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Lanthanide Triflates-Mediated Emulsion Cationic Polymerization of *p*-Alkoxystyrenes in Aqueous Media[1]

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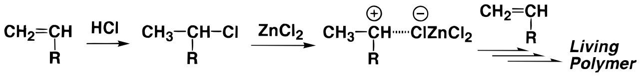
ABSTRACT: Emulsion cationic polymerization in water was achieved with rare earth metal triflates [Ln(OTf)$_3$; Ln = Yb, Sc, Dy, Sm, Gd, and Nd; OTf = OSO$_2$CF$_3$] that are well-known as water-tolerant Lewis acids. Even in the presence of a large amount of surfactants such as dodecylammonium halides, sodium laurylbenzenesulfate, and poly(vinyl methyl ether), Ln(OTf)$_3$ induced cationic polymerizations of *p*-methoxystyrene (pMOS) in aqueous media in conjunction with the pMOS−HCl adduct (**1**) at 30 °C. In particular, the use of cationic surfactants such as dodecyltrimethylammonium chloride accelerated the polymerization and gave polymers of controlled molecular weights and narrower molecular weight distributions (MWDs) ($M_w/M_n \sim 1.4$) than those in the absence of surfactants. The activity of Ln(OTf)$_3$ reduced with decreasing the Lewis acidity or the ionic radii of the central metal. The **1**/Yb(OTf)$_3$ system also induced the polymerization of *p-tert*-butoxystyrene (tBOS) in aqueous media. The homopolymerization of tBOS in water was found to be less controllable than that of pMOS. Random copolymerization of pMOS and tBOS also proceeded in a long-lived fashion in the presence of surfactants. The emulsion cationic polymerization most probably proceeds via the carbocationic species generated from the dormant C−Cl polymer terminal in the organic phase and Ln(OTf)$_3$ entering from the aqueous phase.

Introduction

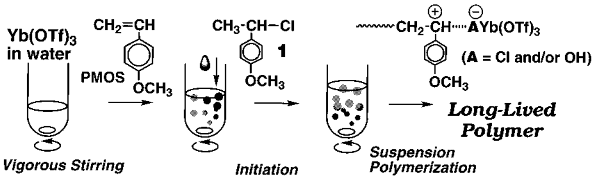
Contrary to the long-time belief that ionic reactions should be carried out under strictly anhydrous conditions, aqueous reactions have recently developed that can undergo even in the presence of a large amount of water.[2−6] Some of these reactions are mediated by lanthanide triflates [Ln(OTf)$_3$; Ln = Yb, Sc, etc.; OTf = OSO$_2$CF$_3$] that are known as water-tolerant Lewis acids. For example, we have found that ytterbium triflate, Yb(OTf)$_3$, induces suspension cationic polymerization of *p*-methoxystyrene (pMOS) in water when coupled with the pMOS−HCl adduct (**1**) (Scheme 1).[7] Even in the presence of a large amount of water, the polymerization is controlled where the number average molecular weights (M_n) increases with monomer conversion, and the molecular weight distributions (MWDs) are relatively narrow ($M_w/M_n \sim 1.4$). This polymerization most probably proceeds in water-suspended organic droplets where the monomer and **1** exist, while the ytterbium salt mostly exists in the aqueous phase due to its high solubility therein. Therefore, it is expected that the polymerization is triggered by a small amount of Yb(OTf)$_3$ which enters into the organic phase to activate the stable and water-tolerant C−Cl bond at the dormant polymer terminal.

This two-phase controlled cationic polymerization originates from the living cationic polymerization in organic solvents, where the covalent but potentially active carbon−halogen bonds at the polymer terminal are activated by metal halides such as ZnCl$_2$, TiCl$_4$, SnCl$_4$, etc., to generate carbocationic species (see, for example, eq 1).[8] In the living cationic polymerization, polymer molecular weight is precisely controlled by the ratio of monomer to alkyl halide initiator, where the initiator generates one polymer chain per molecule via reversible and heterolytic cleavage of carbon−halogen bonds. However, these cationic as well as anionic polymerizations have been believed to be done in rigorously anhydrous organic solvents.[9]



$$\mathrm{CH_2{=}\underset{R}{CH}} \xrightarrow{\mathrm{HCl}} \mathrm{CH_3{-}\underset{R}{CH}{-}Cl} \xrightarrow{\mathrm{ZnCl_2}} \mathrm{CH_3{-}\underset{R}{\overset{\oplus}{C}H}\cdots\overset{\ominus}{Cl}ZnCl_2} \xrightarrow[\longrightarrow]{\mathrm{CH_2{=}\underset{R}{CH}}} \text{Living Polymer} \qquad (1)$$

Scheme 1



Emulsion as well as suspension polymerizations in water are among most commonly used methods for polymer synthesis in industry.[10] Compared to the latter, the emulsion process has several distinct advantages. For instance, the emulsion polymerization afforded precisely sized particles in the submicrometer range, referred to as a latex, which can be used directly without further separation and have established applications for paints, coatings, catalyst supports, and so on.[10,11] It differs from suspension polymerization in many aspects, including the particle size of the products and where the polymerization occurs, while they superficially resemble each other. These two aqueous polymerizations, however, were so far limited to mostly radical processes and a few others.[12,13]

Considering these aspects of cationic polymerizations and emulsion polymerizations, we decided to apply our novel Yb(OTf)$_3$-mediated cationic system[7] to emulsion polymerization of pMOS with the use of surfactants (Scheme 2).[14] In this study, we report that the **1**/Yb(OTf)$_3$ or related lanthanide triflates [Ln(OTf)$_3$; Ln = Sc, Sm, Nd, etc.] initiating systems induced emulsion cationic polymerizations of pMOS and *p-tert*-butoxystyrene (tBOS) in the presence of a large amount of surfactants. Similar to pMOS, the butoxy monomer is cationically polymerizable,[15] and its polymer can readily

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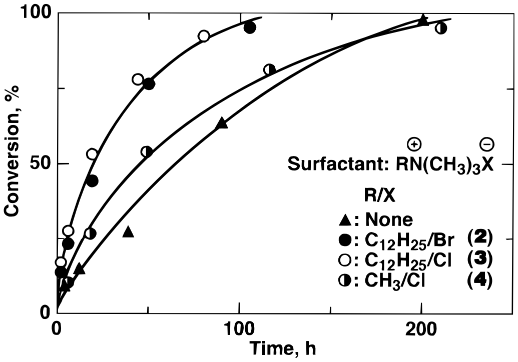
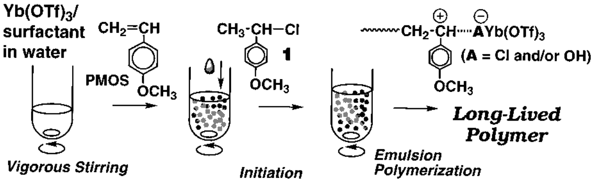


Figure 1. Time−conversion curves of the polymerization of pMOS with **1**/Yb(OTf)$_3$ in water at 30 °C in the presence of ammonium salts: [pMOS]$_0$ = 3.0 M; [**1**]$_0$ = 60 mM; [Yb(OTf)$_3$]$_0$ = 300 mM; [ammonium salt]$_0$ = 100 mM. Ammonium salt: (●) **2**; (○) **3**; (◑) **4**; (▲) none.

Scheme 2



be converted by treatment with protonic acids into poly(vinylphenol), which has versatile applications such as resists.[16]

Results and Discussion

1. Emulsion Cationic Polymerization with Yb(OTf)$_3$. There are mainly three types of surfactants for radical emulsion polymerizations in aqueous media: cationic (alkylammonium salts), anionic (alkylmetal sulfates), and nonionic (polyalcohols or polyethers).[17] Herein, we investigated a series of these surfactants for the pMOS polymerization with **1**/Yb(OTf)$_3$ initiating system in water.

(a) Cationic Surfactants. First, we employed dodecyltrimethylammonium chloride and bromide (**2** and **3**, respectively) as cationic surfactants for the cationic polymerization of pMOS in water with Yb(OTf)$_3$. pMOS was polymerized in the presence of **2** or **3** with the combination of pMOS−HCl adduct (**1**) as an initiator and Yb(OTf)$_3$ as a Lewis acid in water (aqueous/organic phase = 3/5) at 30 °C: [pMOS]$_0$ = 4.8 M and [**1**]$_0$ = 96 mM in the organic phase; [Yb(OTf)$_3$]$_0$ = 800 mM and [ammonium salt]$_0$ = 267 mM in the aqueous phase. The polymerization was initiated by adding an initiator (**1**) solution in CCl$_4$ into an emulsion of pMOS monomer in an aqueous solution of Yb(OTf)$_3$ in the presence of **2** or **3**. The polymerization mixture remained white and milky under stirring[18] throughout the reaction, in contrast to the corresponding systems without surfactants where the oily monomer was dispersed as nearly transparent droplets at first and then the produced polymers precipitated as they formed.[7]

Tetramethylammonium chloride (**4**), which carries shorter alkyl groups and is thus less surface active, did not afford a stable emulsion.

As shown in Figure 1, the polymerizations proceeded smoothly even in the presence of **2** and **3**. Interestingly both surfactants accelerated the polymerizations, in sharp contrast to the conventional living cationic polymerization in anhydrous solvents where the added ammonium salts decreased the Lewis acidity of the activator and then retarded the polymerization. For example, tetrabutylammonium chloride (n-Bu$_4$NCl) should be added to decrease or modify the Lewis acidity of SnCl$_4$ for the living cationic polymerization of vinyl ethers or styrene derivatives with HCl/SnCl$_4$.[19,20] On the other hand, **4**, which did not form a stable emulsion, did not affect the rate of the polymerization.

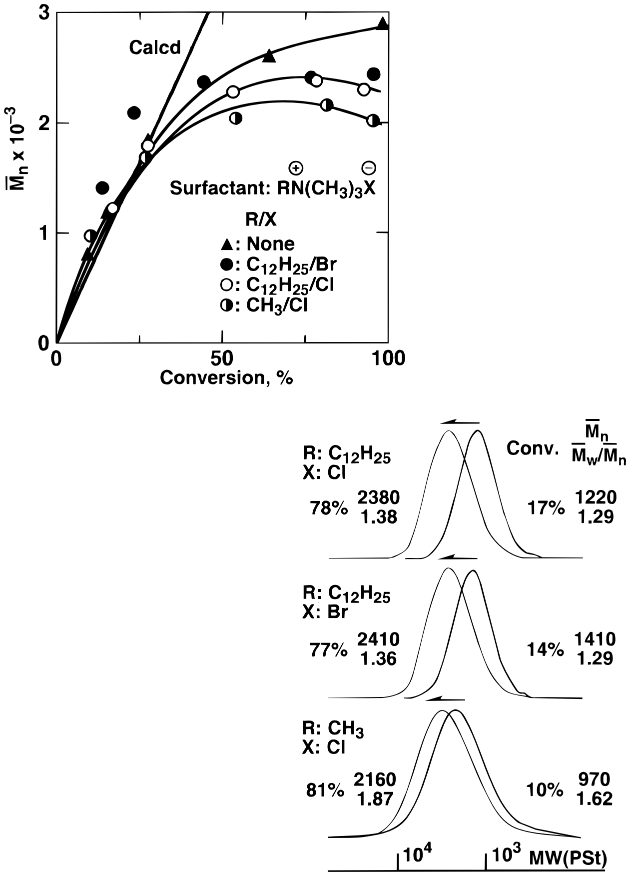


Figure 2. M_n, M_w/M_n and MWD curves of poly(pMOS) obtained in the same experiments as for Figure 1. Ammonium salt: (●) **2**; (○) **3**; (◑) **4**; (▲) none. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per **1** molecule.

Figure 2 shows M_n and MWD curves of the poly(pMOS) obtained in the presence of these ammonium salts. As in the polymerization without the ammonium salts (filled circles), the M_n of the polymers increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one molecule of **1** generates one polymer chain at the early stage of the polymerizations. The increase leveled off at the later stage, however. The MWDs were unimodal and narrower (M_w/M_n ~ 1.3) than those without the surfactants (M_w/M_n ~ 1.4),[7] whereas less surface active **4** afforded the polymers with broader MWDs (M_w/M_n ~ 1.8). These results indicate that the cationic surfactants are effective for the long-lived polymerization of pMOS with the **1**/Yb(OTf)$_3$ system in aqueous media.

The polymerizations most probably proceed in the organic phase, where the C−Cl bonds of **1** or at the polymer growing ends are reversibly activated to generate carbocationic species by a small amount of Yb(OTf)$_3$ transferred from the aqueous phase (Scheme 3). Thus, Yb(OTf)$_3$ enters into the micelles on the organic phase from the aqueous phase similar to the initiating radical

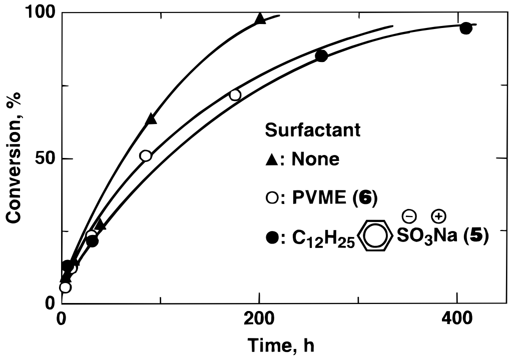
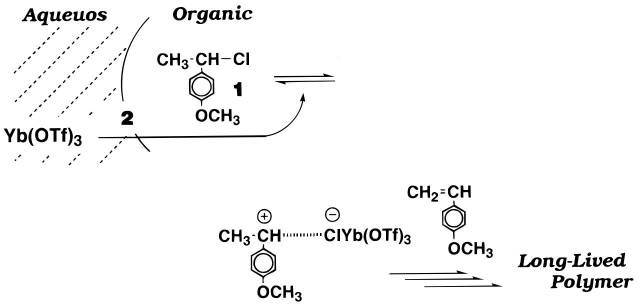


Figure 3. Time–conversion curves of the polymerization of pMOS with **1**/Yb(OTf)$_3$ in water at 30 °C in the presence of surfactants: [pMOS]$_0$ = 3.0 M; [**1**]$_0$ = 60 mM; [Yb(OTf)$_3$]$_0$ = 300 mM; [surfactant]$_0$ = 100 mM. Surfactant: (●) **5**; (○) **6**; (▲) none.

Scheme 3



in emulsion radical polymerization born in the aqueous phase. However, in this cationic case, the polymer chain is generated from **1** in the organic phase via activation of its C–Cl bond with Yb(OTf)$_3$. The molecular weights of the polymers are, therefore, mainly controlled by the ratio of the monomer to **1**, as suggested by Figure 2.

The propagation may also occur via activation of C–OH bond generated from the reaction of the carbocationic species and water. The possibility is less likely because we observed that the adduct of water and pMOS [CH$_3$CH(OH)(4-MeOPh)] did not work as an efficient initiator in conjunction with Yb(OTf)$_3$ under these conditions. However, it cannot be totally excluded because the cation generated from the C–Cl species and Yb(OTf)$_3$ can activate the C–OH bond.

The surfactants increase the surface area of droplets to facilitate the transfer of Yb(OTf)$_3$ into the organic phase, leading to the faster polymerization and the narrow MWDs accordingly. The added salts may also serves as phase transfer agents that help Yb(OTf)$_3$ to enter into the organic phase from the aqueous phase. This equally results in the increase of the concentration of Yb(OTf)$_3$ in the organic phase, which induces the faster polymerization. Furthermore, the interaction between Yb(OTf)$_3$ and these surfactants effects the reversible conversion of the active carbocation to the dormant state, which may make the MWDs of the resultant polymer narrower. The narrower MWDs may be also due to the formation of stable emulsion.

(b) Anionic or Nonionic Surfactants. Other kinds of surfactants were also examined for the pMOS polymerization with **1**/Yb(OTf)$_3$ (Figure 3). As an anionic surfactant, laurylbenzenesulfonic acid sodium salt (**5**)[10,21] was employed for the pMOS polymerization with **1**/Yb(OTf)$_3$ in water at 30 °C. As a nonionic surfactant, poly(vinyl methyl ether) (PVME) (**6**: M_n = 35 800; M_w/M_n = 1.21) prepared by living cationic polymerization[8] was used, because surfactants with active protons such as poly(vinyl alcohol) may trigger side reactions such as chain-transfer.[7] In the presence of these surfactants, polymerizations also proceeded smoothly in water with **1**/Yb(OTf)$_3$. In sharp contrast to the cationic surfactants (**2** and **3**), the polymerizations with **5** or **6** proceeded slower than that without surfactants although they formed apparently similar stable emulsion. These results were probably due to the basic nature of these surfactants, which may reduce the acidity of Yb(OTf)$_3$.

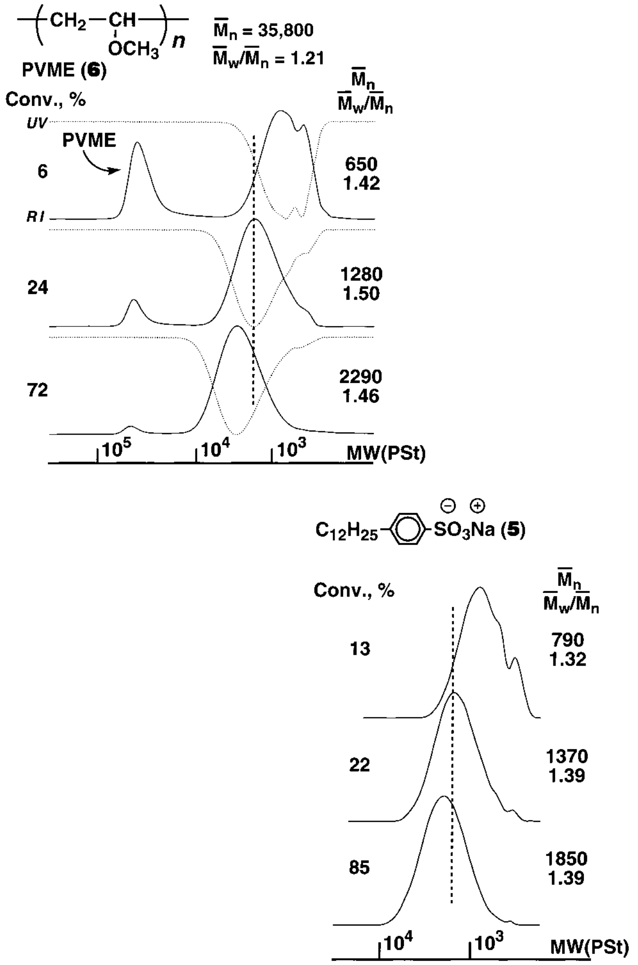


Figure 4. M_n, M_w/M_n and MWD curves of poly(pMOS) obtained in the same experiments as for Figure 3.

Despite the retardation, the anionic or nonionic surfactants gave long-lived polymers. Figure 4 shows the M_n and the MWDs of the polymers thus obtained in the presence of **5** and **6**. The M_n of the polymers also increased with monomer conversion and the MWDs were relatively narrow ($M_w/M_n \sim 1.4$), although the M_n values were lower than those with **2** and **3**. These results suggest that in polymerization of pMOS with **1**/Yb(OTf)$_3$ all of the surfactants, regardless of their nature, do not crucially affect the long-lived nature of the growing end and that the terminal C–Cl bonds survive even in the presence of basic surfactants in water.

2. Effects of Rare Earth Metals. To investigate the effects of the central metals, a series of rare earth triflates [Ln(OTf)$_3$; Ln = Sc, Dy, Sm, Gd, and Nd] were employed for the polymerization in conjunction with **1**. Chart 1 illustrates the periodical table of rare earth metals and shows their ionic radii and electronic

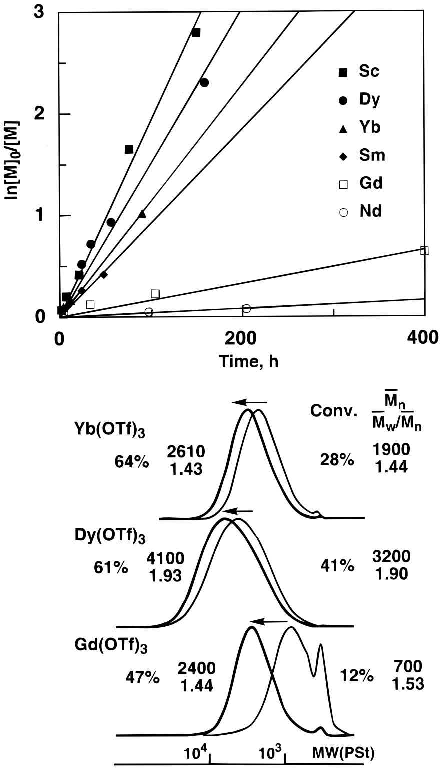
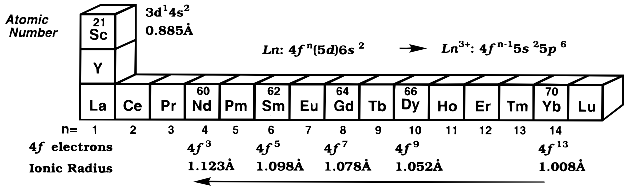


Figure 5. First-order plots and MWD curves for the pMOS polymerization by **1**/Ln(OTf)$_3$ in water at 30 °C: $[\text{pMOS}]_0 = 3.0$ M; $[\mathbf{1}]_0 = 60$ mM; $[\text{Ln(OTf)}_3]_0 = 300$ mM. Ln: (■) Sc; (●) Dy; (▲) Yb; (◆) Sm; (□) Gd; (○) Nd.

Chart 1



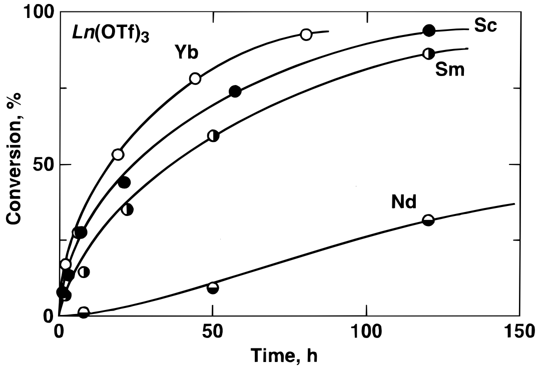


Figure 6. Time–conversion curves of the polymerization of pMOS with **1**/Ln(OTf)$_3$ in water at 30 °C in the presence of **2**: $[\text{pMOS}]_0 = 3.0$ M; $[\mathbf{1}]_0 = 60$ mM; $[\text{Ln(OTf)}_3]_0 = 300$ mM; $[\mathbf{2}]_0 = 100$ mM. Ln: (○) Yb; (●) Sc; (◑) Sm; (◒) Nd.

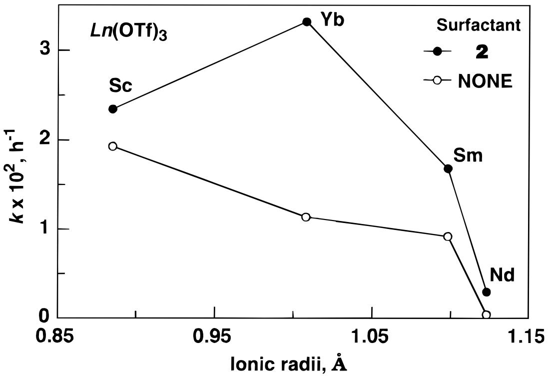


Figure 7. First-order rate constant k for the polymerization of pMOS with **1**/Ln(OTf)$_3$ in water at 30 °C in the absence (○) or the presence (●) of **2**; data from Figures 5 and 6. The horizontal axis is the ionic radii of the central rare earth metal.

orbits.[22] Generally, the acidity of a metal compound depends on the central metals, and it increases as the ionic radius of the metal decreases.

With these Ln(OTf)$_3$ coupled with **1** at 30 °C in water, polymerizations of pMOS was first carried out in the absence of surfactants, where the reagent concentrations were as follows: $[\text{pMOS}]_0 = 4.8$ M and $[\mathbf{1}]_0 = 96$ mM in the organic phase; $[\text{Ln(OTf)}_3]_0 = 800$ mM in the aqueous phase. Quantitative and efficient polymerizations occurred smoothly with most of triflates except Gd and Nd, whereas the polymerization rate remarkably depended on the central metals (Figure 5). In particular, Sc(OTf)$_3$, whose central metal has the smallest ionic radius among them, induced the fastest polymerization, and Nd(OTf)$_3$, with the largest radius, gave no polymers. The M_n of the polymers thus obtained increased with monomer conversion at the early stage in the polymerization, similar to those with Yb(OTf)$_3$. However, some differences in the MWDs were observed. This is probably due to the rate of the interconversion between the dormant and the active species depending on Ln.

Polymerizations with the cationic surfactant **2** were also investigated with **1**/Ln(OTf)$_3$ in water at 30 °C. Emulsion polymerizations took place smoothly with all the triflates (Figure 6). Similar to the polymerization with Yb(OTf)$_3$, the addition of **2** accelerated the polymerizations. Interestingly, Nd(OTf)$_3$, which was ineffective without surfactants, induced pMOS polymerization in the presence of **2**. These results also suggest that **2** can play the role of an emulsifier or a phase transfer agent that helps Ln(OTf)$_3$ to enter into the organic phase to generate carbocationic species via the activation of the dormant polymer terminal.

Figure 7 shows the relationships between the ionic radii of Ln and the apparent first-order rate constants of polymerizations with and without surfactants. The constants highly depend on the central metals and the presence of surfactants. In the absence of **2**, the smaller the ionic radius of Ln, the faster the polymerization proceeded, because the Lewis acidity is generally determined by the ionic radii of the central metals. With all Ln(OTf)$_3$, the polymerizations in water were clearly accelerated by the addition of **2**. The acceleration was largest with Yb(OTf)$_3$ and smallest with Sc(OTf)$_3$. These were probably due to the difference in the coordination number of Ln(OTf)$_3$: Yb(OTf)$_3$ and other lanthanide triflates have high coordination numbers (9–12) because of their 4f orbits, which can interact loosely with basic compounds, in contrast to Sc(OTf)$_3$ without an f orbital.

Figure 8 compares the MWDs of the polymers obtained via suspension and emulsion processes with **1**/Ln(OTf)$_3$. The polymers exhibit narrower MWDs ($M_w/M_n = 1.3$–1.5) in the presence of **2** than those in the absence ($M_w/M_n = 1.4$–3.7). These results indicates that **2** is an effective surfactant for the pMOS polymerizations in water not only with Yb(OTf)$_3$ but also with other Ln(OTf)$_3$ to accelerate the polymerization and make MWDs of the polymers narrower.

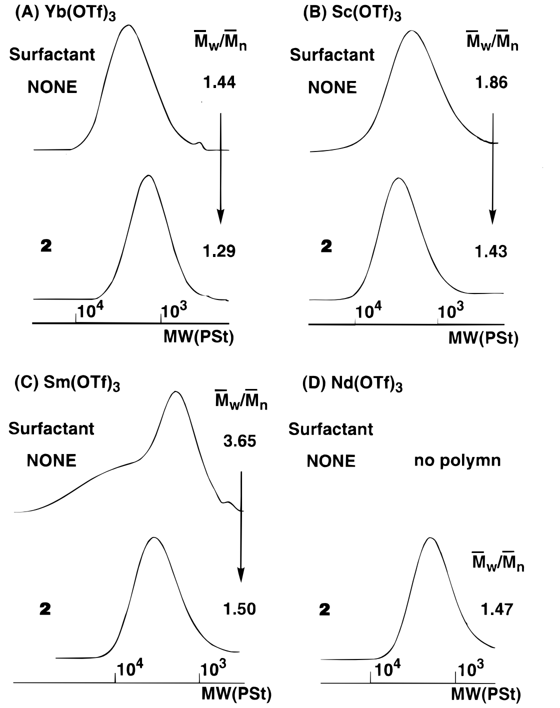


Figure 8. M_w/M_n and MWD curves of poly(pMOS) obtained with **1**/Ln(OTf)$_3$ in water at 30 °C in the absence or the presence of **2**: [pMOS]$_0$ = 3.0 M; [**1**]$_0$ = 60 mM; [Ln(OTf)$_3$]$_0$ = 300 mM; [**2**]$_0$ = 100 mM. Ln: (A) Yb; (B) Sc; (C) Sm; (D) Nd.

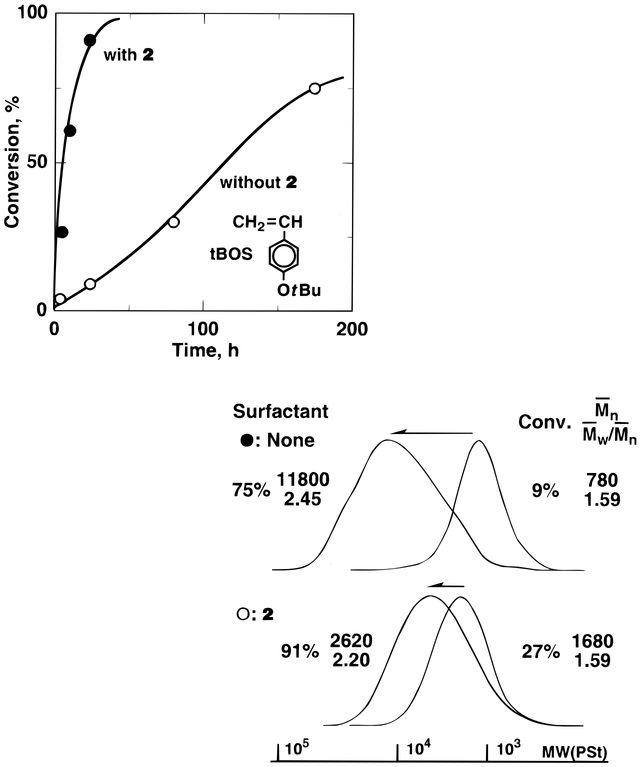


Figure 9. Time–conversion, M_n, M_w/M_n and MWD curves of poly(tBOS) obtained with **1**/Yb(OTf)$_3$ in water at 30 °C in the absence (○) or the presence (●) of **2**: [tBOS]$_0$ = 3.0 M; [**1**]$_0$ = 60 mM; [Yb(OTf)$_3$]$_0$ = 300 mM; [**2**]$_0$ = 100 mM.

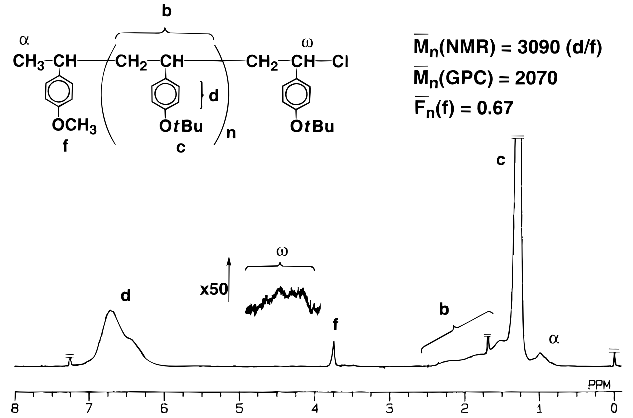
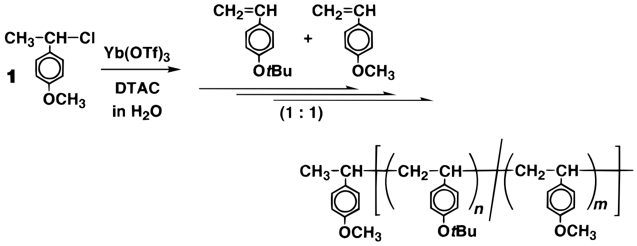


Figure 10. ^{1}H NMR spectra of poly(tBOS) (M_n = 3090, M_w/M_n = 2.00) obtained with **1**/Yb(OTf)$_3$ in water at 30 °C in the presence of **2**: [tBOS]$_0$ = 3.0 M; [**1**]$_0$ = 60 mM; [Yb(OTf)$_3$]$_0$ = 300 mM; [**2**]$_0$ = 100 mM.

Scheme 4



3. Polymerization of tBOS. The homopolymerizations of tBOS under the suspension (without surfactants) and the emulsion (with **2**) conditions were performed with **1**/Yb(OTf)$_3$ in water at 30 °C (Figure 9). In the absence of surfactants, the polymerization proceeded slightly slower than that of pMOS, and the addition of **2** similarly accelerated the polymerization of tBOS. Thus, tBOS was also polymerized in water, although the polymerization was less controllable than that of pMOS. The M_n of the poly(tBOS) increased with monomer conversion, which suggested the long-lived nature of the growing polymer terminal. However, the MWDs obtained without **2** became broader at the later stage of the polymerization, where higher M_n was also observed. This indicates some side reactions, probably caused by the pendant *tert*-butoxy group under aqueous acidic condition. The side reaction can be suppressed by the addition of **2**.

The terminal structure of the poly(tBOS) obtained in water was examined by ^{1}H NMR spectroscopy (Figure 10). The sample [with Yb(OTf)$_3$ and **2**] gave characteristic signals of poly(tBOS): i.e., *tert*-butoxy groups (c), phenyl groups (d), and main-chain aliphatic protons (b). In addition to these large signals, small signals due to the end groups appeared. They are the CH$_3$– (α; 1.0 ppm) and the *p*-CH$_3$O– (f; 3.7 ppm) groups at the α-end and the –CH–Cl (*ω*; 4.3 ppm) groups at the *ω*-end, which are originally from the HCl adduct of pMOS (**1**) as an initiator. This indicates that the polymerization is really initiated from **1** via generation of cationic species. However, the functionality of the α-end methoxy group (f) was 0.67, lower than unity. This reveals the existence of chain transfer during the polymerization to generate new polymer chains without the initiator moiety.

Random copolymerization of tBOS and pMOS was examined (Scheme 4). Equimolar amounts of tBOS and pMOS were polymerized with **1**/Yb(OTf)$_3$ in the presence of **2** in water at 30 °C (Figure 11). Polymerizations of both monomers occurred smoothly and almost simultaneously where pMOS was consumed slightly faster than tBOS. The M_n of the polymer thus obtained also

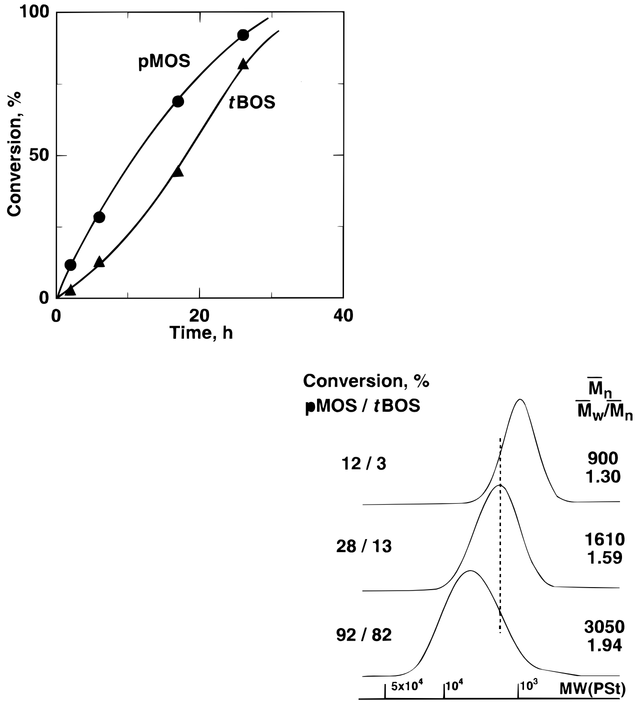


Figure 11. Time−conversion and MWD curves in the tBOS-pMOS random copolymerization with **1**/Yb(OTf)$_3$ in water at 30 °C in the presence of **2**: [tBOS]$_0$ = 1.5 M; [pMOS]$_0$ = 1.5 M; [**1**]$_0$ = 60 mM; [Yb(OTf)$_3$]$_0$ = 300 mM; [**2**]$_0$ = 100 mM.

increased with the consumption of monomers, although the molecular weight distributions (MWDs) became broader as the copolymerization proceeded. Thus, random emulsion copolymerization of tBOS and pMOS was possible with **1**/Yb(OTf)$_3$ in water.

In conclusion, emulsion cationic polymerization of pMOS in water was achieved with the **1**/Ln(OTf)$_3$ initiating system in the presence of surfactants. In particular, cationic surfactants such as dodecyltrimethylammonium halides had some advantages over anionic and nonionic ones in the rate of polymerization and the MWDs of the product polymers. The use of such surfactants will possibly lead to precisely sized particles via emulsion cationic polymerization in water. tBOS can also be polymerized in water with the **1**/Yb(OTf)$_3$ system, which also permitted random copolymerization with pMOS.

Experimental Section

Materials. pMOS (Aldlich; purity 97%) was dried overnight over calcium chloride, distilled over calcium hydride under reduced pressure, and stored at −80 °C. tBOS (Hokko Chemicals) was distilled twice over calcium hydride under reduced pressure and stored at −80 °C. Rare earth triflates [Ln(OTf)$_3$; Ln = Yb, Sc, Dy, Gd, Sm, Nd] (Aldlich) were obtained commercially and used as received. Dodecyltrimethylammonium chloride (Tokyo Kasei; purity > 97%) and bromide (Tokyo Kasei; purity > 99%), laurylbenzenesulfonic acid sodium salt (Tokyo Kasei; purity > 95%), and tetramethylammonium chloride (Wako Chemical; purity > 98%) were used as received after drying under vacuum at room temperature. PVME was prepared by the living cationic polymerization of methyl vinyl ether with the HCl/SnCl$_4$/n-Bu$_4$NCl system in CH$_2$Cl$_2$ at −78 °C.[8] The pMOS−HCl adduct (**1**) was prepared by bubbling dry HCl gas into 1.0 M solution of pMOS at 0 °C, and then dry nitrogen was bubbled to remove excess HCl. Bromobenzene as an internal standard for gas chromatography was dried overnight over calcium chloride, doubly distilled over phosphorus pentoxide and then over calcium hydride before use.

Polymerization Procedures. Polymerization was carried out by the syringe technique under air in glass tubes equipped with a screw cap. A typical example for pMOS polymerization is given below. The polymerization was initiated by adding solution of the pMOS−HCl adduct (**1**) (in CCl$_4$; 0.20 mL) into an aqueous monomer emulsion in the aqueous solution of Yb(OTf)$_3$ and **2** (1.4 mL) containing pMOS (0.65 mL) and bromobenzene (0.15 mL) (see text). The total volume of the reaction mixture was thus 1.6 mL. The reaction was run under vigorous stirring and was terminated with methanol and with excess water and toluene. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with bromobenzene as an internal standard. The polymer was extracted with toluene, washed with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymer.

Measurements. The MWD, M_n, and M_w/M_n values of the polymers were measured in chloroform eluent at 40 °C on three polystyrene gel columns (Shodex K-805L × 3) that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index and 970-UV ultraviolet detectors. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemicals; M_n = 580−1 547 000; M_w/M_n < 1.1) as well as the styrene monomer. ^{1}H NMR spectra were recorded in CDCl$_3$ at 25 °C on a JEOL JNM-GSX270 spectrometer, operating at 270.7 MHz. Polymers for ^{1}H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002).

References and Notes

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(18) The resultant emulsion was not stable and underwent phase separation when it standed without stirring for a long period. This is probably due to the relatively low viscosity of the particles by the presence of CCl_4, which originated from the solvent for **1**. The compound is difficult to isolate because of its low stability under reduced pressure.

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