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Iron Oxides as Heterogeneous Catalysts for Controlled/Living Radical Polymerization of Styrene and Methyl Methacrylate

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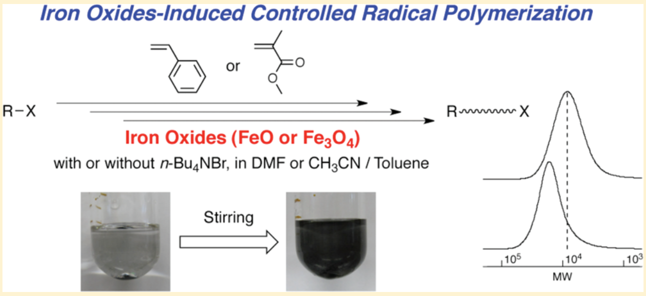
Supporting Information

ABSTRACT: Heterogeneous systems using iron oxides with low-valent Fe(II) components, FeO and Fe_3O_4, were designed for controlled/living radical polymerization of styrene and methyl methacrylate. The polymerizations with FeO in conjunction with an alkyl halide initiator bearing a C−Br bond such as ethyl α-bromophenylacetate proceeded in controlled fashions in the solvent mixtures of *N*,*N*-dimethylformamide/toluene or acetonitrile/toluene to yield polymers with predetermined molecular weights. The controllability of the reactions was improved upon the addition of *n*-Bu_4NBr to give polymers bearing theoretical M_n values and narrower molecular weight distributions. The polymerizations also proceeded using magnetic Fe_3O_4 or zerovalent Fe(0), although the controllability was inferior to FeO. The heterogeneous catalytic mechanisms using FeO were suggested by the effect of stirring on the reaction rate and some other polymerization results.



INTRODUCTION

Controlled/living radical polymerization has remarkably progressed over the past 15 years both in the development of new initiating systems and in their applications for precisely structured polymers with various unique characteristics. One of the major methods, i.e., transition-metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP),[1−3] can control the propagation of vinyl monomers by the reversible activation−deactivation equilibrium between the dormant and the propagating radical species via the homolytic cleavage of the carbon−halogen bonds through one-electron redox processes. Among various metal catalysts capable of inducing living polymerization, iron complexes are especially advantageous in various aspects, including their abundance and low toxicity. Most of the iron catalysts used for controlled/living radical polymerization have been designed in combination with a variety of ligands, such as phosphines,[4] nitrogen-based ligands,[5−11] cyclopentadienyl groups,[12] *N*-heterocyclic carbenes,[13] onium salts with halogen anions,[14,15] or carboxylic acids[16] for divalent iron halides [$Fe(II)X_2$; X = Cl or Br]. Trivalent iron halides [$Fe(III)X_3$] have also been utilized for controlled/living radical polymerization in conjunction with a free-radical initiator (a reverse system)[17] or a reducing agent[18,19] or even without those compounds.[20,21] Despite such a diversification, almost all of the effective systems are comprised of homogeneous catalytic processes.

Iron oxides (Fe_xO_y) are abundantly available, easy to handle, robust, low-cost, nontoxic, and halogen-free metal compounds, which is particularly attractive in terms of industrial applications as well as the recent demand for environmentally benign processes. Recently, living cationic polymerization of vinyl ethers in heterogeneous media has been achieved using α-Fe_2O_3 and Fe_3O_4, which are the main components of red rust and iron sand, respectively, as the catalysts based on their Lewis acidic nature.[22] For further utilization of these attractive compounds, we focused on the possibility of FeO and Fe_3O_4 as heterogeneous catalysts for controlled/living radical polymerization since these oxides have low-valent Fe(II) species that may induce a homolytic cleavage of carbon−halogen bonds in the initiator or growing terminal.

In this paper, we report the first example of controlled radical polymerization of styrene and methyl methacrylate (MMA) with FeO-based heterogeneous systems (Scheme 1). The controlled reactions were successful in conjunction with an alkyl bromide initiator, such as ethyl α-bromophenylacetate (**1**), in *N*,*N*-dimethylformamide (DMF)/toluene or acetonitrile (CH_3CN)/toluene. The magnetic Fe_3O_4 or zerovalent Fe(0) also mediated controlled polymerization under similar conditions.

RESULTS AND DISCUSSION

Polymerization of Styrene and MMA with FeO. The polymerization of styrene was first examined using FeO in conjunction with **1** as an initiator at 80 °C under vigorous stirring (Table 1). The polymerization proceeded under apparently heterogeneous conditions in a solvent mixture of DMF and toluene (4/1 v/v) to produce polymers with moderately controlled number-average molecular weights (M_ns). These values

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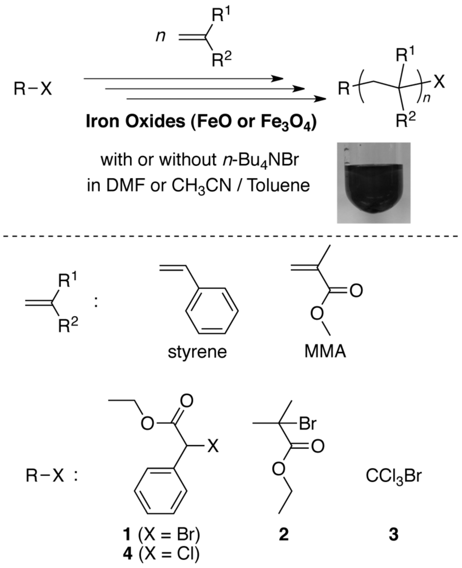
were close to the calculated ones based on the assumption that one molecule of **1** generates one polymer chain, although the molecular weight distributions (MWDs) were relatively broad (entry 1). A better control was obtained when the reaction was conducted with *n*-Bu$_4$NBr as the additive (entry 2). The M_n values linearly increased almost in accordance with the theoretical line, which indicates that the polymerization proceeded in a controlled/living fashion. The well-controlled M_n was also attained in toluene without using DMF as the cosolvent for the styrene polymerization in the presence of *n*-Bu$_4$NBr, but much broader MWDs ($M_w/M_n > 3$, entry 3) were obtained most probably due to a slower interconversion between the dormant and radical species. In contrast to *n*-Bu$_4$NBr, the addition of *n*-Bu$_3$P, Ph$_3$P, and *n*-Bu$_3$N, which are effective ligands for homogeneous living radical polymerizations with iron halides,[4,5] resulted in a worse controllability to give polymers with larger M_ns than the calculated values and/or broader MWDs (Figure S3). The ^{1}H NMR spectra of the polymers obtained with FeO in the presence of *n*-Bu$_4$NBr revealed both the **1**-derived α-end and C−Br *ω*-end termini, of which the M_n values calculated from the α-end methylene and the main-chain peaks agreed with those obtained by size-exclusion chromatography (SEC) analyses (Figure S4).[23]

Scheme 1. Radical Polymerization of Styrene and MMA with Iron Oxide (FeO or Fe$_3$O$_4$)-Based Heterogeneous Systems



Further improvements in the controllability were achieved when the polymerizations were performed in the solvent mixture with a higher amount of toluene (DMF/toluene = 1/2 v/v; entries 4 and 5) or in the mixture of CH$_3$CN with toluene (4/1 v/v; entries 6 and 7).[24] Figure 1 shows the styrene polymerization using FeO in CH$_3$CN/toluene (4/1 v/v). As in the DMF/toluene mixtures, the heterogeneous polymerization smoothly proceeded with FeO in conjunction with **1** as the initiator even in the absence of *n*-Bu$_4$NBr to yield controlled polymers, of which the M_n values linearly increased close to the calculated line (red circles in Figure 1B). The addition of *n*-Bu$_4$NBr further narrowed the MWDs ($M_w/M_n < 1.4$), where the M_n increased in direct proportion to monomer conversion (blue circles in Figure 1B).

The reported homogeneous FeBr$_2$/*n*-Bu$_4$NBr system,[14] which is effective for controlled polymerization of styrene in bulk and nonpolar solvents, was also used under similar conditions containing polar cosolvents such as CH$_3$CN and DMF because the heterogeneous FeO might generate some soluble FeBr$_2$ species. However, the FeBr$_2$/*n*-Bu$_4$NBr system almost lost its activity under similar conditions with CH$_3$CN (entry 11; see

Table 1. Radical Polymerization of Styrene and MMA Using FeO, Fe$_3$O$_4$, Fe(0), or FeBr$_2$[a]

entry	monomer	catalyst	[*n*-Bu$_4$NBr]$_0$ (mM)	solvent (v/v)	time (h)	conv (%)	M_n (calcd)	M_n[b]	M_w/M_n[b]
1	styrene	FeO	0	DMF/toluene (4/1)	51	81	8700	11000	1.88
2			20	DMF/toluene (4/1)	51	85	9100	11700	1.68
3			20	toluene	216	89	9600	9600	3.69
4			0	DMF/toluene (1/2)	75	86	9200	11400	1.70
5			20	DMF/toluene (1/2)	75	87	9300	10300	1.46
6			0	CH$_3$CN/toluene (4/1)	51	75	8100	9900	1.95
7			20	CH$_3$CN/toluene (4/1)	51	85	9100	12200	1.39
8		Fe$_3$O$_4$	0	DMF/toluene (1/2)	508	82	8800	9500	1.65
9			20	DMF/toluene (1/2)	196	29	3200	4000	1.49
10		Fe(0)	20	DMF/toluene (1/2)	51	94	10000	14300	1.67
11[c]		FeBr$_2$	10	CH$_3$CN/toluene (4/1)	51	7			
12[d]			10	DMF/toluene (1/2)	75	77	8200	15400	1.44
13	MMA	FeO	0	DMF/toluene (4/1)	11	77	8000	9200	3.02
14			20	DMF/toluene (4/1)	5	89	9200	10300	2.10
15			20	DMF/toluene (1/2)	6	84	8600	10600	1.86
16			20	CH$_3$CN/toluene (1/2)	7	76	7800	9000	1.90
17		Fe$_3$O$_4$	0	DMF/toluene (1/2)	96	50	5200	5500	5.72
18			20	DMF/toluene (1/2)	75	58	6000	6200	2.90
19		Fe(0)	20	DMF/toluene (1/2)	2.5	81	8400	11200	1.81

[a] [Monomer]$_0$ = 4.0 M, [**1**]$_0$ = 40 mM, [catalyst]$_0$/[**1**]$_0$ = 5 (for FeO), 2 [for Fe$_3$O$_4$ and Fe(0)], or 0.25 (for FeBr$_2$), [*n*-Bu$_4$NBr]$_0$ = 0, 10, or 20 mM, in DMF/toluene (4/1 or 1/2 v/v) or CH$_3$CN/toluene (4/1 or 1/2 v/v) at 80 °C; see Supporting Information for the detailed data. [b] By SEC using polystyrene or poly(MMA) standards. [c] The reaction proceeded in a homogeneous system. [d] An induction period (>30 h) was observed. The reaction medium became opaque after the induction period.

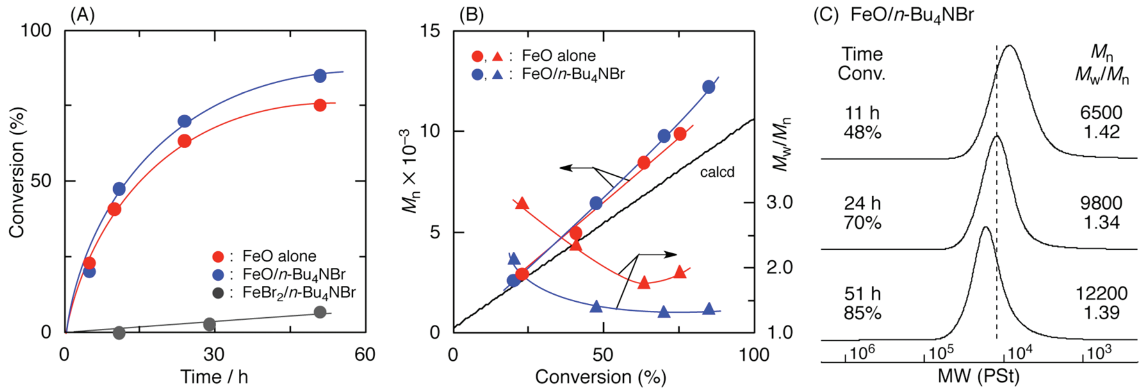


Figure 1. (A) Time−conversion curves, (B) M_n and M_w/M_n curves for the polymerization of styrene using FeO or $FeBr_2$, and (C) MWD curves of the polystyrenes obtained using FeO: [styrene]$_0$ = 4.0 M, [**1**]$_0$ = 40 mM, [n-Bu_4NBr]$_0$ = 0 (red), 10 (gray), or 20 (blue) mM, [FeO]$_0$/[**1**]$_0$ = 5 or [$FeBr_2$]$_0$ = 10 mM in CH_3CN/toluene (4/1 v/v) at 80 °C.

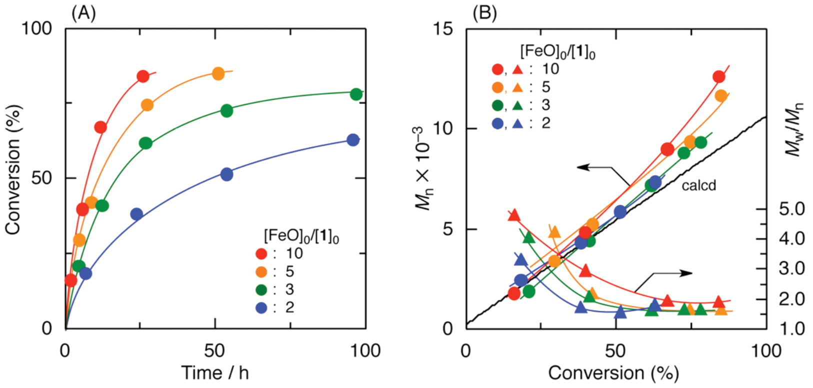


Figure 2. Polymerization of styrene with various amounts of FeO: [styrene]$_0$ = 4.0 M, [**1**]$_0$ = 40 mM, [n-Bu_4NBr]$_0$ = 20 mM, [FeO]$_0$/[**1**]$_0$ = 10 (red), 5 (orange), 3 (green), or 2 (blue) in DMF/toluene (4/1 v/v) at 80 °C.

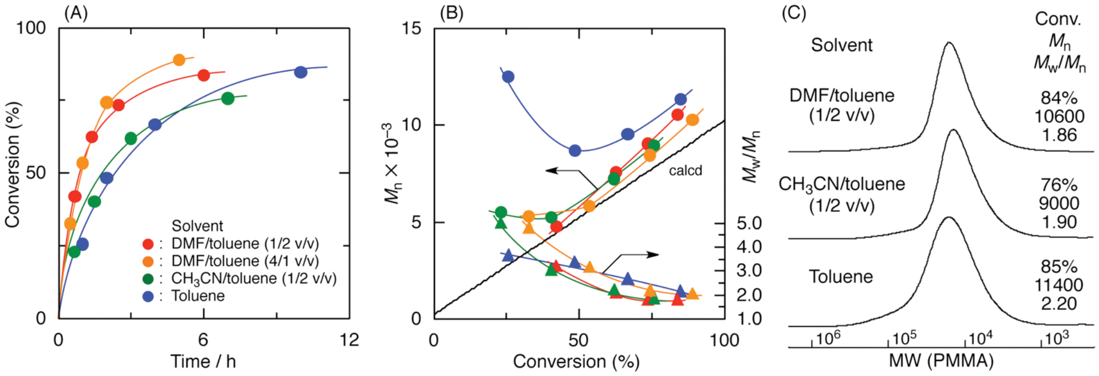


Figure 3. Polymerization of MMA using FeO in DMF/toluene [1/2 (red) or 4/1 (orange) v/v], CH_3CN/toluene (1/2 v/v; green), or toluene (blue): [MMA]$_0$ = 4.0 M, [**1**]$_0$ = 40 mM, [n-Bu_4NBr]$_0$ = 20 mM, [FeO]$_0$/[**1**]$_0$ = 5 at 80 °C.

also Figure 1A). Although the $FeBr_2$/n-Bu_4NBr system was capable of polymerization in another mixed solvent [DMF/toluene (1/2 v/v)] (entry 12), a significant induction period and higher M_ns than the theoretical ones were observed. These results indicate little possibility of $FeBr_2$ alone as the actual catalytic species in the FeO systems, although a small amount of $FeBr_2$ might generate in situ and contribute to the controlled polymerization with FeO as discussed later.

The effect of the catalyst concentration was then investigated by varying the amounts of FeO in the range of [FeO]$_0$/[**1**]$_0$ = 2−10 (Figure 2). The larger the loading amount of FeO became, the faster the styrene polymerization proceeded. The polymers with the M_ns close to the theoretical values were obtained under these conditions irrespective of the amounts of FeO. These results indicate that FeO functioned in the catalytic process of the controlled/living radical polymerization.

MMA could also be polymerized with the FeO-based system using **1** as the initiator. As in the case of the styrene polymerization, MMA reacted in either the presence or absence of n-Bu_4NBr, in which the ammonium salt improved the controllability of the

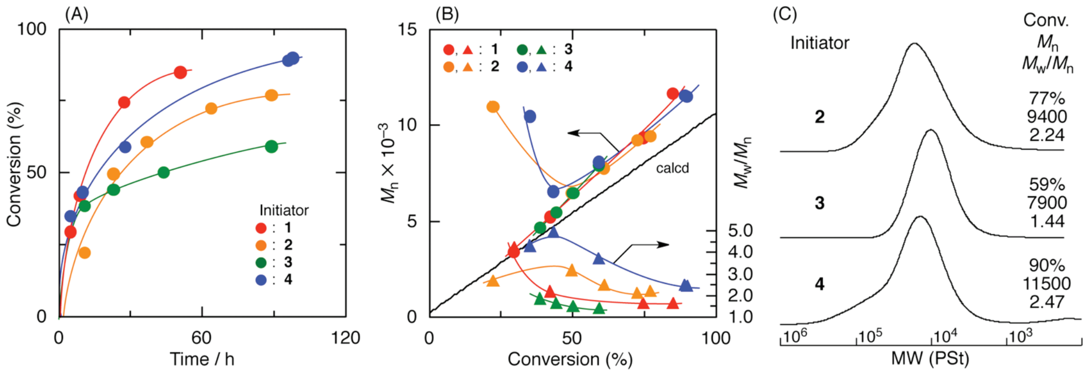


Figure 4. Polymerization of styrene using FeO in the presence of *n*-Bu_4NX (X = Br for **1**−**3**, Cl for **4**) with various initiators: $[styrene]_0 = 4.0$ M, $[initiator]_0 = 40$ mM, $[n\text{-}Bu_4NX]_0 = 20$ mM, $[FeO]_0/[initiator]_0 = 5$ in DMF/toluene (4/1 v/v) at 80 °C.

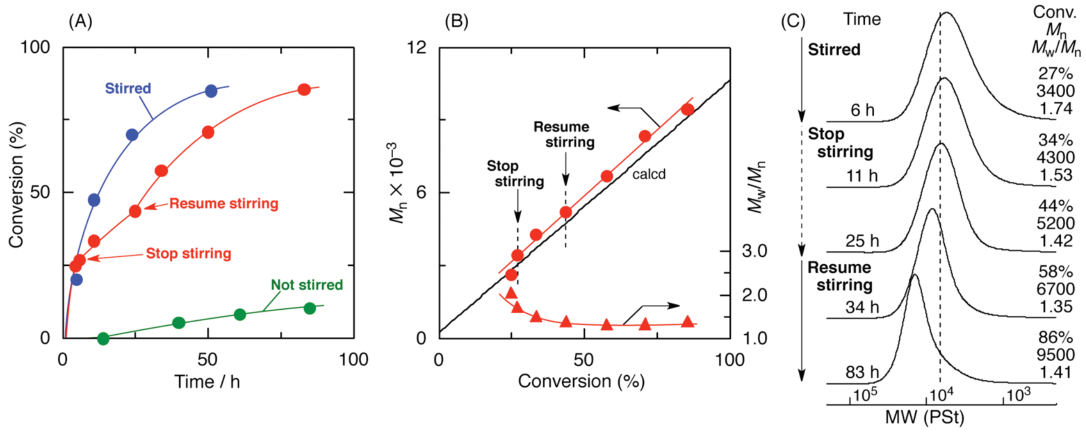


Figure 5. Effect of stirring on the styrene polymerization using FeO: the reaction mixtures were stirred (blue), stirred for first 6 h and after 25 h (red), or not stirred (green); $[styrene]_0 = 4.0$ M, $[\mathbf{1}]_0 = 40$ mM, $[n\text{-}Bu_4NBr]_0 = 20$ mM, $[FeO]_0/[\mathbf{1}]_0 = 5$ in CH_3CN/toluene (4/1 v/v) at 80 °C.

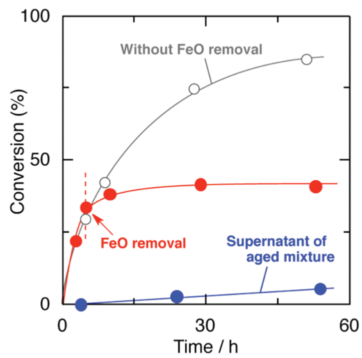


Figure 6. Polymerization of styrene using FeO; the removal of FeO during the reaction (red) or the reaction with the supernatant of the aged mixture of FeO and *n*-Bu_4NBr in DMF at 80 °C for 3 h (blue); FeO was removed under dry nitrogen by a disposable syringe filter (pore size: 0.50 μm): $[styrene]_0 = 4.0$ M, $[\mathbf{1}]_0 = 40$ mM, $[n\text{-}Bu_4NBr]_0 = 20$ mM, $[FeO]_0/[\mathbf{1}]_0 = 5$ in DMF/toluene (4/1 v/v) at 80 °C.

Scheme 2. Possible Mechanisms for Polymerization Using FeO

(A) Activation by Fe(II) species on FeO surface

$$\text{R–Br} + \text{Fe}^{\text{II}}\ (\text{surface}) \rightleftharpoons \text{R}^{\bullet} + \text{Br–Fe}^{\text{III}}\ (\text{surface})$$

(B) Activation by in situ generated soluble Fe(II) species
and function of FeO as reducing agent

$$\text{R–Br} + \text{Fe}^{\text{II}}\ (\text{soluble}) \rightleftharpoons \text{R}^{\bullet} + \text{Br–Fe}^{\text{III}}\ (\text{soluble})$$

$$\text{Fe}^{\text{II}}\ (\text{surface}) + \text{Br–Fe}^{\text{III}}\ (\text{soluble}) \rightleftharpoons \text{Br–Fe}^{\text{III}}\ (\text{surface}) + \text{Fe}^{\text{II}}\ (\text{soluble})$$

polymerization to result in narrower MWDs (entries 13 and 14). A further improvement was achieved by increasing the amount of toluene in the solvents (DMF/toluene = 4/1 vs 1/2 v/v; orange vs red symbols in Figure 3; entries 14 vs 15 in Table 1). Another cosolvent, CH_3CN, was also effective for the controlled polymerization in conjunction with toluene (1/2 v/v; green symbols; entry 16) while the polymerization in toluene without DMF or CH_3CN was less controlled to result in higher M_n values and broader MWDs (blue symbols).

The effects of the initiator on the polymerization of styrene and MMA were examined using a series of alkyl halides, such as ethyl α-bromoisobutyrate (**2**), CCl_3Br (**3**), and ethyl α-chlorophenylacetate (**4**) in place of **1** (Figure 4). The polymerizations of styrene with **2** also attained an increase of the M_n values with monomer conversion, but the controllability was obviously inferior to **1**. This is probably due to the inefficient or slower initiation reactions stemming from the less reactive C−Br bond of **2** than that of **1**. In contrast, the polymerization of MMA with **2** showed a typical behavior involving a very slow initiation,

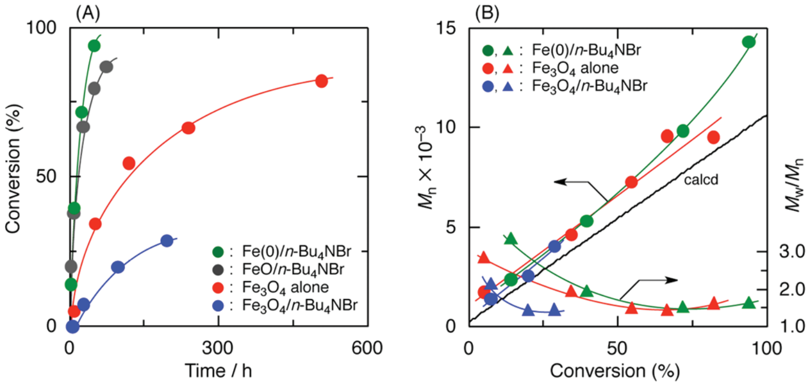


Figure 7. Polymerization of styrene using Fe_3O_4 or Fe(0): $[\text{styrene}]_0 = 4.0$ M, $[\mathbf{1}]_0 = 40$ mM, $[n\text{-}Bu_4NBr]_0 = 0$ or 20 mM, $[\text{Fe compound}]_0/[\mathbf{1}]_0 = 2$ (5 for FeO) in DMF/toluene (1/2 v/v) at 80 °C.

where the M_n values were higher than the calculated values in the initial stage and decreased with conversion to approach the calculated line (see Figure S5). With **3**, the polymerizations of both styrene and MMA proceeded to give polymers with controlled molecular weights that agreed with the calculated M_n and relatively narrow MWDs, although the reaction ceased around a 60% monomer conversion for styrene. As the chloride counterparts of **1** and n-Bu_4NBr, the combination of **4** and n-Bu_4NCl was used for the polymerization to produce less controlled polymers with broader MWDs, probably due to the slower activation−deactivation equilibrium process for the stronger C−Cl bonds.

Heterogeneity during Polymerization. To reveal the heterogeneous catalytic mechanisms, the effect of stirring during the polymerization using FeO was examined (Figure 5). The polymerization of styrene without stirring was much slower than that with vigorous stirring (∼1350 rpm) probably because of less frequent contacts between the surface of FeO and the initiator.[25] The polymerization was immediately retarded upon stopping the stirring at about a 25% monomer conversion, where FeO precipitated on the bottom of the reaction tube. However, upon resuming the stirring, the polymerization was accelerated again at almost the same rate as before and finally reached an almost quantitative monomer consumption. These results indicated that FeO plays a pivotal role in catalyzing the controlled radical polymerization not only at the initiation step but also during the entire processes of the reactions.

Furthermore, to confirm the possibility of bleeding or leaching of any soluble iron species out of the solid FeO, the effect of aging the mixture of FeO and n-Bu_4NBr in DMF was examined for 3 h at 80 °C prior to the initiation (Figure S6). Irrespective of the aging, the polymerizations proceeded to afford polymers with controlled molecular weights. In addition, no polymerization occurred when using supernatant of the aged mixture prepared by removing the solid FeO under nitrogen (blue circles in Figure 6).

The color of the reaction mixtures also provided some meaningful information about the polymerization mechanisms. The supernatant of the polymerization mixture for styrene (the conditions for entry 1) was colorless during the reactions. However, it turned slightly yellow or orange after any of the following three procedures, i.e., pause of the stirring (as in Figure 5), removal of FeO by filtration even under nitrogen (red circles in Figure 6), or exposure to air (Figure S7 for preliminary UV−vis spectra). In all these cases, however, almost no subsequent polymerizations proceeded. Thus, some soluble Fe species leached out while the supernatant alone was less efficient or incapable of catalyzing the polymerization even in conjunction with the initiator.

On the basis of these results as described thus far, two possible roles of FeO are suggested. One is that the Fe(II) species on the surface of FeO participates in both the activation and deactivation of the C−Br bonds to reversibly generate the initiating/propagating radical species (Scheme 2A). The other is that soluble Fe species such as $FeBr_2$ and $FeBr_3$, possibly generated by the reaction between the surface of solid FeO and an alkyl bromide initiator (Scheme S1; similar to the CuO-based system[26]), may be the actual activator and/or deactivator, whereas FeO can function as a reducing agent that converts excess inactive Fe(III) to active Fe(II) similar to reducing agents in ARGET process (Scheme 2B).[27] Even in the latter case, however, the FeO surface is most likely to participate at least in the activation of the initiating C−Br bonds because the aging of FeO and n-Bu_4NBr apparently generated no soluble real catalytic species (vide supra). In any case, the polymerization of styrene and MMA was triggered by the heterogeneous FeO species and resulted in polymers, of which the molecular weights were controlled by the ratio of the monomer to initiator, whereas the MWDs were relatively broad most probably due to the slow activation−deactivation processes originating from the heterogeneity. We are currently elucidating the detailed polymerization mechanisms and further designing the system for a better controllability with FeO.

Polymerization with Fe_3O_4 or Fe(0). Another type of iron oxide, Fe_3O_4, and zerovalent Fe(0),[28−30] which are both insoluble in organic solvents, also induced the polymerization of styrene or MMA in conjunction with **1** and n-Bu_4NBr (entries 8−10 and 17−19; Figure 7 and Figure S8). In both cases with Fe_3O_4 and Fe(0), the polymerizations proceeded in a controlled fashion to produce polymers with controlled molecular weights under similar conditions to those with FeO, in which the former resulted in much slower polymerizations than the FeO system (styrene) or lower monomer consumptions plateaued around 60% (MMA). The lower activity of Fe_3O_4 compared to FeO most probably originated from the considerable amount of inactive Fe(III) components [Fe(II)/Fe(III) = 1/2]. In addition, the polymerization of styrene using Fe_3O_4 in the absence of n-Bu_4NBr was faster than in the presence because the reaction between the surface Fe(III) and n-Bu_4NBr may form Fe(III)−Br species as a possible deactivator. These results suggest that polymerization can be successfully catalyzed by the solid iron species with different oxidation states.

CONCLUSIONS

The FeO- or Fe_3O_4-based heterogeneous systems were used for the controlled/living radical polymerization for the first time. The polymerization of styrene or MMA proceeded in a controlled fashion using the alkyl bromide initiator bearing a C−Br bond. The effect of stirring on the polymerization behavior indicated the participation of FeO in the entire catalytic processes possibly via the direct activation of the C−Br bonds and/or the reduction of some actual soluble iron(II) species. These abundantly available, easy to handle, and environmentally benign heterogeneous catalyst systems would possibly open up new avenues for wide and versatile applications of the controlled/living radical polymerization in industrial fields.

EXPERIMENTAL SECTION

Materials. Styrene (Kishida, 99.5%), MMA (TCI, >99.8%), **1** (Aldrich, 97%), **2** (Aldrich, 98%), **3** (TCI, >98%), and **4** (Aldrich, 97%) were distilled over calcium hydride under reduced pressure before use. DMF (Kanto, 99.5%) was distilled over calcium hydride under reduced pressure and bubbled with dry nitrogen over 10 min before use. CH_3CN (dehydrated solvent; Kanto, >99.5%) was bubbled with dry nitrogen over 10 min before use. *n*-Bu_3N (Wako, >98%) was distilled over calcium hydride. FeO (Aldrich, 99.9%; −10 mesh), Fe_3O_4 (Aldrich, 99.99%), Fe(0) (Nilaco, 99+%; 325 mesh), $FeBr_2$ (Aldrich, 99.999%), $FeBr_3$ (Aldrich, 98%), *n*-Bu_4NBr (TCI, >99.0%), *n*-Bu_4NCl (Fluka, >97%), *n*-Bu_3P (Kanto, >98%), and Ph_3P (Aldrich, 99%) were used as received and handled in a glovebox (VAC Nexus) under a moisture- and oxygen-free argon atmosphere (O_2 <1 ppm). Toluene (Kanto, >99.5%; H_2O <10 ppm) was dried and deoxygenized by passage through columns of Glass Contour Solvent Systems before use.

Polymerization Procedures. Polymerization was carried out under dry nitrogen in a baked glass tube equipped with a three-way stopcock. A typical example for the polymerization procedure is given below. To the glass tube containing FeO (36.4 mg, 0.51 mmol) and *n*-Bu_4NBr (17.4 mg, 0.05 mmol), DMF (1.08 mL), styrene (1.15 mL, 10.0 mmol), and a stock solution of **1** (374 mM in toluene, 0.27 mL) were added successively. The tube was immersed in thermostatic oil bath at 80 °C. During the polymerization, the heterogeneous reaction mixture was maintained stirring using a magnetic stirrer (Koike Precision Instruments HE-20GA; ~1350 rpm) with a small handmade stirring bar made from a thin glass tube and a wire. A small amount (<0.1 mL) of the reaction mixture was extracted for several times to be terminated by cooling and exposure to air. Monomer conversions were determined from the concentrations of residual monomer measured by gas chromatography with DMF as an internal standard (the final product: 85% conversion for 51 h). The quenched reaction mixtures were diluted with toluene, washed with water, evaporated to dryness under reduced pressure, and dried in vacuum to give the product polymers (M_n = 11 700, M_w/M_n = 1.68).

Measurements. The M_n and M_w/M_n of the product polymers were determined by SEC in THF at 40 °C on two polystyrene gel columns [Shodex KF-805 L (pore size: 200−1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate: 1.0 mL/min] connected to a JASCO PU-2080 precision pump and a JASCO RI-2031 detector. The columns were calibrated against 10 standard polystyrene samples (Varian: M_p = 575−2 783 000; M_w/M_n = 1.02−1.10) or 10 standard poly(MMA) samples (Varian: M_p = 875−1 677 000; M_w/M_n = 1.02−1.23). ^1H NMR spectra were recorded on a JEOL ECS-400 spectrometer, operating at 400 MHz. UV−vis spectra were recorded on a JASCO V-550 UV/vis spectrometer with an ETC-505T Peltier-type thermostatic cell holder. A glass cell with 1.0 cm optical path length was used.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Polymerization results, ^1H NMR spectra of the obtained polymers, and UV−vis spectra of the supernatants of the polymerization mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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