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Organotellurium-Mediated Living Radical Polymerization in Miniemulsion

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Controlled/living radical polymerization (CLRP)[1−3] is a powerful tool for synthesis of polymer with predetermined molecular weight, narrow molecular weight distribution (MWD), and various complex architectures (block, graft, and star polymers, etc.). In the past decade, three typical techniques have been developed: nitroxide-mediated polymerization (NMP),[4] atom transfer radical polymerization (ATRP),[5,6] and reversible addition−fragmentation chain transfer polymerization (RAFT).[7] Yamago et al. have recently pioneered organotellurium-mediated living radical polymerization (TERP) as a novel CLRP and studied its mechanism and kinetics in homogeneous systems (bulk, solution).[8−16] TERP comprises two activation processes: thermal dissociation (TD) and degenerative transfer (DT).

In recent years, much effort has been devoted to render CLRP compatible with the aqueous heterogeneous polymerization process, which is a requirement from an industrial perspective. Most success has to date been achieved using the miniemulsion approach.[17−41] All ingredients are located in the monomer droplets in the early stage of a miniemulsion polymerization, and radical polymerization (RP) should ideally occur in the monomer droplets without transportation of ingredients between droplets. However, in NMP and ATRP in miniemulsion, the deactivator is a low molecular weight species, which may exit to the aqueous medium,[26,31,33,39,42,43] thus making the kinetics considerably more complex.

In this Communication, we report the first TERP in miniemulsion, using hydrophobic organotellurium compounds and an azo initiator as the radical source.

The typical procedure is described below. Water and methyl methacrylate (MMA) were deoxygenized by nitrogen bubbling. First, MMA (1 g, 1×10^{-2} mol), 2,2′-azobis(isobutyronitrile) (AIBN) (8.2 mg, 5×10^{-5} mol), ethyl 2-methyl-2-butyltellanylpropionate (EMA−TeBu) (23 μL, 1×10^{-4} mol), dibutyl ditelluride ($(BuTe)_2$) (12.4 μL, 5×10^{-5} mol), and hexadecane (HD) (0.05 g) were mixed under a nitrogen atmosphere. This organic solution was immediately poured into 0.67 g/L sodium dodecyl sulfate (SDS) aqueous solution (15 g) and subsequently ultrasonicated with an ultrasonic homogenizer (Nissei, US-300T) for 30 s in an ice−water bath under a nitrogen atmosphere. The emulsion was then immediately transferred to a glass ampule, degassed using several N_2/vacuum cycles and sealed off under vacuum, and then shaken at 90 cycles/min in a water bath at 60 °C. Conversion was measured by gas chromatography (GC-18A, Shimadzu Co.) and gravimetry. Number-average molecular weight (M_n) and MWD were measured by gel permeation chromatography (GPC) using two styrene/divinylbenzene gel columns (TOSOH Corp., TSKgel GMH$_{HR}$-H) using THF as eluent at 40 °C at a flow rate of 1.0 mL/min, employing refractive index (RI) (TOSOH RI-8020/21) and ultraviolet detectors (UV) (TOYO SODA UV-8II). The columns were calibrated with six standard polystyrene (PS) samples ($1.05 \times 10^3 - 5.48 \times 10^6$, $M_w/M_n = 1.01-1.15$). Theoretical molecular weights ($M_{n,th}$) were calculated according to $M_{n,th} = \alpha[M]_0 M_M/[EMA-TeBu]_0$,where α is monomer conversion, $[M]_0$ and $[EMA-TeBu]_0$ are the initial concentrations of monomer and EMA−TeBu (replaced by polymer-TeBu in the case of seeded TERP), respectively, and M_M is the molecular weight of monomer. Particle size distributions were measured using dynamic light scattering (FPAR-1000, Otsuka Electronics) at room temperature. Number-average particle diameters (d_n) were obtained using the Marquadt analysis routine.

All polymerizations were conducted at 60 °C, at which the activation process of TERP is mainly DT, and TD can be neglected.[12−15] Yamago et al. reported that TERP in bulk of S and acrylates using various organotellurium compounds such as methyl 1-phenylethyl telluride, ethyl 2-methyl-2-methyltellanyl-propionate, and 2-methyl-2-methyltellanyl-propionitrile as TERP agent proceeded with good control, but for methacrylates, poor levels of control were obtained.[8−15] They clarified that the low degree of control for MMA was due to the low exchange constant ($C_{ex} = k_{ex}/k_p = 3.6$) in the MMA/PMMA−TeMe/60 °C system,[14] where k_{ex} and k_p are the exchange and propagation rate constants, respectively. To overcome this problem, dimethyl ditelluride ($(MeTe)_2$) was added, resulting in good control. $(MeTe)_2$ operates as a deactivator, and $MeTe^\bullet$ derived from $(MeTe)_2$ fulfills the role of an efficient activator, resulting in an increase in the number of activation−deactivation cycles experienced by a chain as it grows to a given degree of polymerization (i.e., lower M_w/M_n).[15] In the present work, the hydrophobic organotellurium compounds (EMA−TeBu) and ditelluride $(BuTe)_2$, which have a butyltellanyl group, were selected to minimize partitioning of TERP agent to the aqueous phase (Scheme 1).

Figure 1a shows conversion vs time plots for conventional RP in miniemulsion and miniemulsion TERP of MMA. Both polymerizations proceeded smoothly and reached almost complete conversion within 6 h, with d_n values of 82 and 92 nm for conventional RP and TERP, respectively. The rate of polymerization (R_p), obtained from slopes of the first-order plots, was a factor of ∼5 lower in TERP than in conventional RP (Figure 1b). Such retardation is often observed in RAFT polymerization (where the activation process is DT), and termination between propagating radicals and adduct radicals (cross-termination) or slow fragmentation of the adduct radical has been proposed as reasons.[44] However, TERP does not proceed via adduct radical formation; R_p of TERP in homogeneous systems has been reported to be the same as in conventional RP.[14] Therefore, the retardation observed in the present work must have a different origin.

The chain lengths of propagating radicals in CLRP are shorter than in a conventional system, and thus chain-length-dependent termination would be expected to cause some degree of retardation.[45] Simulations of TERP and the corresponding conventional system were carried out using the software PREDICI[46] (based on the generally accepted TERP mechanism),[14,15] with experimentally obtained C_{ex} (3.6) for the MMA/

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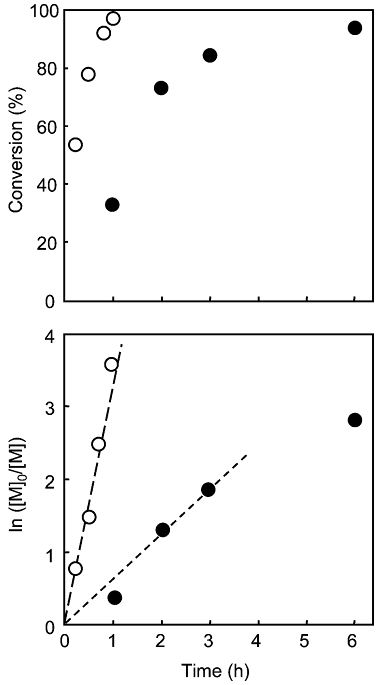
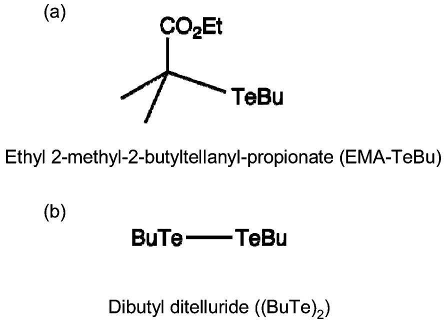


Figure 1. Conversion vs time and first-order plots for miniemulsion RP (○) and miniemulsion TERP (●) of MMA at 60 °C. $[MMA]_0/[EMA{-}TeBu]_0/[(BuTe)_2]_0/[AIBN]_0 = 100/1/0.5/0.5$ in TERP and 100/0/0/0.5 in the conventional polymerization. The twin broken lines are guides to the eye only.

Scheme 1. Organotellurium Compound (a) and Ditelluride (b)



PMMA−TeMe/60 °C system[14] and chain-length-dependent k_t of MMA. Chain-length dependence of k_t was included in the model according to the composite model:[47]

$$k_t^{i,i} = \begin{cases} 1.0 \times 10^9 i^{-0.5} & (i \leq 100) \\ 2.09 \times 10^8 i^{-0.16} & (i > 100) \end{cases}$$

where i is the chain length of propagating radical. The cross-termination rate coefficients were obtained on the basis of the geometric mean model:[47]

$$k_t^{i,j} = (k_t^{i,i} k_t^{j,j})^{0.5}$$

Other rate constants used were as follows: k_p[48] $= 833$ M^{-1} s^{-1}; k_d[49] $= 9.6 \times 10^{-6}$ s^{-1}; $[MMA]_0 = 8.9$ M; $[PMMA\text{-}TeMe]_0 = 8.9 \times 10^{-2}$ M; $[AIBN]_0 = 4.4 \times 10^{-2}$ M, where k_d is the decomposition rate constant of AIBN. According to the simulations, R_p was a factor of 1.4 lower in TERP than in conventional RP. The difference in the ratio of R_p (TERP) to R_p (conventional RP) between the experiment (~5) and simulation (1.4) suggests that the retardation in the present work cannot be explained by k_t chain-length dependence only. It therefore seems likely that the retardation observed in this study is caused by the heterogeneous nature of the system, possibly related to the exit of small radicals. The AIBN radicals and the propagating radicals may add to the initial TERP agent, which generates another small radical. This small radical may also exit to the aqueous phase. The presence of the TERP agent therefore provides an additional pathway to exit.

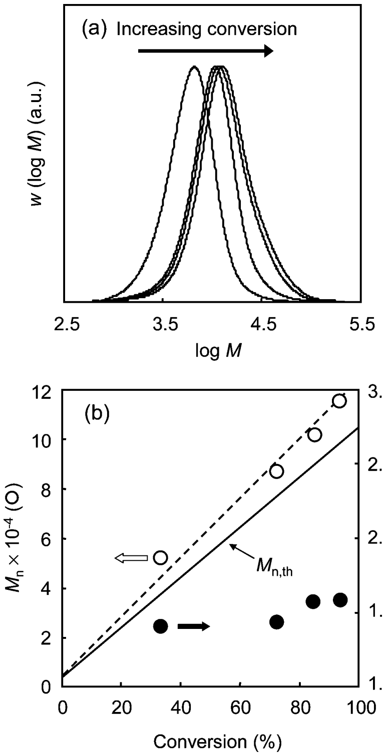


Figure 2. MWD (a) and M_n and M_w/M_n (b) of PMMA−TeBu prepared by miniemulsion TERP at 60 °C at various conversions. $[MMA]_0/[EMA{-}TeBu]_0/[(BuTe)_2]_0/[AIBN]_0 = 100/1/0.5/0.5$ in TERP and 100/0/0/0.5 in the conventional polymerization. Full line: $M_{n,th}$; broken line: guide to the eye only.

Figure 2a shows the MWDs of PMMA−TeBu prepared by miniemulsion TERP at various conversions. The MWDs shifted to higher molecular weights with increasing conversion, indicating that the polymerization proceeded in a living manner. As shown in Figure 2b, experimental M_n increased linearly with increasing conversion, with $M_n \approx M_{n,th}$.

The MWD of PMMA in the present work ($M_w/M_n = 1.55$ at the 96% conversion) was broader than the results in TERP in bulk using a similar organotellurium compound with a methyltellanyl group, as reported by Yamago et al. ($M_w/M_n = 1.15$ at 98% conversion).[10−12] This lower degree of control might be caused by the heterogeneous nature of the system and/or by the lower k_{ex} of organotelluriums compound with a butyltellanyl group as opposed to a methyltellanyl group. In the case of the S/AIBN/60 °C bulk system, k_{ex} of PS−TeBu (3.5×10^3) was lower than that of PS−TeMe (5.7×10^3), resulting in less control.[16] These k_{ex} values for S are not applicable to the present MMA system, but the relatively broad MWDs can at least partially be attributed to the butyltellanyl group.

Polymerizations of S and butyl acrylate (BA) were also carried out under the same conditions as for MMA. In both cases, $(BuTe)_2$ was not employed because the C_{ex} values of S and methyl acrylate (MA) respectively with PS−TeMe and poly(methyl acrylate)−TeMe at 60 °C are sufficiently high[14] (17 and 19, respectively). The polymerizations generally proceeded in a controlled/living manner to high conversion, and stable polymer latexes were obtained. However, MWD of PS−TeBu

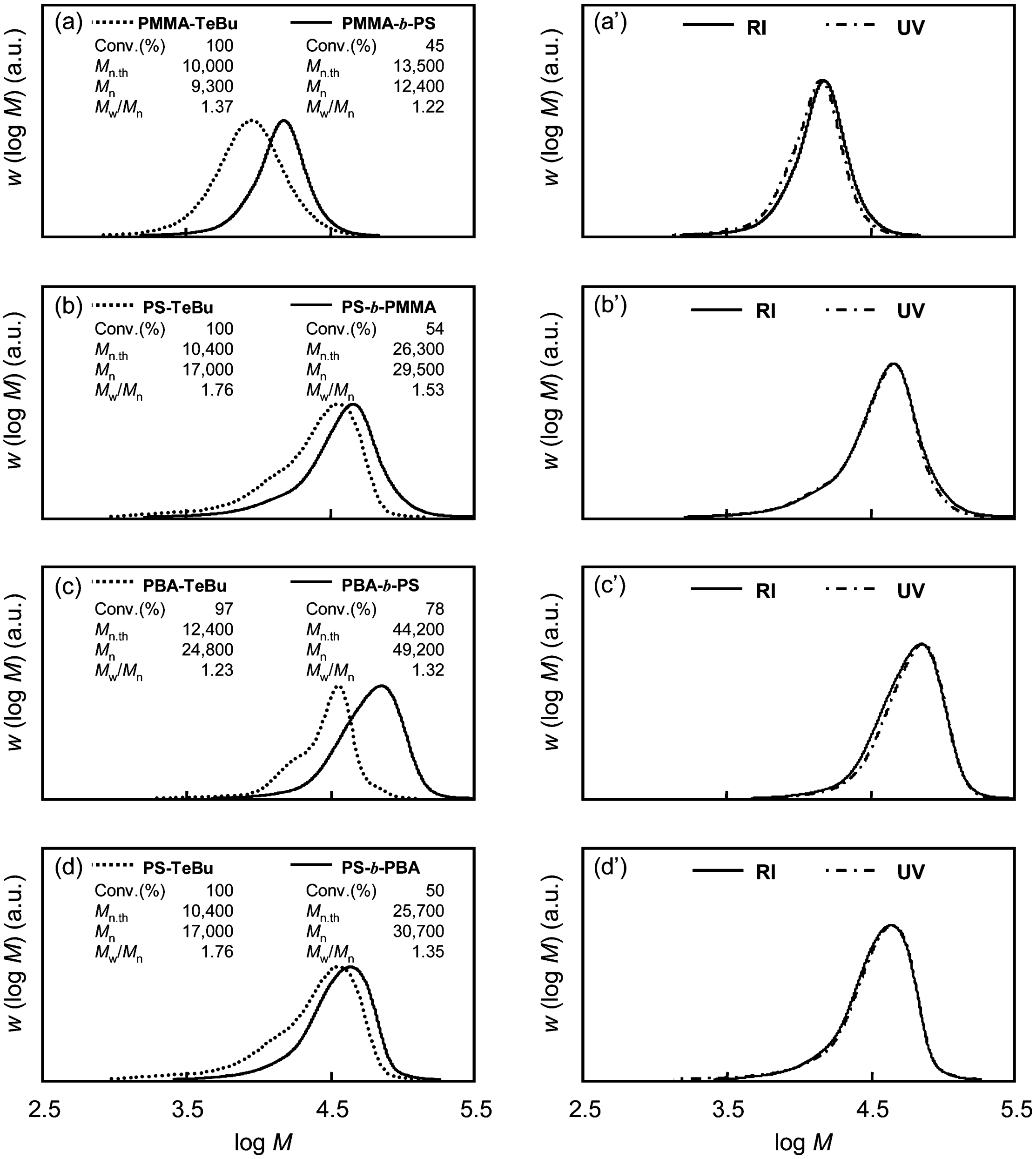


Figure 3. MWDs of various homopolymers prepared by miniemulsion TERP (dotted lines) and the corresponding chain extensions by seeded TERP (solid lines) (a−d; RI detection) measured using RI and UV detection (dot-dash line) (a′−d′).

was relatively broad and had a molecular weight shoulder ($M_{n,th}$ = 10 400, M_n = 7000, M_w/M_n = 1.76 at 100% conversion). The MWD of poly(*n*-butyl acrylate) (PBA)−TeBu was narrow, but a low molecular weight shoulder was present ($M_{n,th}$ = 12 400, M_n = 26 200, M_w/M_n = 1.23 at 97% conversion; data not shown).

Not only can TERP be employed for the synthesis of a wide variety of homopolymers, it is also not sensitive to the order of polymerization when preparing block copolymers.[9,11,12,14] In the present work, seeded emulsion polymerization of various monomers in TERP (seeded TERP) was carried out with various polymer−TeBu seed particles prepared by miniemulsion TERP. Figure 3 shows the MWDs of PMMA-*b*-PS−TeBu, PS-*b*-PMMA−TeBu, PBA-*b*-PS−TeBu, and PS-*b*-PBA−TeBu prepared by seeded TERP. In all cases, the MWDs shifted to higher molecular weight while maintaining a narrow MWD. In addition, the MWDs detected by RI and UV corresponded well, indicating that these polymerizations proceeded with good control/livingness and that virtually all of the reacted second stage monomer had added onto propagating radicals originating from the original homopolymer with a butyltellanyl active chain end. These results clearly demonstrate the successful synthesis of block copolymers independent of the order of monomer addition also in a heterogeneous dispersed system.

In conclusion, miniemulsion TERP has been performed successfully for the first time using various monomers (MMA, S, and BA). The polymerizations reached high conversion, and chain extensions revealed high degrees of livingness. Various block copolymers were prepared using a two-step procedure, carried out entirely in aqueous dispersed systems. The successful application of the present techniques to various monomers demonstrates the applicability of TERP in aqueous heterogeneous systems.

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