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# Heterogeneously Catalyzed Living Cationic Polymerization of Isobutyl Vinyl Ether Using Iron(III) Oxide

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We have synthesized various well-defined and stimuli-responsive poly(vinyl ether)s[1] such as block copolymers,[2] gradient copolymers,[3] and star polymers[4] by living cationic polymerization using a Lewis acid in the presence of an added base. A typical initiating system consisted of $Et_xAlCl_{3-x}$ ($x = 1, 1.5$) and an added base, such as an ester or ether.[5] Recently, a wide variety of Lewis acids, not only conventional $SnCl_4$, $FeCl_3$, $TiCl_4$, and $ZnCl_2$ but also $ZrCl_4$, $HfCl_4$, $SiCl_4$, $GeCl_4$, $GaCl_3$, and $BiCl_3$, have been shown to induce living cationic polymerization with a base.[6] These exhibited different polymerization behaviors, especially in terms of polymerization rate. For example, $SnCl_4$[7] or $FeCl_3$,[8] when combined with an appropriate base, induced fast living cationic polymerization (complete in seconds). $SnCl_4$ was also effective in achieving living polymerization of monomers that were difficult to control.[7] These reactions as well as other living cationic polymerization reactions[9] of vinyl ethers, isobutene, or styrene derivatives were invariably conducted in homogeneous systems.

Solid acids such as metal oxides, heteropolyacids, or silica-supported metal halides are insoluble in organic solvents but are reactive enough to catalyze various organic reactions in a heterogeneous mixture.[10] Important advantages of heterogeneous catalyst systems are easy catalyst removal and the possibility of their reuse. Nevertheless, heterogeneously catalyzed living cationic polymerization using solid acids has never been achieved, although cationic polymerization with metal oxides,[11] metal sulfate−sulfuric acid complexes,[12] modified Ziegler-type catalysts,[13] heteropolyacids,[14] yttrium-decorated silica,[15] and ion-exchange resin[16] has been reported.

We have investigated the heterogeneously catalyzed cationic polymerization of vinyl ethers using a metal oxide in the presence of an added base. In this study, polymerization with $Fe_2O_3$ was examined first since it has been used for acid-catalyzed heterogeneous reactions such as Friedel−Crafts benzylation.[17] Here we report the first example of a heterogeneously catalyzed living cationic polymerization.

$Fe_2O_3$ (Aldrich, 99+%, identified as $\alpha$-$Fe_2O_3$ by powder XRD, average diameter = 1.0 $\mu$m) was crushed with a mortar and heated at ca. 400 °C for 8 min under $N_2$ atmosphere in the reaction container before use. Next, toluene, an added base, isobutyl vinyl ether (IBVE), and an adduct of IBVE with HCl (IBVE−HCl) in toluene solution were successively added at 0 °C to start the polymerization. The heterogeneous solution was magnetically stirred throughout the reaction. After quenching the polymerization with methanol containing a small amount (0.1%) of aqueous ammonia, the catalyst was removed by centrifugation and subsequent decantation. The product polymer was obtained by evaporating the remaining toluene, added base, and monomer.

Heterogeneously catalyzed cationic polymerization of IBVE using $Fe_2O_3$ in conjunction with IBVE−HCl was conducted in the absence and presence of an added base. Without the base, the reaction proceeded smoothly to reach almost quantitative conversion in 8 h at 0 °C. The resulting polymer had a unimodal molecular weight distribution (MWD) without oligomeric products (Table 1, entry 1). This suggested that the polymerization using the heterogeneous catalyst proceeded via a relatively simple mechanism. Ethyl acetate and 1,4-dioxane are effective bases for homogeneous living cationic polymerization of vinyl ethers with various metal halides.[6] In the presence of such a base, the heterogeneous catalytic system of $Fe_2O_3$ induced a controlled reaction to produce polymers with very narrow MWDs (Table 1, entries 2 and 4). In addition, $M_n$ of the product polymers increased in direct proportion to the monomer conversion, and their MWDs were very narrow throughout the polymerization ($M_w/M_n \leq 1.1$, Figure 1A). Controlled polymerization also occurred even at higher temperature (30 °C) (Table 1, entries 3 and 5).[5a]

***Table 1.*** Heterogeneously Catalyzed Living Cationic Polymerization of IBVE Using $Fe_2O_3$[a]

| entry | added base[b] | $T$/°C | time/h | conv/% | $M_n$ (calcd) | $M_n$[c] | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 1 | none | 0 | 8 | 80 | 15200 | 31000 | 2.14 |
| 2 | EA | 0 | 8 | 96 | 18300 | 18200 | 1.08 |
| 3 | EA | 30 | 5 | 99 | 18700 | 15500 | 1.08 |
| 4 | DO | 0 | 8 | 85 | 16100 | 16500 | 1.06 |
| 5 | DO | 30 | 5 | 99 | 18800 | 13700 | 1.11 |
| 6[d] | DO | 0 | 5.5 | 95 | 18100 | 15300 | 1.11 |

[a] $[IBVE]_0 = 0.76$ M, $[Fe_2O_3] = 2.6$ mol % to IBVE, $[IBVE{-}HCl]_0 = 4.0$ mM, [added base] = 1.0 M, [heptane] = 5 vol % (entries 1, 2, 4, 6), in toluene. [b] EA: ethyl acetate, DO: 1,4-dioxane. [c] By GPC (polystyrene calibration). [d] With $[H_2O]_0 = 12$ mM.

The livingness of the polymerization was confirmed by a monomer addition experiment. A fresh feed of monomer was added to the reaction mixture after the first feed was almost quantitatively consumed. This second stage of polymerization also proceeded smoothly, and the GPC curves of the polymer shifted toward higher molecular weight, maintaining the unimodal and narrow MWD (Figure 1B). These results supported the occurrence of heterogeneously catalyzed living cationic polymerization in this system.

Polymerization with reused $Fe_2O_3$ was examined according to the following procedure: after the first polymerization, the product polymer was removed by the above-mentioned method, and the remaining catalyst was vacuum-dried and heat-treated. Toluene, base, IBVE, and IBVE−HCl solution were then added successively to start the second polymerization. Living polymerization was again achieved, yielding a polymer with a very narrow MWD (Figure 1C). Upon repetition of this procedure, it was found that catalytic activity was maintained until at least the fifth use.

The $M_n$ values of the polymers are plotted against the $[IBVE]_0/[IBVE{-}HCl]_0$ ratios in Figure 2. The correspondence between the experimental and theoretical values of $M_n$ indicated that IBVE−HCl functioned as a cationogen and that $Fe_2O_3$ catalyzed the living cationic polymerization of IBVE. No polymerization occurred in

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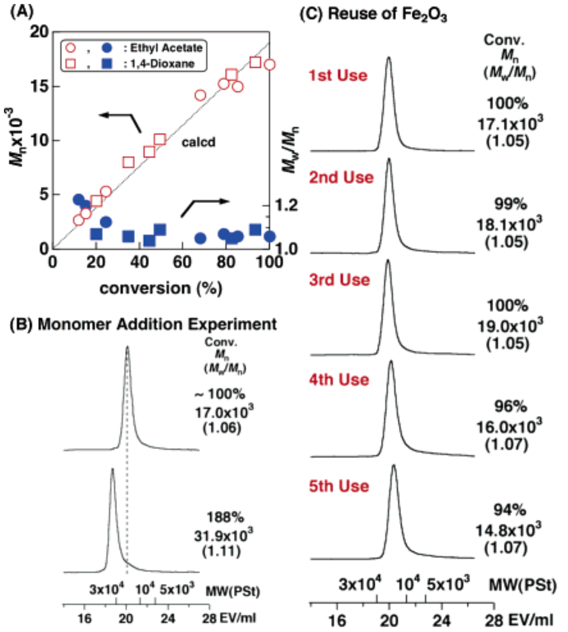


***Figure 1.*** (A) $M_n$ and $M_w/M_n$ for the polymerization of IBVE, (B) MWD curves for poly(IBVE) in the monomer addition experiment [added base: ethyl acetate], and (C) MWD curves for poly(IBVE) in the polymerization with reused $Fe_2O_3$ [added base: ethyl acetate, polymerization time: 8 h] ($[IBVE]_0 = 0.76$ M, $[Fe_2O_3] = 2.6$ mol % to IBVE, $[IBVE-HCl]_0 = 4.0$ mM, [added base] $= 1.0$ M, in toluene at 0 °C).

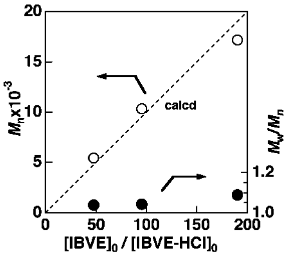
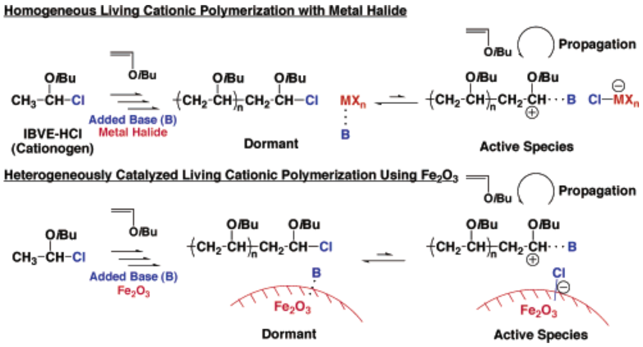


***Figure 2.*** $M_n$ and $M_w/M_n$ versus the $[IBVE]_0/[IBVE-HCl]_0$ ratio ($[IBVE]_0 = 0.76$ M, $[Fe_2O_3] = 2.6$ mol % to IBVE, $[IBVE-HCl]_0 = 4.0$, 8.0, and 16 mM, [1,4-dioxane] $= 1.0$ M, in toluene at 0 °C).

***Scheme 1.*** Estimated Mechanisms of Living Cationic Polymerization



the absence of cationogen or by the use of other initiators, such as the adduct of IBVE with acetic acid or trifluoroacetic acid. These results indicated that the polymerization was not initiated by water unexpectedly contained in a solution or adsorbed on the catalyst, nor did initiation occur via scission of the C−O bond of an adduct with $Fe_2O_3$. Furthermore, a small amount of purposely added water (12 mM) had no effect on the livingness of the reaction, which shows any water present in the system caused neither initiation nor undesired reactions such as termination or transfer (Table 1, entry 6).

The electronically unsaturated $Fe^{3+}$ species and the hydroxy groups from adsorbed water on the surface of $Fe_2O_3$ are regarded as acidic species judging from several experiments using an adsorbate such as carbon monoxide or pyridine.[18] In the polymerization system in this study, either or both of these would have interacted strongly with the chlorine atom of the propagating end to break the C−Cl bond (Scheme 1). The added base is likely to moderate the Lewis acidity of $Fe_2O_3$, realizing an appropriate equilibrium between the active and dormant species for living polymerization, as observed with homogeneous living process. UV−vis spectroscopic analysis revealed that there was no possibility of activation by impurities such as $FeCl_3$. The polymerization mechanism is now under detailed investigation.

In conclusion, heterogeneously catalyzed living ionic polymerization with a solid catalyst has been achieved for the first time. In the presence of an added base, $Fe_2O_3$ catalyzed polymerization of IBVE in a heterogeneous system to produce polymers with very narrow MWDs. The catalyst maintained its activity after the polymerization, and its repeated reuse was shown to be possible. This robust and environmentally benign system is expected to open new avenues for practical and industrial uses of living cationic polymerization involving vinyl monomers.

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**Supporting Information Available:** Experimental procedures, the XRD data, and several polymerization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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