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Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization of Butyl Acrylate[†]

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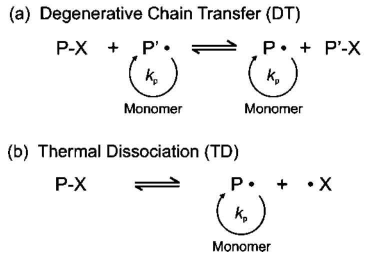
ABSTRACT: Organotellurium-mediated living radical polymerization (TERP) of *n*-butyl acrylate (BA) in emulsifier-free emulsion polymerization system was carried out for the first time, using the in situ nucleation technique via self-assembly of the propagating amphiphilic polymer chains derived from water-soluble TERP agent, poly(methacrylic acid)−methyltellanyl, with water-soluble thermal initiator, 4,4′-azobis(4-cyanovaleric acid), as a radical source at 60 °C. The polymerization proceeded with high control/livingness to high conversion without coagulation, resulting in nanosized poly(BA) particles. The difference in the stirring rates of the polymerization system, where the whole monomer dispersed as droplets at a high rate or it existed as an upper layer on the aqueous medium at a low rate, had a great influence both on the rate of polymerization and on the degree of the control/livingness. On both of them, the polymerization with the high stirring rate gave more desirable results than those with the low rate.

Introduction

Controlled/living radical polymerization (CLRP)[1−3] techniques have been considerably improved and achieving various polymer synthesis well-defined on molecular weights distribution (MWD) and molecular architectures (multiblock, star, and surface-initiated polymer, so on). Among the past 15 years, nitroxide-mediated polymerization (NMP),[4,5] atom transfer radical polymerization (ATRP),[6,7] and reversible addition−fragmentation chain transfer (RAFT) polymerization[8,9] have been successively established as three standard techniques, and then organotellurium-mediated living radical polymerization (TERP), pioneered by Yamago et al., has been followed.[10−17] Their mechanistic/kinetic research in a homogeneous system has revealed that TERP proceeded via both activation processes, as shown in Scheme 1: [degenerative chain transfer (DT) (a) such as RAFT and thermal dissociation (TD) (b) such as NMP].

As well as conventional radical polymerization, CLRP in aqueous dispersed systems[9,18−44] also attracts much attention for both academic interest and industrial application, and these detailed improvements and successful implementations with good colloidal stability and control/livingness have been mainly achieved by employing miniemulsion polymerization. In miniemulsion polymerization, the nucleation takes place in each monomer droplet already broken up by any mechanistic shear (such as ultrasonication) with emulsifier and including all ingredients prior to the polymerization, growing up to polymer particles directly. Thus, miniemulsion polymerization can be treated as the small scale of bulk polymerization, so that the complexity of the mass transfer of CLRP species to the locus of the polymerization, which is the most problematic barrier to apply CLRP in emulsion polymerization, can be eliminated. However, because of their mechanistic shear application, miniemulsion polymerization is fundamentally much restricted of their appreciable reaction scale, mainly adopted for laboratory small scale, not industrial large scale. Thus, the high-level achievement of CLRP in emulsion polymerization is one of the final objectives in this area.

Scheme 1. Reversible Activation Process in Organotellurium-Mediated Living Radical Polymerization (X = TeMe in This Work)



Recently, as one of the elegant means of overcoming the above issue in emulsion polymerization, in RAFT,[45−47] and NMP,[48−51] self-assembly approaches have been reported. Their polymerizations started from water-soluble CLRP species in aqueous phases homogeneously, namely poly(acrylic acid) (PAA)-RAFT and PAA-NMP, respectively, in the absence of emulsifier micelles. Then these propagating chains become amphiphilic character in accordance with addition reaction of hydrophobic monomer, and consequently self-assemble by themselves, resulting in nucleation micelles. Therefore, CLRP species can be introduced into the locus of the polymerization smoothly at the beginning of particle nucleation process, whereas in typical emulsion polymerization where the monomer-swollen emulsifier micelles such as sodium dodecyl sulfate (SDS) are formed, it is difficult to migrate CLRP species into the locus of the polymerization.

In a previous article,[52] we carried out TERP in miniemulsion polymerization system (miniemulsion TERP) for the first time and achieved the synthesis of submicron-sized polymer emulsion comprising various homopolymers or block copolymers maintaining good colloidal stability and control/livingness. In this article, the application of TERP will be extended for the first time to emulsifier-free emulsion polymerization (emulsion TERP) of *n*-butyl acrylate (BA), using in situ nucleation technique via self-assembly of propagating amphiphilic polymer chains. As described above, self-assembly approaches have used PAA as the water-soluble anchor of the CLRP species, namely PAA-RAFT and PAA-NMP agents. However, it was reported that PAA chains, which stabilize forming particles, cause the retardation of the rate of the polymerization (R_p) because they catch free radicals which enter into and exit from the par-

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ticle.[53,54] Therefore, to avoid the problem, water-soluble TERP agent, poly(methacrylic acid) (PMAA)−methyltellanyl (TeMe) ($PMAA_{30}$-TeMe), is employed for emulsion TERP to give PMAA as the water-soluble anchor of the CLRP specie and protective layer at particle.

Experimental Part

Materials. BA (Nacalai Tesque, Japan) was purified by distillation under reduced pressure in a nitrogen atmosphere. Deionized water with a specific resistance of 5×10^6 Ω·cm was distilled prior to use. 4,4′-Azobis(4-cyanovaleric acid) (V-501, Wako Pure Chemicals, Japan) was purified by recrystallization in water. $PMAA_{30}$-TeMe (degree of polymerization of PMAA, 30; PDI, 1.1) was supplied from Otsuka Chemical Co., Ltd., Osaka, Japan, and trimethylsilyldiazomethane (TMSD, Nacalai Tesque) was used as received.

Emulsion TERP. A typical procedure is described below. Water and BA were deoxygenized by nitrogen bubbling. First, water (45 g) and V-501 (10.5 mg, 37.8 μmol) were added into a round-bottom Schlenk flask, sealed off with a silicon rubber septum, and then degassed using several N_2/vacuum cycles. $PMAA_{30}$-TeMe (234 μL, 0.113 M aqueous solution neutralized by NaOH, 37.8 μmol) was injected into the system via syringe, and the solution was stirred until mixing equally. After BA (0.92−3.68 g, 7.6−30.0 mmol) was poured, the flask was then placed in a water bath at 60 °C (taken to be the start of the polymerization, $t = 0$), and polymerization was allowed to proceed at a given time at two stirring rates (220 and 1000 rpm) with a magnetic stirrer. Before gel permeation chromatography (GPC) the polymers were modified by methylation of the carboxyl group using trimethylsilyldiazomethane according to the previous work as follows.[52] After acidification of the medium, the polymers were recovered by drying polymer emulsion. They were dissolved in a mixture of DMF and methanol at room temperature. The yellow solution of trimethylsilyldiazomethane was added dropwise at room temperature into the polymer solution and reacted overnight. After excess trimethylsilyldiazomethane was destroyed by acetic acid, the polymer solution was mixed with THF and used for GPC measurement.

Characterization. Conversion was measured by gravimetry. Number-average molecular weight (M_n) and molecular weight distribution (MWD) were measured by GPC using two styrene/divinylbenzene gel columns (TOSOH Corp., TSKgel GMH_{HR}-H, 7.8 mm i.d × 30 cm) using THF as an 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 ($1.05 \times 10^3 - 5.48 \times 10^6$, $M_w/M_n = 1.01-1.15$). Theoretical molecular weight ($M_{n,th}$) was calculated by following equation:

$$M_{n,th} = MW_{PMAA_{30}\text{-TeMe}} + \frac{[M]_0 MW_M \alpha}{[\text{PMAA-TeMe}]_0}$$

where α is the conversion of monomer, $MW_{PMAA_{30}\text{-TeMe}}$ and MW_M are the molecular weights of $PMAA_{30}$-TeMe and BA, respectively, and $[M]_0$ and $[PMAA_{30}\text{-TeMe}]_0$ are the initial concentrations of monomer and $PMAA_{30}$-TeMe, respectively. Particle size distribution was measured using dynamic light scattering (FPAR-1000, Otsuka Electronics, Osaka, Japan) at the light scattering angle of 90° at 24.8 °C. Number-average particle diameter (d_n) was obtained using the Marquadt analysis routine.

Results and Discussion

Emulsifier-Free Emulsion TERP. In this study, all polymerizations were carried out at 60 °C, employing the water-soluble initiator, V-501 as the radical source, where the activation process of TERP proceeds exclusively via DT, avoiding the complexity of the TD included.

Figure 1a shows conversion versus time plot for emulsion TERP with the initial molar ratio of BA/$PMAA_{30}$-TeMe/V-501 = 400/1/1 and solids content = 4 wt % (experiment 1) at a low stirring rate of 220 rpm, at which BA floated as layer on the water phase. The polymerization reached to high conversion without coagulation, and the final product (91% conversion) at $t = 16$ h was almost transparent polymer emulsion. The d_n of the particles, measured by DLS, was 19 nm and showed a unimodal distribution, whereas d_w showed a bimodal distribution (Figure 2). The polymer emulsion was so stable that any coagulation and precipitation did not appear for several months at room temperature. In this study typical emulsifier such as SDS was not employed into the system. Thus, it is indicated that the $PMAA_{30}$ anchor of the initial TERP agent, $PMAA_{30}$-TeMe, could play the role of an electrosteric stabilizer, dispersing PBA particles stably.

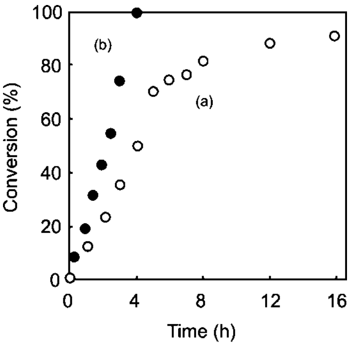

Figure 1. Conversion versus time plots for emulsion TERP of BA using $PMAA_{30}$-TeMe and V-501 at stirring rates of 220 rpm (a) (experiment 1) and 1000 rpm (b) (experiment 2) at 60 °C. BA/$PMAA_{30}$-TeMe/V-501 (molar ratio) = 400/1/1 and 4 wt % solids content.

Figure 3 shows MWDs of the products (after methylation) obtained at the stirring rate of 220 rpm and M_n and M_w/M_n as function of the conversion. As shown in Figure 3a, the MWD shifted to higher with increasing conversion, indicating that the polymerization proceeded maintaining good controlled manner and M_n increased with conversion, although it gradually deviated from the theoretical line with a higher value (Figure 3b). Figure 3a also shows that a part of the initial TERP agent, $PMAA_{30}$-TeMe, has been remaining until around 50% conversion. In a general emulsion polymerization, low molecular weight emulsifier molecules forming micelles above critical micelle concentration are consumed to adsorb and stabilize forming polymer particles in the early stage of the polymerization (interval I < ca. 20% conversion). In the emulsion TERP, once initial TERP agents have activated via DT and gotten a free radical activity, they directly led to propagation with monomer, followed by either self-assembly nucleation in the early stage of the polymerization or adsorption onto polymer particles (main reaction locus). It did, however, seem to take a long time to consume whole initial TERP agents completely, and they have remained in the aqueous phase unless they have experienced an activation process. Nevertheless, because free radicals were formed in aqueous phase from water-soluble initiator, V-501, in the middle of the polymerization almost all of initial TERP agents could be consumed and belong to the reaction. The M_w/M_n values of the overall MWD curves including the initial TERP agents (black circle) show a higher value above 2 over the polymerization. On the other hand, M_w/M_n values of only $PMAA_{30}$-*b*-PBA-TeMe propagating chains (cross symbol) after exclusion of the low-MW shoulder due to unreacted $PMAA_{30}$-TeMe were in the range of 1.5−2 until around 50% conversion. Those values indicate that in this system the degree of control/livingness is not good so much. The cause will be discussed below.

The above results suggest that emulsion TERP employing water-soluble TERP agents, $PMAA_{30}$-TeMe, could produce the PBA emulsion maintaining colloidal stability and control/livingness, although the latter value was not good so much.

Scheme 2. TERP in Emulsifier-Free Emulsion Polymerization (Emulsion TERP) Using in Situ Nucleation via Self-Assembly

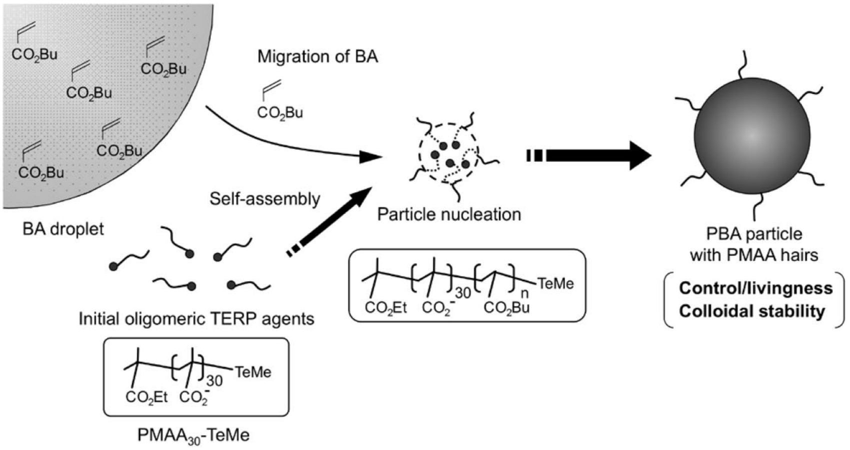

Table 1. Recipes of Emulsion TERP of BA Using $PMAA_{30}$-TeMe and V-501 at Two Stirring Rates at 60 °C

	BA (wt %)[a]	$PMAA_{30}$-TeMe (mmol)	V-501 (mmol)	initial molar ratio	stirring rates (rpm)	states of monomer phase[b]
exp 1	4	0.836	0.836	400:1:1	220	layer
exp 2	4	0.836	0.836	400:1:1	1000	droplets
exp 3	2	0.836	0.836	200:1:1	220	layer
exp 4	8	0.836	0.836	800:1:1	220	layer

[a] Based on the overall. [b] Before the polymerizations.

Table 2. Experimental ($d_{n,exp}$) and Calculated ($d_{n,calc}$) Number-Average Particle Diameters and Calculated Numbers of Particles (N_p) at Different Solids Contents at Each Final Conversion

	BA (wt %)	stirring rate (rpm)	conversion[a] (%)	measured d_n[b] (nm)	calculated d_n (nm)	N_p (numbers/mL)
exp 1	4	220 (layer)	91	19	19[c]	1.07×10^{16}
exp 2	4	1000 (dispersion)	100	22		0.76×10^{16}
exp 3	2	220 (layer)	79	15		0.94×10^{16}
exp 4	8	220 (layer)	100	27	25[c]	0.83×10^{16}

[a] Measured by gravimetry. [b] Measured by dynamic light scattering. [c] Calculated based on the $d_{n,exp}$ (=15 nm) at 2 wt % content monomer assuming a constant number of particles.

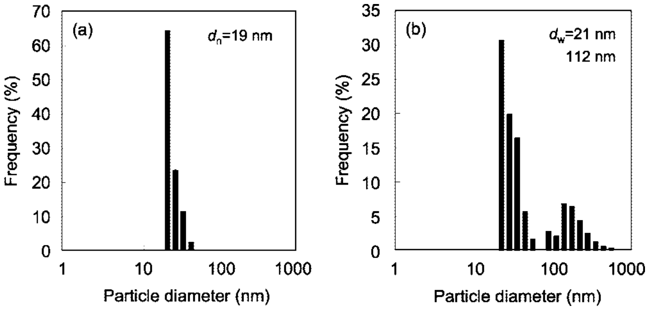

Figure 2. Particle size distribution (number (a) and weight (b) distributions) of $PMAA_{30}$-*b*-PBA-TeMe emulsion at 91% conversion prepared by emulsion TERP using $PMAA_{30}$-TeMe and V-501 at the low stirring rate (220 rpm). BA/$PMAA_{30}$-TeMe/V-501 (molar ratio) = 400/1/1 and 4 wt % solids content (experiment 1).

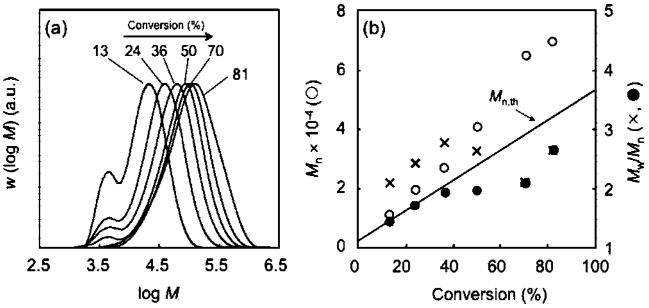

Figure 3. (a) MWD and (b) M_n (open circle), and M_w/M_n corresponding to the overall MWD (cross symbol), and M_w/M_n of $PMAA_{30}$-*b*-PBA-TeMe after exclusion of the low-MW shoulder (closed circle) at different conversions (as indicated in %) of emulsion TERP using $PMAA_{30}$-TeMe and V-501 with the low stirring (220 rpm). BA/$PMAA_{30}$-TeMe/V-501 (molar ratio) = 400/1/1 and 4 wt % solids content (experiment 1). Full line is $M_{n,th}$.

Effect of Stirring Condition. Emulsion TERP at a high stirring rate of 1000 rpm at which whole monomer was dispersed as droplets with the initial ratio of BA/PMAA-TeMe/V-501 = 400/1/1 and solids content of 4 wt %, which were the same as those in experiment 1 except for stirring rate, was performed (experiment 2). The polymerization proceeded smoothly and reached high conversion within 4 h (Figure 1b), which was faster than that at 220 rpm (Figure 1a). The final product was transparent, and measured d_n was 22 nm, showing a unimodal distribution (Figure 4). We have checked that the effect of pH on the particle size measured by DLS can be considered negligible in the pH range from 8.0 to 11.3. The MWDs of the preparing polymer chains (after methylation), as shown in the Figure 5a, shifted to the high conversion with increasing conversion, and M_n linearly increased with the conversion while they deviated from the theoretical line with a higher value (Figure 5b). The MWDs show much narrower over the polymerization. The M_w/M_n values of the overall MWD curves including unreacted $PMAA_{30}$-TeMe TERP agents (closed circle) was less than 2, and those after exclusion of the low MW shoulder due to the unreacted TERP agents (cross symbol) was in the range of 1.0−1.5. These results indicate that this polymerization proceeded maintaining better controlled manner than that at 220 rpm. Ferguson et al. reported that dispersed monomer droplets in the reaction system during the nucleation period should be avoided to keep out the propagating polymer chains adsorbing into droplet/water interface and subsequent

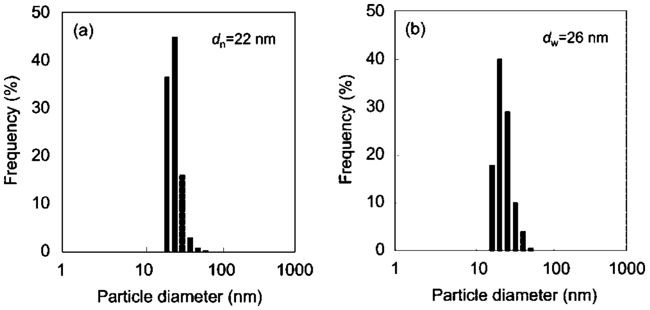

Figure 4. Particle size distribution (number (a) and weight (b) distributions) of PMAA$_{30}$-*b*-PBA-TeMe emulsion at 100% conversion prepared by emulsion TERP using PMAA$_{30}$-TeMe and V-501 at the low stirring rate (1000 rpm). BA/PMAA$_{30}$-TeMe/V-501 (molar ratio) = 400/1/1 and 4 wt % solids content (experiment 2).

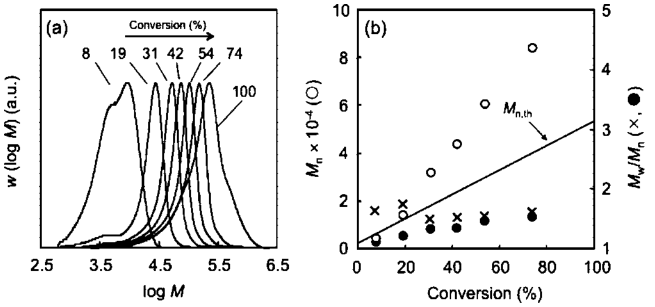

Figure 5. (a) MWD and (b) M_n (open circle), and M_w/M_n corresponding to the overall MWD (cross symbol) and M_w/M_n of PMAA$_{30}$-*b*-PBA-TeMe after exclusion of the low-MW shoulder (closed circle) at different conversions of emulsion TERP using PMAA$_{30}$-TeMe and V-501 with a high stirring rate (1000 rpm). BA/PMAA$_{30}$-TeMe/V-501 (molar ratio) = 400/1/1 and 4 wt % solids content (experiment 2). Full line is $M_{n,th}$.

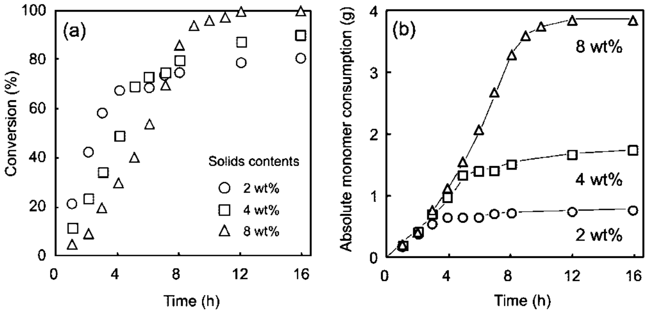

Figure 6. (a) Conversion and (b) absolute monomer consumption versus time plots for emulsion TERPs of BA using PMAA$_{30}$-TeMe and V-501 at the low stirring rate of 220 rpm at 60 °C. BA/PMAA$_{30}$-TeMe/V-501 (molar ratio): open circles, 200/1/1 (experiment 3); open squares, 400/1/1 (experiment 1); open triangles 800/1/1 (experiment 4). Solids content (wt %): circles, 2; open squares, 4; open triangles, 8.

droplets nucleation.[45,46] If droplets nucleation were the exclusive mechanism, it would be impossible to produce such nanoparticles, ~20 nm, rather much larger particle would be prepared. Moreover, if self-assembly nucleation and droplets nucleation took place at a similar degree, MWD would make the bimodal peak and M_w/M_n would indicate higher values. Both hypotheses are opposite to the obtained experimental results. Thus, although whether droplets nucleation took place or not is not clear, almost all of the nucleation occurs via self-assembly of propagating amphiphilic polymer chains so that the possibility and the influence of droplets nucleation could be neglected, resulting in desirable polymer nanoparticles maintaining colloidal stability and control/livingness. The storage stability of the polymer emulsion was, however, less than that obtained at the low stirring rate (220 rpm), so that precipitation has appeared after a few weeks. At 220 rpm, the particle size distribution was bimodal, and a significant fraction of large particles were obtained; on the other hand, only small particles were obtained at 1000 rpm. Therefore, it seems that the total surface area of particles prepared at 1000 rpm was larger than that of 220 rpm, and the number of PMAA$_{30}$ chains per unit area at 220 rpm was larger than that at 1000 rpm, resulting in the higher colloidal stability at 220 rpm.

As described above, both on R_p and the degree of control/livingness, the more desirable result was achieved when the polymerization was performed at the high stirring rate. In general, R_p (M s^{-1}; here expressed as rate of conversion dx/dt in s^{-1}) in the conventional emulsion polymerization can be described by

$$R_p = \frac{dx}{dt} = \frac{k_p[M]_p N_p}{N_A n_M^0}\tilde{n}$$

where x is fractional conversion, k_p is the propagation rate coefficient of monomer, $[M]_p$ is monomer concentration in the particles, N_p is particle number per unit volume of aqueous phase, N_A is Avogadro constant, n_M^0 is initial number of moles of monomer present per unit volume of aqueous phase, and $\bar{n}$ is the average number of radical per particle.[55] When this equation is applied to controlled/living radical polymerization, the different processes from the conventional radical polymerization such as activation–deactivation are included in the $\bar{n}$ term. Therefore, this expression can be used as a basis for discussion of R_p in the present work.

We can consider the possibility in terms of $[M]_p$ of the reason why R_p in the high stirring rate was higher than that in the low stirring rate. In the low stirring rate, whole monomer floated as monomer layer on the aqueous medium, even if the monomer droplets were existed the droplets size was very large as a mm order in the reaction system, minimizing the monomer/water interfacial area, so the diffusion of the monomer from monomer phase throughout water phase into particle could be much restricted and could not overtake the consumption by propagation, and each particle would be monomer-starved (lower $[M]_p$) during the course of the polymerization, resulting in lower R_p. On the other hand, at the high stirring rate, monomer phase was dispersed as droplets sufficiently in reaction system so that each particle was monomer-saturated (higher $[M]_p$) until the droplets disappear, resulting in higher R_p.

About the difference in the degree of control/livingness between both polymerizations, from the difference of the $[M]_p$ one speculation can also be assumed. The higher $[M]_p$ in the high stirring rate leads to lower weight fraction of polymer, w_p, whereas the lower $[M]_p$ in the low stirring rate leads to higher w_p. DT is a reaction between two polymer chains: one with free-radical active chain end and the other with dormant chain end-capped by the methyltellanyl group. Moreover, the alternative chain ends of the propagating polymer are water-soluble PMAA anchor (except one derived from conventional initiator and one initiated from monomer radical by transfer to monomer), and therefore they are anchored at the interface of the particle. In these situations, the chain exchange rate coefficient, k_{ex}, might become severely diffusion-controlled; the higher w_p is, the lower k_{ex} might be, and vice verca. On the other hand, propagation is a reaction between a polymer radical and a small monomer molecule, so that k_p is generally known as chemically controlled even at quite high w_p.[56] Thus, the exchange constant, C_{ex} (= k_{ex}/k_p), might be influenced by $[M]_p$, namely w_p. In the case of RAFT, the activation process also proceeds via DT because k_{ex} is typically many orders of magnitude higher than k_p, so that even if k_{ex} were somewhat altered by the influence of the system, practically C_{ex} would be enough large, which

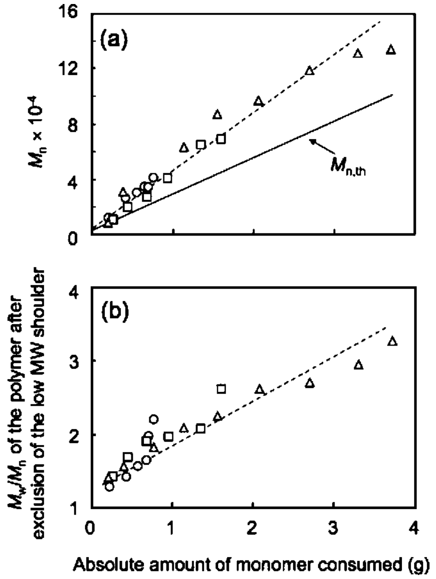

Figure 7. (a) M_n and (b) M_w/M_n of PMAA$_{30}$-*b*-PBA-TeMe prepared by emulsion TERP of BA using PMAA$_{30}$-TeMe and V-501 at the low stirring rate of 220 rpm after exclusion of the low-MW shoulder due to residual PMAA$_{30}$-TeMe as function of absolute amount of monomer consumped. BA/PMAA$_{30}$-TeMe/V-501 (molar ratio): open circles, 200/1/1 (experiment 3); open squares, 400/1/1 (experiment 1); open triangles 800/1/1 (experiment 4). Solids content (wt %): circles, 2; open squares, 4; open triangles, 8. Full line: $M_{n,th}$; broken line: guide to the eye only.

would be negligible in the influence on control/livingness. On the other hand, in TERP, k_{ex} is originally not so much higher corresponding to k_p (=19 for methyl acrylate),[16] although the value is sufficient to achieve high degree of control/livingness in homogeneous polymerizations such as bulk and solution. A decrease in k_{ex}, namely C_{ex}, would result in loss in control. Moreover, unlike in bulk and solution polymerizations, where w_p increase dependently on increasing conversion especially at high conversion, in emulsion polymerization these trends would last from the beginning of the polymerization until monomer droplets (layer) have been disappeared, so the influence would appear more remarkable. Moreover, chain transfer to polymer may occur at high w_p,[57,58] resulting in an increase of PDI. Therefore, in emulsion TERP it is required that monomer is transferred smoothly into the locus of the polymerization.

We have visually observed that the PMAA$_{30}$-TeMe was primarily located at the oil/water interface in the absence of stirring (under the oil layer) before polymerization. The surface tension of PMAA aqueous solution was lower than that of pure water, which indicates that PMAA is surface active. In addition, it has been reported that PMAA has an ability to emulsify a monomer.[59] At the high stirring rate, the initial TERP agent was easily desorbed into aqueous phase, resulting in smoothly propagation and rapidly micelles formation. Consequently, as shown in Figure 5a, the initial TERP agent has been already consumed at about 30% conversion. On the other hand, at the low stirring rate, the TERP agents at the oil/water interface were more difficult to desorbed into aqueous phase, leading to inhomogeneous propagation of initial TERP agents. From that reason, in the low stirring rate initial TERP agent still remained even at 50% conversion, as shown in Figure 3a. This inhomogeneous propagation of initial TERP agent has given the harmful influences to control, resulting in the high M_w/M_n value as shown in Figure 3a.

Effect of Monomer Concentration. To further prove above explanation, the effect of monomer content was investigated. Emulsion TERPs, where the initial concentrations of PMAA$_{30}$-TeMe and V-501 were fixed at constant values, were carried out at the monomer contents of 2, 4, and 8 wt % (experiments 3, 1, and 4, respectively). Figure 6 shows conversion versus time plots for the emulsion TERPs at the low stirring rate of 220 rpm at 60 °C. Alternatively, these plots were described again as the absolute monomer consumption versus time plots in Figure 6b. On the latter description, it is found that the absolute monomer consumption increased with the time independently of solids contents. The final PBA emulsion at high conversion was so stable that any coagulation and precipitation have not appeared for several months at room temperature. In each polymerization the number of polymer particles was approximately equal during the course of the polymerization. In Figure 7, M_n linearly increased independent of the monomer content, while they deviated from the theoretical line with a higher value. M_w/M_n of propagating polymer chains (Figure 7b) also increased with increasing absolute amount of monomer consumed independent of the monomer content while they deviated from the theoretical line with a higher value. In the polymerization systems with different monomer contents at the low stirring rate, where whole monomer floated as monomer layer on the aqueous medium because the solubility of BA in water is extremely low, particle nucleation in the aqueous media was the same. It seems that the particle nucleation, which was caused by via self-assembly of propagating amphiphilic polymer chains derived from PMAA$_{30}$-TeMe in the aqueous medium, completed around the amount of consumed monomer to be 2 wt %. This idea is supported by the result that the numbers of particles formed in the three polymerizations were nearly the same.

Conclusions

Emulsion TERP of BA has been carried out for the first time, using the in situ nucleation technique via self-assembly of propagating amphopholic chains derived from water-soluble TERP agents, PMAA$_{30}$-TeMe. The polymerization reached to high conversion maintaining control/livingness with no coagulation, resulting in nanosized PBA particles. The difference in the stirring rates of the reaction system had a great influence both on the R_p and on the degree of the control/livingness and on both of which the polymerization with the high stirring rate gave more desirable results than that with the low stirring rate, which would be caused by the difference of the $[M]_p$.

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