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Iron-Catalyzed Suspension Living Radical Polymerizations of Acrylates and Styrene in Water[1]

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ABSTRACT: Iron(II)-catalyzed suspension living radical polymerizations of acrylates and styrene have been achieved for the first time in water. In the presence of a large amount of water (water/organic = 1/1 v/v), a half-metallocene type iron complex [Fe(Cp)I(CO)$_2$] induced a smooth polymerization of *n*-butyl acrylate in conjunction with $(CH_3)_2C(CO_2Et)I$ as an initiator to give polymers of narrow molecular weight distributions (MWDs) (M_w/M_n = 1.2−1.3) and controlled number-average molecular weights, in direct proportion to monomer conversion. Reaching 90% conversion in 4 h, the polymerizations proceeded much faster than in toluene without water. Similarly, methyl acrylate, *tert*-butyl acrylate, and styrene were polymerized with the same initiating system under aqueous suspension conditions to afford living polymers of controlled molecular weights and narrow MWDs (M_w/M_n = 1.2−1.3). The suspension systems can be applied to the controlled synthesis of block and random copolymers of acrylates and styrene.

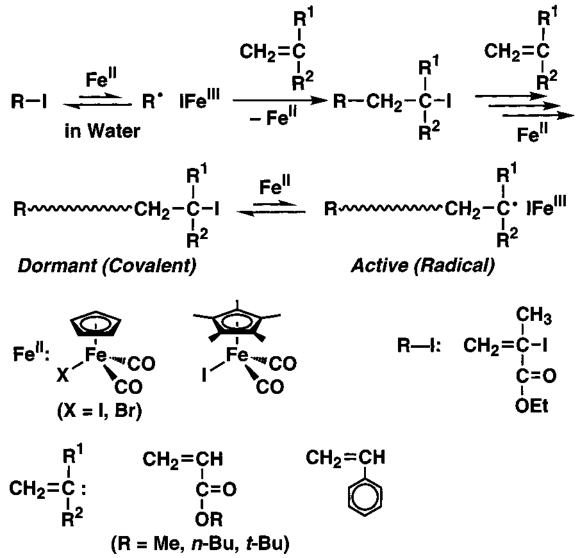
Introduction

In radical polymerization, water-based suspension, dispersion, and emulsion systems are favorably employed in industry processes for several reasons; e.g., water is the most abundant solvent and can solve thermal and viscosity problems to control polymerization.[2] In addition to such economical or practical advantages, water has recently attracted much attention as a nontoxic and environmentally friendly medium for organic reactions and polymerizations.[3,4] However, water, a protic compound, sometimes poisons reactions and catalysts and thereby lowers product yield and/or selectivity. Thus, new systems must be developed that either enhance or do not adversely affect the activity or controllability in the presence of water.

Living polymerization, one of the most effective methods to synthesize polymers of controlled molecular weights and architectures,[5] is usually conducted under anhydrous conditions. This is primarily because most living polymerizations have been based on ionic reactions that are highly susceptible to water. However, recent progress has permitted precision reaction control even in the presence of water, where the mechanisms include ring-opening metathesis,[6] cationic,[7,8] ring-opening anionic,[9] and radical polymerizations via metal-catalyzed,[10−26] nitroxide-mediated,[27−34] or reversible addition−fragmentation[35,36] system, where the radical processes are among the most robust systems because the growing radical species are inherently water-tolerant.

We have been investigating transition-metal-catalyzed living radical polymerizations[37] of methacrylates, acrylates, and styrenes with various metal complexes of ruthenium, iron, nickel, rhenium, etc. To adapt the metal-catalyzed systems to water-based polymerizations, water-tolerant metal catalysts should of course be employed. In this aspect, ruthenium is one of the most promising metals due to its low oxophilicity, and we have indeed found Ru(II)-mediated living radical polymerization of methacrylates in water.[10,11] Other metals such as copper,[12−24] nickel,[25] and palladium[26] can also be employed for similar purposes. However, these systems may have some problems in their costs and environmental aspects originating from the nature of the metals.

Scheme 1



On the other hand, iron, a group 8 element as ruthenium, is one of the most abundant metals on earth and is nontoxic, while most of its complexes, unlike the ruthenium counterparts, are generally unstable in water. This has prevented iron complexes from being used for water-based living polymerizations thus far, despite its environmentally and economically favorable nature. However, this view is not always correct because iron complexes such as ferrocene are highly stable in water, and some iron catalysts even work in the presence of moisture.[38]

This study is thus to employ a series of half-metallocene type iron(II) complexes [Fe(Cp)X(CO)$_2$ (X = I, Br) and Fe(Cp*)I(CO)$_2$; Cp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl] for living radical polymerizations of acrylates and styrene in suspension with water (Scheme 1). As we have already reported, an iron(II)

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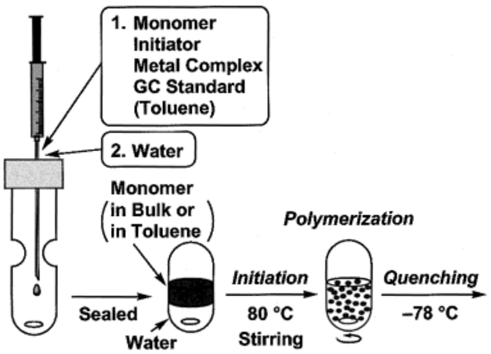
Scheme 2



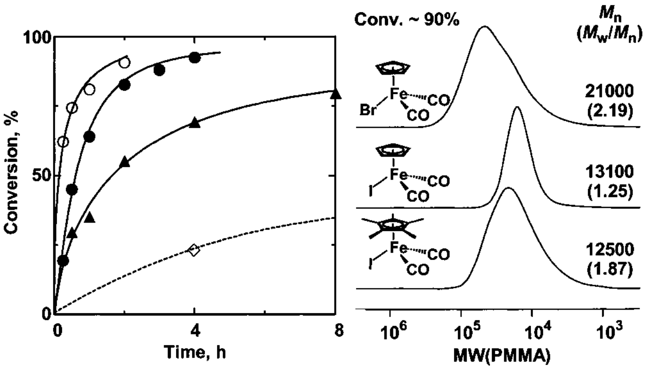


Figure 1. Suspension polymerizations of nBA with the $(CH_3)_2C(CO_2Et)I$/iron complex systems in water/toluene mixtures (nBA/toluene = 1.8/1 v/v, water/organic phase = 1/1 v/v) at 80 °C: $[nBA]_0 = 4.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 40$ mM; [iron complex]$_0$ = 40 mM. Iron complex: Fe(Cp)Br$(CO)_2$ (○); Fe(Cp)I$(CO)_2$ (●); Fe(Cp*)I$(CO)_2$ (▲). The dotted line with ◇: homogeneous polymerization of nBA with $(CH_3)_2C(CO_2Et)I$/Fe(Cp)I$(CO)_2$/Ti(O*i*-Pr)$_4$ in toluene at 80 °C: $[nBA]_0 = 4.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 40$ mM; $[Fe(Cp)I(CO)_2]_0 = 40$ mM; $[Ti(O\textit{i}\text{-}Pr)_4]_0 = 40$ mM.

catalyst, Fe(Cp)I$(CO)_2$, induces living radical polymerizations of styrenes[39,40] and acrylates[41] in toluene to give polymers of controlled molecular weights and narrow molecular weight distributions (MWDs) ($M_w/M_n = 1.1-1.2$), when coupled with an organic iodide as an initiator and a metal alkoxide additive. This study reports that the $(CH_3)_2C(CO_2Et)I$/Fe(Cp)I$(CO)_2$-initiating system is effective for acrylates [$CH_2{=}CH(CO_2R)$; R = Me, *n*-Bu, *t*-Bu] and styrene even in the presence of a large amount of water, where the suspension living polymerizations proceeded much faster than in toluene.

Results and Discussion

1. Stability of Iron Complexes against Water. Prior to polymerization, we examined the stability of iron complexes such as Fe(Cp)I$(CO)_2$ and $FeBr_2(PPh_3)_2$ toward water; the former catalyst is effective in living radical polymerization of acrylates and styrene in organic solvents,[39−41] whereas the latter are effective for methacrylates.[42] In some experiments, the toluene solvent was omitted in the organic phase (see below), and all of the ingredients were dissolved in bulk monomer before mixing with water.

On mixing toluene solutions of the catalysts with water, followed by stirring at room temperature for 3 min, the dark brown organic layer of the half-metallocene complex remained unchanged in color and homogeneity. In contrast, the solution of $FeBr_2(PPh_3)_2$ changed from orange to colorless on mixing. Thus, $FeBr_2(PPh_3)_2$ is not stable and is hydrolyzed in the presence of water, while Fe(Cp)I$(CO)_2$ can elude partitioning into water even after exposure to water under vigorous stirring. This is probably due to its less hydrophilic nature originating from the Cp and carbonyl groups.

2. Suspension Living Radical Polymerization of Acrylates. (a) *n*-Butyl Acrylate. We thus employed half-metallocene iron complexes [Fe(Cp)I$(CO)_2$, Fe(Cp)Br$(CO)_2$, and Fe(Cp*)I$(CO)_2$] for polymerization of *n*-butyl acrylate (nBA) in conjunction with $(CH_3)_2C(CO_2Et)I$ as an initiator in water/toluene mixtures (1/1 v/v; see Scheme 2 and the Experimental Section). Unlike the previously reported systems in toluene,[39−41] no metal alkoxide additives were employed. The reaction was started by heating mixtures of water and the organic layer containing the monomer, toluene (as a solvent for the catalyst), *n*-octane (an internal standard for gas chromatography), the initiator, and the Fe(II) catalyst under continuous magnetic stirring. Under these conditions, the stirred suspensions remained brown irrespective of the iron catalysts. Stirring was stopped at predetermined intervals, and the mixtures were allowed to cool to room temperature to regenerate a two-layer mixture. The resulting polymers were isolated from the upper organic phase.

As shown in Figure 1, the three catalysts invariably induced smooth and fast polymerizations. The rate increased in the order Fe(Cp*)I$(CO)_2$ < Fe(Cp)I$(CO)_2$ < Fe(Cp)Br$(CO)_2$. With the two Cp complexes, fast polymerizations proceeded to reach ~90% conversion in 2−4 h. The polymerization with Fe(Cp)I$(CO)_2$ was much faster than that in toluene, where no polymerization occurred without additives. In the presence of Ti(O*i*-Pr)$_4$, moreover, the reaction in the organic solvent reached only 23% conversion in 4 h (open diamonds and dotted line in Figure 1).[41] This suggests that water interacts with Fe(Cp)I$(CO)_2$ to afford a highly active catalyst/activator; this possibility is now under investigation in our group.

The polymers obtained with Fe(Cp)I$(CO)_2$ had narrow MWDs ($M_w/M_n = 1.25$) and controlled number-average molecular weights (M_n) that agreed well with the calculated values assuming that one molecule of initiator generates one living polymer chain. In contrast, Fe(Cp*)I$(CO)_2$ and Fe(Cp)Br$(CO)_2$ resulted in broad MWDs, as in toluene in the presence of metal alkoxides.[41] Similar results were obtained in the reactions at higher monomer concentration without toluene solvent.

Figure 2 shows the dependence of the M_n on conversion in the $(CH_3)_2C(CO_2Et)I$/Fe(Cp)I$(CO)_2$-mediated suspension polymerization with and without toluene. The toluene-free suspension polymerization reached nearly quantitative conversion in 6 h. The M_n increased in direct proportion to monomer conversion and agreed well with the calculated values. In both cases, the MWDs were very narrow ($M_w/M_n \sim 1.2$) at the latter stages of the polymerizations, while broader in the initial stages, predominantly due to slow interconversion between the dormant and radical species. These results demonstrate that the $(CH_3)_2C(CO_2Et)I$/Fe(Cp)I$(CO)_2$ initiating system induced living radical polymerization of nBA under suspension conditions even without additives or in bulk monomer as the organic phase.

(b) Methyl Acrylate. Methyl acrylate (MA) was also polymerized with $(CH_3)_2C(CO_2Et)I$/Fe(Cp)I$(CO)_2$ in tolu-

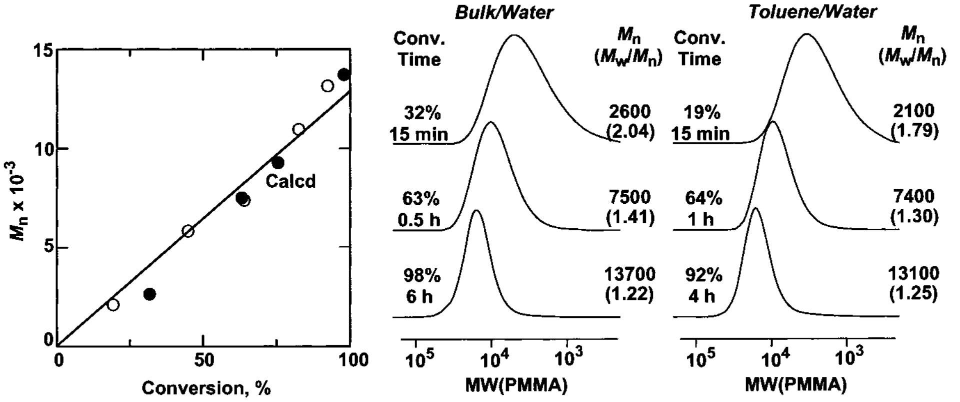


Figure 2. Living radical suspension polymerization of nBA in water. M_n and SEC curves of poly(nBA) obtained with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ in water (●) (water/organic phase 5/1 v/v; $[nBA]_0 = 6.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 60$ mM; $[Fe(Cp)I(CO)_2]_0 = 60$ mM) or in water/toluene (○) (nBA/toluene = 1.8/1 v/v, water/organic phase = 1/1 v/v; $[nBA]_0 = 4.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 40$ mM; $[Fe(Cp)I(CO)_2]_0 = 40$ mM) at 80 °C.

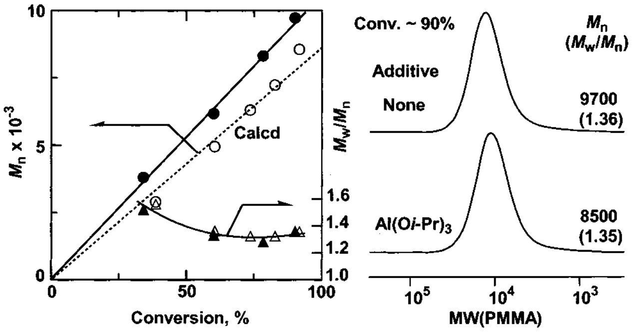


Figure 3. Living radical suspension polymerization of MA in water. M_n, M_w/M_n, and SEC curves of poly(MA) obtained with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ in water/toluene (MA/toluene = 1/1.6 v/v, water/organic phase = 1/1 v/v) in the presence (○, △) or absence (●, ▲) of Al(O*i*-Pr)$_3$: $[MA]_0 = 4.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 40$ mM; $[Fe(Cp)I(CO)_2]_0 = 40$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. The diagonal dotted line indicates the calculated M_n assuming the formation of one living polymer per $(CH_3)_2C(CO_2Et)I$ molecule.

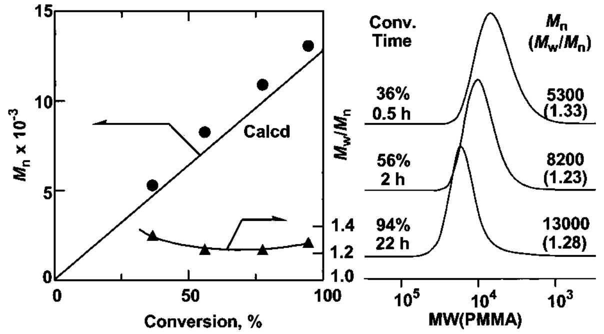


Figure 4. Living radical suspension polymerization of tBA in water. M_n, M_w/M_n, and SEC curves of poly(tBA) obtained with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ in water/toluene (tBA/toluene = 2/1 v/v, water/organic phase = 1/1 v/v): $[tBA]_0 = 4.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 40$ mM; $[Fe(Cp)I(CO)_2]_0 = 40$ mM. The diagonal solid line indicates the calculated M_n assuming the formation of one living polymer per $(CH_3)_2C(CO_2Et)I$ molecule.

ene/water under similar conditions but with and without Al(O*i*-Pr)$_3$ (Figure 3). The additive had little effect on the rate (~90% conversion in 9–10 h in both cases), in contrast to the polymerizations in toluene, which require metal alkoxides to achieve appreciable rates and narrow MWDs.[41] The aluminum compound certainly undergoes hydrolysis in the presence of water into hydrophilic derivatives that move into the aqueous phase and thus does not affect the polymerization that eventually occurs in the organic phase.

The resulting polymers, in both the absence and presence of Al(O*i*-Pr)$_3$, had narrow MWDs ($M_w/M_n \sim 1.3$) and controlled M_n. The molecular weights were in direct proportion to monomer conversion, and close to the calculated values, although slightly higher in the absence of additives.

(c) *tert*-Butyl Acrylate. A living suspension polymerization was also possible with *tert*-butyl acrylate (tBA) in the absence of additives as shown in Figure 4. The polymerization was completed in 1 day, which was slower than those of nBA and MA. The M_n increased in direct proportion to monomer conversion and agreed well with the calculated values. The MWDs were narrow throughout the polymerizations ($M_w/M_n = 1.2$–1.3). The pendent *tert*-butyl groups, which can be removed and converted into carboxylic acid groups, remained intact during the polymerizations.[43] These results demonstrate that the $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ initiating system is effective in suspension living radical polymerization of acrylates of various alkyl groups.

3. Suspension Living Radical Polymerization of Styrene. The half-metallocene type iron complexes are also effective for living radical polymerizations of styrene in toluene in the presence of additives.[39,40] Thus, the $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ initiating system was employed for the possible suspension polymerization of styrene in water.

The polymerization proceeded smoothly without additives and also with and without toluene in the oil/droplet phase, to reach almost quantitative conversion in 3–4 days, similar to those in toluene with Ti(O*i*-Pr)$_4$ as an additive.[39,40] The resulting polymers had narrow MWDs ($M_w/M_n \sim 1.2$) and controlled M_n in direct proportion to monomer conversion and in agreement with the calculated values (Figure 5). Thus, living radical suspension polymerization in water is possible for styrene with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$.

The effects of additives such as Ti(O*i*-Pr)$_4$ and Al(O*i*-Pr)$_3$ were also examined (Table 1). There were no significant effects of additives on the rate, the molecular weights, and the MWDs. Polymers with controlled M_n and narrow MWDs were obtained. This is in sharp contrast to the corresponding results in toluene, where the initiating system induces living radical polymerization in the presence of additives but results in only oligomers in their absence.[39,40] The oligomers most

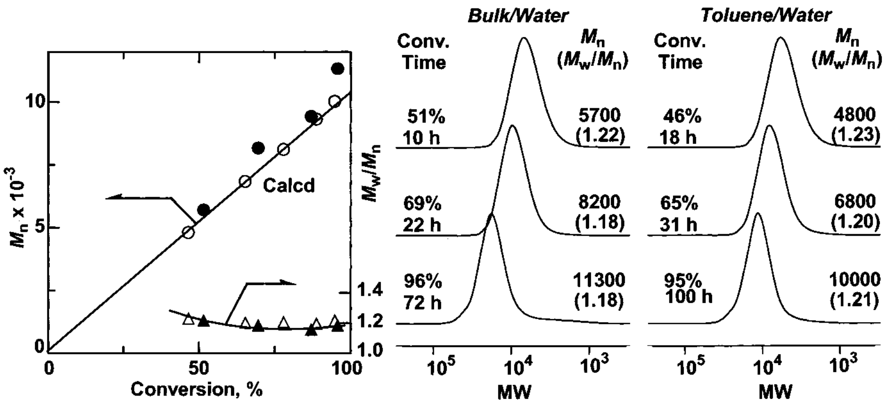


Figure 5. Living radical suspension polymerization of styrene in water. M_n, M_w/M_n, and SEC curves of polystyrene obtained with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ in water (●, ▲) (water/organic phase 5/1 v/v; $[styrene]_0 = 7.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 70$ mM; $[Fe(Cp)I(CO)_2]_0 = 70$ mM) or water/toluene (○, △) (styrene/toluene = 1/1 v/v, water/organic phase = 1/1 v/v; $[styrene]_0 = 4.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 40$ mM; $[Fe(Cp)I(CO)_2]_0 = 40$ mM) at 80 °C. The diagonal solid line indicates the calculated M_n assuming the formation of one living polymer per $(CH_3)_2C(CO_2Et)I$ molecule.

Table 1. Effects of Additives on Styrene Suspension Polymerization with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$[a]

additive	time (h)	conv (%)	M_n(calcd)[b]	M_n[c]	M_w/M_n[c]
none	100	95	10100	10000	1.21
$Ti(Oi\text{-}Pr)_4$	144	94	10000	9800	1.18
$Al(Oi\text{-}Pr)_3$	90	92	9800	9900	1.20

[a] $[styrene]_0 = 4.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 40$ mM; $[Fe(Cp)I(CO)_2]_0 = 40$ mM; $[additive]_0 = 0$ or 40 mM; water/toluene (styrene/toluene = 1/1 v/v, water/organic phase = 1/1 v/v); 80 °C. [b] $M_n(calcd) = ([styrene]_0/[(CH_3)_2C(CO_2Et)I]_0) \times 104.1 \times conversion + 242.1$. [c] Measured by SEC.

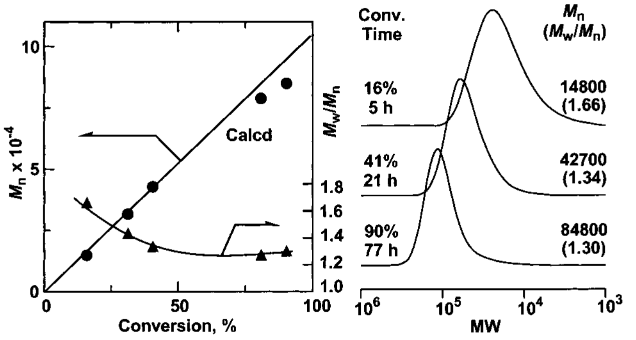


Figure 6. Synthesis of high molecular weight polystyrene with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ in water (water/organic phase 5/1 v/v) at 80 °C: $[styrene]_0 = 8.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 8.0$ mM; $[Fe(Cp)I(CO)_2]_0 = 8.0$ mM.

probably form via a cationic mechanism in toluene at high temperature, which is inhibited in the suspension systems in the presence of water. These results again show that water affects the iron complex by converting it into an active catalyst for living radical polymerizations.

Figure 6 summarizes the results for the synthesis of higher molecular weight polymers [M_n(calcd) ~ 10^5; $DP_n = 1000$] in water without toluene (water/organic phase 5/1 v/v). It proceeded smoothly without an induction period and reached 90% in 77 h. The resulting polymers had unimodal and narrow MWDs. The M_n increased in direct proportion to monomer conversion up to 8.5×10^4 (or $DP_n = 850$) and were close to the calculated values, assuming that one molecule of the initiator generates one living polymer chain. Thus, the suspension polymerization enables the synthesis of high molecular weights and narrow MWDs. Despite such high molecular weights and nearly bulk conditions in the organic phase, the products remained in finely dispersed droplets of the organic phase without forming larger flocculants or precipitates during the reaction.

4. Block and Random Copolymerization. We then employed the iron-based living radical suspension polymerization of styrene for the synthesis of block and random copolymers with acrylates.

(a) Block Copolymerization. Sequential block copolymerizations from nBA or tBA to tBA or styrene were examined with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ in water/toluene mixtures. For example, a feed of tBA, equimolar to the initially added nBA, was added into the living poly(nBA) when the nBA feed was almost consumed (94% conversion in 5 h; Figure 7A). After the monomer addition, the second-phase polymerizations ensued smoothly. The size-exclusion chromatography (SEC) curves of the resulting polymers remained unimodal and shifted to higher molecular weight with consumption of the second monomer, although a small shoulder originating from the remaining prepolymer was observed (Figure 7B).

The result was better with nBA and styrene pair, where the block copolymerization was carried out from a living poly(nBA) with a narrow MWD (Figure 7C). The SEC curves of the resulting block copolymers shifted to higher molecular weight without remaining prepolymer (Figure 7D). In contrast, the products obtained with living poly(tBA) (Figure 7E) and styrene showed a small shoulder, although the main peak of the SEC curves shifted to higher molecular weight (Figure 7F). This is due to a slight loss of the C−I end groups during such a long reaction period needed for consumption of the first monomer.

These results indicate that the iron-based initiating system is useful for the synthesis of block copolymers of acrylates and styrene under suspension conditions containing a large amount of water. The blocking efficiency is high but not complete because of some side reactions originating from the weak C−I dormant terminal.

(b) Random Copolymerization. Random copolymerizations of nBA and tBA or styrene were also investigated. Thus, equimolar mixtures of nBA and tBA or styrene were polymerized with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ in water/toluene mixtures. Both monomers were polymerized almost simultaneously at almost the same rates for nBA and tBA (Figure 8A), while styrene

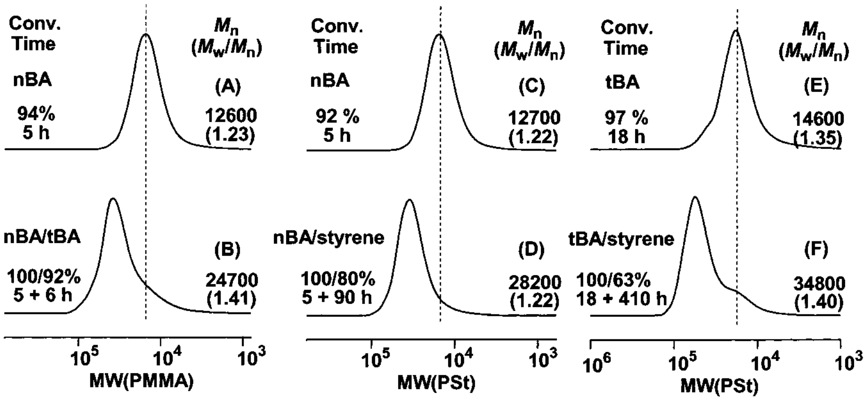


Figure 7. Block copolymerizations with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ in water (water/organic phase 1/1 v/v) at 80 °C: (A) prepolymer of nBA, (B) nBA−tBA block copolymer; (C) prepolymer of nBA; (D) nBA−styrene block copolymer; (E) prepolymer of tBA (F) tBA−styrene block copolymer. [first monomer]$_0$ = [second monomer]$_{add}$ = 4.0 M; [$(CH_3)_2C(CO_2Et)I$]$_0$ = 40 mM; [Fe(Cp)I(CO)$_2$]$_0$ = 40 mM. The diagonal solid line indicates the calculated M_n assuming the formation of one living polymer per $(CH_3)_2C(CO_2Et)I$ molecule.

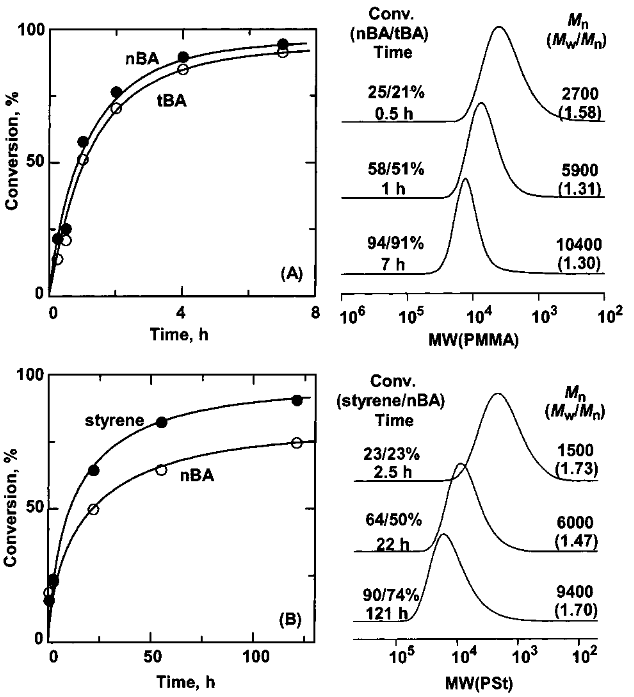


Figure 8. Random copolymerizations of nBA/tBA (A) and nBA/styrene (B) with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ in water (water/organic phase 1/1 v/v) at 80 °C: [nBA]$_0$ = [tBA]$_0$ = [styrene]$_0$ = 2.0 M; [$(CH_3)_2C(CO_2Et)I$]$_0$ = 40 mM; [Fe(Cp)I(CO)$_2$]$_0$ = 40 mM.

was consumed faster than nBA (Figure 8B). These reactivity orders are similar to those in conventional free radical copolymerizations of these monomers.[44] The MWDs of the copolymers of nBA and tBA were unimodal and narrowed with conversions [M_w/M_n = 1.30, conversion = 94/91% (nBA/tBA)], similar to those obtained in their homopolymerizations. The copolymers of nBA and styrene showed broader MWDs (M_w/M_n = 1.5−1.7) than those of the respective homopolymers (M_w/M_n = 1.2−1.3). This may be due to the differences in cross-propagation rates and in reactivities of the dormant carbon−halogen bonds derived from the two monomers that belong to different families of monomers. This point should be investigated further.

In conclusion, iron catalysis works under suspension conditions with water to induce living radical polymerizations of acrylates and styrene. The $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ initiating system is more active in the presence of water than in organic solvents only and does not necessarily need additives for acceleration and better molecular weight control. Controlled block and random copolymers of acrylates and styrene can be prepared under suspension conditions with the iron-based initiating systems.

Experimental Section

Materials. nBA (>98%), MA (>98%), tBA (>97%), and styrene (>99%), all from Wako Chemicals, were dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. Fe(Cp)I(CO)$_2$ (Aldrich; >97%), Al(O*i*-Pr)$_3$ (Aldrich; >99.99%), and Ti(O*i*-Pr)$_4$ (Kanto Chemicals; >97%) were used as received. Fe(Cp*)I(CO)$_2$ was synthesized by the method of King et al.[45] Anal. Calcd for $C_{12}H_{15}O_2IFe$: C, 38.54; H, 4.05; I, 33.93. Found: C, 38.32; H, 3.95; I, 33.92. Fe(Cp)Br(CO)$_2$ was synthesized by the method of Fischer et al.[46] Calcd for $C_7H_5O_2BrFe$: C, 32.73; H, 1.96; Br, 31.11. Found: C, 32.66; H, 1.86; Br, 31.05. $FeBr_2(PPh_3)_2$ was synthesized by the method of Gooth et al.[47] Calcd for $C_{36}H_{30}P_2Br_2Fe$: C, 58.41; H, 4.08; Br, 21.59. Found: C, 58.34; H, 4.11; I, 21.68. All metal compounds were handled in a glovebox (M.Braun Labmaster 130) under a moisture- and oxygen-free argon atmosphere (H_2O, <1 ppm; O_2, <1 ppm). Ethyl 2-iodoisobutyrate [$(CH_3)_2C(CO_2Et)I$], as an initiator, was prepared by the method of Curran et al.;[48] bp 50 °C/9 Torr; identified by 500 MHz ^{1}H NMR. Anal. Calcd for $C_6H_{11}O_2I$: C, 29.8; H, 4.58; I, 52.4. Found: C, 29.7; H, 4.59; I, 52.3. Toluene (solvent), tetralin, and *n*-octane (internal standards for gas chromatographic analysis of the monomers) were dried overnight over calcium chloride, distilled twice over sodium benzophenone ketyl (for toluene) or calcium hydride (for tetralin and *n*-octane), and bubbled with dry nitrogen over 15 min immediately before use. Water (Wako Chemicals, distilled) was similarly degassed before use.

Polymerization Procedures. Polymerization was carried out by the syringe technique under dry nitrogen in glass tubes equipped with a three-way stopcock or in baked and sealed glass vials. A typical example for the polymerization of styrene with $(CH_3)_2C(CO_2Et)I/Fe(Cp)I(CO)_2$ is given below: In a 50 mL round-bottomed flask was placed Fe(Cp)I(CO)$_2$ (8.5 mg, 0.028 mmol), tetralin (0.26 mL), styrene (3.21 mL, 28.0 mmol), and a solution of $(CH_3)_2C(CO_2Et)I$ (0.037 mL of 750 mM in toluene, 0.028 mmol) at room temperature. The total volume of reaction mixture was 3.5 mL. Immediately after mixing, five aliquots (0.40 mL each) of the solutions were injected into backed glass tubes. Distilled and degassed water (2.0 mL) was added to this homogeneous organic solution. The total volume of the reaction mixture was thus 2.40 mL (i.e., organic/water phase 1/5 v/v). The reaction vials were sealed (except for some runs that used a stopcock) and placed in an oil bath kept at 80 °C under vigorous stirring. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C. Monomer conversion was determined from the residual monomer concentration by gas chromatography with tetralin as an internal standard. The quenched reaction solutions were diluted with methanol (ca. 20 mL) and rigorously shaken with an absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical] (ca. 5 g) to remove the metal-containing residues. After the absorbent was separated by filtration (Whatman 113V), the filtrate was washed with water and evaporated to dryness to give the products, which were subsequently vacuum-dried overnight.

Measurements. The MWD, M_w, and M_w/M_n ratios of the polymers were measured by SEC in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: 20−1000 Å; 8.0 mm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index and a Jasco 970-UV ultraviolet detectors. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemical; $M_n = 580-1\,547\,000$; $M_w/M_n < 1.1$) or 11 standard poly(MMA) samples (Polymer Laboratories; $M_n = 630-1\,200\,000$; $M_w/M_n = 1.04-1.22$) as well as monomers. ^1H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz. Polymers for ^1H NMR analysis were fractionated by preparative SEC as $CHCl_3$ eluent (column: Shodex K-2002) to remove traces of the catalyst and low-molecular-weight residues.

References and Notes

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