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Registry No. **2**, 83646-11-1; **3**, 124156-68-9; **4**, 124156-69-0; 4-amino-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 14691-88-4.

Living Cationic Polymerization of *p*-Methoxystyrene by the HI/ZnI_2 and HI/I_2 Initiating Systems: Effects of Tetrabutylammonium Halides in a Polar Solvent

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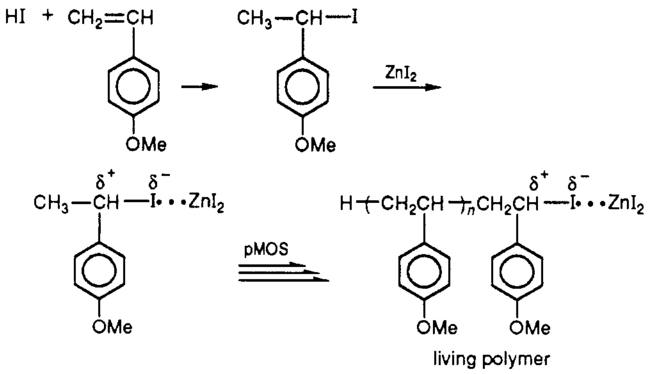
ABSTRACT: The effects of added salts (nBu_4NX; X = I, Br, Cl, ClO_4) on the cationic polymerization of *p*-methoxystyrene (pMOS) by the hydrogen iodide/zinc iodide (HI/ZnI_2) or hydrogen iodide/iodine (HI/I_2) initiating systems were investigated at −15 and +25 °C in methylene chloride (CH_2Cl_2) as a polar solvent. In salt-free CH_2Cl_2, the molecular weight distributions (MWDs) of the polymers were bimodal, where the higher molecular weight polymer peak was nonliving, whereas the lower molecular weight polymer fraction had a long lifetime. When a small amount of nBu_4NI (1.0 mol % to HI) was added in the solvent, the higher polymer fraction was completely eliminated to give polymers with very narrow MWDs ($\bar{M}_w/\bar{M}_n \leq 1.1$) that turned out to be living (at −15 °C with HI/I_2 and even at +25 °C with HI/ZnI_2). The number-average molecular weight ($\bar{M}_n$) of the polymers increased in direct proportion to pMOS conversion, continued to increase upon sequential addition of pMOS feeds, and were in good agreement with the calculated values assuming one living chain per HI. Very similar living polymerizations occurred when nBu_4NBr or nBu_4NCl was employed in place of the iodide salt; however, the use of nBu_4NClO_4 did not effect such a living process at all. It is concluded that through their high nucleophilicity, the added halide anions efficiently eliminate a dissociated nonliving growing species (**1**), thereby selectively permitting living propagation via the nondissociated living counterpart (**2**) (Scheme I).

Introduction

Recently, we have found living cationic polymerization of *p*-methoxystyrene (pMOS) to proceed with the hydrogen iodide/zinc iodide (HI/ZnI_2) initiating system in toluene solvent.[1] This finding permitted the first synthesis of nearly monodisperse styrenic polymers of controlled molecular weights under cationic conditions even at room temperature. A similar but less controlled polymerization of pMOS has been achieved by us using iodine as an initiator in carbon tetrachloride, in which process the growing species also exhibits the living character.[2,3] These living pMOS polymerizations specifically employ nonpolar solvents.

In general, solvent polarity remarkably affects the rate of cationic polymerization and the molecular weight distribution (MWD) of the polymers. For example, the use of a polar solvent usually increases the polymerization rate but renders the propagating carbocations more ionically dissociated and hence less stable than in nonpolar media. It is therefore expected that living cationic polymerization would be more difficult to occur in polar solvents.



Another complexity associated with polar solvents is the involvement of multiple growing species with different ionic dissociation states, the existence of which is shown by bimodal MWDs of product polymers.[4] The typical examples of the double-peaked distribution have been found for the polymerizations of styrene,[5,6] *p*-methylstyrene,[7,8] and pMOS[2,7] initiated by perchloric acid, acetyl perchlorate, or iodine, all being carried out in relatively

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polar media like methylene chloride (CH_2Cl_2) or its mixtures with toluene or carbon tetrachloride.

The multiple intermediates in these reactions consist of dissociated and nondissociated species that independently and simultaneously yield higher and lower polymer fractions, respectively.[4] The nondissociated growing species is similar in nature to the single intermediate in nonpolar solvents and, importantly, it predominates over the dissociated counterpart even in a polar solvent if a common ion salt is added therein. Thus, for example, the styrene polymerization by acetyl perchlorate in salt-free CH_2Cl_2 gives polymers with a bimodal MWD, whereas only the lower polymer (from the nondissociated species) forms in the same solvent but in the presence of tetra-*n*-butylammonium perchlorate (nBu_4NClO_4).[5]

Such *changes in polymer MWD suggest that one can* control the ionic dissociation of, and in turn the stability of, the propagating carbocations in polar media by use of added salts. Despite some fragmentary evidence,[2] however, it is unknown how the multiplicity of the propagating species in polar solvents affects living cationic polymerization or which one of the two intermediates possesses livingness.

In this study, therefore, we investigated the possibility of living cationic polymerization of pMOS by the HI/ZnI_2 and HI/I_2 initiating systems in CH_2Cl_2 as a polar solvent. The nature of the propagating species therein is also discussed on the basis of the effects of added tetra-*n*-butylammonium halides and perchlorate (nBu_4NX; X = I, Br, Cl, ClO_4).

Experimental Section

Materials. pMOS was prepared from *p*-methoxyacetophenone by the literature method[9] and purified by double distillation over calcium hydride under reduced pressure. The gas chromatographic purity of the monomer exceeded 99.8%. Anhydrous hydrogen iodide was obtained as an *n*-hexane solution as previously reported.[10] Iodine was sublimed at 100 °C in the presence of potassium iodide and stored in sealed glass vials under dry nitrogen in the dark. ZnI_2 (Aldrich, purity > 99.99%), nBu_4NX (X = I, Br, Cl; Wako, purity ca. 98%), and nBu_4ClO_4 (Fluka, purity > 98%) were all used as commercially supplied. After prolonged drying in vacuo, these hygroscopic salts were handled in a drybox under nitrogen. Immediately before use, ZnI_2 was dissolved in diethyl ether,[11] whereas iodine and the ammonium salts were in CH_2Cl_2. Solvents (CH_2Cl_2, *n*-hexane, and diethyl ether) and tetrahydronaphthalene as an internal standard for gas chromatography were purified by the usual methods[10] and distilled at least twice over calcium hydride just before use.

Procedures. Polymerization of pMOS was carried out under dry nitrogen in baked glass tubes each equipped with a three-way stopcock. The reaction was initiated by sequential addition of a prechilled hydrogen iodide solution (in *n*-hexane, 10 vol % to the reaction mixture) and a solution of ZnI_2 or iodine into a monomer solution in CH_2Cl_2 containing 7 vol % tetrahydronaphthalene as an internal standard for gas chromatography. Immediately before use, the zinc salt was dissolved in diethyl ether,[11] whereas iodine was in CH_2Cl_2, both solutions being handled in the dark and 10 vol % to the reaction mixture. For the polymerizations in the presence of nBu_4NX, it was dissolved in the monomer solution before addition of hydrogen iodide. After predetermined intervals, the polymerization was terminated with prechilled ammoniacal methanol, and monomer conversion was determined from its residual concentration by gas chromatography.

The quenched reaction mixtures were washed with aqueous sodium thiosulfate solution (10 %, w/v) and then with water to remove the initiator residues, evaporated to dryness below 40 °C under reduced pressure, and vacuum dried to give the produced polymers. The MWD of the products was measured by size-exclusion chromatography in chloroform at room temperature on a Jasco Trirotar-II chromatograph equipped with three polystyrene gel columns (Shodex K-802, -803, and -804) and refractive index/ultraviolet dual detectors. The number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) of the polymers were calculated from size-exclusion eluograms on the basis of a polystyrene calibration.

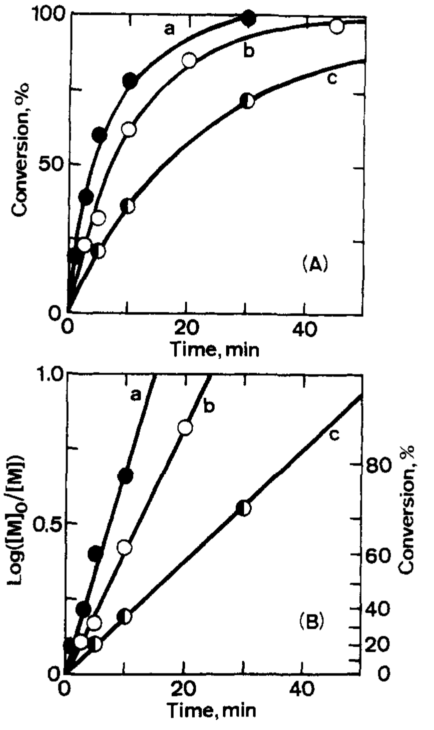


Figure 1. Time–conversion curves (A) and first-order plots (B) for the polymerization of pMOS by HI/ZnI_2 at −15 °C: $[M]_0$ = 0.50 M; $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 5.0 mM. Solvent: (●) CH_2Cl_2; (○) CH_2Cl_2 with nBu_4NI (0.10 mM); (◐) toluene.

Results and Discussion

1. Polymerization by HI/ZnI_2. Effects of a Common Ion Salt.

This section discusses the possibility of living pMOS polymerization by the HI/ZnI_2 system in a polar solvent (CH_2Cl_2), as an extension of the corresponding process in toluene previously reported by us.[1]

Polymerization Rate and Polymer MWD. With HI/ZnI_2, pMOS was polymerized in CH_2Cl_2 much faster than in toluene at −15 to +25 °C. Figure 1A compares the time–conversion curves for the polymerizations at −15 °C in CH_2Cl_2 (curve a) and in toluene[1] (curve c), both of which proceeded quantitatively without an induction phase. The polymerization mixtures were all homogeneous and colorless throughout; despite the relatively high polarity of CH_2Cl_2 solvent, ZnI_2 alone could not polymerize pMOS at all. The HI/ZnI_2-mediated polymerizations in CH_2Cl_2 and toluene both proved first order in monomer, giving linear plots of ln ($[M]_0/[M]$) against time, where the subscript 0 indicates the initial concentration (Figure 1B).

In contrast to the similarity in kinetics, the polymerizations in the two media led to polymers with completely different MWDs. As reported previously,[1] the poly(pMOS) samples obtained in toluene exhibit sharp and nearly monodisperse MWDs. On the other hand, the MWD for CH_2Cl_2 solvent turned out to be bimodal, particularly notable at low conversions (Figure 2A). As the polymerization proceeded, the molecular weight of the lower polymer fraction clearly increased, while such an increase was absent for the higher polymer fraction,

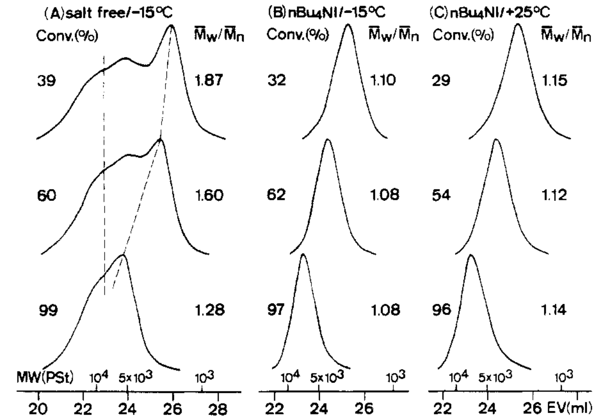


Figure 2. MWD of poly(pMOS) obtained with HI/ZnI_2 in CH_2Cl_2 in the absence (A) and presence (B and C) of nBu_4NI (0.10 mM) at various conversions: $[M]_0$ = 0.50 M; $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 5.0 mM. Polymerization temperature (°C): (A) -15; (B) -15; (C) +25.

and thereby the two peaks increasingly overlapped at higher conversions.

Bimodal MWDs similar to the above have been observed in cationic polymerization of styrene derivatives[2,8] and attributed to the coexistence of dissociated (1) and nondissociated (2) intermediates, the latter of which is responsible for the lower polymer fraction (see Introduction and Scheme I).[4] The progressive increase in molecular weight of the lower polymer thus indicates the nondissociated species to have a long lifetime. In order to achieve a living pMOS polymerization in CH_2Cl_2, it is thus necessary to generate selectively the nondissociated species. A method to this end is addition of a common ion salt, which suppresses the ionic dissociation of the propagating carbocations.[4]

Effects of a Common Ion Salt. The pMOS polymerization by HI/ZnI_2 was thus carried out in CH_2Cl_2 at -15 and +25 °C in the presence of a small amount of nBu_4NI (1.0 mol % to HI). As shown in Figure 1A, the polymerization was slightly slower than in the absence of the salt but was faster than in toluene. More important, the MWDs of the polymers (Figure 2B,C) now consist of a single narrow peak that corresponds to the lower polymer fraction formed in salt-free CH_2Cl_2 (Figure 2A). As expected, the molecular weight of this peak increased with increasing conversion.

Living Polymerization. Figure 3 plots the $\bar{M}_n$ of the polymers obtained in the presence of nBu_4NI as a function of conversion. Independent of polymerization temperature, the $\bar{M}_n$ increased in direct proportion to monomer conversion and was in good agreement with the calculated value assuming that one polymer chain forms per molecule of hydrogen iodide (the solid line in Figure 3). The MWDs of the polymers were very narrow and nearly monodisperse ($\bar{M}_w/\bar{M}_n \leq 1.1$) even at room temperature.

The livingness of the polymers was further confirmed by so-called "monomer addition" experiments in which fresh feeds of pMOS were added to completely polymerized reaction mixtures (Figure 4). On addition of a pMOS feed, a second-stage polymerization immediately ensued at both -15 and +25 °C. In the reaction at -15 °C, the $\bar{M}_n$ of the polymers continued to increase even after the second monomer addition, again in direct proportion to conversion, and was very close to the calculated value for a living polymer (the solid line in Figure 4), while the polymer MWD stayed very narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$).

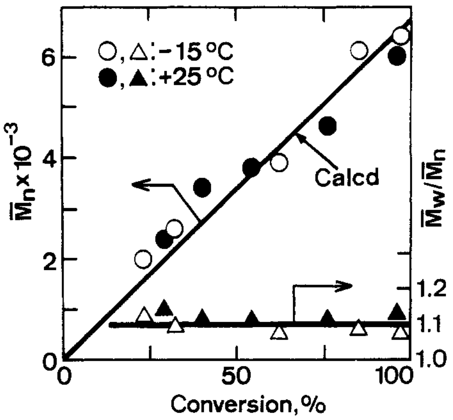


Figure 3. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(pMOS), as a function of conversion, obtained with HI/ZnI_2 in CH_2Cl_2 in the presence of nBu_4NI (0.10 mM) at -15 (○, △) and +25 °C (●, ▲): $[M]_0$ = 0.50 M; $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 5.0 mM. The diagonal solid line indicates the calculated $\bar{M}_n$ values assuming one living chain per HI.

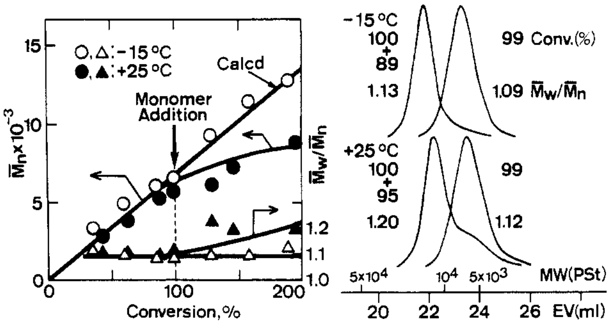


Figure 4. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(pMOS) obtained with HI/ZnI_2 in monomer addition experiments in CH_2Cl_2 in the presence of nBu_4NI (0.10 mM) at -15 (○, △) and +25 °C (●, ▲): $[M]_0 = [M]_{added}$ = 0.50 M; $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 5.0 mM. The diagonal solid line in the $\bar{M}_n$-conversion profile indicates the calculated $\bar{M}_n$ values assuming one living chain per HI.

At +25 °C, the monomer addition indeed led to an increase in polymer molecular weight, but it was no longer linear and soon leveled off with increasing conversion. The MWD of the polymers in the second phase had a low molecular weight tailing and was hence broader than that before the monomer addition.

The presence of nBu_4NI thus allowed living cationic polymerization of pMOS to proceed in a polar solvent. Under these conditions, the living process is most likely mediated by the nondissociated species alone where the counteranion strongly interacts with the carbocationic active center. When compared with the counterpart in toluene,[1] the polymerization in salt-containing CH_2Cl_2 is very similar to that at -15 °C (both perfectly living) but less controllable at +25 °C, as evidenced by the failure of a linear increase in $\bar{M}_n$ after a second monomer addition; note that in toluene, a perfectly living process is feasible even at room temperature.[1]

Another difference is that the polymerization in CH_2Cl_2 with nBu_4NI is clearly faster than in toluene (cf. Figure 1A), although in both processes the growing species is all nondissociated. The nondissociated species in the polar solvent seems more polarized, more reactive, and hence more susceptible to chain transfer at room temperature.

2. Polymerization by HI/I_2. Clear effects of added nBu_4NI, similar to the above, were observed when pMOS was polymerized in CH_2Cl_2 at -15 and +25 °C by the HI/I_2 initiating system instead of HI/ZnI_2. For example, the polymerization without the iodide salt produced polymers with bimodal MWDs that are very similar to

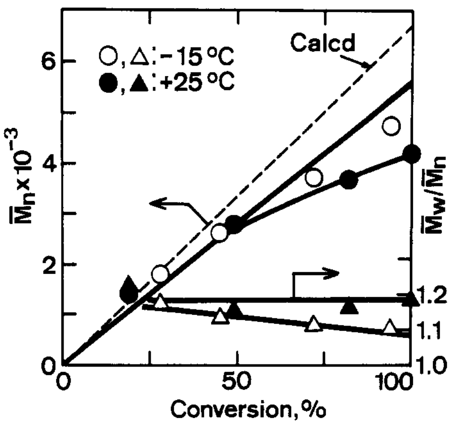


Figure 5. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(pMOS), as a function of conversion, obtained with HI/I_2 in CH_2Cl_2 in the presence of nBu_4NI (0.10 mM) at -15 (○, △) and +25 °C (●, ▲): $[M]_0$ = 0.50 M; $[HI]_0$ = 10 mM; $[I_2]_0$ = 5.0 mM. The diagonal broken line indicates the calculated $\bar{M}_n$ values assuming one living chain per HI.

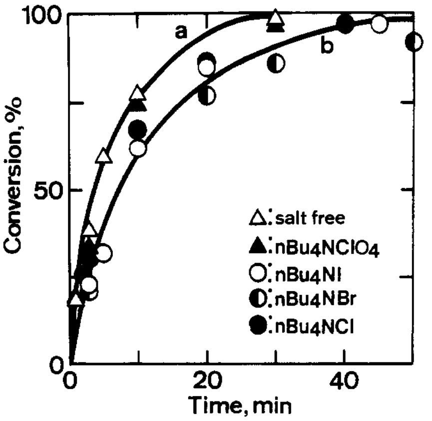


Figure 6. Time-conversion curves for the polymerization of pMOS by HI/ZnI_2 in CH_2Cl_2 at -15 °C in the presence of nBu_4NX (0.10 mM): $[M]_0$ = 0.50 M; $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 5.0 mM. X of nBu_4NX: (○) I; (◐) Br; (●) Cl; (▲) ClO4; (△) salt free.

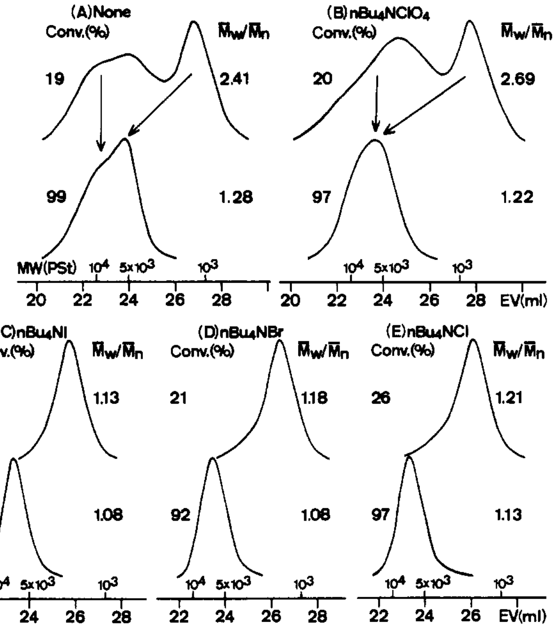


Figure 7. MWD of poly(pMOS) obtained with HI/ZnI_2 in CH_2Cl_2 at -15 °C in the presence of nBu_4NX (0.10 mM) at low and high conversions: $[M]_0$ = 0.50 M; $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 5.0 mM. X of nBu_4NX: (A) salt free; (B) ClO4; (C) I; (D) Br; (E) Cl.

those with HI/ZnI_2 (cf. Figure 2A). On addition of nBu_4NI (1.0 mol % to HI), the MWD of the products became unimodal and fairly narrow ($\bar{M}_w/\bar{M}_n$ = 1.1-1.2), consisting of a low polymer fraction only. As shown in Figure 5, the $\bar{M}_n$ for -15 °C increased to monomer conversion but was slightly smaller than the calculated value for living polymers (one living chain per HI; the broken line). The latter fact suggests that the living process with HI/I_2 is accompanied by polymerization by iodine alone.

The HI/I_2-mediated polymerization in salt-containing CH_2Cl_2 is no longer perfectly living at +25 °C. Although the MWD of the polymers was unimodal and fairly narrow ($\bar{M}_w/\bar{M}_n$ = 1.2), the $\bar{M}_n$-conversion plot is curved, where the $\bar{M}_n$ is considerably smaller than that at -15 °C (Figure 5).

3. Polymerization in the Presence of Various Tetra-*n*-butylammonium Salts.

As described above, nBu_4NI turned out to be essential to attaining living cationic polymerization of pMOS in CH_2Cl_2. It is of interest then to investigate the effects of added ammonium salts other than nBu_4NI on the living process, and for this we employed a series of its analogues (nBu_4NX) carrying counteranions, the nucleophilicity of which is higher (X = Br, Cl) or lower (X = ClO_4) than the iodide anion (X = I).

Polymerization Rate and Polymer MWD. The polymerization of pMOS by HI/ZnI_2 was thus carried out at -15 °C in CH_2Cl_2 solvent in the presence of nBu_4NX (X = Br, Cl, ClO_4; 1.0 mol % to HI). The rates of the polymerizations with nBu_4NBr and nBu_4NCl were almost the same as that with nBu_4NI (Figure 6, curve b), whereas the rate with the prechlorate counterpart was greater and similar to the rate in salt-free CH_2Cl_2 (Figure 6, curve a).

The MWDs of the polymers produced in the presence of nBu_4NBr and nBu_4NCl were unimodal, narrow, and almost identical with those in nBu_4NI, all of which shift toward higher molecular weight with increasing conversion (Figure 7C-E). The use of nBu_4NClO_4 had no effect on polymer MWD and resulted in polymers with bimodal MWDs (Figure 7B) that are very similar to the distributions obtained without an added salt (Figure 7A).

Living Polymerization. In accordance with the unimodality and narrowness of the MWDs, the $\bar{M}_n$'s of the polymers with nBu_4NBr and nBu_4NCl increased in direct proportion to conversion (Figure 8). Equally important, the $\bar{M}_n$'s were independent of the halide anions type (X = I, Br, Cl) and were in good agreement with the calculated values (one living chain per HI; the solid line in Figure 8). It should be noted that the addition of halide anions, whether or not it is the common ion for the growing species, leads to living polymerization of pMOS in CH_2Cl_2. In view of the failure of such a living process with use of the less nucleophilic perchlorate counterpart, the high nucleophilicity of the halide anions appears to be the primary factor that determines the livingness of pMOS in the polar medium.

Scheme I illustrates a possible pathway that accounts for the effects of the added bromide and chloride anions. In the absence of the ammonium salts (X = I, Br, Cl), the growing species is either a dissociated species (1) or a nondissociated species (2), both of which carry the iodide anion, derived from hydrogen iodide, that is associated by zinc iodide as an activator.[11] The coexistence of species 1 and 2 then leads to polymers having a bimodal MWD as shown in Figure 2A. Because our standard conditions employ a ZnI_2 concentration lower than that of hydrogen iodide, the nondissociated form 2 should be in

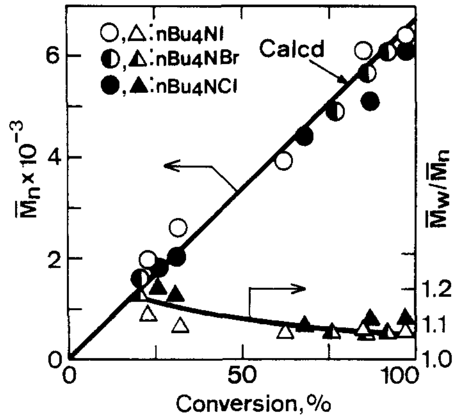
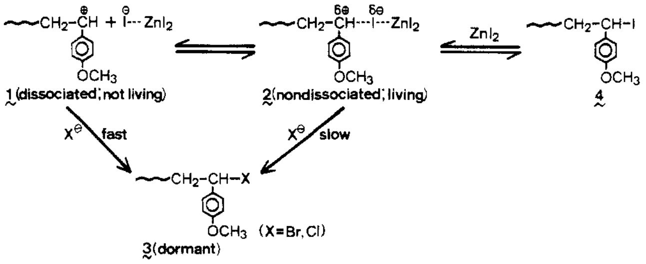


Figure 8. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(pMOS), as a function of conversion, obtained with HI/ZnI_2 in CH_2Cl_2 at −15 °C in the presence of nBu_4NX (0.10 mM): $[M]_0$ = 0.50 M; $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 5.0 mM. X of nBu_4NX: (○, △) I; (◐, ▲) Br; (●, ▲) Cl. The diagonal solid line indicates the calculated $\bar{M}_n$ values assuming one living chain per HI.

Scheme I



a rapid equilibrium with a dormant, nonactivated species (4) that carries a carbon–iodine terminal bond free from the activation by zinc iodide.

In the presence of nBu_4NI (a common ion salt), the dissociated species 1 is suppressed and the propagating species is entirely the nondissociated form 2 that eventually gives living polymers of a narrow MWD (Figure 2B,C).

When nBu_4NBr or nBu_4NCl, instead of the iodide counterpart, is added to a polymerization mixture initiated with HI/ZnI_2, the nucleophilic bromide or chloride anion may react with the dissociated propagating species 1 to convert it into a dormant species 3 with a C–Br or C–Cl terminal linkage, which is similar to another dormant form 4. Namely, the added bromide and chloride anions may act as quenchers that efficiently eliminate the uncontrolled propagation via the nonliving, dissociated species 1 and thereby permit living polymerization to occur selectively via the nondissociated species 2.

Since the concentration of species 1 is much lower than that of 2, transformation of 1 into 3 would not seriously affect the concentration of the living species 2; i.e., [3] + [1] ≪ [2]. Thus, [2] would in turn remain almost equal to the initial amount of hydrogen iodide $[HI]_0$. The $\bar{M}_n$ values of the living polymers are then independent of the type of the added halide anions.

When 1 is trapped by the bromide or chloride anions into 3, the equilibrium between 1 and 2 would shift and reproduce the former. This interconversion, however, is much slower than living propagation from 2 and therefore would not affect the living polymerization; if it were indeed faster, the MWD of polymers obtained in salt-free CH_2Cl_2 would not be bimodal but unimodal and broad.

Effects of Salt Concentration. Supporting evidence for Scheme I was obtained, when the polymerization was carried out in CH_2Cl_2 at −15 °C at a higher concentration of nBu_4NI or nBu_4NCl (5.0 mM; 50 mol % to HI), where effects of the counteranions in the added salts were now clearly observed. Under these conditions, for example, the polymerizations needed 3 h (with nBu_4NI) and 32 h (with nBu_4NCl) to reach 50% conversion, being much slower than at the lower salt concentration (1.0 mol % to HI; 50% conversion in 6 min; see Figure 6, curve b) that was invariably employed for the experiments discussed in the preceding sections.

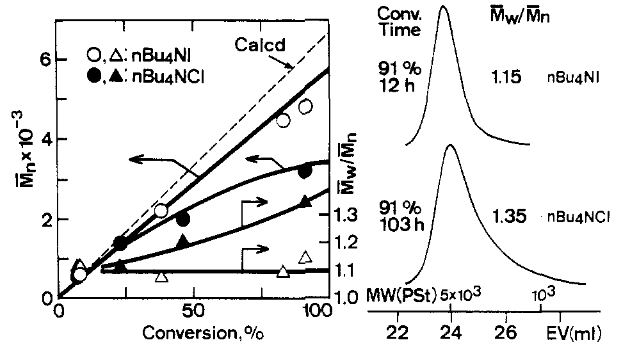


Figure 9. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of poly(pMOS) obtained with HI/ZnI_2 in CH_2Cl_2 at −15 °C at a high salt concentration (5.0 mM): $[M]_0$ = 0.50 M; $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 5.0 mM. Added salt: (○, △) nBu_4NI; (●, ▲) nBu_4NCl. MWD: (a) with nBu_4NI, conversion = 91%, 12 h; (b) with nBu_4NCl, conversion = 91%, 103 h. The diagonal broken line indicates the calculated $\bar{M}_n$ values assuming one living chain per HI.

Even added at the higher concentration, nBu_4NI allowed the formation of living polymers of narrow MWDs, with their $\bar{M}_n$ increasing proportionally to monomer conversion (Figure 9). In contrast, the use of the large amount of the chloride counterpart turned out to adversely affect living polymerization; as pMOS conversion increased, the $\bar{M}_n$ of the polymers became progressively smaller than the calculated value, while polymer MWD severely broadened ($\bar{M}_w/\bar{M}_n$ up to 1.3 or greater).

The observed effects of the added salt concentration indeed show that there is a strong interaction of the chloride anion with the growing carbocation. When employed at a high concentration, the halide anion may react not only with the dissociated species 1 but, though slowly, with the less reactive nondissociated intermediate 2, converting it into 3. The concentration of the dormant species 3 is thus higher than at the low salt concentration, and the polymerization is slowed accordingly. The increased contribution of 3 may also broaden the polymer MWD and in turn reduce the polymer's $\bar{M}_n$, because its activation and subsequent propagation via the activated form are much slower than that via 2.

Quite recently, Nuyken and Kröner reported a living cationic polymerization of isobutyl vinyl ether initiated with hydrogen iodide in CH_2Cl_2 in the presence of a series of nBu_4NX (X = I, NO_3, ClO_4, etc.), where addition of ZnI_2 or similar Lewis acid activators is unnecessary for the polymerization to occur.[12] It is unknown so far, however, whether Nuyken's HI/nBu_4NI system can polymerize pMOS.

In conclusion, this study has demonstrated the coexistence of the dissociated and nondissociated propagating species (1 and 2, respectively) in the polymerization of pMOS by HI/ZnI_2. Such multiplicity in the growing end has not been established for the corresponding reactions of vinyl ethers,[13] although some indirect evidence has been reported.[14] The use of added halide salts also permitted living cationic polymerization of pMOS to proceed in a polar solvent even at room temperature to give

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nearly monodisperse polymers of controlled molecular weights.

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Copolymerization of Styrene and Substituted Styrenes with $Ti(OMen)_4$–Methylaluminoxane Catalyst

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ABSTRACT: Copolymerizations of styrene and substituted styrenes were carried out at room temperature with a $Ti(OMen)_4$–methylaluminoxane catalyst and the monomer reactivity ratios (r) were estimated by using the Fineman–Ross method. From the plot of log r versus σ in the Hammett equation, $\log r = \rho\sigma$, ρ was approximately −1.2. The negative value of ρ suggested that polymerization of these styrene monomers proceeds not via a coordinated anionic but via a coordinated cationic mechanism. The results of copolymerization between styrene and α-olefins supported the mechanism.

Introduction

Ishihara et al.[1] have succeeded in preparing syndiotactic polystyrene by using a kind of Kaminsky–Sinn catalysts composed of some titanium compounds and methylaluminoxane (MAO). Zambelli et al.[2,3] later found that some zirconium compounds are also effective for the syndiotactic polymerization of styrene when MAO is used as cocatalyst. Ishihara et al.[4] have recently reported that corresponding syndiotactic polymers can also be similarly obtained for ring-substituted styrenes (*p*- and *m*-methylstyrene, *p*-*tert*-butylstyrene, *p*- and *m*-chlorostyrene, *p*-fluorostyrene, etc.) with a similar catalyst system. More recently, Grassi et al.[5] have also carried out the polymerization of substituted styrenes and found that syndiotactic polymer is obtained from *p*-methylstyrene, whereas atactic polymers are obtained from *p*-methoxystyrene and *p*-, *m*-, and *o*-chlorostyrene.

It is evident that MAO plays an important role in producing syndiotactic polystyrene. However, the catalyst system composed of Cp_2MCl_2 (M = Ti, Zr) and MAO, which is well-known to catalyze olefin polymerization, does not give syndiotactic polystyrene, whereas the $Ti(OR)_4$–MAO system, which produces syndiotactic polystyrene, also gives polyolefins[6] but not copolymers of styrene and olefins. These facts may indicate that the active species that produce syndiotactic polystyrene are different from those producing polyolefins.

To obtain more information on the active species for syndiotactic polymerization of styrene, we have carried out the copolymerization of styrene and analyzed the results by using the Hammett law.

Experimental Section

Materials. Styrene and substituted styrenes commercially obtained from Kanto Chemical Co. were washed with an aqueous solution of sodium hydroxide, dried over calcium hydride for 12 h, and distilled under reduced pressure. Toluene used as solvent was purified by refluxing over calcium hydride for 24 h, followed by fractional distillation. $Ti(OMen)_4$ was prepared from $TiCl_4$ and L-(−)-menthol and purified by distillation. $AlMe_3$ (TMA) and $CuSO_4{\cdot}5H_2O$ were commercially obtained and used without further purification. Methylaluminoxane (MAO) was prepared from TMA and $CuSO_4{\cdot}5H_2O$ according to the literature[7] and reserved as stock solution in toluene, 0.40 mmol/dm^3. Nitrogen of 99.9989% purity was used after passing it through a column of 3A molecular sieve.

Polymerization and Analytical Procedures. Polymerizations were carried out in a 100-cm^3 glass reactor equipped with a magnetic stirrer. Polymerization was stopped by adding a mixture of hydrochloric acid and methanol, filtered, and dried under reduced pressure at 60 °C. The structures and compositions of the copolymers were determined by ^{1}H NMR, ^{13}C

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