respectively, and $[M]_0$ and $[PMAA_{30}\text{-}TeMe]_0$ are the initial concentrations of monomer and $PMAA_{30}$-TeMe, respectively. Before GPC measurement, the prepared polymers were modified by methylating the carboxyl group of MAA units using TMSD according to a previous report.[43] In brief, after acidification of the media, the polymers were recovered by drying the polymer emulsions. They were dissolved in mixtures of dimethylformamide and a small amount

of methanol at room temperature. The yellow solution of TMSD was added dropwise at room temperature to the polymer solutions and allowed to react overnight. After the excess TMSD had been neutralized by acetic acid, each polymer solution was mixed with THF and used for GPC measurement.

The number-average particle diameters (d_n, respectively) were measured using a dynamic light scattering (DLS, FPAR-1000 RK, Fiber-optics particle analyzer, Photal Otsuka Electronics, Osaka, Japan) at a perpendicular light scattering angle at room temperature using the CONTIN analysis routine. One to two droplets of emulsion samples withdrawn from the reactor were diluted with approximately 8 mL of distilled water before measurement using the dilution mode. The polydispersity index was obtained from cumulant analysis.

Results and Discussion

1. Bulk TERP of Styrene

To compare with emulsion TERP, bulk TERPs of styrene were carried out at 60°C using EMA-TeMe as a control agent and AIBN as an initiator, in which the target $M_{n,th}$ values at 100% conversion ($M_{n,th\,(100\,\%)}$) were set at 0.5 $\times 10^6$ and 1.0 $\times 10^6$. Figure 1 shows conversion versus time plots of the bulk TERPs. The polymerizations did not

proceed to high conversion and reached only 5% conversion in 48 h especially in the latter polymerization (the target $M_{n,th\ (100\ \%)}$ value=1.0 $\times 10^6$), where low conversion was caused by a smaller initiator concentration compared to that in the case of the target $M_{n,th\ (100\ \%)}$ of 0.5 $\times 10^6$.

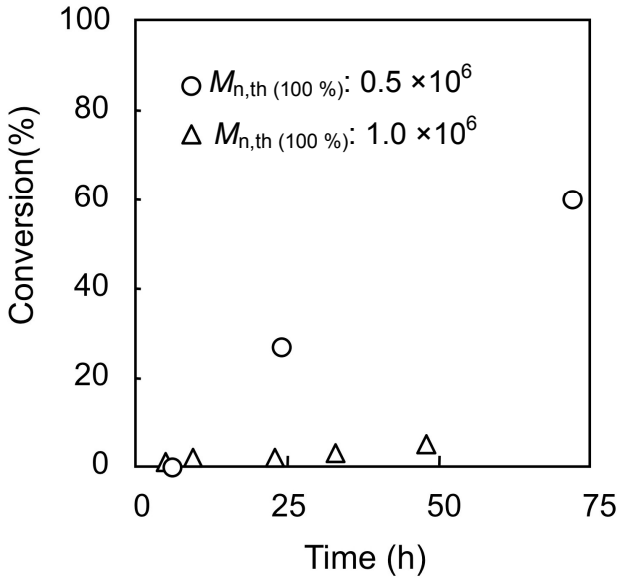


Figure 1 Conversion versus time plots for bulk TERPs of styrene using EMA-TeMe and AIBN at 60°C. Target $M_{n,th}$ values at 100 % conversion ($M_{n,th\ (100\ \%)}$) are 0.5 $\times 10^6$ (open circles) and 1.0 $\times 10^6$ (open triangles).

Figure 2 shows MWDs, M_n and M_w/M_n values of PS prepared by the bulk TERPs. In the case of the target $M_{n,th\ (100\ \%)}$ of 0.5 $\times 10^6$, MWD shifted to a higher molecular weight on conversion, but the experimental M_n was below 1.0 $\times 10^5$ even at 60%

conversion, which was much smaller than the corresponding $M_{n,th\ (60\ \%)}$ values (3.0×10^5). At the target $M_{n,th\ (100\ \%)}$ of 1.0×10^6, MWD was not shifted to a higher molecular weight with increasing conversion, in which the concentration of the control agent would be significantly low. The M_n value only reached $\sim 1.0 \times 10^4$. These results indicate the difficulty of synthesizing high MW PS by bulk TERP.

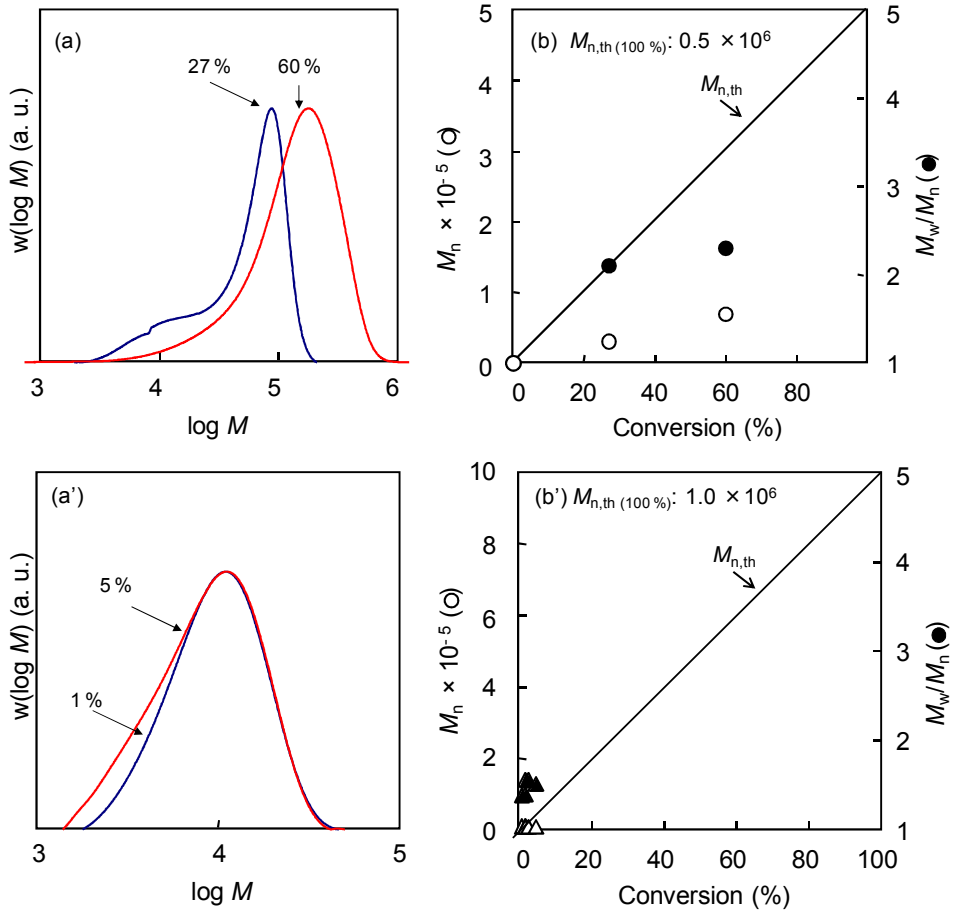


Figure 2 MWD (a, a'), M_n (open circles, open triangles) and M_w/M_n (closed circles, closed triangles) (b, b') of PS measured with GPC (detector: refractive index) at

different conversions (as indicated in %) of the bulk TERPs using EMA-TeMe and AIBN. Target $M_{n,th\,(100\,\%)}$ values are 0.5×10^6 (a, b) and 1.0×10^6 (a', b').

In contrast to the bulk system, emulsion polymerization offers important kinetics for synthesizing ultra-high MW polymers based on the segregation effect. Radicals are separated in polymer particles as a small container, and the segregation effect results in suppression of radical termination during the polymerization. Therefore, emulsion polymerization offers much promise for the synthesis of the high molecular weight polymers.

In emulsion CLRP systems, the general strategy is based on the polymerization-induced self-assembly nucleation mechanism reported by Hawkett et al.[44] Emulsion CLRP is generally carried out at a low or middle monomer concentration of less than 30 wt % solid content at the fundamental research level; it is worth noting that Cunnigham et al. successfully achieved a high solid content (50%) with an emulsion CLRP system.[45] To achieve the ultra-high MW PS, the emulsion CLRP must be controlled with ca. 0.3 mM of control agent. To date, many research groups have reported the successful synthesis of stable polymer particles via this strategy. The Hawkett group is a pioneer of emulsion RAFT. In their work, the macro-chain transfer

agent concentration was 1.6 – 6.3 mM.[44] Charleux et al. reported on emulsion RAFT with a wide range of water-soluble control agents. When they performed emulsion RAFT with 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid (TTCA) as a water-soluble RAFT agent having a short chain length, the concentration was ca. 8.7 mM.[46] In the case of poly(ethylene oxide) (PEO)- and poly(*N*,*N*-dimethylacrylamide)-based macro-chain transfer agents, the concentrations were 7.0 – 14 mM and 4.0 – 17.9 mM, respectively.[47-49] D'Agosto, Lansalot and their coworkers reported on emulsion RAFT using a poly(acrylic acid) (PAA) macro-chain transfer agent at 5.05 mM concentration.[50] Lacroix-Desmazes and coworkers have successfully demonstrated reversible iodine transfer polymerization (RITP) in an emulsion polymerization system, where the control agents were formed *in situ* from the initiator and I_2, and the I_2 concentration was 6.17 mM.[51] In these ways, the control agent concentrations were one order greater than the theoretical concentration (<0.3 mM) for synthesis of ultra-high MW PS.

We carried out the emulsion TERP with a low monomer solid content (ca. 3 wt%) with one order smaller concentration (0.25 mM) of the water-soluble macro-chain transfer agent compared to the emulsion RAFT systems above discussed. However, homogeneous nucleation concurrently occurred in addition to self-assembly nucleation

in the emulsion TERP system. The particle nucleation step is a critically important one in the emulsion polymerization system.[40, 52] The self-assembly nucleation was caused by *in situ* formed amphiphilic macro-chain transfer agents, resulting in incorporation of macro-chain transfer agents in the particles. It was clarified that the particles formed from the homogeneous nucleation did not contain a sufficient concentration of the macro-chain transfer agent, resulting in a low MWD control. To overcome the problem based on homogeneous nucleation, optimization of the initiator decomposition rate as well as the stirring rate was done to obtain polymer particles based on self-assembly nucleation.[33-35] Herein, we selected the optimal polymerization temperature as well as stirring conditions (60°C and 1,000 rpm) for the emulsion TERP with a lower macro-chain transfer agent concentration (0.25 mM).[33-36]

Figure 3 shows conversion versus time plots in emulsion TERPs of styrene at 60°C with 1000 rpm stirring rate, in which the target $M_{n,th\ (100\%)}$ values were set at 0.5×10^6, 1.0×10^6 and 1.5×10^6 by changing the styrene concentration (solid contents at 100% conversion were 11.2, 20.1 and 27.4 wt%, respectively). The polymerization proceeded smoothly, and conversions reached > 90 % in 21 h. In addition, the obtained PS emulsions were very stable without coagulation.

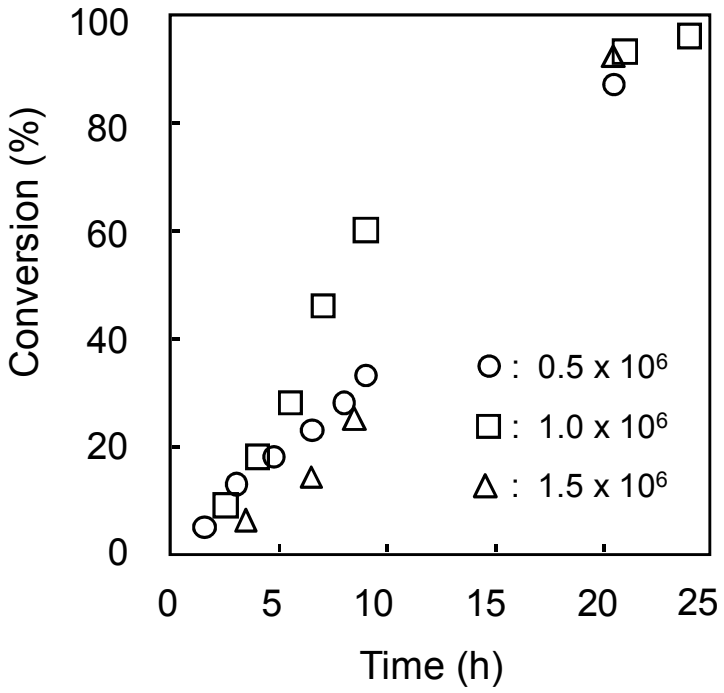


Figure 3 Conversion versus time plots for emulsifier-free, organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of styrene using $PMAA_{30}$-TeMe and V-501 at 60°C with 1000 rpm stirring. Target $M_{n,th(100\,\%)}$ are set at 0.5×10^5 (open circles), 1.0×10^6 (open squares) and 1.5×10^6 (closed triangles) by changing styrene concentration.

Table 1 shows d_n and its polydispersity index values of the prepared PS particles by the emulsion TERP at the three target $M_{n,th}$ values. The d_n values increased with increasing target $M_{n,th}$ because of the increase of solid content although the

polydispersity index values were higher. In our previous study, PS particles prepared by emulsion TERP with low solid contents (ca. 3 wt%) also had the broad distribution, and such broad particle size distribution measured by DLS was confirmed by TEM observations.[34] The high polydispersity index value may be caused by the long particle nucleation period at an initial stage of the emulsion TERP although the $PMAA_{30}$-TeMe was completely consumed even with low conversion in all polymerizations (discussed below). Figure 4 shows the d_n values (a) and the number of PS particles (N_p) at various conversions in the emulsion TERP at the three target $M_{n,th\ (100\ \%)}$ values. The d_n values in all polymerizations increased with conversions, while the N_p values remained in a similar order during the polymerizations. In addition, the final log(N_p) values at all polymerizations were similar, indicating that the different monomer concentrations did not affect the particle nucleation step. In addition, particle coagulation did not occur after the particle nucleation period even with a high solid content (ca. 27 wt%), indicating that the PMAA hairy layer at the surface of the particles formed based on self-assembly nucleation was endowed with high colloidal stability to the PS particles.

Table 1 d_n, polydispersity index measured by DLS and the number of PS particles (N_p) in the emulsion TERPs at various target $M_{n,th}$ values

$M_{n,th}$ (100 %)	Conversion (%)	Solids content (wt %)	d_n (nm)	Polydispersity index	Log (N_p) (/mL)
0.5×10^5	87	9.74	56	0.125	15.1
1.0×10^6	93	18.7	89	0.099	14.8
1.5×10^6	92	25.2	113	0.094	14.7

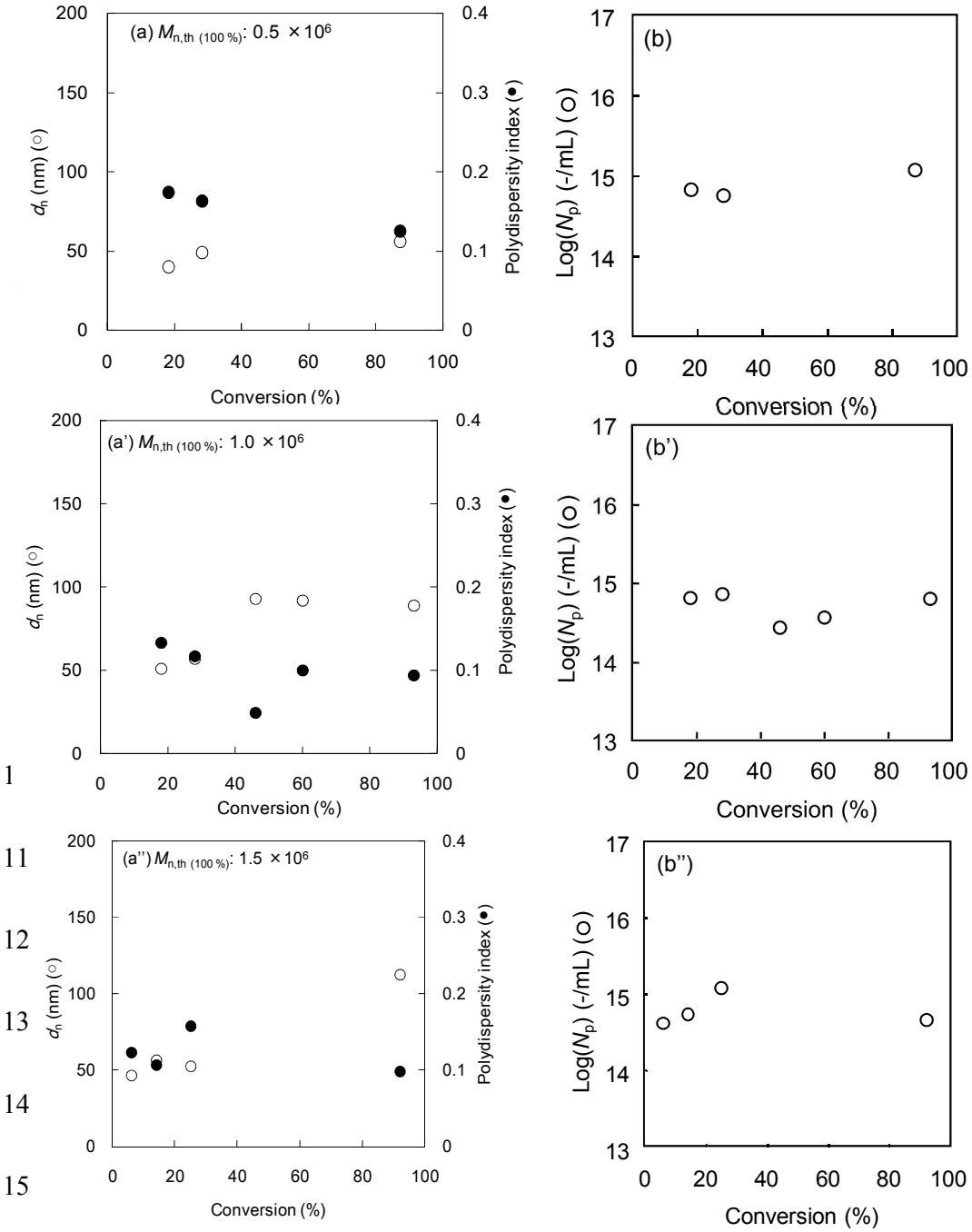


Figure 4 d_n and polydispersity index (a) (by DLS measurements) and N_p values (b) of PS particles prepared by the emulsion TERP with $PMAA_{30}$-TeMe and V-501 with 1000 rpm stirring at 60°C. Target $M_{n,th\,(100\,\%)}$ values are 0.5 ×10^6 (a, b), 1.0 ×10^6 (a', b') and 1.5 ×10^6 (a'', b'').

Figure 5 shows MWDs (a), M_n and M_w/M_n values (b) of PS prepared by emulsion TERPs, where the MW of the methylated PMAA unit was included in the M_n values. However, the MW (M_n: ca. 2700) can be considered negligible because it was significantly small compared to our target MW values of PS. The MWD was shifted to higher MW and the M_n value increased linearly with increasing conversion, maintaining low M_w/M_n values. The M_n values at high conversion were slightly smaller than the corresponding $M_{n,th}$ values, although M_w/M_n values at the highest conversions were the smallest. In addition, the MWDs obtained from the RI detector at various conversions accorded well with those from the UV detector in all polymerizations, as shown in Figure 6. The RI detector detected all polymer species contained in the polymerization systems, while the polymer species containing styrene units were detected by the UV detector. Of the MWDs detected by the RI detector, the peak due to free $PMMA_{30}$-TeMe was not observed even at 6 – 9 % conversions in all polymerization systems. These results clearly indicate that the $PMAA_{30}$-TeMe was completely consumed at the low conversions. M_w/M_n values were maintained at low values throughout the polymerizations. From the above results, we concluded that ultra-high MW ($M_n \sim 1.2 \times 10^6$) PS having narrow MWD (PDI ~1.3) was successfully synthesized by emulsion TERP.

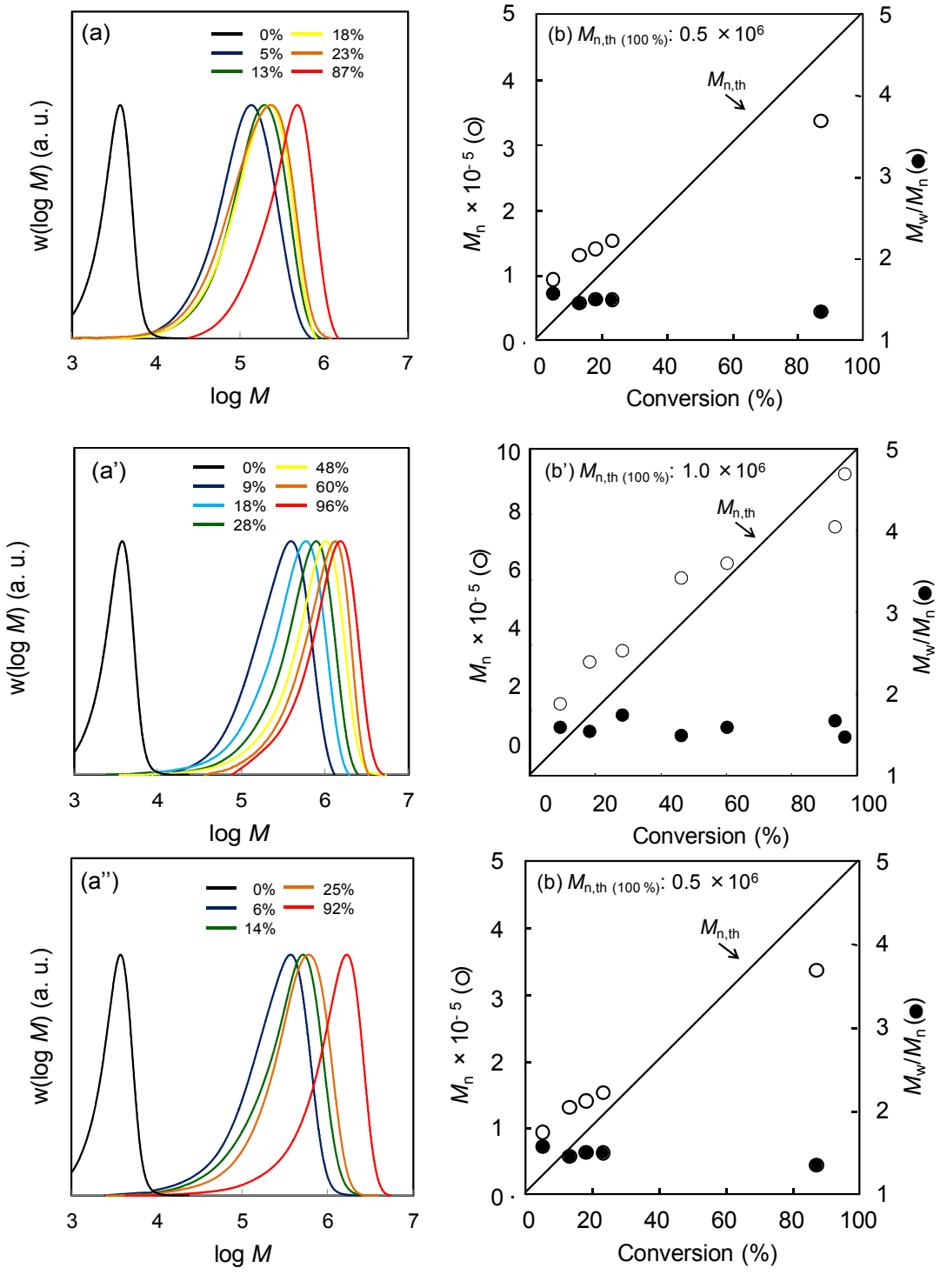


Figure 5 MWD (a, a', a''), M_n (open circles) and M_w/M_n (closed circles) (b, b', b'') of

PMMA$_{30}$-*b*-PS-TeMe measured with GPC (detector: refractive index) after methylation of PMAA$_{30}$ block at different conversions (as indicated in %) of the emulsion TERP using PMAA$_{30}$-TeMe and V-501 at 60˚C with 1000 rpm stirring. Target $M_{n,th\,(100\%)}$ values are 0.5 ×10^6 (a, b), 1.0 ×10^6 (a', b') and 1.5 ×10^6 (a'', b'').

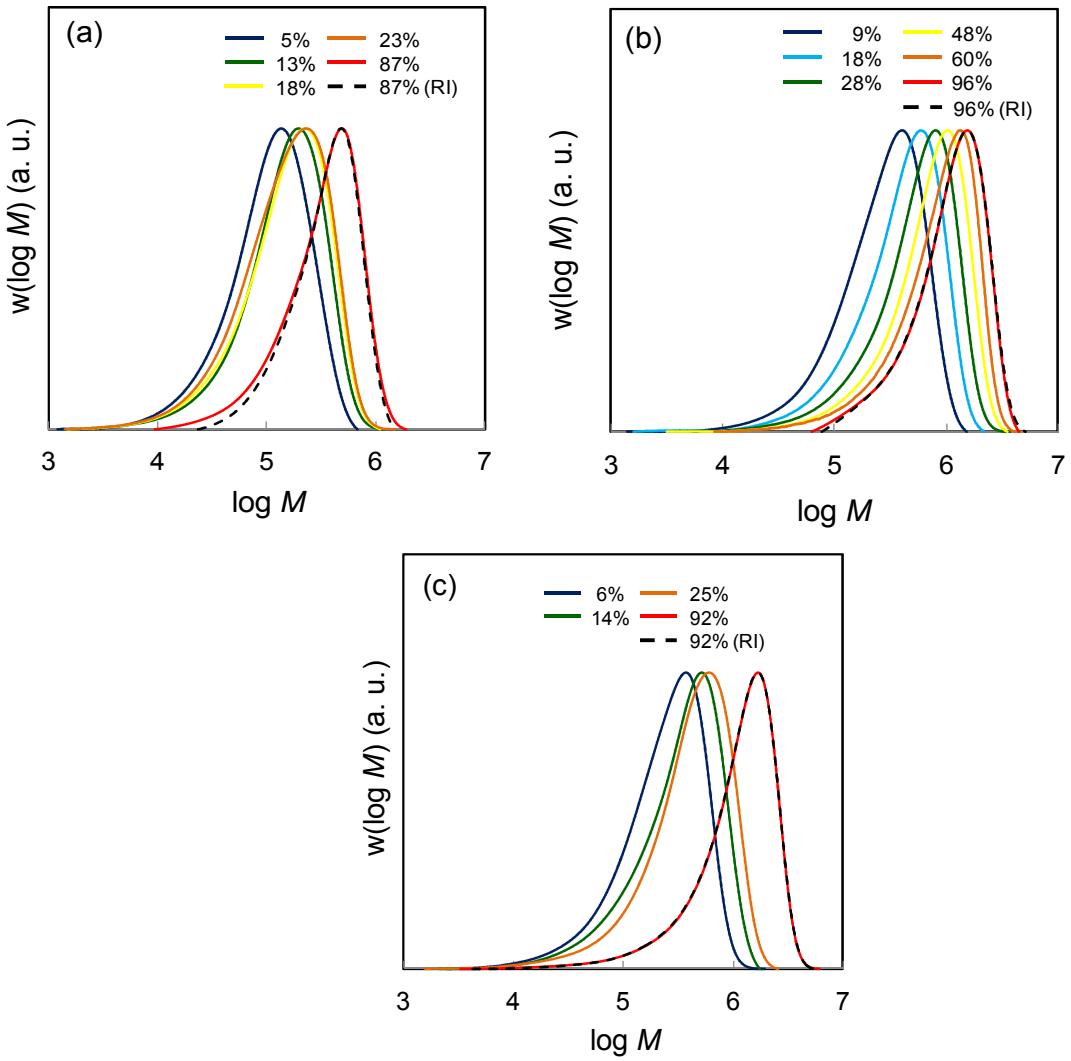


Figure 6 MWDs of PMMA$_{30}$-*b*-PS-TeMe measured with GPC (detector: UV) after methylation of PMAA$_{30}$ block at different conversions (indicated as %) of the emulsion

TERP using $PMAA_{30}$-TeMe and V-501 at 60˚C with 1000 rpm stirring. Target $M_{n,th\ (100\%)}$ values are 0.5×10^6 (a), 1.0×10^6 (b) and 1.5×10^6 (c). Black dashed lines indicate MWDs of $PMMA_{30}$-*b*-PS-TeMe at the highest conversion detected by the RI detector.

Conclusions

A versatile synthetic route of ultra-high MW PS (~ 1.2×10^6) having narrow MWD (PDI ~ 1.3) by emulsion TERP based on DT mechanism was successfully demonstrated at 60°C under ordinary pressure (1 atm). In homogeneous systems, high MW PS cannot be obtained, indicating the value of the segregation effect in the emulsion polymerization system. The polymerization proceeded smoothly and could be completed in almost 24 h. The obtained PS particles of < 150 nm in size showed good colloidal stability without coagulation due to the electrosteric repulsion of the $PMAA_{30}$ hairy layer, where the final solid content of the PS emulsion reached ca. 25 wt%.

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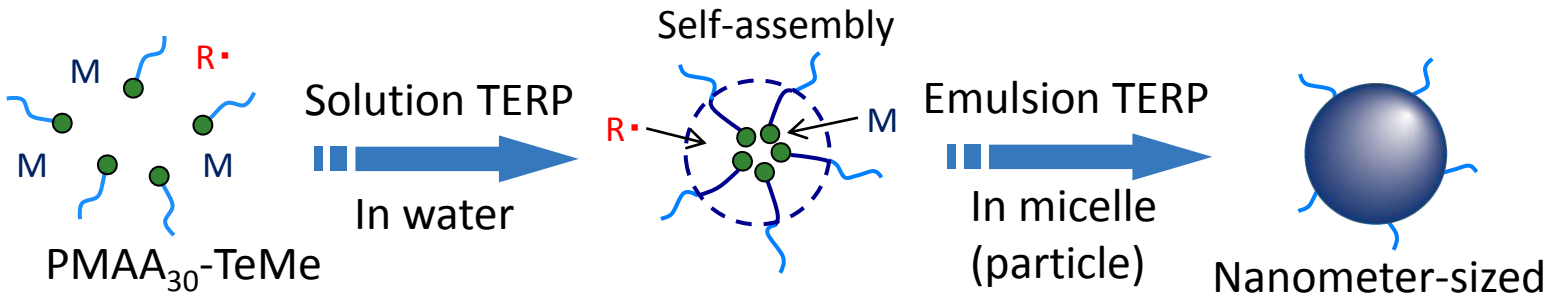
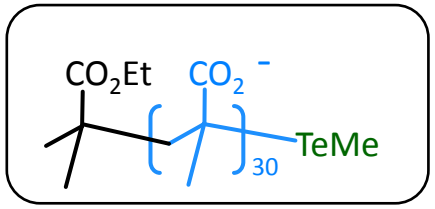
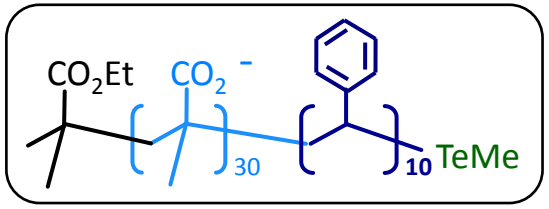
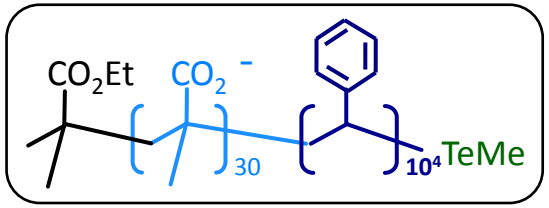
◆ ***Self-assembly nucleation***

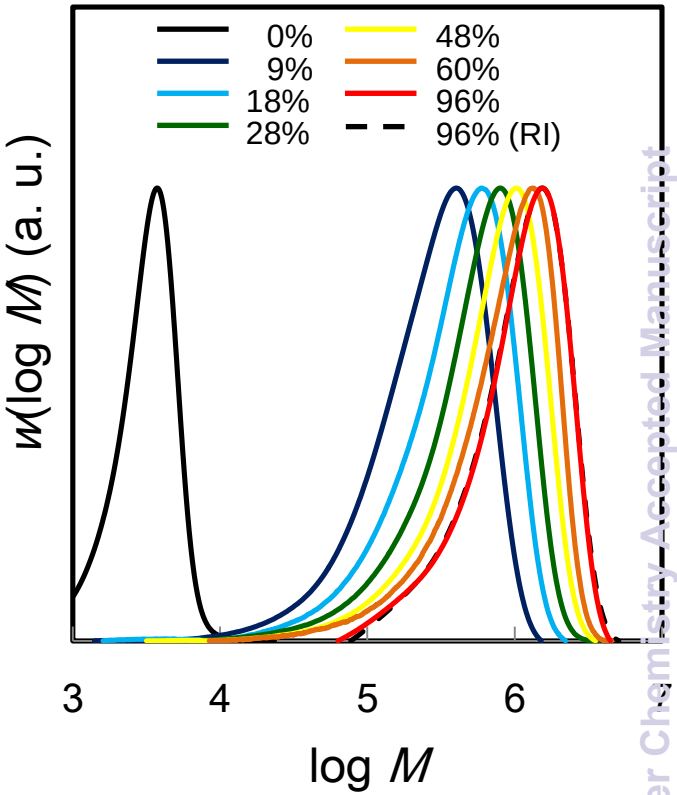
R·:Initiator radical M :Monomer (styrene)











Segregation effect In Emulsion TERP → ***High Molecular Weight (>10⁶) Polystyrene***