Living Cationic Polymerization of Styrene: New Initiating Systems Based on Added Halide Salts and the Nature of the Growing Species[1]

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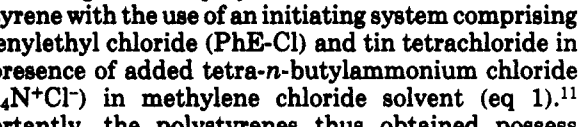
ABSTRACT: In methylene chloride at −15 °C, the living cationic polymerization of styrene has been achieved with a series of new initiating systems: mixtures of 1-phenylethyl halide (PhE-X; X = Br, Cl) and tin tetrachloride in conjunction with added tetra-*n*-butylammonium halide (nBu$_4$N$^+$Y$^-$; Y$^-$ = I$^-$, Br$^-$, Cl$^-$), where the halogens X and Y may be either the same or different. Without nBu$_4$N$^+$Y$^-$, the PhE-X/SnCl$_4$ systems form polymers with bimodal molecular weight distributions (MWDs), but with the added salt, living polystyrenes with very narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.1–1.2) are formed. The number-average molecular weights ($\bar{M}_n$) of these living polymers are directly proportional to conversion, close to the calculated values with the assumption that one polymer chain is generated per PhE-X molecule, and are independent of the concentrations of SnCl$_4$ and nBu$_4$N$^+$Y$^-$. On the basis of these dependencies and other facts, the roles of PhE-X (initiator), SnCl$_4$ (activator), and nBu$_4$N$^+$Y$^-$ (added salt) have been established. Thus, the PhE-X/SnCl$_4$ systems generate two independent propagating species, a dissociated nonliving species and a nondissociated living species, of which the former is suppressed by added nBu$_4$N$^+$Y$^-$. ^{1}H NMR model experiments on the mixtures of the three components show that, whether initiated with the chloride (PhE-Cl) or the bromide (PhE-Br), the growing ends (and the PhE-Br initiator) rapidly undergo halogen exchange with SnCl$_4$ activator to generate a chloride-type species. The occurrence of the halogen exchange suggests that, upon addition to monomer, the activated growing end most likely assumes an ionic form.

Introduction

Because of its lack of a strongly electron donating substituent, styrene is among the poorly reactive monomers in cationic polymerizations. When polymerized with conventional cationic initiators, styrene forms an unstable growing carbocation that is prone to undergo chain transfer, termination, and other undesirable side reactions. As a result, the living cationic polymerization of styrene has been considered theoretically difficult,[2] in marked contrast to the recent development of well-defined living cationic polymerization processes for a variety of vinyl monomers,[3] including vinyl ethers,[4] isobutylene,[5] *p*-alkoxystyrenes,[6] and *N*-vinylcarbazole,[7] most of which bear electron-donating substituents.

Despite such a rather pessimistic prediction, work by Pepper and Goethals[8] suggests that the polystyrene generated with a perchlorate counteranion at a low temperature is long-lived, and Kennedy and his associates[9] recently reported the possibility of living cationic polymerization of styrene with several BCl$_3$- and TiCl$_4$-based initiating systems, though in some cases the living nature of the polymerization was somewhat obscured by the broad molecular weight distribution (MWD) of the polymers obtained. More recently,[10] we have found that a near-perfect living cationic polymerization is indeed feasible for styrene with the use of an initiating system comprising 1-phenylethyl chloride (PhE-Cl) and tin tetrachloride in the presence of added tetra-*n*-butylammonium chloride (nBu$_4$N$^+$Cl$^-$) in methylene chloride solvent (eq 1).[11] Importantly, the polystyrenes thus obtained possess narrow MWDs ($\bar{M}_w/\bar{M}_n \leq 1.15$) and controlled number-average molecular weights ($\bar{M}_n$).



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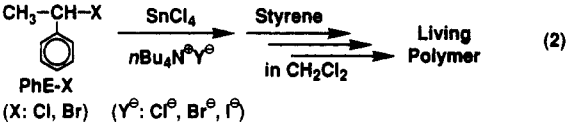
The underlying concept for the living cationic polymerization of styrene with the PhE-Cl/SnCl$_4$ initiating system is the "nucleophilic stabilization of the unstable growing carbocation" and related control of its ionic dissociation.[3] Relative to this principle, the marked features of this living process involve the use of the following: (a) a highly nucleophilic counteranion (the chloride anion from PhE-Cl) to ensure an effective nucleophilic stabilization of the growing styryl carbocation;[3] (b) a strong Lewis acid (SnCl$_4$) to induce the efficient initiation of a relatively unreactive monomer (styrene) with PhE-Cl; and perhaps most important, (c) an added chloride salt (nBu$_4$N$^+$Cl$^-$) to provide a sufficient concentration of the chloride anion, which seemingly exerts an additional carbocation stabilization. Though our prior work established the effectiveness of this particular initiating system,[10] the generality and mechanistic implications of these features still await further clarification.

To this end, the primary objectives of this study are (i) to explore new initiating systems (eq 2)[11] for living cationic



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polymerization of styrene by generalizing the three features (a–c) and (ii) to uncover the nature of the (living) growing species generated therefrom. Thus, we employed a variety of combinations of 1-phenylethyl halide (PhE-X; X = Cl, Br), metal halides (MX_n = SnCl$_4$, SnBr$_4$, EtAlCl$_2$), and added salts (nBu$_4$N$^+$Y$^-$; Y$^-$ = Cl$^-$, Br$^-$, I$^-$, ClO$_4^-$) as new initiating systems for living styrene polymerization (for objective i). The nature of the growing species in the living styrene polymerization with these new initiating systems was also studied by the direct analysis of relevant model reactions by ^{1}H NMR spectroscopy (for objective ii). Additionally, kinetic experiments were carried out to determine the roles of the three components of the initiating systems, i.e., PhE-X, MX_n, and nBu$_4$N$^+$Y$^-$.

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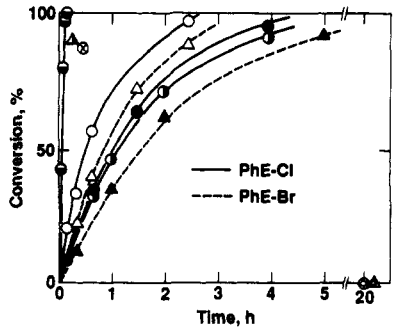


Figure 1. Time–conversion profiles for the polymerizations of styrene ($[M]_0$ = 1.0 M) with PhE-Cl/$SnCl_4$ (—) and PhE-Br/$SnCl_4$ (- - -) (20 mM PhE-X and 100 mM $SnCl_4$) in the presence of nBu$_4$N$^+$Y$^-$ (40 mM) at −15 °C in CH_2Cl_2: (⊗) PhE-Cl, no salt; (⊖) PhE-Cl, nBu$_4$N$^+$ClO$_4^-$; (○) PhE-Cl, nBu$_4$N$^+$Cl$^-$; (●) PhE-Cl, nBu$_4$N$^+$Br$^-$; (◑) PhE-Cl, nBu$_4$N$^+$I$^-$; (△) PhE-Br, no salt; (△) PhE-Br, nBu$_4$N$^+$Cl$^-$; (▲) PhE-Br, nBu$_4$N$^+$Br$^-$; (◉) PhE-Cl or (△) PhE-Br alone (without $SnCl_4$ and nBu$_4$N$^+$Y$^-$).

Results and Discussion

1. PhE-X/$SnCl_4$/nBu$_4$N$^+$Y$^-$: New Initiating Systems for Living Cationic Polymerization of Styrene. The first phase of this study was directed toward exploring the new initiating systems, consisting of various combinations of PhE-X, MX_n, and nBu$_4$N$^+$Y$^-$ (eq 2) for living cationic polymerization of styrene. Unless otherwise specified, the polymerizations were carried out in CH_2Cl_2 solvent at −15 °C at the following initial concentrations of reagents: styrene, 1.0 M; PhE-X, 20 mM; MX_n ($SnCl_4$), 100 mM; nBu$_4$N$^+$Y$^-$, 40 mM.

Effects of Added Salts (nBu$_4$N$^+$Y$^-$). The previous work with the PhE-Cl/$SnCl_4$ initiating system[10] indicated that addition of nBu$_4$N$^+$Cl$^-$ is mandatory for living styrene polymerization to occur. Herein we first examined ammonium salts with varying anions Y$^-$ (nBu$_4$N$^+$Y$^-$; Y$^-$ = Br$^-$, I$^-$, ClO$_4^-$) as alternatives for the chloride salt in the polymerization initiated with PhE-Cl/$SnCl_4$. Figure 1 shows the time–conversion profiles for these polymerizations, where the results with the PhE-Cl are shown with circular data points connected through solid lines.

In the absence of nBu$_4$N$^+$Y$^-$, styrene was rapidly polymerized with PhE-Cl/$SnCl_4$,[10] and an even faster quantitative polymerization occurred with a salt carrying the less nucleophilic ClO$_4^-$ anion. By comparison, nucleophilic halide anions (Y$^-$ – Cl$^-$, Br −, I$^-$) led to slower quanitative polymerizations. The overall reaction rates decreased with the salts' anions Y$^-$ in the order: ClO$_4^-$ > none ≫ Cl$^-$ > Br$^-$ > I$^-$.

Figure 2, series A, shows the MWDs of polystyrenes thus obtained. The PhE-Cl/$SnCl_4$-initiated polymerization without nBu$_4$N$^+$Y$^-$ yielded polymers with a distinct bimodal MWD (Figure 2a),[10] which is attributed to a parallel propagation of two independent growing species (see eq 3 below).[3a,12] On addition of the perchlorate salt (nBu$_4$N$^+$ClO$_4^-$), the MWD became broadly unimodal (Figure 2e). By contrast, the bromide and iodide salts (nBu$_4$N$^+$Br$^-$, nBu$_4$N$^+$I$^-$) gave unimodal and very narrow MWDs ($\bar{M}_w/\bar{M}_n$ < 1.15) (Figure 2c,d), similar to that obtained with the chloride counterpart (nBu$_4$N$^+$Cl$^-$) (Figure 2b).[10] The single-peaked MWDs correspond to the low molecular weight population of the bimodal distribution for the salt-free system (Figure 2a); all the relatively narrow peaks shift to higher molecular weights as conversion increases. The narrow unimodal MWDs with the added halide salts (nBu$_4$N$^+$Y$^-$; Y$^-$ = Cl$^-$, Br$^-$, I$^-$) suggest the living nature of the polymerization, as will be discussed later.

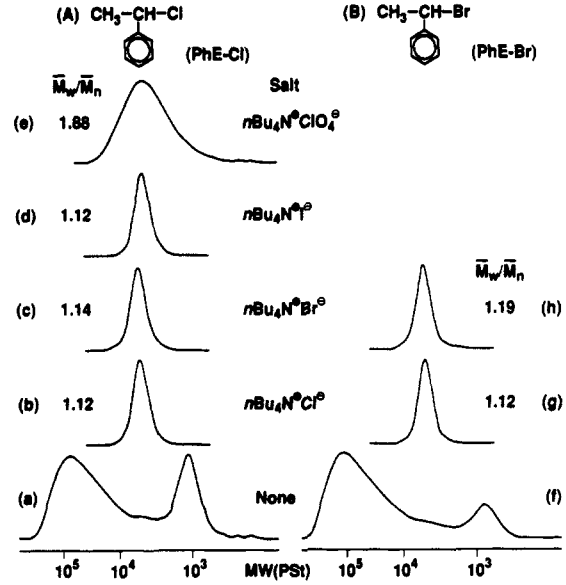


Figure 2. MWDs of the polystyrenes ($[M]_0$ = 1.0 M) obtained with PhE-X/$SnCl_4$ (20 and 100 mM, respectively) in the presence and absence of nBu$_4$N$^+$Y$^-$ (40 mM) at −15 °C in CH_2Cl_2 at a conversion of >90%. Combinations of PhE-X and nBu$_4$N$^+$Y$^-$ as indicated.

Effects of 1-Phenylethyl Halides (PhE-Cl versus PhE-Br). In addition to varying the anions Y$^-$ in nBu$_4$N$^+$Y$^-$ salts, the use of PhE-Br, in place of PhE-Cl, was also examined. Thus, styrene was polymerized with the PhE-Br/$SnCl_4$ system in the presence of nBu$_4$N$^+$Cl$^-$ or nBu$_4$N$^+$Br$^-$ (Figure 1). Like PhE-Cl,[10] PhE-Br alone did not polymerize styrene under our reaction conditions. When coupled with $SnCl_4$, however, PhE-Br indeed induced efficient styrene polymerizations where the overall rates followed the same dependence on the anions Y$^-$ in nBu$_4$N$^+$Y$^-$ (none > Cl$^-$ > Br$^-$). In the presence of a particular nBu$_4$N$^+$Y$^-$ salt, the polymerization with PhE-X/$SnCl_4$ was slightly slower for PhE-Br than for PhE-Cl. For the five combinations of PhE-X and nBu$_4$N$^+$Y$^-$ (with $SnCl_4$ as metal halide), the overall reaction rates decreased in the following order (X/Y$^-$): Cl/Cl$^-$ > Br/Cl$^-$ > Cl/Br$^-$ ~ Cl/I$^-$ > Br/Br$^-$.[13]

Figure 2, series B, shows the MWDs of the polymers obtained with the PhE-Br/$SnCl_4$ system in the absence and presence of the two ammonium salts (Y$^-$ = Cl$^-$, Br$^-$). The overall results were similar to those obtained with the PhE-Cl/$SnCl_4$ counterpart, namely, a bimodal MWD for the salt-free system (Figure 2f) and narrow and unimodal distributions for the systems with the added salts (Figure 2g,h; $\bar{M}_w/\bar{M}_n$ < 1.2).

Living Cationic Polymerizations. In Figure 3 are plotted the number-average molecular weights ($\bar{M}_n$) as a function of conversion for the polymers initiated with the PhE-Cl/$SnCl_4$ and the PhE-Br/$SnCl_4$ systems in conjunction with the added nBu$_4$N$^+$Y$^-$ salts. For both initiating systems, the molecular weights with the halide salts (Y$^-$ = Cl$^-$, Br$^-$, I$^-$) are directly proportional to conversion, almost independent of the type of the halide anions Y$^-$, and invariably close to the calculated values based on the assumption that one polymer chain is formed per PhE-X molecule. Note that all these polymers also exhibited very narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.1–1.2; Figure 2b–d,g,h). By contrast, the $\bar{M}_n$'s of the polystyrenes obtained with the perchlorate salt (Figure 3) incleased nonlinearly with conversion and then leveled off as the reaction proceeded.

Thus, a variety of combinations of the PhE-X/$SnCl_4$ intiating systems and added halide salts (nBu$_4$N$^+$Y$^-$; Y$^-$ = Cl$^-$, Br$^-$, I$^-$) have been found to induce living cationic

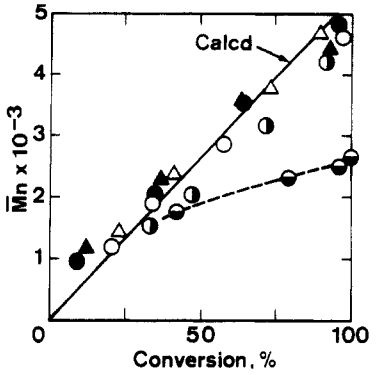


Figure 3. $\bar{M}_n$'s of the polystyrenes ($[M]_0 = 1.0$ M) obtained with PhE-X/$SnCl_4$ (20 and 100 mM, respectively) in the presence of n-$Bu_4N^+Y^-$ (40 mM) at −15 °C in CH_2Cl_2, as a function of conversion: (⊖) PhE-Cl, n-$Bu_4N^+ClO_4^-$; (○) PhE-Cl, n-$Bu_4N^+Cl^-$; (●) PhE-Cl, n-$Bu_4N^+Br^-$; (◑) PhE-Cl, n-$Bu_4N^+I^-$; (△) PhE-Br, n-$Bu_4N^+Cl^-$; (▲) PhE-Br, n-$Bu_4N^+Br^-$. The diagonal straight line indicates the calculated $\bar{M}_n$ values based on the formation of one polymer chain per PhE-X molecule.

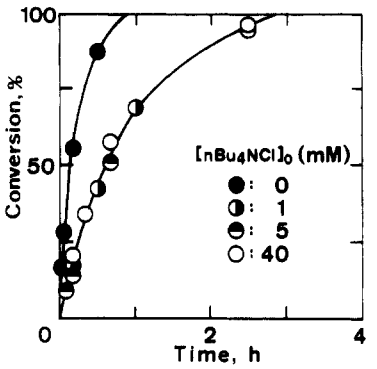


Figure 4. Time–conversion profiles for the polymerization of styrene ($[M]_0 = 1.0$ M) with PhE-Cl/$SnCl_4$ (20 and 100 mM, respectively) at varying concentrations of n-$Bu_4N^+Cl^-$ in CH_2Cl_2 at −15 °C.

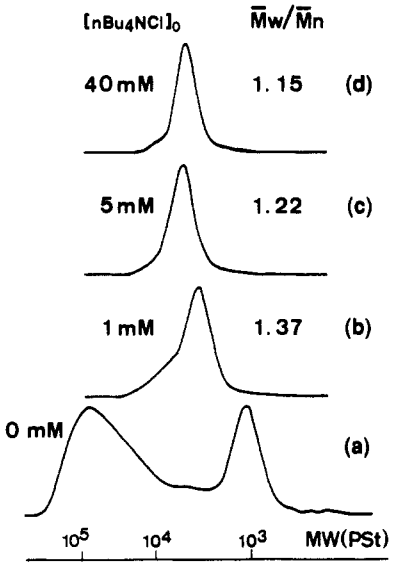


Figure 5. MWDs of the polystyrenes ($[M]_0 = 1.0$ M) obtained with PhE-Cl/$SnCl_4$ (20 and 100 mM, respectively) at varying concentrations of n-$Bu_4N^+Cl^-$ in CH_2Cl_2 at −15 °C at a conversion of >90%.

polymerization of styrene; the previously reported system, PhE-Cl/$SnCl_4$ coupled with n-$Bu_4N^+Cl^-$,[10] belongs to this generalized category.

In these initiating systems, X (in PhE-X) and Y (in n-$Bu_4N^+Y^-$) should be all halides (Cl, Br, I), but X and Y may be either the same or different from each other; i.e., X = Y or X ≠ Y. The failure of living polymerization with the perchlorate salt (n-$Bu_4N^+ClO_4^-$) indicates that, among other factors, the nucleophilicity of the salts' anions is important in attaining the living styrene polymerization (see sections 2 and 3 below).

Effects of Metal Halides (MX_n). Other than $SnCl_4$, the strong Lewis acids (MX_n), tin tetrabromide and ethylaluminum dichloride, were used with PhE-X to initiate styrene polymerization in CH_2Cl_2 solvent at −15 °C (PhE-X/MX_n, 20 and 100 mM, respectively). However, these Lewis acids turned out to be unsuitable for living polymerization of styrene. For example, even in the absence of n-$Bu_4N^+Y^-$, the PhE-Br/$SnBr_4$ system induced a very slow polymerization (83% conversion in 120 h); the produced polymers showed apparent bimodal MWDs in which the higher polymer fraction predominated. The PhE-Cl/$EtAlCl_2$ system indeed gave 100% conversion within 2 min in the presence of n-$Bu_4N^+Cl^-$ (40 mM), but the MWD of the products was very broad ($\bar{M}_w/\bar{M}_n \sim 5$; $\bar{M}_n = 1600$).

2. Polymerization with PhE-Cl/$SnCl_4$/n-$Bu_4N^+Cl^-$: Effects of Reagent Concentrations and Solvent Polarity. After the generalized formula of the initiating systems (PhE-X/$SnCl_4$/n-$Bu_4N^+Y^-$; X, Y = Cl, Br, I) was established, we examined the details of the living cationic polymerization of styrene using the PhE-Cl/$SnCl_4$/n-$Bu_4N^+Cl^-$ initiating system in CH_2Cl_2 at −15 °C. More specifically, experiments were directed to identify the role of each of the three components therein, the effects of their concentrations, and the effects of solvent polarity.

Effects of Salt (n-$Bu_4N^+Cl^-$) Concentration. To clarify the role of the added ammonium salt, the polymerization of styrene ($[M]_0 = 1.0$ M) with the PhE-Cl/$SnCl_4$ system (20/100 mM) was carried out at varying concentrations of n-$Bu_4N^+Cl^-$ (0, 1, 5, and 40 mM). As seen in the time–conversion profiles in Figure 4, the reaction was slower in the presence of the salt than in its absence, but when the salt was present, the overall rate was apparently independent of its concentration.

In contrast to this independence, the MWD of the product polymers (Figure 5) clearly depended on the salt concentration. As already reported,[10] the MWD for the salt-free system was bimodal (Figure 5a) and consisted of a broad population of high molecular weight polymer and a relatively narrow fraction of low molecular weight polymer. Addition of a small amount of the salt (1.0 mM; Figure 5b) dramatically suppressed the formation of the former, the relative amount of which decreased with increasing salt concentration (Figure 5b–d) to give a nearly monodisperse, very narrow distribution with 40 mM n-$Bu_4N^+Cl^-$ ($\bar{M}_w/\bar{M}_n < 1.15$; Figure 5d).

Figure 6 shows the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the polymers obtained in these salt-present systems as a function of conversion. The polymer molecular weights were nearly independent of the salt concentration within the range employed (1.0–40 mM), were directly proportional to conversion, and were invariably close to the calculated values based on the formation of one polymer chain per PhE-Cl molecule. The MWDs were very narrow throughout the reactions, except for the lowest salt concentration (1.0 mM), where the $\bar{M}_w/\bar{M}_n$ was initially above 1.9 and continued to decrease as conversion increased.

These observations show that the polymerization with PhE-Cl/$SnCl_4$ is living only at or above a certain concentration of salt, n-$Bu_4N^+Cl^-$. Under our reaction conditions (Figures 4–6), the threshold would be around 5.0 mM for obtaining narrowly distributed living polymers with controlled molecular weights. Overall, the added salt retards

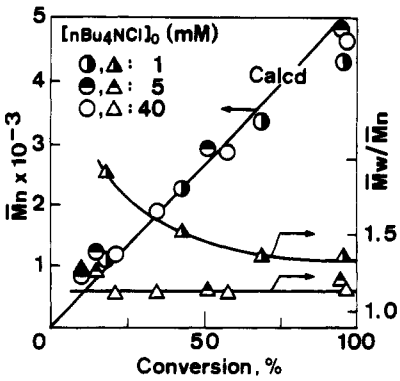


Figure 6. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the polystyrenes ($[M]_0$ = 1.0 M) obtained with PhE-Cl/$SnCl_4$ (20 and 100 mM, respectively) at varying concentrations of n-$Bu_4N^+Cl^-$ in CH_2Cl_2 at −15 °C. The diagonal straight line indicates the calculated $\bar{M}_n$ values based on the formation of one polymer chain per PhE-Cl molecule.

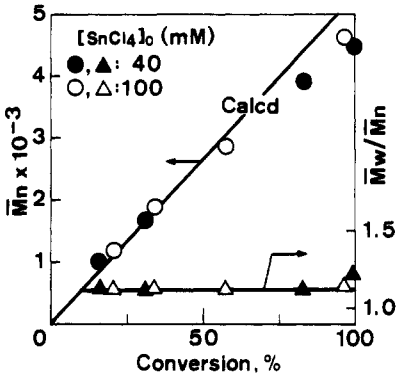


Figure 7. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the polystyrenes ($[M]_0$ = 1.0 M) obtained with PhE-Cl/$SnCl_4$ ($[PhE\text{-}Cl]_0$ = 20 mM) in the presence of n-$Bu_4N^+Cl^-$ (40 mM) at varyng concentrations of $SnCl_4$ in CH_2Cl_2 at −15 °C. The diagonal straight line indicates the calculated $\bar{M}_n$ values based on the formation of one polymer chain per PhE-Cl molecule.

the polymerization (Figure 4), suppresses the formation of the nonliving, broadly distributed, high molecular weight polymer fraction (Figure 5), and eventually results in living polystyrene (Figure 6). The implications of these effects of the added salt, relative to the living nature of the polymerization, will be discussed later in this paper.

Effects of Metal Halide ($SnCl_4$) Concentration. In this regard, styrene ($[M]_0$ = 1.0 M) was polymerized at varying concentrations of $SnCl_4$ (0, 40, and 100 mM), with the initial amounts of PhE-Cl (20 mM) and n-$Bu_4N^+Cl^-$ (40 mM) kept constant. Virtually no consumption of styrene took place at least within 20 h in the absence of $SnCl_4$ (see Figure 1).[10] However, an efficient polymerization occurred when $SnCl_4$ was present, and the reaction was accelerated with increasing $SnCl_4$ concentration. The rate dependence on the $SnCl_4$ concentration was apparently not of first order and was rather complicated. No further attempts were made to clarify this point.

Despite such an acceleration, the tin chloride concentration altered neither the narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.15$) nor the molecular weights of the polymers (Figure 7). The $\bar{M}_n$'s were consistently in direct proportion to conversion (living polymerization) and in close agreement with the calculated values based on the formation of one polymer chain per PhE-Cl molecule.

Effects of Solvent Polarity. In addition to the three components of the initiating systems (PhE-X, $SnCl_4$, n-$Bu_4N^+Y^-$), solvent polarity turned out to be an important factor that affected the rate and the living nature of the styrene polymerization with PhE-X/$SnCl_4$. The results

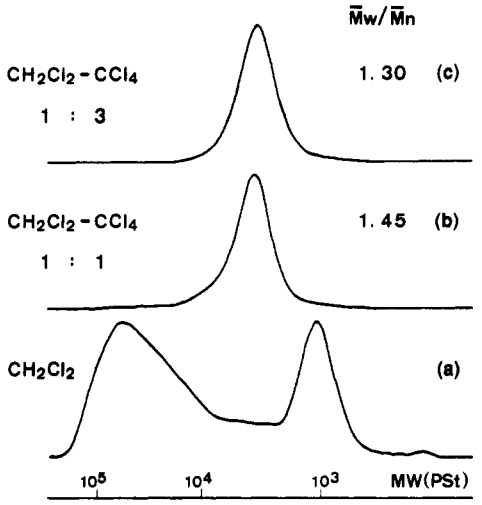


Figure 8. Effects of solvent polarity of the MWDs of the polystyrenes ($[M]_0$ = 1.0 M) obtained with PhE-Cl/$SnCl_4$ (20 and 100 mM respectively) in the presence of n-$Bu_4N^+Cl^-$ (40 mM) at −15 °C at a conversion of >85%. Solvent: CH_2Cl_2/CCl_4 (% v/v).

are a clue to understanding the role of n-$Bu_4N^+Y^-$ in more detail.

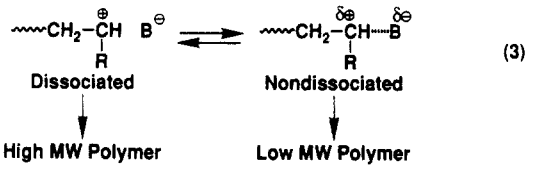
Figure 8 compares the MWDs of the polymers produced with the PhE-Cl/$SnCl_4$ system (without n-$Bu_4N^+Y^-$) at −15 °C in three CH_2Cl_2/CCl_4 solvent mixtures with different polarity. When solvent polarity was decreased by addition of nonpolar carbon tetrachloride to CH_2Cl_2, the overall rate of polymerization decreased considerably. For example, typical results of these experiments with respect to solvent composition (CH_2Cl_2/CCl_4, v/v), reaction time, and percent conversion were as follows: 100/0, 0.5 h, 88%; 50/50, 48 h, 76%; 25/75, 192 h, 86%.

Along with such a decrease in reaction rate, the polymer MWDs (for conversions of 80–90%) changed from a bimodal distribution with pure CH_2Cl_2 (Figure 8a) to unimodal and narrower distributions with the less polar CH_2Cl_2/CCl_4 mixtures (Figure 8b, c), and in the latter solvent mixtures, the MWDs became progressively narrower with decreasing solvent polarity. Importantly, in the least polar CH_2Cl_2/CCl_4 mixture (25/75 v/v), the $\bar{M}_n$ of the polymers was directly proportional to conversion, indicating the occurrence of a living polymerization. A similar effect of solvent polarity on styrene polymerization with PhE-Cl/$SnCl_4$ has recently been reported preliminarily by Choi et al.[14]

Bimodal MWD and Two Growing Species. Comparison of Figures 5 and 8 shows that the observed changes in MWD (from bimodal to unimodal and narrow) are the same for the products obtained upon the addition of the halide salt (n-$Bu_4N^+Y^-$) (Figure 5) and upon decrease in solvent polarity (Figure 8). In either way, a unimodal MWD resulted by the elimination of the high molecular weight polymer fraction and is indicative of a living styrene polymerization.

Such effects of added salts and solvent polarity on polymer MWDs have also been observed in the polymerizations of styrene initiated with acetyl perchlorate,[12] perchloric acid,[15] and other oxygen-containing protonic acids,[16] as well as those of other monomers[3a] such as p-alkoxystyrenes (with iodine[17] and hydrogen iodide/zinc iodide[6]). All of these lead to polymers with bimodal MWDs in polar media without added salts. From these effects, the bimodal MWDs have been attributed to the coexisting two growing species that propagate simultaneously but independently of each other,[3a,12] and the same is equally

true for the polymerization with PhE-X/$SnCl_4$ in salt-free CH_2Cl_2 solvent (eq 3; B^- = counteranion).



(3)

Of these two propagating species, the one for the high molecular weight polymer fraction is "dissociated" (favored in polar media) and more reactive; the other for the lower polymer fraction is "nondissociated" and less reactive.[10,12,16b] Because of its nondissociated nature, the latter growing species predominates in nonpolar media or in the presence of an added common ion salt (a neutral salt that possesses the same anion as that associating with the growing carbocation), where the ionic dissociation of carbocationic species is suppressed. Specifically for the polymerization of styrene with the PhE-X/$SnCl_4$ systems, this and preceding studies[10] have further demonstrated that the dissociated species for the higher polymer is not living (transfer-dominant), whereas the nondissociated species for the lower polymer is indeed living.

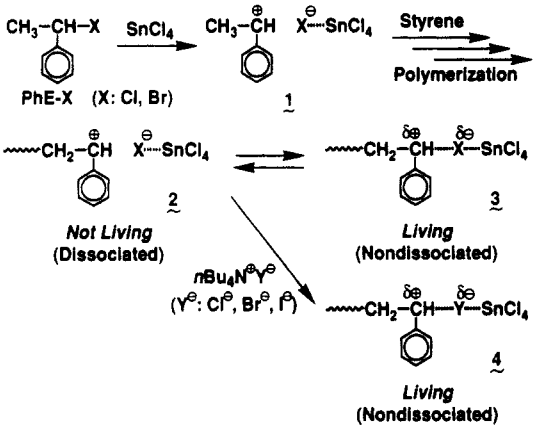
Roles of the Three Components of the Initiating Systems. As shown above, the $\bar{M}_n$ of the PhE-Cl/$SnCl_4$-initiated polymers is independent of the initial concentrations of both $SnCl_4$ (Figure 7) and $nBu_4N^+Cl^-$ (Figure 6) but is invariably close to the calculated value with the assumption that one polymer chain is formed from one PhE-Cl molecule (Figures 3, 6, and 7; the straight lines through the origin). Separate experiments indicated that the $\bar{M}_n$ of the polymers increases with decreasing initial PhE-Cl concentration, while the overall polymerization rate decreases. These facts show that the living growing end is generated quantitatively and entirely from PhE-Cl (or PhE-Br).

However, the other two components, $SnCl_4$ and $nBu_4N^+Cl^-$ (or $nBu_4N^+Y^-$ in general), are equally indispensable to induce the living styrene polymerization, despite the absence of their effects on polymer molecular weights. On one hand, $SnCl_4$ is critically needed to polymerize styrene with PhE-X, which is inert per se, and an increase in the $SnCl_4$ concentration accelerates the living polymerization. The added salt $nBu_4N^+Y^-$, on the other hand, is critically needed to form the living polystyrene with unimodal and narrow MWDs. Another effect of the added salts is a slight deceleration of the polymerization reaction (Figure 4). As discussed above, these salt effects stem from their ability in suppressing the formation of the reactive and dissociated growing species, which forms the nonliving higher polymer fraction.

Thus, PhE-X is a source of the growing end, $SnCl_4$ facilitates its generation from PhE-X, and $nBu_4N^+Y^-$ retains its living nature.

Polymerization Pathway. On the basis of these considerations, we propose the reaction sequence shown in Scheme I[11] as a generalized pathway for the living cationic polymerization initiated with the PhE-X/$SnCl_4$ systems in the presence of $nBu_4N^+Y^-$ (X, Y = Cl, Br, I). Thus, the polymerization starts with interaction between PhE-X and $SnCl_4$, by which the latter metal halide "activates" the carbon–halogen bond of PhE-X (schematically shown as 1) so that this originally inert *sec*-alkyl halide can react with styrene to commence propagation. The resulting growing end, therefore, most likely involves a carbocation associated by a binary counteranion like $^-X\cdots SnCl_4$ (see section 3 below for further discussion of this point). In this regard, PhE-X may be called "*initiator*", whereas $SnCl_4$ is the "*activator*".[3]

Scheme I
Living Cationic Polymerization of Styrene with PhE-X/$SnCl_4$/$nBu_4N^+Y^-$



Through the interaction of the two components, the PhE-X/$SnCl_4$ systems generate two independent growing species (dissociated (2) and nondissociated (3); eq 3) in CH_2Cl_2 solvent. For the living styrene polymerization to occur, $nBu_4N^+Y^-$ with a halide anion must be added.

The similarity of the effects of the added salt and solvent polarity (Figures 5 and 8, respectively) strongly suggests that the role of $nBu_4N^+Y^-$ is to suppress the ionic dissociation of the growing end, to eliminate the dissociated and nonliving species (2), and to selectively generate the nondissociated and living counterpart (like 3). However, in view of the fact that the salt's anion Y^- should be the halide ion but may not necessarily be the same as X^- from the initiator PhE-X (see section 1 and Figure 3), $nBu_4N^+Y^-$ cannot be regarded as a so-called "common ion" salt but can simply be an additive (halide donor) that most likely contributes to the stabilization of the growing species by supplying a nucleophilic halide anion so as to suppress the formation of the nonliving dissociation species 2. This stabilization should involve conversion of nonliving species 2 into another nondissociated species 4, which is the same as 3 (for Y = X) or different from 3 (for Y ≠ X). The nature of the living growing species will be further discussed in the following section.

3. ^{1}H NMR Analysis of Model Reactions: Nature of the Growing Species. To obtain further insight into the nature of the growing species in the living cationic polymerization with the PhE-X/$SnCl_4$ systems in the presence of $nBu_4N^+Y^-$, reactions of PhE-X with $SnCl_4$ and/or $nBu_4N^+Y^-$ (X, Y = Cl, Br) were directly analyzed by 270-MHz ^{1}H NMR spectroscopy. Except for the absence of styrene, the model reaction conditions were set to closely mimic those for the corresponding polymerizations in CH_2Cl_2, i.e., in CD_2Cl_2 at −40 °C (unless otherwise specified) at the following initial concentrations: PhE-X, 20 mM; $SnCl_4$, 100 mM; $nBu_4N^+Y^-$, 40 mM. Though employed originally as the initiator, PhE-X can be regarded as the simplest and most direct model of the polymer chain end to be generated from the PhE-X/$SnCl_4$ initiating systems.

The focus of the ^{1}H NMR analysis was on the interaction of PhE-X with $SnCl_4$ and/or $nBu_4N^+Y^-$ where X and Y differ from each other and on the nature of the intermediate(s) resulting therefrom, in relation to the possible halogen exchange[18] of PhE-X with the other components. Importantly, PhE-Cl and PhE-Br can readily be distinguished spectroscopically on the basis of their character-

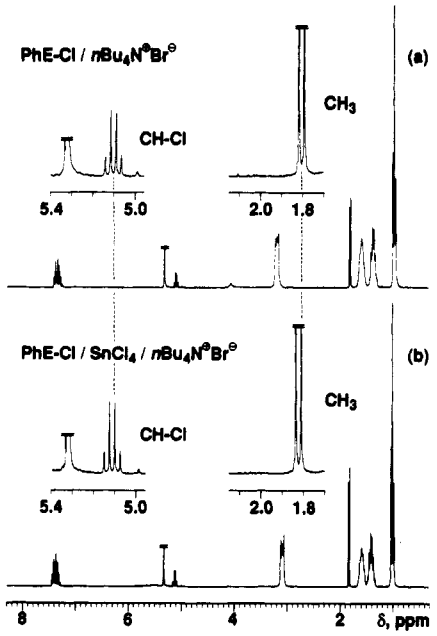


Figure 9. ^{1}H NMR spectra of PhE-Cl solutions in CD_2Cl_2 at −40 °C: (a) PhE-Cl + nBu$_4$N$^+$Br$^-$; (b) PhE-Cl + nBu$_4$N$^+$Br$^-$ + $SnCl_4$, 40 min after the addition of $SnCl_4$ into mixture a. $[PhE\text{-}Cl]_0$ = 20 mM; $[n\text{Bu}_4\text{N}^+\text{Br}^-]_0$ = 40 mM; $[SnCl_4]_0$ = 100 mM. The four signals appearing at 3.2–3.0 and 1.7–0.9 ppm are due to the n-butyl groups of nBu$_4$N$^+$Br$^-$; the peak at ca. 5.3 ppm is from CH_2Cl_2 in the deuterated solvent.

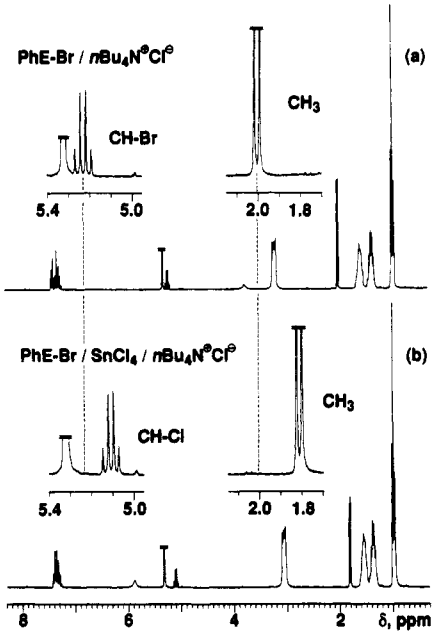
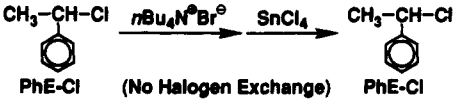


Figure 10. ^{1}H NMR spectra of PhE-Br solutions in CD_2Cl_2 at −40 °C: (a) PhE-Br + nBu$_4$N$^+$Cl$^-$; (b) PhE-Br + nBu$_4$N$^+$Cl$^-$ + $SnCl_4$, 4 min after the addition of $SnCl_4$ into mixture a. $[PhE\text{-}Br]_0$ = 20 mM; $[n\text{Bu}_4\text{N}^+\text{Cl}^-]_0$ = 40 mM; $[SnCl_4]_0$ = 100 mM. The four signals appearing at 3.2–3.0 and 1.7–0.9 ppm are due to the n-butyl groups of nBu$_4$N$^+$Cl$^-$; the peak at ca. 5.3 ppm is from CH_2Cl_2 in the deuterated solvent.

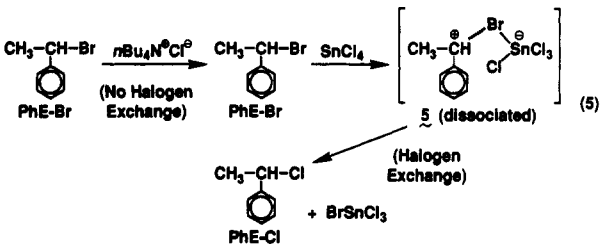
istic methyl and methine signals (CH_3/CH; δ, ppm): PhE-Cl, 1.81/5.10 (cf. Figure 9a); PhE-Br, 2.00/5.23 (cf. Figure 10a).

PhE-Cl/$SnCl_4$/nBu$_4$N$^+$*Br*$^-$ System. When PhE-Cl was mixed with nBu$_4$N$^+$Br$^-$, the spectrum of PhE-Cl remained unchanged from that of its original solution (Figure 9a). To this quiescent mixture was added $SnCl_4$ at −78 °C, and the temperature was raised to −40 °C. The spectrum remained unchanged after 1 h at this temperature (Figure 9b) and also at least for an additional 30 min after the temperature was raised to 0 °C. Thus, neither $SnCl_4$ nor nBu$_4$N$^+$Br$^-$ undergoes halogen exchange with PhE-Cl (eq 4).



(4)

PhE-Br/$SnCl_4$/nBu$_4$N$^+$*Cl*$^-$ System. Results contrasting with the above were obtained for this heterohalogen system. The spectrum of PhE-Br did not change on mixing it with nBu$_4$N$^+$Cl$^-$ (no halogen exchange; Figure 10a). On further addition of $SnCl_4$, however, the PhE-Br was rapidly converted into PhE-Cl (100% in 4 min), as evidenced by the complete disappearance of both methyl and methine resonances of PhE-Br and the immediate appearance of the corresponding quartet and doublet of PhE-Cl, respectively (Figure 10b). The spectral change apparently began during the initial treatment with $SnCl_4$ at −78 °C and immediately progressed during the subsequent fast warming of the mixture to −40 °C. The rapid conversion demonstrates that PhE-Br undergoes quantitative halogen exchange with chlorine in the presence of $SnCl_4$ and nBu$_4$N$^+$Cl$^-$ (eq 5).

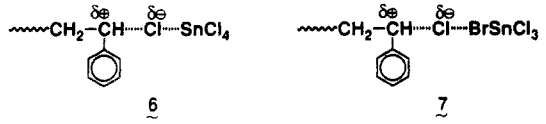


(5)

A similar halogen exchange was also observed at −40 °C on mixing PhE-Br with $SnCl_4$ alone, but no such exchange was detectable in a binary mixture of PhE-Br and nBu$_4$N$^+$Cl$^-$ alone. For the latter PhE-Br/nBu$_4$N$^+$Cl$^-$ pair, however, a partial conversion from PhE-Br into PhE-Cl indeed occurred slowly at +25 °C (ca. 50% in 72 h). In the halogen-exchange reaction in the PhE-Br/$SnCl_4$/nBu$_4$N$^+$Cl$^-$ system (eq 5), therefore, the chlorine in the newly formed PhE-Cl primarily comes from those in $SnCl_4$, although partial contribution from nBu$_4$N$^+$Cl$^-$ cannot be ruled out completely, particularly in the presence of the tin chloride (see below).

The halogen exchange between PhE-Br and $SnCl_4$, in turn, shows that $SnCl_4$ (activator) in fact interacts with PhE-Br (initiator) and, more important, that the interaction generates an *ionic* or a *dissociated* intermediate (schematically shown as **5** in eq 5), where the resulting mixed halide counteranion [$(BrSnCl_4)^-$] subsequently releases a chloride anion to afford PhE-Cl. Though undetectable by definition, a similar halogen exchange via an ionic intermediate should occur between PhE-Cl and $SnCl_4$ (i.e., PhE-*Cl** + $SnCl_4$ → PhE-Cl + *Cl**$SnCl_3$).

Nature of the Growing Species. Relative to the living cationic polymerization of styrene with the PhE-X/$SnCl_4$/nBu$_4$N$^+$Y$^-$ system (cf. Scheme I), the observation of halogen exchange in the model reactions leads to the following conclusions: (a) whether initiated with the chloride (PhE-Cl) or the bromide (PhE-Br), the growing end and the PhE-X initiators rapidly undergo a halogen exchange with the $SnCl_4$ activator (e.g., eq 5) to give such chloride-type intermediates as **6** and **7** (cf. species **3** in Scheme I); (b) when reacting with styrene to propagate, the growing end assumes an *ionic* or a *dissociated* form. Analogous anion exchange and involvement of ionic



6 7

intermediates have been observed for the living cationic polymerization of vinyl ethers with the hydrogen halide/zinc halide initiating systems.[18]

The occurrence of the rapid halogen-exchange reaction indicates that, in the presence of $SnCl_4$ and $nBu_4N^+Cl^-$, most of the polymer terminals carry a chloride terminal [$\sim CH_2CH(C_6H_5)$-Cl]. As shown by the absence of polymerization with PhE-Cl alone, the chloride-capped polymers cannot propagate by themselves but must be activated by $SnCl_4$ so as to propagate (as in the form of 6). In this regard, the chlorine-capped polymers are "dormant" species, and their activation by $SnCl_4$ most likely generates the nondissociated species (cf. 3 and 4, Scheme I). Although the identification of the exact nature of the nondissociated growing species still awaits further clarification, our NMR analysis indicates that the activation of the dormant species leads to an ionic species.

End-Group Analysis of Polymers. The $SnCl_4$-assisted exclusive formation of the chloride-type growing species (conclusion) was further corroborated by ^1H NMR structural analysis of the polystyrene samples obtained in the living polymerizations with the PhE-X/$SnCl_4$/$nBu_4N^+Y^-$ systems (quenched with methanol; $\bar{M}_n$ = 2000–5000, $\bar{M}_w/\bar{M}_n$ = 1.1–1.2). Thus, regardless of conversion and the types of the halogens X and Y in PhE-X and $nBu_4N^+Y^-$, the isolated polymers showed a broad signal around δ 4.3–4.5 ppm that is assignable to the methine proton of the chloride terminal [$\sim CH_2CH(C_6H_5)$-Cl].[19] No resonances were detected for other possible end groups such as an indan, an olefin, or a methoxide (though the polymerization was quenched with methanol).

The absence of the terminal methoxide indicates a strong interaction between the terminal carbon and chlorine, unlike the corresponding vinyl ether polymer chain ends [$\sim CH_2CH(OR)$-Z activated with zinc halide; Z = Cl, Br, I], which quantitatively give methoxides on quenching with methanol.[20] The absence of the indan and the olefinic terminals further supports the living nature of the styrene polymerization, which is free from chain transfer and termination expected to give these end groups.

Experimental Section

Materials. Styrene and bromobenzene (internal standard for gas chromatography) were purified by the usual methods[12a,16] and distilled twice over calcium hydride under reduced pressure. Commercial PhE-Cl, PhE-Br, and $SnCl_4$ (over phosphorus pentoxide) were distilled twice under reduced pressure. The five as-distilled reagents were sealed into brown ampules under dry nitrogen and stored in a freezer; gas chromatographic purity (except for $SnCl_4$) >99.5%. $SnBr_4$ (Aldrich, purity >99%, 1.0 M solution in CH_2Cl_2) and $EtAlCl_2$ (Kanto Chemical, purity >99%, 1.0 M solution in *n*-hexane) were used as received and handled under dry nitrogen. $nBu_4N^+Y^-$ (Y^- = Cl^-, Br^-, I^-, ClO_4^-) (all from Tokyo Kasei, purity >98%) were used as commercially supplied after drying in vacuo. CH_2Cl_2 (solvent) was washed with aqueous 10% sodium hydroxide solution and then with deionized water, dried overnight with calcium chloride, and distilled at least twice over calcim hydride into a glass flask containing 3-Å molecular sieves just before use. CD_2Cl_2 (Aldrich, >99.96% atm D) was used as received in sealed glass ampules.

Polymerization Procedures. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock.[10] Liquid reagents were transferred via dry syringes against a continuous nitrogen flow; solid reagents were taken into glass vessels in a nitrogen-filled drybox. The reaction was initiated by adding a solution of $SnCl_4$ in CH_2Cl_2 (0.50 mL) to a mixture (4.50 mL) of styrene (0.58 mL), PhE-X, $nBu_4N^+Y^-$, and bromoenzene (0.10 mL) in the same solvent at −15 °C and was quenched with prechilled methanol (2 mL) containing a small amount of ammonia. Conversion was determined from the residual concentration of styrene by gas chromatography with bromobenzene as an internal standard.

The quenched reaction mixtures were diluted with toluene (20 mL), washed with 2% hydrochloric acid and then with deionized water to remove the tin-containing residues, evaporated to dryness under reduced pressure, and dried in vacuo overnight to give the product polymers. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios of the polymers were measured by size-exclusion chromatography in chloroform on three polystyrene gel columns (Shodex K-802, K-803, and K-804, calibrated against 10 standard polystyrene samples in the molecular weight range from 10^2 to 3×10^5) that were connected to a Jasco 880-PU precision pump and a Jasco 830-RI refractive index detector. ^1H NMR spectra of the polymers were recorded at 270 MHz in $CDCl_3$ at 25 °C on a JEOL GSX-270 spectrometer.

^1H NMR Analysis of Model Reactions. The analysis on a typical mixture of PhE-X, $SnCl_4$, and $nBu_4N^+Y^-$, as well as on the other binary mixtures (such as PhE-X/$SnCl_4$), was carried out as follows. A mixture of PhE-X and $nBu_4N^+Y^-$ (40 and 80 mM, respectively) in CH_2Cl_2 (0.40 mL), from a stock solution prepared beforehand in a stopcocked flask, was injected into a septum-capped NMR sample tube (i.d. 5 mm) via a dry syringe under dry nitrogen, and the solvent was evaporated off under vacuum. The residue was immediately redissolved in 0.40 mL of CD_2Cl_2, and the solution was cooled to −78 °C in a dry ice/methanol bath. In a septum-capped small vial was dissolved $SnCl_4$ (neat, distilled; via a microsyringe) in CD_2Cl_2, and a portion of the cooled solution (200 mM, 0.40 mL) was injected into the NMR tube, followed by vigorous manual mixing. The tube was immediately inserted into the NMR probe port, which was kept at −78 °C in advance, and the first spectrum was measured at this temperature. Subsequently, the solution was warmed to −40 °C by quickly raising the probe temperature of the instrument, and additional spectra were taken. The ^1H NMR spectra were recorded under the following conditions: instrument, JEOL GSX-270; frequency, 270 MHz; spectral width, 6002.4 Hz (22.17 ppm); pulse width, 4.3 μs (45-deg pulse); data acquisition time plus pulse delay, 30 s; data points, 32 768; spectral accumulation, 16 transients (8.00 min/spectrum). The chemical shifts were determined relative to the signal of the residual CH_2Cl_2 (δ 5.32 ppm) in the deuterated solvent.

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(11) The triple arrow indicates the repeated addition (propagation reaction) of styrene to the growing end.

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(13) This trend indicates that the polymerization is fastest with the "all-chloride system" (i.e., PhE-Cl/$SnCl_4$/$nBu_4N^+Cl^-$) and decelerates in the following order: with a particular salt ($nBu_4N^+Y^-$), PhE-Cl > PhE-Br; with a particular PhE-X, $nBu_4N^+Cl^- > nBu_4N^+Br^-$ ($\geq nBu_4N^+I^-$). In view of the halogen exchange between PhE-Br and $SnCl_4$ (see section 3 of this paper), the slower polymerization with PhE-Br/$SnCl_4$ is probably due to the formation of $SnCl_3Br$, a Lewis acid weaker than $SnCl_4$.

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(19) The observed NMR signal is too far upfield for the corresponding terminal bromide [$\sim CH_2CH(C_6H_5)$-Br] (or the iodide), as indicated by the chemical shift difference between the methine signals of PhE-Cl and PhE-Br (Figures 9 and 10, respectively). The presence of the terminal chloride was also supported by elemental analysis: Miyashita, K.; Kamigaito, M.; Sawamoto, M.; Higashimura, T., to be submitted to *Macromolecules*.

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