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Controlled Cationic Polymerization of *p*-Methoxystyrene in Aqueous Media with $Yb(OTf)_3$[1]

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ABSTRACT: This study shows that ytterbium triflate [$Yb(OTf)_3$; OTf = OSO_2CF_3] induces cationic polymerizations of isobutyl vinyl ether (IBVE) and *p*-methoxystyrene (pMOS) *in aqueous media* in conjunction with the hydrogen chloride−vinyl monomer adduct [$CH_3-CHR-Cl$; R = O*i*Bu, $C_6H_4-OCH_3$] as the initiator at room temperature. These "suspension" polymerizations are carried out by adding neat monomer and then a solution of the initiator into an aqueous solution of $Yb(OTf)_3$ under vigorous stirring, and the polymerizations occur smoothly without being inhibited by water. Under these conditions, IBVE polymerization was uncontrolled, but pMOS can be polymerized in a controlled fashion where the molecular weight distributions (MWDs) are relatively narrow ($\bar{M}_w/\bar{M}_n \sim 1.4$) and the molecular weights increase in proportion to monomer conversion. The reactions proved to be cationic, being quenched by NaOH and EtOH but not by 1,4-benzoquinone. The aqueous hydrochloric acid/$Yb(OTf)_3$ initiating system also generates similar long-lived pMOS polymer in water. The success in such controlled cationic polymerizations in aqueous media is due to the stability of $Yb(OTf)_3$ as well as the dormant C−Cl poly(pMOS) terminal in water.

Introduction

Aqueous media are seldom employed for controlled ionic reactions because even a small amount of water usually deactivates or decomposes catalysts and ionic intermediates. However, water as a solvent is attracting much attention from the viewpoint of environmental aspect,[2] and in special cases aqueous media can indeed be used for organic reactions such as Diels−Alder,[3a] Aldol,[3b] Michael reactions,[3c] etc. Some of these reactions are induced by ytterbium triflate [$Yb(OTf)_3$; OTf = OSO_2CF_3], which serves as a water-resistant Lewis acid that maintains catalyst activity even in aqueous solution[3b,c] where usual Lewis acids ($TiCl_4$ etc.) immediately decompose.

As for polymerizations, water is widely used in suspension and emulsion radical polymerizations.[4] These techniques are invaluable to industrial polymer synthesis because of the easier control of the reactions (e.g., heat dissipation) and easier handling of the products. However, the techniques have been limited to radical polymerizations, where the neutral radical intermediates are tolerant to water. Recently, living ring-opening metathesis polymerization catalyzed by a ruthenium complex was carried out in aqueous media to give polymers with controlled molecular weights and distributions, where the propagating species and the catalyst are stable in water.[5] We have also found that the ruthenium complex-mediated living radical polymerization is feasible even in water under suspension/dispersion conditions.[6]

In contrast to such robust systems, living anionic and cationic polymerizations should be done in highly purified and anhydrous organic solvents to afford polymers with controlled structures, because water acts as a terminator or a chain-transfer agent in these ionic processes. Living ionic polymerization systems are widely employed for the precision polymer synthesis in laboratory scale but are not suited for practical use because of the required stringent conditions.

We have been investigating living cationic polymerizations of vinyl monomers such as vinyl ethers and styrenes and found that the cationic polymerizations can be controlled by initiating systems consisting of a protonic acid like hydrogen chloride and a Lewis acid like zinc chloride (eq 1).[7] The protonic acid forms a stable adduct with monomer, and the Lewis acid activates the generated C−Cl bond subsequently to induce living cationic polymerizations. For achievement

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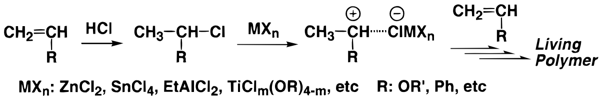
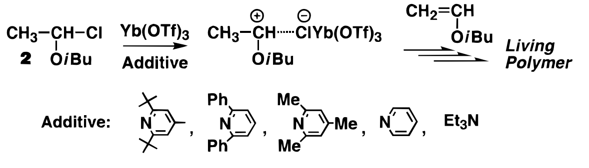


(1)

of such living polymerizations, the selection of Lewis acids proved important, and the Lewis acids thus far employed are almost invariably halides of boron, aluminum, tin, titanium, and zinc, all of which are of course highly sensitive to moisture and decompose or transform into less effective very weak Lewis acids. Thus, controlled cationic polymerization has been impossible in aqueous media.

Recently, we reported that Yb(OTf)$_3$ led to living cationic polymerization of isobutyl vinyl ether (IBVE) coupled with the IBVE−HCl adduct (initiator) in CH$_2$Cl$_2$ at −15 °C in the presence of Lewis bases such as not only sterically bulky pyridines (e.g., 2,6-di-*tert*-butyl-4-methylpyridine) but also unsubstituted pyridines or amines (eq 2).[8] The high activity of Yb(OTf)$_3$ even in the presence of nitrogen bases is due to the high Lewis acidity of Yb(OTf)$_3$ where the triflate group acts as a strong electron-withdrawing group as well as due to the large radius and high coordination number of Yb(III).[9] We also showed that the Yb(OTf)$_3$ can be recovered from the quenched reaction mixture and reused to induce living cationic polymerization.



(2)

This paper reports the first example of *suspension* cationic polymerizations of IBVE and *p*-methoxystyrene (pMOS) *in water* with the use of Yb(OTf)$_3$ as a Lewis acid. Yb(OTf)$_3$ induced cationic polymerizations of the monomers quantitatively when coupled with hydrogen chloride adduct initiator even in the presence of large amount of water. Especially for pMOS, the polymerization proceeds in a controlled fashion where the molecular weights increase with conversion as in living polymerizations. This is also the first example of controlled cationic polymerization of vinyl monomers in aqueous media.

Results and Discussion

1. Living Cationic Polymerization of pMOS with Yb(OTf)$_3$ in Nonaqueous Media. Prior to studies on the possible cationic polymerization of pMOS in aqueous media, we investigated cationic polymerization of pMOS in nonaqueous media. As reported in our previous paper,[8] Yb(OTf)$_3$ mediates living cationic polymerization of IBVE in CH$_2$Cl$_2$/THF (9/1) in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP). Thus, pMOS was polymerized with the pMOS−HCl adduct (**1**)/Yb(OTf)$_3$/DTBMP initiating system in CH$_2$Cl$_2$/THF (9/1) at 10 °C. The **1**/Yb(OTf)$_3$ system induced a quantitative polymerization of pMOS without an induction phase, where the conversion reached 99% in 13 h (Figure 1).

The obtained polymers had broad molecular weight distributions (MWDs; $\bar{M}_w/\bar{M}_n \sim 2.1$) and number-average molecular weights ($\bar{M}_n$) remained unchanged throughout the reaction ($\bar{M}_n \sim 4500$), whereas the $\bar{M}_n$ was close to the calculated values assuming that one molecule of **1** generates one living polymer chain. This is probably due to slow equilibrium between the dormant and the activated species, which would slow the initiation step relative to propagation and result in broader MWDs.

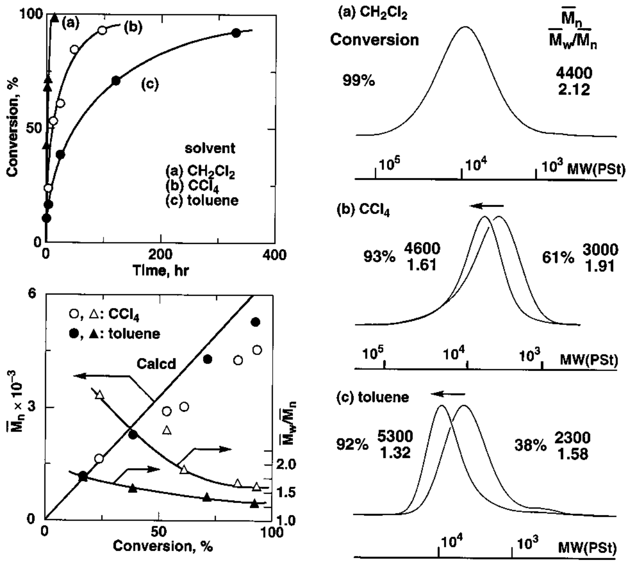


Figure 1. Time−conversion and polymer molecular weights data for the polymerization of pMOS with **1**/Yb(OTf)$_3$ in the presence of DTBMP at 10 °C in anhydrous organic media. Solvents (including 10 vol % of THF): (a) CH$_2$Cl$_2$; (b) CCl$_4$; (c) toluene. $[\text{pMOS}]_0 = 0.50$ M; $[\mathbf{1}]_0 = 10$ mM; $[\text{Yb(OTf)}_3]_0 = 2.0$ mM; $[\text{DTBMP}]_0 = 2.0$ mM. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per **1** molecule.

On the other hand, polymerization in less polar solvents such as CCl$_4$/THF (9/1) or toluene/THF (9/1) proceeded much slower than in CH$_2$Cl$_2$/THF. In particular, monomer conversion reached 92% in 330 h in toluene, and the MWDs became narrower ($\bar{M}_w/\bar{M}_n \sim$ 1.4). The $\bar{M}_n$ of the polymer increased in direct proportion to monomer conversion and agreed with the calculated values assuming that one polymer chain is formed per one molecule of **1**. These results indicated that the **1**/Yb(OTf)$_3$/DTBMP initiating system is effective in controlled cationic polymerization of pMOS in toluene to give polymers with controlled molecular weights and MWDs.

2. Cationic Polymerization in Aqueous Media. Yb(OTf)$_3$ is known as a unique Lewis acid characterized by its tolerance toward water and strong Lewis acidity even in water.[3,8] These features prompted us to investigate cationic polymerization of IBVE and pMOS in aqueous media with Yb(OTf)$_3$.

(a) Polymerization of IBVE. For this, we polymerized IBVE in the presence of a large amount of water (organic/aqueous phase = 1/1 v/v) with the IBVE−HCl adduct (**2**)/Yb(OTf)$_3$ initiating system. Thus, neat monomer and a solution of **2** in CCl$_4$ were added to an aqueous solution of Yb(OTf)$_3$, and the mixture was vigorously stirred to form a suspension: $[\text{IBVE}]_0 = 5.6$ M and $[\mathbf{2}]_0 = 260$ mM in the organic phase, $[\text{Yb(OTf)}_3]_0 = 300$ mM in the aqueous phase. Despite excess water, IBVE polymerization proceeded to give poly(IBVE) in 2 h in high yields at room temperature whereas Yb(OTf)$_3$ or **2** alone did not induce polymerizations at all. Also, trifluoromethanesulfonic acid, a strong protonic acid that would form from Yb(OTf)$_3$ via hydrolysis, was much less effective in such aqueous media to result in much lower yield (yield = 0.7% for 2 h). These suggest

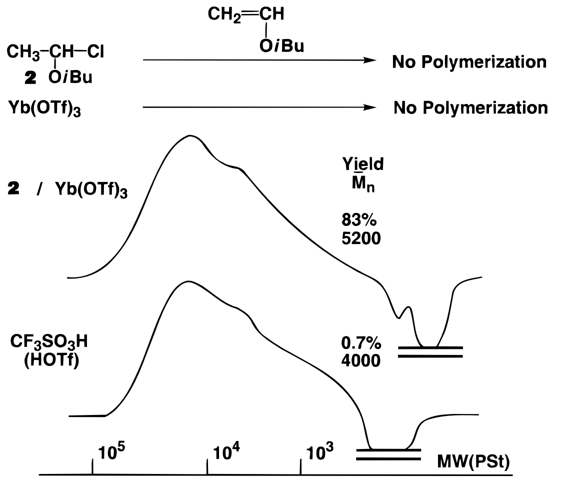


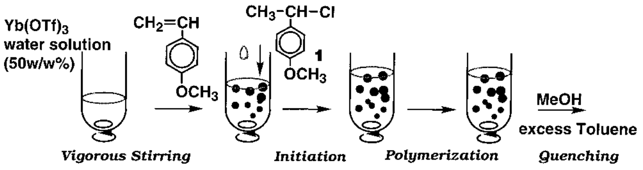
Figure 2. Polymerization of IBVE in water at 30 °C for 2 h: $[\text{IBVE}]_0$ = 2.8−3.8 M; $[\mathbf{2}]_0$ = 130 mM; $[\text{Yb(OTf)}_3]_0$ = 150 mM; $[\text{CF}_3\text{SO}_3\text{H}]_0$ = 190 mM.

that Yb(OTf)_3 is stable without hydrolysis or decomposition even in water and that it can be an effective activator for cationic polymerization of IBVE in conjunction of **2**. The polymerization is most probably initiated via formation of cationic species from **2** and Yb(OTf)_3.

Figure 2 shows a sample of poly(IBVE) obtained with **2**/Yb(OTf)_3: yield 83%; $\bar{M}_n$ = 5200; $\bar{M}_w/\bar{M}_n$ = 3.4. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values were less reproducible and scattered around 3000−6000 and 2.5−3.0, respectively, depending on yields (61−83%). The yellow products contained low molecular weight oligomers, which are due to the conjugated polyene structures caused by β-proton elimination followed by consecutive release of alcoholic groups from poly(VE).[10] These results are due to the sensitive C−Cl dormant bond of poly(vinyl ether), which forms on unstable hemiacetal with water.

(b) Controlled Polymerization of pMOS. Polymerizations of pMOS in aqueous media (organic/aqueous phase = 5/3) were also investigated with a combination of **1** and Yb(OTf)_3 at 30 °C. Scheme 1 illustrates the procedure for the pMOS polymerization with **1**/Yb(OTf)_3 in aqueous media. The polymerization was initiated by adding the initiator (**1**) solution (in CCl_4) into a vigorously stirred suspension of pMOS in the aqueous solution of Yb(OTf)_3. The stirred mixture of pMOS in the Yb(OTf)_3 aqueous solution forms a fine suspension where the oily monomer is distributed as small, nearly transparent droplets. The added initiator solution in CCl_4 apparently diffuses and mixes into these droplets. At the beginning, when the stirring is terminated, the dispersion readily phase-separates into two layers, but as the polymerization proceeded, the suspension turns milky and the phase separation became slower, probably due to the higher viscosity of the organic phase. Upon quenching with methanol followed by dilution with an excess toluene, the suspension became a two-layered mixture.

Scheme 1



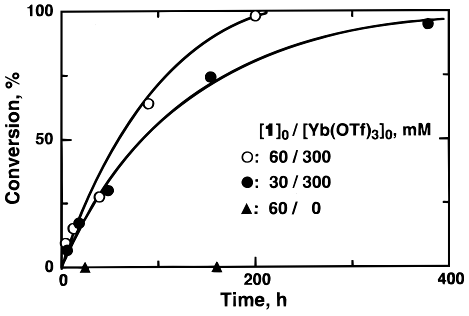


Figure 3. Time−conversion curves for the polymerization of pMOS with **1**/Yb(OTf)_3 in aqueous media at 30 °C: $[\text{pMOS}]_0$ = 3.0 M; $[\mathbf{1}]_0/[\text{Yb(OTf)}_3]_0$ = 60/300 (○); 30/300 (●); 60/0 (▲) mM: aqueous phase/organic phase = 3/5.

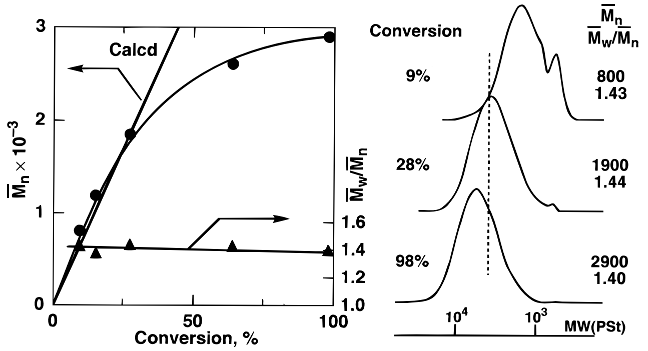


Figure 4. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(pMOS) obtained with **2**/Yb(OTf)_3 in water at 30 °C: $[\text{pMOS}]_0$ = 3.0 M; $[\mathbf{1}]_0$ = 60 mM; $[\text{Yb(OTf)}_3]_0$ = 300 mM. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per **1** molecule.

As shown in Figure 3, **1** alone did not induce the pMOS polymerization at all (filled triangles). In contrast, a quantitative and efficient polymerization occurred smoothly without an induction phase in conjunction with the **1**/Yb(OTf)_3 initiating system at 30 °C. Monomer conversion reached 98% in 200 h (open circle), where the reagent concentrations were as follows: $[\text{pMOS}]_0$ = 4.8 M and $[\mathbf{1}]_0$ = 96 mM in the organic phase; $[\text{Yb(OTf)}_3]_0$ = 800 mM in the aqueous phase. The polymerization rate also depends on the concentration of **1**, and as expected, it decreases at a lower initiator concentration; the reaction was retarded (filled circles).

Figure 4 shows the $\bar{M}_n$ and MWDs of the poly(pMOS) thus obtained. At the early stage of the polymerizations, the $\bar{M}_n$ increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one molecule of **1** generates one polymer chain, although the increase leveled off at the later stage. The MWDs were unimodal and relatively narrow ($\bar{M}_w/\bar{M}_n \sim 1.4$) throughout the reaction. These results suggest the formation of long-lived polymers of pMOS with the **1**/Yb(OTf)_3 in aqueous media.

Figure 5 shows the matrix-assisted, laser desorption−ionization, time-of-flight mass spectrometry (MALDI-TOF-MS) spectra of poly(pMOS) obtained in water. These spectra consist of the sharp peaks separated by a 134 Da interval each, which corresponds to the molecular weight of pMOS monomer. A set of peaks of homologous-series polymers shifted to higher molecular weight regions without significant formation of another set of peaks as the polymerization proceeds. These results also indicate that the pMOS polymerization with **1**/Yb(OTf)_3 in water proceeds in controlled fashion to

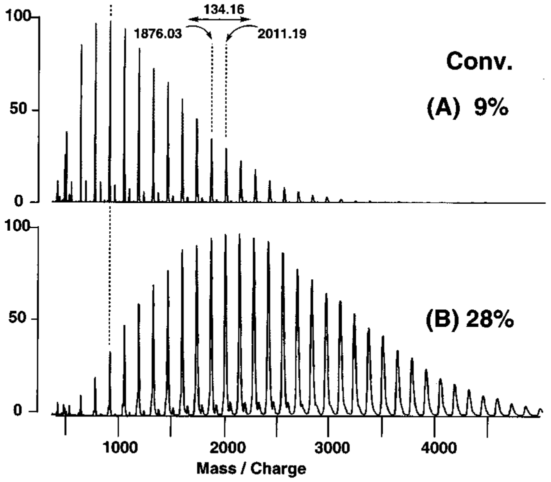
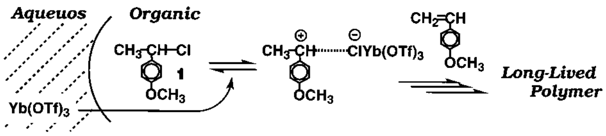


Figure 5. MALDI-TOF-MS spectra of poly(pMOS) obtained in the same experiments as for Figure 4: monomer conversion = 9% (**A**); 28% (**B**).

give long-lived polymers without significant side reactions.

The polymerization probably proceeds in the organic phase (droplets) via a carbocationic species generated from **1** and Yb(OTf)$_3$, where the carbon−chlorine bond in **1** was activated by Yb(OTf)$_3$ similarly to polymerizations in anhydrous organic solvents (Scheme 2), because both **1** and Yb(OTf)$_3$ are necessary for the polymerization (see also Figure 3). However, the solubility of Yb(OTf)$_3$ in the organic phase that contains monomer and **1** is very low compared with its high solubility in water; i.e., most of Yb(OTf)$_3$ exists in the aqueous phase. Thus, it is expected that the polymerization is triggered by a small amount of Yb(OTf)$_3$ transferred into the organic phase under vigorous stirring or that the polymerization occurs near the boundary between the organic and aqueous phase.

Scheme 2



The terminal structure of the polymers obtained with **1** and Yb(OTf)$_3$ in water was examined by ^{1}H NMR spectroscopy. Figure 6 shows the ^{1}H NMR spectra of the product polymers obtained with **1**/Yb(OTf)$_3$ in water (A) and those obtained in CCl$_4$ (B). The polymers obtained in CCl$_4$ exhibit characteristic signals assigned to the CH$_3$ group (a; 1.0 ppm) at the α-end and the −CH−OCH$_3$ group (f; 3.0 ppm) at the ω-end (due to quenching the polymerization with methanol). In contrast, the polymers obtained in water are free from such a methoxy ω-end. They instead showed a new absorption at 4.1 ppm ascribed to the methine proton (−CH−Cl) adjacent to a chlorine.[11] The functionality of the chlorine group is 0.35, lower than unity, which suggests some loss of living growing polymer terminal as also indicated by the lower molecular weights than calculated values. The existence of the terminal chlorine in the polymers was also confirmed by elemental analysis.[12] This shows that the polymerization proceeds via the reversible activation of the C−Cl bond at the polymer terminal by Yb(OTf)$_3$ even in water to give long-lived polymers.

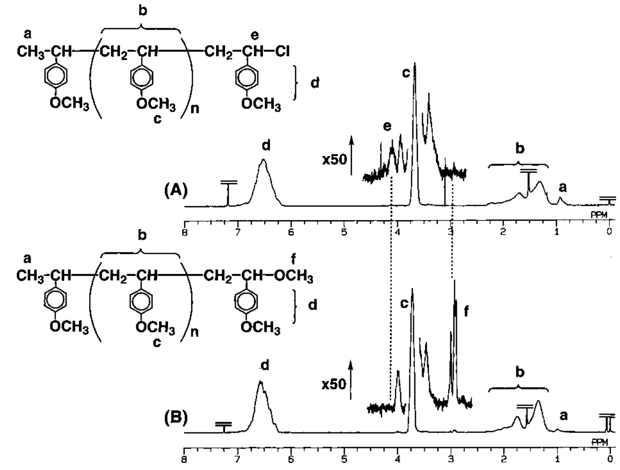


Figure 6. ^{1}H NMR spectra of poly(pMOS) obtained in the polymerization with **1**/Yb(OTf)$_3$ in water (A) and CCl$_4$ (B) at 30 °C: (A) [pMOS]$_0$ = 3.0 M; [**1**]$_0$ = 60 mM; [Yb(OTf)$_3$]$_0$ = 300 mM, M_n = 2000, M_w/M_n = 1.40. (B) [pMOS]$_0$ = 0.50 M; [**1**]$_0$ = 10 mM; [Yb(OTf)$_3$]$_0$ = 2.0 mM, M_n = 3850, M_w/M_n = 2.20.

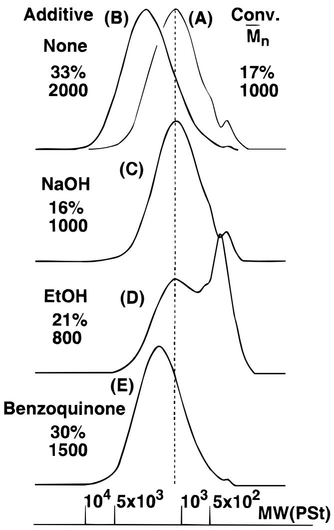


Figure 7. Effects of additives on the pMOS polymerization with **1**/Yb(OTf)$_3$ in aqueous media at 30 °C: [pMOS]$_0$ = 3.0 M; [**1**]$_0$ = 60 mM; [Yb(OTf)$_3$]$_0$ = 300 mM; [additive]$_{add}$/[**1**]$_0$ = 3.3 (NaOH), 45 (EtOH), 3.3 (benzoquinone); time for (A) = 12 h; time for (B−E) = 56 h.

(c) Evidence for Cationic Polymerization. To confirm the carbocationic mechanism of the polymerization, effects of additives such as NaOH, ethanol, and 1,4-benzoquinone were investigated in the long-lived polymerization of pMOS with **1**/Yb(OTf)$_3$ in water. The first two compounds are known as terminators and/or chain transfer agents for cationic polymerization; the third one is a typical radical inhibitor that has no acidic proton. The polymerization was first run without additives, where conversion reached 17% in 12 h and 33% in 56 h (chromatograms A and B in Figure 7, respectively). At about 17% conversion, the additives, excess to the initiator (**1**), were added to the suspension polymerization mixtures.

In the presence of NaOH, conversion did not increase any more, and the polymerization clearly ceased even if it was kept unquenched beyond 56 h. The molecular weight did not increase, either, and stayed unchanged after the addition (trace C). Upon the addition of ethanol, side reactions such as chain transfer and subsequent addition reactions to monomer took place

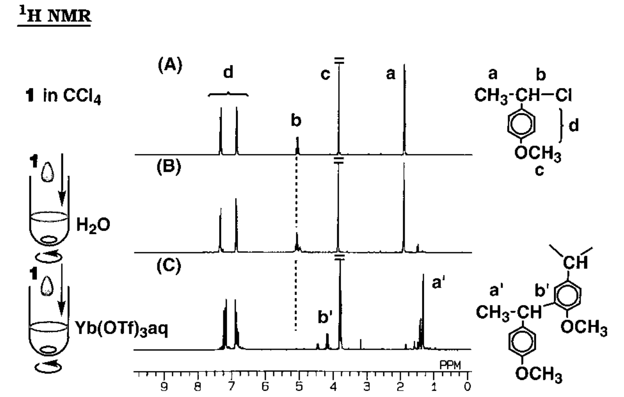


Figure 8. ^{1}H NMR spectra of **1** (A) **1** treated with water for 1 day (B) and the products obtained with **1** and Yb(OTf)$_3$ in water for 1 day (C). The spectra were recorded in CDCl$_3$ at 25 °C.

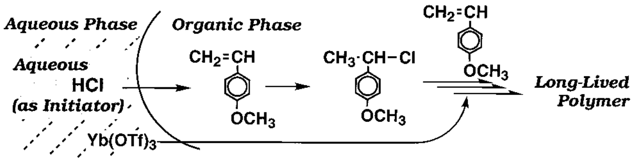
during the prolonged time. This caused a slight increase in monomer conversion along with a decrease of molecular weights due to the formation of low molecular weight oligomers. However, the position of the peak-top molecular weight still remained unchanged (trace D). ^{1}H NMR analysis indicated that the terminal groups of these products were changed from a chlorine to a hydroxy or an ethoxy group by substitution.

In contrast, the addition of 1,4-benzoquinone did not affect the long-lived polymerization of pMOS in water. As in the additive-free systems, the $\bar{M}_n$ increased further with conversion after the addition of the quinone (trace E). These results show that the long-lived suspension polymerization of pMOS occurs via the cationic mechanism generated from **1** and Yb(OTf)$_3$, where the propagating cationic species keeps its activity even in the presence of water.

The carbocation formation from **1** and Yb(OTf)$_3$ was also confirmed by ^{1}H NMR analysis of a model reaction between **1** and Yb(OTf)$_3$ in water (Figure 8). In CCl$_4$, adduct **1** alone gives a clean spectrum where the methine proton (b), adjacent to the chlorine, is seen at 5.2 ppm and the α-methyl protons (a) at 1.9 ppm (Figure 8A). Interestingly, the spectrum did not change at all when a solution of **1** (in CCl$_4$) was mixed with water and kept stirred for 1 day, as seen in Figure 8B. This indicates the stability of the carbon−chlorine bond of **1** in water. In sharp contrast, the mixing of **1** with an aqueous solution of Yb(OTf)$_3$ ([**1**]$_0$/[Yb(OTf)$_3$]$_0$ = 200/400 mM) led to the change in spectrum in 1 day (Figure 8C). The products are considered as a set of compounds generated via intermolecular Friedel−Crafts reactions between carbocation derived from the C−Cl bond and the pendant phenyl rings of **1**. This also supports that Yb(OTf)$_3$ is active and effective in water to generate a carbocation from **1** which would induce the cationic polymerization in the presence of monomer.

(d) Aqueous HCl as an Initiator. Subsequently, we used hydrochloric acid as a water-soluble initiator in place of its adduct **1** in the organic phase (Scheme 3). The polymerization was initiated by addition of pMOS into an aqueous solution of HCl and Yb(OTf)$_3$ under vigorous stirring at 30 °C.

Scheme 3



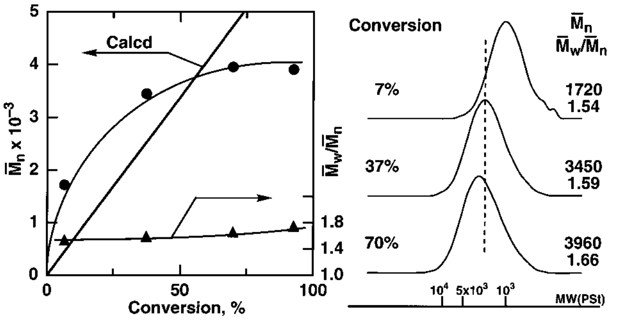


Figure 9. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(pMOS) obtained with aqueous HCl/Yb(OTf)$_3$ in water at 30 °C: [pMOS]$_0$ = 3.0 M; [HCl]$_0$ = 60 mM; [Yb(OTf)$_3$]$_0$ = 400 mM. The diagonal bold line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per HCl molecule.

pMOS consumption occurred smoothly and quantitatively without an induction phase. The obtained polymer also had long-lived nature where the $\bar{M}_n$ increased with monomer conversion (Figure 9). The higher $\bar{M}_n$ than the calculated values in the early stage of the polymerizations are due to slow initiation where HCl should transfer from the aqueous to the organic phase for the addition reaction to the monomer. And the lower $\bar{M}_n$ in the later stage indicates some chain transfer reaction similarly to the polymerization with **1**/Yb(OTf)$_3$ (cf. Figure 4). Thus, aqueous HCl is also an effective initiator for pMOS polymerization with Yb(OTf)$_3$ in aqueous media to give long-lived polymers.

In conclusion, we have demonstrated cationic polymerization of IBVE and pMOS with a combination of HCl adduct or aqueous HCl and Yb(OTf)$_3$ in water at 30 °C without additives such as pyridines. To our knowledge this is the first example of the cationic polymerization of vinyl monomers in aqueous media. The pMOS polymerization proceeds via long-lived species generated from a stable carbon−chlorine bond and Yb(OTf)$_3$ similarly to the living cationic polymerization in organic solvents.

Experimental Section

Materials. IBVE (Tokyo Kasei; purity >99%) was washed with 10% aqueous sodium hydroxide solution and then water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride before use. pMOS (Aldlich; purity 97%) was dried overnight over calcium chloride, distilled over calcium hydride under reduced pressure, and stored at −80 °C. Yb(OTf)$_3$ (Aldlich) was obtained commercially as a hydrate. For the polymerization in aqueous media, it was used as received. In the case on the anhydrous condition, the hydrate salt was vacuum-dried at 200 °C for 6 h and was immediately dissolved in dry THF containing DTBMP [Yb(OTf)$_3$ and DTBMP, 20 mM each] under dry nitrogen.[13] The pMOS−HCl adduct (**1**) and IBVE−HCl adduct (**2**) were prepared by bubbling dry HCl gas into 1.0 M solution of the corresponding monomer at −78 or 0 °C, and then dry nitrogen was bubbled to remove excess HCl. Aqueous hydrogen chloride solution (6.0 N; Wako Chemicals) and 2,6-di-*tert*-butyl-4-methylpyridine (Aldlich; purity 98%) were used as received. CH$_2$Cl$_2$ and CCl$_4$ as solvents and bromobenzene as an internal standard for gas chromatography were dried overnight over calcium chloride and doubly distilled over phosphorus pentoxide and then over calcium hydride before use. Toluene was dried overnight over calcium chloride and doubly distilled over calcium hydride before use. THF was distilled over LiAlH$_4$ before use. Distilled deionized water was used for the polymerizations without degassing.

Polymerization Procedures. Polymerization in organic solvent was carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for pMOS polymerization is given below. The polymerization was initiated by adding solutions of pMOS−HCl adduct (**1**) (in CCl_4 or toluene; 0.30 mL) and $Yb(OTf)_3$/DTBMP (in THF; 0.30 mL), sequentially in this order, into a monomer solution (2.4 mL) containing pMOS (0.20 mL) and bromobenzene (0.11 mL). The total volume of the reaction mixture was thus 3.0 mL. The polymerization was terminated with prechilled methanol (1.5 mL). Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with bromobenzene as an internal standard. The quenched reaction mixture was washed with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymer.

Polymerization in aqueous media was initiated by adding solution of the pMOS−HCl adduct (**1**) (in CCl_4) into monomer suspension in aqueous $Yb(OTf)_3$ solution (monomer/water = 1/1; see text). The reaction was run under vigorous stirring and was terminated with methanol and with excess water and toluene. The polymer was extracted with toluene and purified by the same method for the polymerization in organic solvent.

Measurements. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at room temperature on three polystyrene gel columns (Shodex K-802 + K-803 + K-804) that were connected to a Jasco Trirotar-V precision pump and a Jasco 830-RI refractive index detector. The columns were calibrated against 11 standard poly(styrene) samples (Polymer Laboratories; $\bar{M}_n = 630-220\,000$; $\bar{M}_w/\bar{M}_n = 1.06-1.22$) as well as monomer. ^1H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-GSX270 spectrometer, operating at 270.7 MHz. Polymers for ^1H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002). MALDI-TOF-MS spectra were measured on a KRATOS KOMPACT IV spectrometer with dithranol (1,8,9-anthracenetriol) as an ionizing matrix.

References and Notes

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(11) The chemical shift of the methine proton of polymer terminal group is upfielded in comparison to that of the model compound (cf. Figure 6). For example, the methine proton of chlorine-terminal polystyrene absorbs at 4.3 ppm, whereas that of 1-phenylethyl chloride at 5.1 ppm.

(12) The absence of methoxy terminal group after quenching with methanol is most probably due to that the added methanol existed in water rather than in the organic layer where the polymer dissolved and thus interacted with $Yb(OTf)_3$ preferentially to deactivate the polymerization.

(13) In the absence of DTBMP, the dried $Yb(OTf)_3$ induces cationic ring-opening polymerization of THF.

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