Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization of Styrene†

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Summary: Emulsifier-free organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of styrene was successfully carried out using a water-soluble TERP agent, poly(methacrylic acid)-methyltellanyl ($PMAA_{30}$-TeMe) (degree of polymerization of PMAA, 30) and a water-soluble thermal initiator, 4,4′-azobis(4-cyanovaleric acid) (V-501), which were neutralized with NaOH, at 60 °C with stirring at 220 rpm, where most of monomer floated as a layer onto an aqueous medium. The polymerization proceeded without an induction period and completed within 20 h, resulting in a stable PS emulsion without any coagulation, although the particle size distribution was bimodal. The polymerization livingness was maintained, although the experimental number-average molecular weight (M_n) differed from theoretical M_n, and polydispersity (M_w/M_n) reached a slightly high value (2.1) at the completion of the polymerization.

Keywords: emulsion polymerization; organotellurium-mediated living radical polymerization (TERP); particle; self-assembly; styrene

Introduction

Controlled/living radical polymerization (CLRP) has been developed in homogeneous systems such as bulk and solution polymerizations for the syntheses of polymers having narrow molecular weight distributions, predominant molecular weight and a complex structure such as macromonomers, functional polymers, block polymers and graft polymers.[1–3] CLRP has the potential to become commercially feasible because it shows all the desirable traits of conventional radical polymerization. At present, there are three main well established techniques: nitroxide-mediated radical polymerization (NMP),[4–6] atom transfer radical polymerization (ATRP),[7–10] and reversible addition fragmentation chain transfer polymerization (RAFT),[11,12] More recently, a novel CLRP technique, organotellurium-mediated living radical polymerization (TERP),[13–18] which proceeds with both thermal dissociation (TD) and degenerative chain transfer (DT), was discovered by Yamago and coworker.

Recently, much attention has been devoted to apply CLRP to aqueous dispersed systems.[19,20]. Most success has been achieved using a miniemulsion approach.[21–24] In miniemulsion systems, ideally all ingredients are located in monomer droplets and radical polymerization should ideally occur in the monomer droplets without transportation of ingredients between droplets, and each droplet is converted to polymer particles. In a previous work, we have successfully applied TERP to the miniemulsion system (miniemulsion TERP) using several monomers for the first time and synthesized the polymer particles having narrow molecular weight distributions (MWDs).[25] In addition, several block copolymer particles were also prepared by subsequent seeded TERPs.[25]

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With the development of CLRP in miniemulsion systems, attention has also been devoted at emulsion polymerization systems without mechanistic shear forces. A conventional emulsion polymerization (conventional EP) has many advantages compared to homogeneous polymerizations such as bulk and solution polymerizations, i.e., higher polymerization rate and higher molecular weight due to compartmentalization, and higher rate of heat transfer to the aqueous medium during the polymerization and more environmentally friendly character.[26–29]

Most examples of application of CLRP to the emulsion polymerization system have many problems such as low polymerization control and poor colloidal stability. These problems were caused by the difficulty of the control agent to transport to the micelles across the aqueous phase.[30–33] However, recently, a very efficient novel method for CLRP to apply in emulsifier-free emulsion polymerization systems, which is based on a mechanism via self-assembly of water soluble control agent reacting with hydrophobic monomer in an aqueous medium, was proposed by Gilbert and coworkers.[34] Several successful researches of applying CLRP in the emulsion system have been reported utilizing NMP[35–40] and RAFT.[41–48] We also have successfully applied TERP of butyl acrylate (BA) to emulsifier-free emulsion polymerization using poly(methacrylic acid) (PMAA)–methyltellanyl (TeMe) ($PMAA_{30}$-TeMe) (degree of polymerization of PMAA, 30) utilizing the self-assembly approach (emulsion TERP) for the first time.[49] In the previous study, it was clarified stirring conditions greatly affected the CLRP behavior.

In the present research, emulsion TERP of styrene is carried out at a low stirring rate, and controlled/livingness and particle formation will be discussed.

Experimental Part

Materials

Styrene (NacalaiTesque, Japan) was purified by distillation under reduced pressure in a nitrogen atmosphere. Deionized water used in all experiments was obtained from Elix® UV (Millipore Japan) purification system and had a resistivity of $18.2\,M\Omega\cdot cm^{-1}$. 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, M_w/M_n: approximately 1.1) was supplied from Otsuka Chemical Co., Ltd., Osaka, Japan and trimethylsilyldiazomethane (TMSD, NacalaiTesque) was used as received.

Emulsion TERP of Styrene

A typical procedure is described below. Water and styrene were deoxygenized by nitrogen bubbling. First, NaOH aqueous solution (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, then degassed using several N_2/vacuum cycles, where the amount of NaOH was to the same equivalent to that of carboxyl groups of V-501. $PMAA_{30}$-TeMe (295 μl, 0.127 M aqueous solution neutralized by NaOH, 37.8 μmol) was injected into the system via syringe. After styrene (1.57 g, 15 mmol) was injected via syringe, the flask was then placed in a water bath at 60 °C (taken to be the start of the polymerization, $t = 0$. In all polymerizations, stirring rate with a magnetic stirrer was fixed at 220 rpm, where most of monomer existed as a layer above the aqueous phase.

In comparison with emulsion TERP, emulsifier-free conventional emulsion polymerization (conventional EP) was carried out at the same conditions except for absence of the $PMAA_{30}$-TeMe.

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 Corporation, TSKgel GMHHR-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 (1.05×10^3–5.48×10^6, $M_w/M_n = 1.01$–1.15). Theoretical molecular weight ($M_{n,th}$) was calculated by following equation:

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

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 gel permeation chromatography (GPC) measurement, the polymers were modified by methylation of the carboxyl group of MAA units using TMSD according to the previous work[25] as follows. After acidification of the medium, the polymers were recovered by drying polymer emulsion. They were dissolved in a mixture of dimethylfolmamide and methanol at room temperature. The yellow solution of TMSD was added dropwise at room temperature into the polymer solution and reacted overnight. After excess TMSD was destroyed by acetic acid, the polymer solution was mixed with THF and used for GPC measurement.

Number-average and weight-average particle diameters (d_n and d_w, respectively) were measured using a dynamic light scattering (DLS, FPAR-1000 RK, Fiber-optics particle analyzer, PhotalOtsuka electronics, Osaka, Japan) at the light scattering angle 90° at room temperature using the Contin analysis routine. 1–2 droplets of emulsion samples withdrawn from the reactor were diluted with approximately 8 ml of distilled water before measurement in the dilution mode.

Polymer particles were observed with transmission electron microscopy (TEM, JEOL JEM-1230 electron microscope). Each emulsion was diluted to approximately 50 ppm, and then a drop was placed on a carbon-coated copper grid and dried at room temperature in a desiccator.

Results and Discussion

Emulsion TERP of styrene was carried out using $PMAA_{30}$-TeMe as control agent and V-501 as initiator at 60 °C, at which the activation process of TERP proceeds only via DT without TD with 220 rpm stirring, where most of monomer floated as a layer onto the aqueous phase.[16] $PMAA_{30}$-TeMe propagated with monomer after chain transfer from primary radical and/or oligomer radical in an aqueous medium, resulting in a low molecular weight amphiphilic $PMAA_{30}$-*b*-PS-TeMe block copolymer in an early stage of the polymerization. The amphiphilic block copolymers self-assemble, resulting in micelles, which solubilize monomer and play an important role as polymerization loci, and then the polymerization would proceed predominantly therein, $PMAA_{30}$-TeMe is also expected to have a potential to provide high colloidal stability because ionized PMAA part must localize at formed particle surfaces and colloidally stabilize them.

Figure 1 shows conversion versus time plots for emulsifier-free conventional emulsion polymerization (conventional EP) and for emulsion TERP at 60 °C. The difference in the recipes of the former and latter polymerizations was only absence or presence of $PMAA_{30}$-TeMe. The conventional EP of styrene slowly proceeded after an induction period of approximately 8 h and the conversion was still less than 30% after 30 h. On the other hand, in the emulsion TERP proceeded without the induction period faster than the conventional EP, and almost completed within 20 h. In the conventional EP a small amount of aggregates were observed after the polymerization for 30 h (conv., 28%), but in the emulsion TERP any aggregation was not observed until 100% conversion and even further after several months. These results suggest that ionized PMAA ''hairy'' surface layer stabilized formed PS particles.

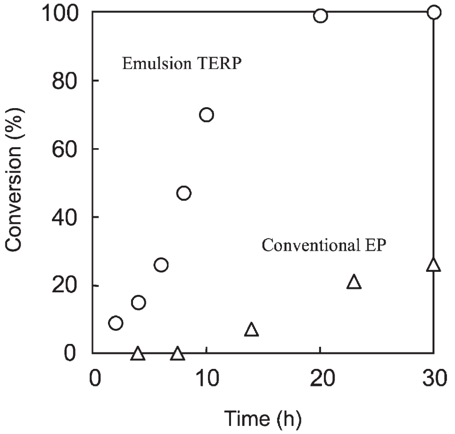

Figure 1.
Conversion versus time plots for emulsifier-free conventional emulsion polymerization (conventional EP) of styrene using V-501 at 60 °C (open triangles) and emulsifier-free organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of styrene using PMAA$_{30}$-TeMe and V-501 at 60 °C (open circles) at a stirring rate of 220 rpm. Syrene/PMAA$_{30}$-TeMe/V-501 (molar ratio) = 400/1/1.

The rate of emulsion TERP of styrene was slower than that of BA, in which the polymerization almost finished at 16 h.[49] The difference between the two polymerizations seems to be caused by the differences in the solubilities of the monomers in the aqueous phases (i.e. transfer rate of monomer from the monomer phase to the polymerizing particles via the aqueous phase) and their propagation rate constants (k_p).

Figure 2 shows MWD, M_n and M_w/M_n at various conversions of the emulsion TERP. The carboxyl groups of the samples were modified by methylation described in the experimental part before the GPC measurement. The MWD (obtained using a reflective index detector) was shifted to higher molecular weight with increasing conversion, and the M_n linearly increased until 70% conversion. Above 70% the M_n values were apart from the line to the lower value side and apparently decreased after 99% conversion. The M_w/M_n ratio gradually increased linearly with the conversion upto 70% conversion, but it attained 2.0 at 99% conversion and 2.1 at 100%. The MWDs obtained using an ultraviolet (UV) detector at 70, 99 and 100% conversions are shown in Figure 3. The UV detector detected only polymer chains containing styrene units, i.e. the original PMAA$_{30}$-TeMe peak was not detected. The peak top ($\log M = 5.5$) from 70 to 99% conversion was shifted to higher molecular weight, and it from 99 to 100% conversion was not shifted. The amount of the lower molecular weight component ($\log M = 4.5$) was always increased with the conversion from 70 to 100%. These results indicate that the decrease of M_n in the final stage was caused by increasing number of the newly formed low M_n polymer chains ($\log M = 4.5$).

As the reason for the newly formed low M_n, it was first thought that some PMAA$_{30}$-TeMe chains, which had been adsorbed at the styrene/water interface, moved to the aqueous phase based on the disappearance of the monomer layer at 70% conversion, resulting in the formation of new low M_n polymer chains and a discontinuous increase of total number of polymer chains around 70% conversion. In Figure 2(a), the peak due to methylated PMAA$_{30}$-TeMe ($\log M = 3.5$) rapidly decreased in the early stage of the polymerization, but approximately 25% of the original PMAA$_{30}$-TeMe remained at 70% conversion and still 20% at 100% conversion. That is, the consumption of the PMAA$_{30}$-TeMe proceeded only 5% in the final stage (conv. 70–100%), which was not enough amount to form the low M_n polymer chains for the "decrease" of M_n in the final stage. Moreover, in the case of the emulsion TERP of BA, in which M_n similarly decreased in the final stage of polymerization (conversion > 80%), PMAA$_{30}$-TeMe was completely consumed before the final stage. Therefore, it seems that the remain of PMAA$_{30}$-TeMe in the aqueous phase in the final stage is not a main reason that the number of the low M_n polymer chains was markedly increased therein. However, the remain of PMAA$_{30}$-TeMe throughout the polymerization is a main reason that M_n was higher than $M_{n.th}$ and M_w/M_n linearly increased with the conversion. When the $M_{n.th}$ was recalculated using

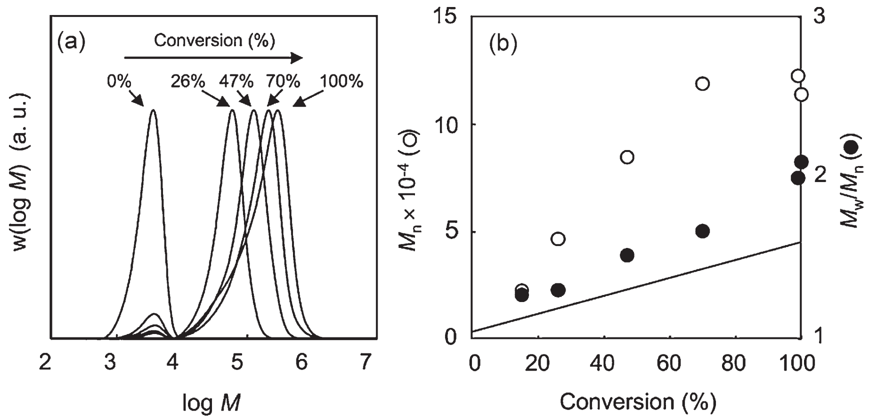

Figure 2.
MWD (a), M_n (open circles) and M_w/M_n (closed circles) (b) of PMAA$_{30}$-*b*-PS-TeMe at different conversions (as indicated in %) of emulsion TERP using PMAA$_{30}$-TeMe and V-501 at 60 °C with 220 rpm. Styrene/PMAA$_{30}$-TeMe/V-501 (molar ratio) = 400/1/1. MWD was measured with GPC (detector: refractive index) after methylation of PMAA$_{30}$ block. Full line in (b) is $M_{n,th}$.

the actual amount of the consumed PMAA$_{30}$-TeMe instead of the initial amoubnt of PMAA$_{30}$-TeMe, the obtained $M_{n.th}$ slightly closed to M_n. Because the consumption rate of PMAA$_{30}$-TeMe affects $M_n/M_{n,th}$ as described above, the problem of the remain will be discussed in detail in a following article.

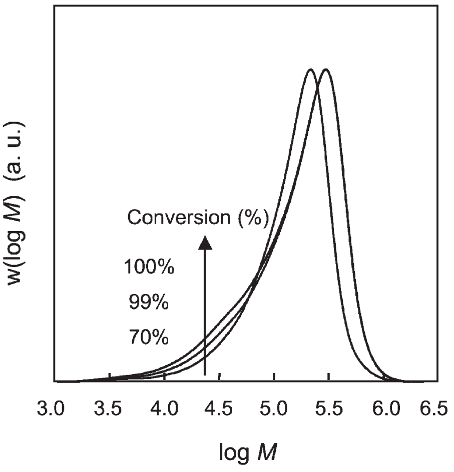

Figure 3.
MWD of PMAA$_{30}$-*b*-PS-TeMe measured with GPC (detector: ultraviolet) after methylation of PMAA$_{30}$ block in the final stage of emulsion TERP using PMAA$_{30}$-TeMe and V-501 at 60 °C with 220 rpm. Styrene/PMAA$_{30}$-TeMe/V-501 (molar ratio) = 400/1/1.

Figures 4 and 5 show weight-average size distributions of PS emulsions prepared by the conventional EP and the emulsion TERP, respectively. In Figure 4, the size of obtained PS particles at 30% conversion of the conventional EP was a monomodal submicrometer (d_n, 666 nm; d_w/d_n, 1.05). On the other hand, in Figure 5 the particle size distribution by the emulsion TERP was bimodal, which was a similar with the result when using BA as monomer. The PS

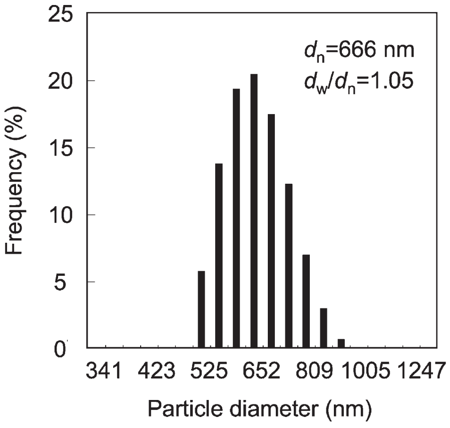

Figure 4.
Weight-avarage size distribution of PS emulsion at 30% conversion prepared by conventional EP using V-501 at 60 °C for 30 h with 220 rpm.

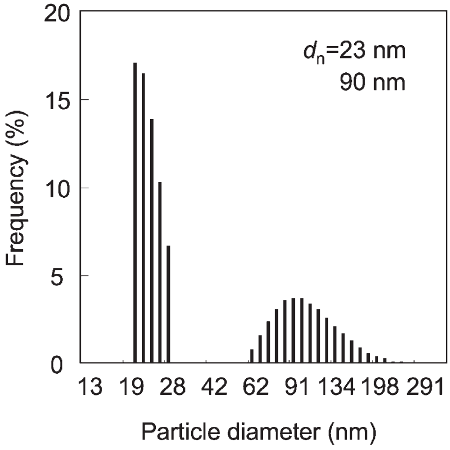

Figure 5.
Weight-avarage size distribution of PS emulsion at 100% conversion prepared by emulsion TERP using $PMAA_{30}$-TeMe and V-501 at 60 °C for 30 h with 220 rpm. Styrene/$PMAA_{30}$-TeMe/V-501 (molar ratio) = 400/1/1.

particles obtained at 100% conversion of the emulsion TERP were much smaller than that at the 30% conversion of the conventional EP.

The consumption of remaining $PMAA_{30}$-TeMe in the final stage of polymerization may cause the new particle formation. In order to clarify whether the smaller particles are formed by the self-assembly nucleation of amphiphili block copolymer derived from the remained $PMAA_{30}$-TeMe in the final stage of polymerization, the fractions of larger ($d_n = 113$ nm) and smaller ($d_n = 35$ nm) particles were obtained by a centrifugate separation of the PS emulsion (at 100% conversion) having the bimodal particle size distribution, which was confirmed with TEM observation (data not shown) and DLS measurement (Figure 6).

Table 1 shows M_n and M_w/M_n values of both fractionated PS particles. If the smaller particles are formed from the remaining $PMAA_{30}$-TeMe in the final stage of polymerization, the M_n value of smaller particles must be much lower than that of the larger particles. However, the M_n value of the smaller particles (1.0×10^5) was only slightly smaller than that of the larger particles, and the M_w/M_n of the smaller particles was a similar to that of the fraction of larger particles. These results indicate that the smaller particles were not byproducts formed in the final stage after disappearance of the monomer layer, but main ones formed in the relationally early stage of the polymerization as well as the large particles. In other words, the formation of the smaller particles is not the cause for the decrease in M_n in the final stage. That is, the remain of $PMAA_{30}$-TeMe in

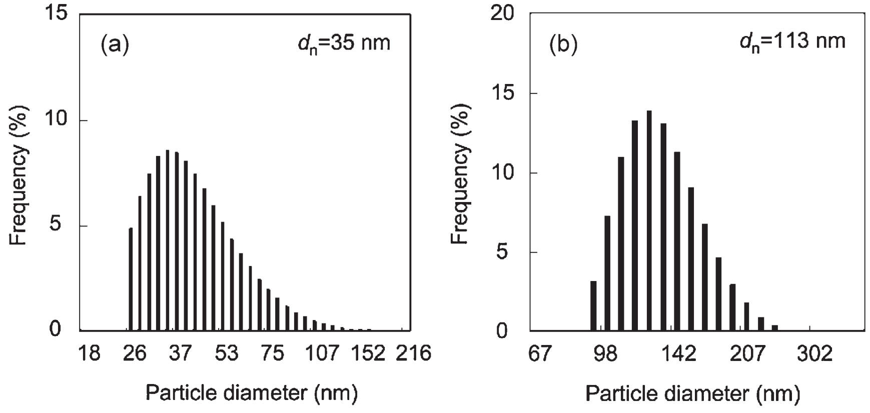

Figure 6.
Weight-average size distribution of two fractionated PS particles by centrifugation: (a) small particle fraction; (b) large particle fraction. Original PS particles were prepared by emulsion TERP using $PMAA_{30}$-TeMe and V-501 at 60°C (conversion 100%).

Table 1.
M_w, M_n and M_w/M_n of small and large particle fractions.

	d_n (nm)	M_w	M_n	M_w/M_n
Small particle fraction	35	2.4×10^5	1.0×10^5	2.4
Large particle fraction	113	3.6×10^5	1.4×10^5	2.6

the final stage is not the reason. We are now considering it as follows. Approximately 80% of V-501 initiator remained at the 70% conversion (polymerization time: 10 h). At the 99% and 100% conversions, the polymerization times were 20 h and 30 h, at which 66% and 54% initiators still remained, respectively. Therefore, a sufficient number of radicals were generated from the initiator in the final stage of polymerization, where the monomer concentration is extremely low, resulting in the genertion of additional low M_n polymer chains. This problem should also be improved to keep narrow molecular weight distribution at the completion of emulsion TERP. The particle formation in the emulsion TERP system will be discussed in more details in the future.

Conclusion

Emulsion TERP of styrene was successfully carried out using $PMAA_{30}$-TeMe and V-501 as conventional initiator at 60 °C with 220 rpm stirring. The emulsion TERP smoothly proceeded relative to a conventional EP because of formation of self-assembled micelles. The livingness was maintained in the emulsion TERP of styrene, although the M_n differed from $M_{n,th}$ and the M_w/M_n value was slightly high (approximately 2.1) and a part of $PMAA_{30}$-TeMe remained in the emulsion TERP of styrene even at the final stage of polymerization, which was not observed in the emulsion TERP of BA. The obtained PS emulsion prepared by the emulsion TERP had a high colloidal stability and much smaller particle size relative to that prepared by conventional EP, although the PS emulsion had bimodal distribution.

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[1] K. Matyjaszewski, T. P. Davis, "*Handbook of Radical Polymerization*", Wiley-Interscience, New York **2002**.
[2] K. Matyjaszewski, "*Advances in Controlled/Living Radical Polymerization*", American Chemical Society, Washington, DC **2003**.
[3] K. Matyjaszewski, "*Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT*", American Chemical Society, Washington, DC **2000**.
[4] D. H. Solomon, E. Rizzardo, P. Cacioli, *U. S. Patent* 4, **1986**.
[5] C. J. Hawker, A. W. Bosman, E. Harth, *Chem. Rev.* **2001**, *101*, 3661.
[6] M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer, *Macromolecules* **1993**, *26*, 2987.
[7] J. S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614.
[8] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, *28*, 3689.
[9] K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921.
[10] M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689.
[11] J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1998**, *31*, 5559.
[12] G. Moad, E. Rizzardo, S. H. Thang, *Aust. J. Chem.* **2005**, *58*, 379.
[13] S. Yamago, K. Lida, J. Yoshida, *J. Am. Chem. Soc.* **2002**, *124*, 2874.
[14] S. Yamago, K. Iida, M. Nakajima, J. Yoshida, *Macromolecules* **2003**, *36*, 3793.
[15] S. Yamago, K. Lida, J. Yoshida, *J. Am. Chem. Soc.* **2002**, *124*, 13666.
[16] A. Goto, Y. Kwak, T. Fukuda, S. Yamago, K. Iida, M. Nakajima, J. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 8720.
[17] S. Yamago, *J. Polym. Sci. part A Polym. Chem.* **2006**, *44*, 1.

[18] Y. Kwak, M. Tezuka, A. Goto, T. Fukuda, S. Yamago, *Macromolecules* **2007**, *40*, 1881.

[19] P. B. Zetterlund, K. Kagawa, M. Okubo, *Chem. Rev.* **2008**, *108*, 3747.

[20] M. F. Cunningham, *Prog. Polym. Sci.* **2008**, *33*, 365.

[21] G. F. Pan, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *Macromolecules* **2001**, *34*, 481.

[22] J. Qiu, B. Charleux, K. Matyjaszewski, *Prog. Polym. Sci.* **2001**, *26*, 2083.

[23] M. F. Cunningham, *Prog. Polym. Sci.* **2002**, *27*, 1039.

[24] P. B. Zetterlund, M. N. Alam, H. Minami, M. Okubo, *Macromol. Rapid Commun.* **2005**, *26*, 955.

[25] Y. Sugihara, Y. Kagawa, S. Yamago, M. Okubo, *Macromolecules* **2007**, *40*, 9208.

[26] G. R. Gilbert, "*Emulsion polymerization:A Mechanistic Approach*", Academic Press, London 1995, p. 362.

[27] P. A. Lovell, M. S. El-Aasser, "*Emulsion Polymerization and Emulsion Polymers*", Wiley, New York 1997, p. 207.

[28] J. M. Asua, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1025.

[29] S. C. Thickett, R. G. Gilbert, *polymer* **2007**, *48*, 6965.

[30] M. J. Monteiro, J. de Barbeyrac, *Macromolecules* **2001**, *34*, 4416.

[31] S. W. Prescott, M. J. Ballard, E. Rizzardo, G. R. Gilbert, *Macromolecules* **2002**, *35*, 5417.

[32] S. W. Prescott, M. J. Ballard, E. Rizzardo, G. R. Gilbert, *Aust. J. Chem.* **2002**, *55*, 415.

[33] I. Uzulina, S. Kanagasabapathy, J. Claverie, *Macromol. Symp.* **2000**, *150*, 33.

[34] C. J. Ferguson, R. J. Hughes, D. Nguyen, B. T. T. Pham, G. R. Gilbert, A. K. Serelis, C. H. Such, B. S. Hawkett, *Macromolecules* **2005**, *38*, 2191.

[35] J. Nicolas, B. Charleux, O. Guerret, S. Magnet, *Angew Chem Int Ed* **2004**, *43*, 6186.

[36] J. Nicolas, B. Charleux, O. Guerret, S. Magnet, *Macromolecules* **2005**, *38*, 9963.

[37] J. Nicolas, B. Charleux, S. Magnet, *J Polym Sci Part A: Polym Chem* **2006**, *44*, 4142.

[38] H. Maehata, X. Liu, M. Cunningham, B. Keoshkerian, *Macromol. Rapid Commun.* **2008**, *29*, 479.

[39] R. W. Simms, M. D. Hoidas, M. Cunningham, *Macromolecules* **2008**, *41*, 1076.

[40] C. Dire, F. Magnet, L. Couvreur, B. Charleux, *Macromolecules* **2009**, *42*, 95.

[41] F. Stoffelbach, L. Tibiletti, J. Rieger, B. Charleux, *Macromolecules* **2008**, *41*, 7850.

[42] C. J. Ferguson, R. J. Hughes, B. T. T. Pham, B. S. Hawkett, R. G. Gilbert, A. K. Serelis, C. H. Such, *Macromolecules* **2002**, *35*, 9243.

[43] C. J. Ferguson, R. J. Hughes, D. Nguyen, B. T. T. Pham, R. G. Gilbert, A. K. Serelis, C. H. Such, B. S. Hawkett, *Macromolecules* **2005**, *38*, 2191.

[44] E. Sprong, J. S. K. Leswin, D. J. Lamb, C. J. Ferguson, B. S. Hawkett, B. T. T. Pham, D. Nguyen, C. H. Such, A. K. Serelis, R. G. Gilbert, *Macromol. Symp.* **2006**, *231*, 84.

[45] J. Hartmann, C. Urbani, M. R. Whittaker, M. J. Monteiro, *Macromolecules* **2006**, *39*, 904.

[46] M. Manguian, M. Save, B. Charleux, *Macromol. Rapid Commun.* **2006**, *27*, 399.

[47] D. E. Ganeva, E. Sprong, H. d. Bruyn, G. G. Warr, C. H. Such, B. S. Hawkett, *Macromolecules* **2007**, *40*, 6181.

[48] A. M. dos Santos, J. Pohn, M. Lansalot, F. D'Agosto, *Macromol. Rapid Commun.* **2007**, *28*, 1325.

[49] M. Okubo, Y. Sugihara, Y. Kitayama, Y. Kagawa, H. Minami, *Macromolecules* **2009**, *42*, 1979.