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Metal Triflates and Tetrafluoroborates as Water-Tolerant Lewis Acids for Cationic Polymerization in Aqueous Media[1]

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ABSTRACT: Metal triflates or tetrafluoroborates, such as $Zn(OTf)_2$, $Cu(OTf)_2$, $Sn(OTf)_2$, and $Zn(BF_4)_2$ ($OTf = -OSO_2CF_3$), were employed as water-tolerant Lewis acids for the emulsion cationic polymerization of *p*-methoxystyrene (pMOS) in heterogeneous aqueous media. All these metal compounds, in addition to rare earth metal triflates such as $Yb(OTf)_3$ already reported by us, induced the polymerization of pMOS in conjunction with the pMOS−HCl adduct (**1**) (initiator) and dodecyltrimethylammonium chloride (surfactant) at 30 °C in water. The pMOS polymerization was controlled, where the molecular weights of the polymer increased with monomer conversion and the molecular weight distributions were relatively narrow ($M_w/M_n \sim 1.4$). ^1H NMR analysis of the obtained polymers showed that the chlorine atom originating from **1** was attached to the growing polymer terminal. In addition, the water tolerance of these catalysts was confirmed by ^{19}F NMR analysis. Thus, the emulsion cationic polymerization proceeds via reversible activation of the C−Cl terminal mediated by the water-tolerant Lewis acid, which enters from the aqueous phase into the organic phase.

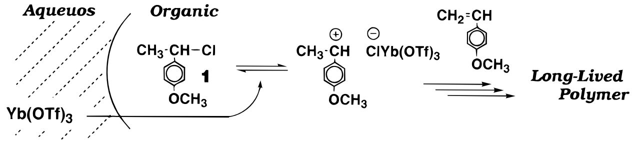
Introduction

Water is evidently the most abundant and environmentally friendly solvent and has the industrial advantages that it can be used in large amounts without hazardous wastes.[2] However, water easily decomposes ionic intermediates as well as metal compounds that catalyze ionic reactions, and thus it has rarely been employed as a reaction medium for organic reactions except for radical reactions like suspension or emulsion radical polymerization. Irrespective of these facts, water-based reactions are of interest, particularly as environmentally benign processes.[3] One of the important developments in this area is that water-tolerant Lewis acids, mostly rare earth metal triflates [$Ln(OTf)_3$; Ln = Yb, Sc, Sm, etc.; $OTf = OSO_2CF_3$], effectively induce Diels−Alder reactions, aldol condensations, Michael additions, etc., even in aqueous media.[4−7]

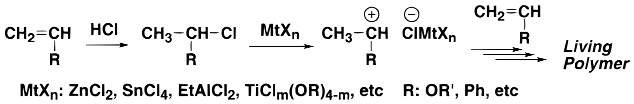
We have found that $Ln(OTf)_3$ can mediate cationic polymerization of *p*-methoxystyrene (pMOS) even in heterogeneous aqueous media with the pMOS−HCl adduct (**1**) as an initiator (Scheme 1).[8] The dispersion polymerizations were fairly controlled, where the number-average molecular weights (M_n) increased with monomer conversion, and the molecular weight distributions (MWDs) were relatively narrow ($M_w/M_n \sim 1.4$). Furthermore, the **1**/$Ln(OTf)_3$-mediated polymerization was improved by the addition of cationic surfactants such as dodecyltrimethylammonium halides, which accelerated the pMOS polymerization in water and made the MWDs of the resultant poly(pMOS) narrower.[9]

This novel aqueous cationic polymerization is based on the two-component initiating systems employed in living cationic polymerization in anhydrous organic solvents, where a protonic acid (HA) or its adduct with a monomer is an initiator and a Lewis acid (MtX_n) is a catalyst that activates the covalent dormant linkage in the initiator or at the polymer terminal into a carbocationic species (Scheme 2).[10−12] A key to the living cationic polymerization lies in the selection of the Lewis acid as well as the initiator so that the former can reversibly activate the covalent polymer terminal derived from the latter. In particular, the Lewis acidity should be controlled by the central metal and its substituents,[13,14] and the effective Lewis acids include the halides and alkoxides of Zn,[15] Al,[16] Sn(II),[17] Sn(IV),[18] Ti,[19] and B.[20]

Scheme 1



Scheme 2



The requisites for controlled cationic polymerization in water, however, are not only to meet these for the living cationic polymerization in organic solvents but also to use water-tolerant Lewis acids.[8,9] They should be stable in aqueous media, and thus elude decomposition, and should reversibly activate dormant polymer terminals. Most of the water-tolerant Lewis acids thus far employed for organic reactions are lanthanide triflates (except for a few compounds of copper, zinc, and others),[21,22] because other Lewis acids are highly moisture sensitive.

In this paper, therefore, we employed a series of metal triflates other than lanthanides for the emulsion cationic polymerization of pMOS in water and examined the effects of the central metals on the polymerization and on the stability in water (Scheme 3). We also herein found that a metal tetrafluoroborate [$Zn(BF_4)_2$] is also water-tolerant and can be used for emulsion cationic polymerization.

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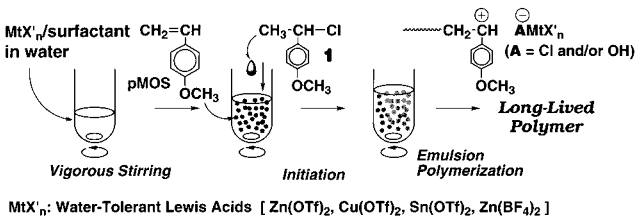
Scheme 3



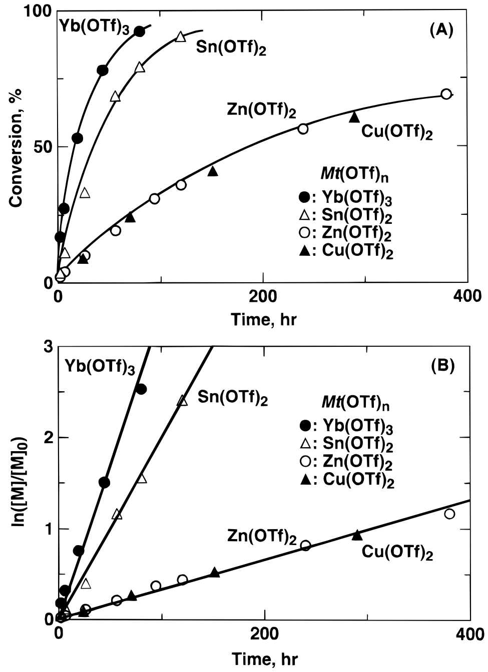


Figure 1. Time−conversion curves (A) and first-order plots (B) for the polymerization of pMOS with **1**/Mt(OTf)$_n$ in water at 30 °C in the presence of DTAC: $[\text{pMOS}]_0 = 3.0$ M; $[\mathbf{1}]_0 = 60$ mM; $[\text{Mt(OTf)}_n]_0 = 300$ mM; $[\text{DTAC}]_0 = 100$ mM. Mt: (●) Yb; (△) Sn; (○) Zn; (▲) Cu.

Results and Discussion

Polymerization of pMOS. Two-valent metal triflates [Sn(OTf)$_2$, Zn(OTf)$_2$, and Cu(OTf)$_2$] were employed as Lewis acids for the emulsion cationic polymerization of pMOS in water. pMOS was polymerized with the combination of these triflates and the adduct **1** as an initiator in water (aqueous/organic phase = 3/5) at 30 °C in the presence of dodecyltrimethylammonium chloride (DTAC) as a surfactant: $[\text{pMOS}]_0 = 4.8$ M and $[\mathbf{1}]_0 = 96$ mM in the organic phase; $[\text{Mt(OTf)}_n]_0 = 800$ mM and $[\text{DTAC}]_0 = 267$ mM in the aqueous phase. Regardless of the central metal (Mt) in the triflates, pMOS emulsion polymerization occurred smoothly without an induction period. The reaction rate critically depended on the metals (Yb > Sn > Zn ~ Cu), mainly because of the difference in Lewis acidity (Figure 1A). The lower activity of Cu(II) and Zn(II) was also reported in the Lewis-acid-catalyzed aldol reactions in aqueous media.[22] The linear first-order plots indicate almost no irreversible termination and no loss of activity of the catalysts during the polymerization (Figure 1B).

These catalysts afforded polymers of controlled molecular weights and molecular weight distributions (MWDs), as did Yb(OTf)$_3$.[8] Figure 2 shows M_n and MWD curves of the poly(pMOS) produced in water. During the early stage of the polymerization, the M_n increased in direct proportion to monomer conversion, although the increase of M_n leveled off at the late stage due to chain-transfer reaction. The MWDs were unimodal and relatively narrow ($M_w/M_n = 1.2-1.4$) throughout the polymerization. These results indicate that metal triflates other than rare earth metal derivatives can induce controlled emulsion cationic polymerization of pMOS even in the presence of a large amount of water. However, Sn(OTf)$_2$ caused gelation of the reaction mixture and formation of low molecular weight oligomers at the late stage of the polymerization. This suggests that it is unstable and decomposed by water via some side reactions.

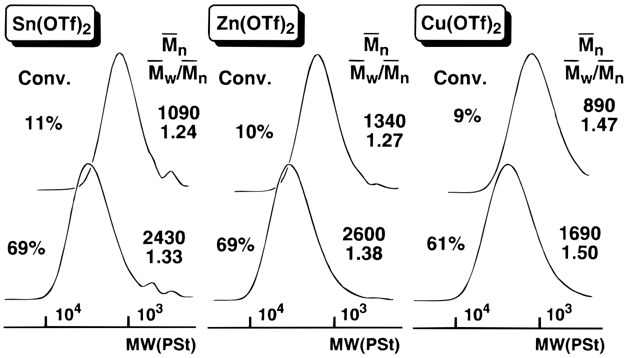


Figure 2. M_n, M_w/M_n, and MWD curves of poly(pMOS) obtained in the same experiments as for Figure 1.

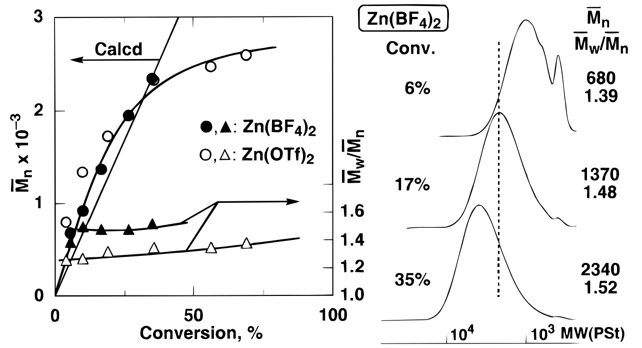


Figure 3. M_n, M_w/M_n, and MWD curves of poly(pMOS) obtained with **1**/Zn(BF$_4$)$_2$ or Zn(OTf)$_2$ in water at 30 °C in the presence of DTAC: $[\text{pMOS}]_0 = 3.0$ M; $[\mathbf{1}]_0 = 60$ mM; $[\text{Lewis acid}]_0 = 300$ [for Zn(OTf)$_2$], 600 [for Zn(BF$_4$)$_2$] mM; $[\text{DTAC}]_0 = 100$ mM. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per **1** molecule.

Another possible water-tolerant Lewis acid is Zn(BF$_4$)$_2$, which has the strongly electron-withdrawing tetrafluoroborate (BF$_4$). The zinc salt was thus employed as a Lewis acid for the pMOS polymerization in the presence of DTAC in water at 30 °C. The pMOS polymerization with **1**/Zn(BF$_4$)$_2$ was much slower than that with **1**/Zn(OTf)$_2$, where conversion reached only 35% in 150 h, even with a higher concentration of the catalyst (1.6 M in aqueous phase). The slower polymerization is probably because of the lower Lewis acidity of Zn(BF$_4$)$_2$.

During the early stage of the polymerization, the M_n of the polymers obtained with Zn(OTf)$_2$ and Zn(BF$_4$)$_2$ increased in direct proportion to monomer conversion and were in good agreement with the calculated values on the assumption that one polymer chain forms per one initiator **1** molecule (Figure 3). However, the M_n values were lower than the calculated in the later stage of the polymerization, suggesting some chain-transfer reaction. These results show that metal tetrafluoroborate is also an effective Lewis acid for cationic

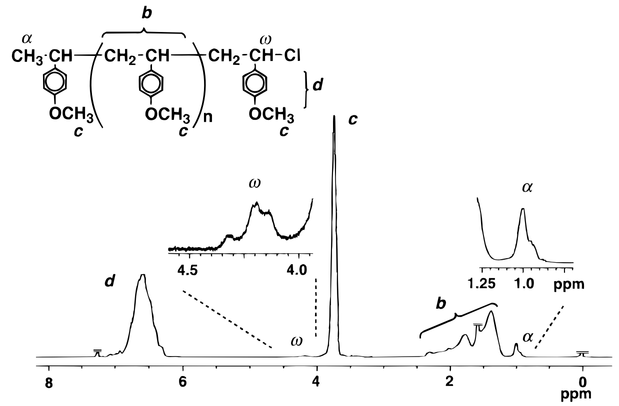


Figure 4. ^{1}H NMR spectrum of poly(pMOS) ($M_n = 3380$, $M_w/M_n = 1.23$) obtained with **1**/Zn(BF_4)$_2$ in water at 30 °C in the presence of DTAC: $[\text{pMOS}]_0 = 3.0$ M; $[\mathbf{1}]_0 = 60$ mM; $[\text{Zn}(BF_4)_2]_0 = 600$ mM; $[\text{DTAC}]_0 = 100$ mM.

Table 1. Poly(pMOS) Obtained with 1/Lewis Acid in Emulsion Polymerization[a]

				F_n	
Lewis acid	time, h	conv, %	M_n (SEC)	$CH_3{}^{\alpha-b}$	$-CH^{\omega}-Cl^{c}$
Yb(OTf)$_3$	6	38	2780	1.22	0.37
Zn(OTf)$_2$	94	31	2890	1.14	0.44
Sn(OTf)$_2$	24	33	2740	1.22	0.35
Zn(BF$_4$)$_2$	100	27	3380	1.20	0.56

[a] $[\text{M}]_0/[\mathbf{1}]_0/[\text{Lewis acid}]_0/[\text{DTAC}]_0 = 3000/60/300$ [for Mt(OTf)$_n$] or 600 [for Zn(BF$_4$)$_2$]/100 mM, in water, at 30 °C. [b] M_n(NMR)/M_n(SEC): M_n(NMR) was determined by the peak intensity ratio of α and *c*; see Figure 4. [c] M_n(NMR)/M_n(SEC): M_n(NMR) was determined by the peak intensity ratio of *ω* and *c*.

polymerization in water to give long-lived polymers of pMOS.

Polymer Analysis. The terminal structures of the polymers obtained with **1**/Mt(OTf)$_n$ or Zn(BF$_4$)$_2$ were examined by ^{1}H NMR spectroscopy. Figure 4 shows the ^{1}H NMR spectrum of the polymer produced by **1**/Zn(BF$_4$)$_2$ coupled with DTAC in water. The sample exhibited characteristic signals of poly(pMOS); i.e., the methoxy groups (c), the phenyl groups (d), and the main-chain aliphatic protons (b). It showed an additional small absorption at 1.0 ppm (α) ascribed to the methyl protons (C*H*$_3$−), probably derived from the initiator **1**, and another at 4.1 ppm (*ω*) for the methine proton (−C*H*−Cl) adjacent to the chlorine at the *ω*-end.[9] The polymers obtained with **1**/Mt(OTf)$_n$ showed similar spectra. Table 1 summarizes the functionalities of these α- and *ω*-groups (pMOS conversion ∼ 30%). Whereas the functionalities of the CH$_3$ group are almost unity ($F_n = 1.1-1.2$) in all cases, those of the chlorine groups are lower than unity, which suggests some chain-transfer reaction as also indicated by the molecular weights lower than the calculated values. Survival of the terminal chlorine in the polymers clearly depends on Lewis acids, where Zn(BF$_4$)$_2$ provides the highest C−Cl functionality. These results suggest that the proper selection of metal centers and substituents in Lewis acids might lead to water-based living cationic polymerization.

^{19}F NMR Analysis: Water Tolerance of Lewis Acids. The polymerization most probably proceeds via the Lewis acid-mediated activation of carbon−halogen bonds. However, there is a possibility that the Lewis acids may hydrolyze into protonic acids such as CF_3SO_2H and HBF_4, which may catalyze the observed cationic polymerization. To confirm their tolerance toward water, ^{19}F NMR analysis of Zn(OTf)$_2$, Yb(OTf)$_3$, and Zn(BF$_4$)$_2$ was thus carried out in water/THF mixture at 30 °C (Figure 5).

Even in the presence of water, Zn(OTf)$_2$ exhibited the same single absorption at −80.31 ppm as in anhydrous THF (Figure 5A). This signal was different from the corresponding peak of trifluoromethanesulfonic acid (−80.34 ppm), which would form via hydrolysis of Zn(OTf)$_2$. As shown in Figure 5B, Yb(OTf)$_3$ exhibited a fairly broad signal (centered at −75.75 ppm) in anhydrous THF probably due to as aggregated or polymeric structure. Upon addition of water, the peak was remarkably sharpened and shifted upfield to −79.68 ppm. The upfield shift is not due to the hydrolysis of Yb(OTf)$_3$ but due to hydration. The spectra of both triflates remained unchanged after 23 h. These results indicate that these triflates are certainly stable in the presence of water and free from hydrolysis and decomposition.

Similar analysis was carried out for Zn(BF$_4$)$_2$ (Figure 5C). Even in the presence of water, no peaks were observed at −153.3 ppm, where tetrafluoroboronic acid exhibited a signal under the same conditions. However, Zn(BF$_4$)$_2$ apparently decomposed after the hydrate salt had been vacuum-dried at 200 °C for 6 h,[23,24] where some undefined peaks and the peak of tetrafluoroboronic acid appeared. This indicates that Zn(BF$_4$)$_2$ is water-tolerant, but it is thermally less stable than lanthanide triflates.

In conclusion, Sn, Zn, and Cu triflates and tetrafluoroborates, along with rare earth salts,[8,9] are effective as activators (Lewis acids) for emulsion cationic polymerization of pMOS in water and afford polymers with controlled molecular weights. The polymerization proceeds via the Lewis-acid-catalyzed reversible activation of the carbon−halogen polymer terminal into carbocationic growing species.

Experimental Section

Materials. pMOS (Aldrich, 97%) was dried overnight over calcium chloride, distilled from calcium hydride under reduced pressure, and stored at −80 °C. Yb(OTf)$_3$·xH$_2$O ($x = 1-2$) and Zn(BF$_4$)$_2$·xH$_2$O ($x = 6-7$) (both Aldrich, 99%) were commercially obtained as hydrates and used as received. Sn(OTf)$_2$ (Aldrich, 97%), Zn(OTf)$_2$ (Aldrich, 97%), and Cu(OTf)$_2$ (Tokyo Kasei, 98%) were also used as received. Dodecyltrimethylammonium chloride (DTAC) (Tokyo Kasei, 97%) was used after drying a commercial product under vacuum at room temperature. The pMOS−HCl adduct (**1**) was prepared by bubbling dry HCl gas into 1.0 M CCl$_4$ solution of pMOS at 0 °C, and then dry nitrogen was bubbled to remove excess HCl.[25] The complete conversion of pMOS into **1** was confirmed by ^{1}H NMR; no residual HCl or pMOS was detected. Bromobenzene (Wako, >98%) as an internal standard for gas chromatography and carbon tetrachloride (Wako, >99%) as solvent for **1** were dried overnight over calcium chloride and doubly distilled from phosphorus pentoxide and then from calcium hydride before use.

Measurements. The MWD, M_n, and M_w/M_n values of polymers were measured in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: $10-10^5$ Å; 8.0 mm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] connected to the same pump/detector combination as above. 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-LA 500 spectrometer, operating at 500.16 MHz. ^{19}F NMR spectra were recorded in THF-d_8 or its mixture with water at 30 °C on a JEOL JNM-LA 500 spectrometer, operating at 470.40 MHz.

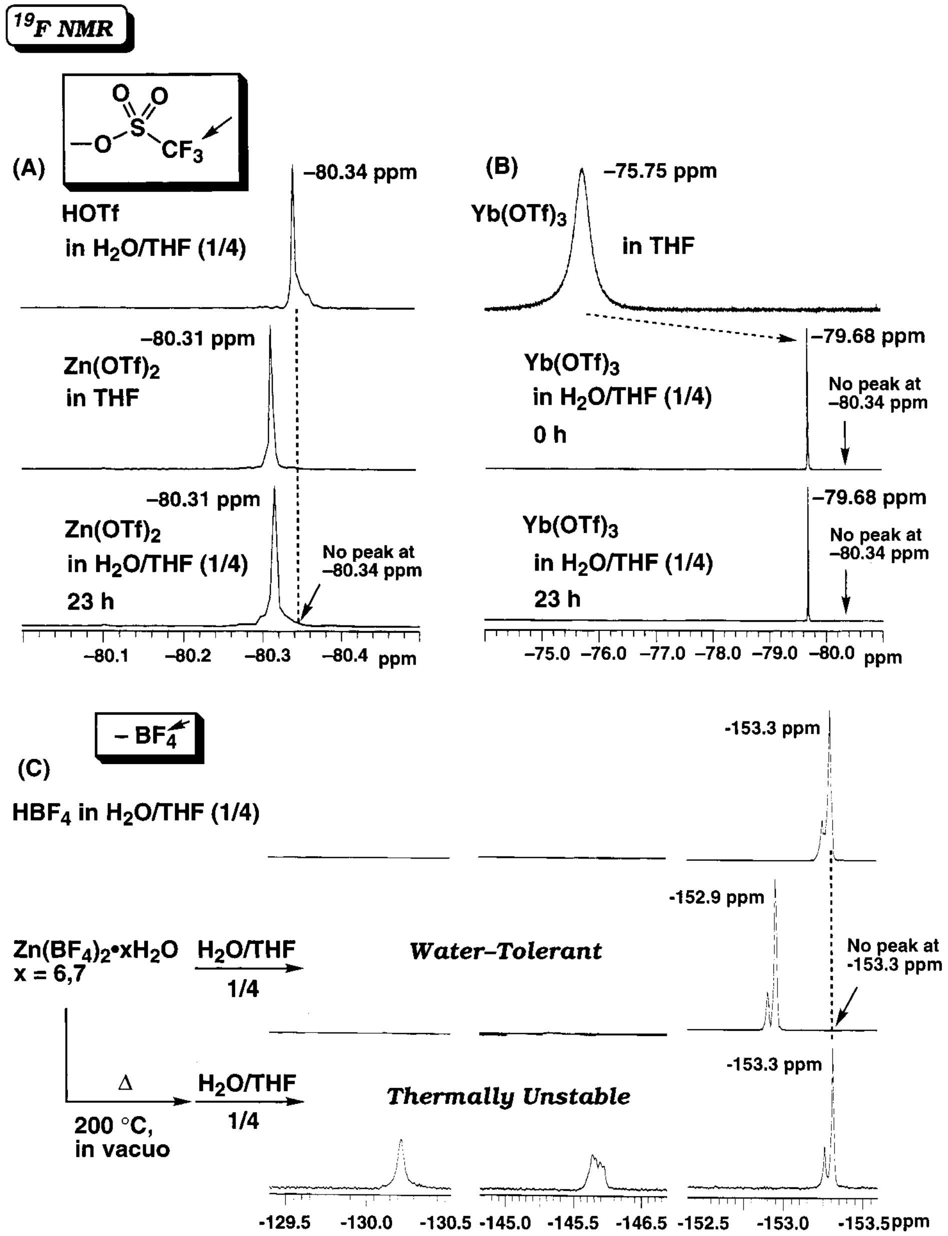


Figure 5. ^{19}F NMR spectra of (A) $Zn(OTf)_2$, (B) $Yb(OTf)_3$, and (C) $Zn(BF_4)_2$. The spectra were recorded at 30 °C in THF-d_8 or its mixture with water (4/1).

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 a solution of the pMOS−HCl adduct (**1**) (0.096 mmol; 0.20 mL of 0.48 M in CCl_4) into an aqueous monomer emulsion in the aqueous solution (1.4 mL) of $Zn(OTf)_2$ (0.48 mmol; 177.4 mg) and DTAC (0.16 mmol; 42.2 mg) containing pMOS (4.8 mmol; 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 and residual surfactant. Products yield were thus higher than those expected from the conversions. Polymer samples for ^1H NMR were isolated by precipitation into *n*-hexane.

References and Notes

(1) This work was presented in part at the following meetings: (a) The 47th Annual Meeting of the Society of Polymer Science, Kyoto, Japan, May 1998; paper I-4-06: Satoh, K.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1998**, *47* (2), 171. (b) The 47th Symposium on *Macromolecules*, Society of Polymer Science, Nagoya, Japan, Oct 1998; paper 1Pf026: Satoh, K.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1998**, *47* (7), 1239. (c) IUPAC International Symposium on Ionic Polymerization, Kyoto, Japan, July 1999; paper C1-212: Satoh, K.; Kamigaito, M.; Sawamoto, M. IP'99 Preprints, p 58. (d) The 218th National Meeting on the American Chemical Society, New Orleans, LA, Aug 1999; POLY 240: Satoh, K.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1999**, *40* (2), 895.

(2) For example, see: *Green Chemistry*; Anastas, P. T., Williamson, T. C., Eds.; ACS Symposium Series 626; American Chemical Society: Washington, DC, 1996.

(3) For example, see: *Aqueous-Phase Organometallic Catalysis*; Cornils, B., Herrmann, W. A., Eds.; Willey-VCH: Weinheim, 1998.

(4) Kobayashi, S. *Synlett* **1994**, 689.

(5) Engberts, J. B. F. N.; Feringa, B. L.; Keller, E.; Otto, S. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 457.
(6) Kobayashi, S. In *Aqueous-Phase Organometallic Catalysis*; Cornils, B., Herrmann, W. A., Eds.; Willey-VCH: Weinheim, 1998; p 519.
(7) Xie, W.; Jin, Y.; Wang, P. G. *CHEMTECH* **1999**, *29* (2), 23.
(8) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3827.
(9) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 4660.
(10) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111.
(11) Kennedy, J. P.; Iván, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser: Munich, 1992.
(12) *Cationic Polymerizations*, Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996.
(13) Kamigaito, M.; Maeda, Y.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1993**, *26*, 2670.
(14) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 5671.
(15) Sawamoto, M.; Okamoto, C.; Higashimura, T. *Macromolecules* **1987**, *20*, 2693.
(16) Aoshima, S.; Higashimura, T. *Polym. Bull.* **1986**, *15*, 417.
(17) Kojima, K.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1989**, *22*, 1552.
(18) Ishihama, Y.; Sawamoto, M.; Higashimura, T. *Polym. Bull.* **1990**, *23*, 361.
(19) Kaszas, G.; Puskas, J. E.; Kennedy, J. P. *Polym. Bull.* **1988**, *20*, 413.
(20) Faust, R.; Kennedy, J. P. *Polym. Bull.* **1986**, *15*, 317.
(21) Otto, S.; Bertoncin, F.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1996**, *118*, 7702.
(22) Kobayashi, S.; Nagayama, S.; Busujima, T. *J. Am. Chem. Soc.* **1998**, *120*, 8287.
(23) The hydrate triflates such as $Yb(OTf)_3$ can be easily vacuum-dried into anhydrous form at 200 °C for 6 h: Kobayashi, S.; Hachiya, I.; Takahori, T. *Synthesis* **1993**, 371.
(24) Satoh, K.; Katayama, H.; Kamigaito, M.; Sawamoto, M. In *Catinoic Polymeriztion: Fundamentals and Applications*; Faust, R., Shaffer, T. D., Eds.; ACS Symposium Series 665; American Chemical Society: Washington, DC, 1997; Chapter 10.
(25) Katayama, H.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 3747.

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