# "Living" Cationic Polymerization of Styrene in the Presence of Tetrabutylammonium Salts

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ABSTRACT: The effect of tetrabutylammonium chloride on the kinetics and the molecular weight distribution in the cationic polymerization of styrene initiated by 1-phenylethyl chloride/$SnCl_4$ was investigated. This "living" system resembles classic cationic systems but proceeds with a lower instantaneous concentration of active carbocations. The carbenium ions form covalent species reversibly. The fraction of unpaired carbocations can be suppressed by addition of salts with common anions. When molecular weights are low enough, the transfer reactions cannot be easily detected and polymers with low polydispersities are formed. For this system, the upper limit of the molecular weight control is in the range of $M_n \approx 5000$ at 20 °C. Polymerization rates decrease approximately 5 times in the presence of a small amount of salt ([salt]/[$SnCl_4$] < 0.1), remain fairly constant until [salt]/[$SnCl_4$] ≈ 1, and then rapidly decrease at ratios [salt]/[$SnCl_4$] > 1. The changes in the structure of Lewis acid and anions were monitored by $^{119}Sn$ NMR. One average signal was observed at low salt concentrations due to a rapid exchange between $SnCl_4$ and $SnCl_5^-$. At ratios [salt]/[$SnCl_4$] > 1 very broad signals were found which were converted to a sharp signal of the $SnCl_6^{2-}$ anion at ratios [salt]/[$SnCl_4$] ≥ 2. The unusual kinetics and $^{119}Sn$-NMR data were explained by nearly equal ionization ability of $SnCl_4$ and the $SnCl_5^-$ anion and by the formation of inactive oligomeric anions ($Cl-[SnCl_5^-]_n$) at ratios [salt]/[$SnCl_4$] > 1.

## Introduction

The cationic polymerization of alkenes is difficult to control due to the high reactivity of carbenium ions. Propagation is rapid and is accompanied by termination and transfer in many systems. These side reactions, slow initiation, and slow exchange between various active sites result in low molecular weights and high polydispersities when polymerization is carried out at ambient and higher temperatures. Some "new living" cationic polymerization systems involving vinyl ethers,[1,2] styrene,[3,4] and isobutene[5,6] have been reported recently. They are based on the rapid equilibration between small amounts of active carbenium ions and large amounts of either dormant covalent species or dormant onium ions.[7] The total concentration of active centers (the sum of the concentration of both carbenium ions and dormant species) is usually equal to the initial concentration of initiator, $[I]_0$. Since $[I]_0$ is relatively high, these systems are less sensitive to impurities than classic systems operating at much lower $[I]_0$. A high initiator concentration also leads to a high concentration of growing chains and a relatively low degree of polymerization. Transfer reactions may not be detectable at lower molecular weights. If the initiating system is chosen correctly, initiation will be fast compared to propagation. In addition, due to the low transient concentrations of carbenium ions, polymerizations are slower and therefore easier to control.

The synthesis of polymers with narrow molecular weight distributions requires that the various active species in the polymerization system have similar reactivity or that they exchange rapidly compared to propagation.[7,8] Although at ambient temperatures the active ions and ion pairs in cationic polymerization seem to have similar reactivities,[9–11] their lifetimes are usually very different[12] which leads to high polydispersities. Thus, the broad and multimodal molecular weight distributions observed in classic cationic polymerizations may originate from slow exchange between various active sites having different reactivities or different lifetimes.

The lifetime of carbenium ions can be reduced by the addition of nucleophiles which rapidly form onium species. The proportion of free ions and their lifetimes can also be reduced by adding salts with anions capable of forming covalent species reversibly. This salt effect has been used successfully for improving the "livingness" of polymerizations of vinyl ethers,[13] *N*-vinylcarbazole,[14] isobutene,[15] and styrene.[16,17] In this paper the effect of adding tetrabutylammonium chloride on the polymerization of styrene initiated by 1-phenylethyl chloride/$SnCl_4$ in $CH_2Cl_2$ is reported.

## Experimental Section

Styrene was treated with KOH or NaOH, dried, and distilled from $CaH_2$ under reduced pressure. $CH_2Cl_2$ was washed with fuming acid until the acid layer remained colorless, washed with aqueous $NaHCO_3$ and distilled water, dried over $CaCl_2$, and distilled from $CaH_2$ at least twice under an inert atmosphere. 1-Phenylethyl chloride was prepared by bubbling HCl through 1-phenylethyl alcohol and purified by distillation from $CaH_2$ under reduced pressure. Tetra-*n*-butylammonium chloride was dried under high vacuum at 90 °C. $SnCl_4$ (Aldrich, 99.999% pure) was used as received.

Reactions were performed under nitrogen in a Vacuum Atmospheres drybox ([$H_2O$] and [$O_2$] < 1 ppm) or in a septum-sealed NMR tube purged with dry inert gas. A mixture of $SnCl_4$ and salt dissolved in $CH_2Cl_2$ was added to a mixture of initiator (1-phenylethyl chloride) and monomer dissolved in $CH_2Cl_2$. Polymerizations were terminated by the addition of a large excess of pyridine in methanol.

Polymerizations were monitored by $^1H$ NMR using either a GE GN-300 (300 MHz) or an IBM NR-300 (300 MHz) spectrometer at various reaction temperatures (±1 °C control). $^{119}Sn$ NMR spectra were obtained using an IBM NR-300 NMR (112 MHz).

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) in THF using a Waters GPC with three Ultrastyragel columns (100 Å, 500 Å and linear) in series. The calculation of molecular weights and polydispersities was based on polystyrene standards.

## Results and Discussion

Tin tetrachloride was used very early as a catalyst in the cationic polymerization of styrene.[18] In fact it is a coinitiator, because the true initiator[19] is either a proton source (such as water, alcohols, protonic acids) or an alkyl ester. The polystyrene formed in polymerizations coini-

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**Scheme I. "Living" Cationic Polymerization of Styrene Initiated by 1-Phenylethyl Chloride/$SnCl_4$ in the Presence of Salts**

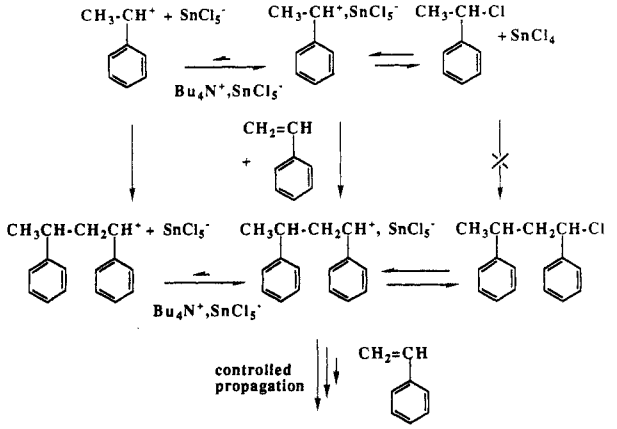
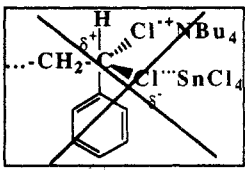



**Chart I. Previously Proposed Species with a Formally Pentacoordinated Carbon Atom**




tiated by $SnCl_4$ at ambient temperatures is usually of relatively low molecular weight with broad or even bimodal molecular weight distribution.[17] The ionic nature of this process has been postulated based on greater polymerization rates in more polar solvents[20] and on model studies in which racemization of optically active precursors is faster than their incorporation into polymer chains.[21] The bimodal molecular weight distributions observed in this work and before[17] may therefore originate from propagation by both free ions and ion pairs having different lifetimes. Thus, scavenging of free ions could produce polymers with low polydispersities (Scheme I). This was reported recently[4,17] but explained by the interaction of the ammonium salt chloride anion with the partially positively charged carbon atom from a covalent species activated by $SnCl_4$ (Chart I). However, the presence of this species with a formally pentacoordinated carbon atom is quite unlikely, and the interaction with a monomer molecule, required for the chain growth, is sterically restricted. In order to understand this system better, we have investigated the effect of added salt on the kinetics and molecular weight distribution and also followed changes in the structure of the Lewis acid and the anions with $^{119}Sn$ NMR and UV–vis spectroscopy.

**1. Kinetic Studies.** The polymerization of styrene was initiated by 1-phenylethyl chloride/$SnCl_4$ in $CH_2Cl_2$, in both the presence and absence of tetrabutylammonium chloride. As shown in Figure 1, the polymerization is internally first order in monomer. This indicates that monomer is consumed in the rate-determining step. Figures 2 and 3 demonstrate that the slopes of the kinetic plots (also rates of polymerization) increase linearly with both [1-phenylethyl chloride]$_0$ and $[SnCl_4]_0$. This indicates that the rate-determining step involves species which are created by interactions of the alkyl chloride and tin tetrachloride.

Figure 4 demonstrates that the addition of a small amount of $Bu_4N^+Cl^-$ slows the polymerization, as would be expected if it removes free ions from the system. Since the equilibrium constants for the equilibria between covalent species and ion pairs ($K_i^1$ in Scheme II) and

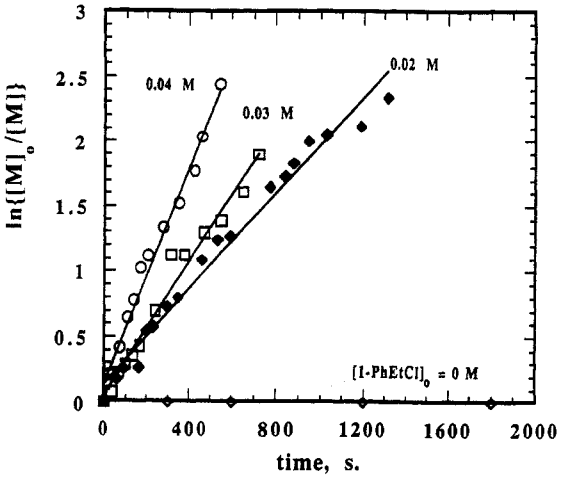



**Figure 1.** Kinetic plots for polymerization of styrene in $CD_2Cl_2$ at 20 °C ([styrene]$_0$ = 1 mol/L, $[SnCl_4]_0$ = 0.1 mol/L, $[Bu_4NCl]_0$ = 0.040 mol/L, [1-phenylethyl chloride]$_0$ = 0, 0.02, 0.03, and 0.04 mol/L).

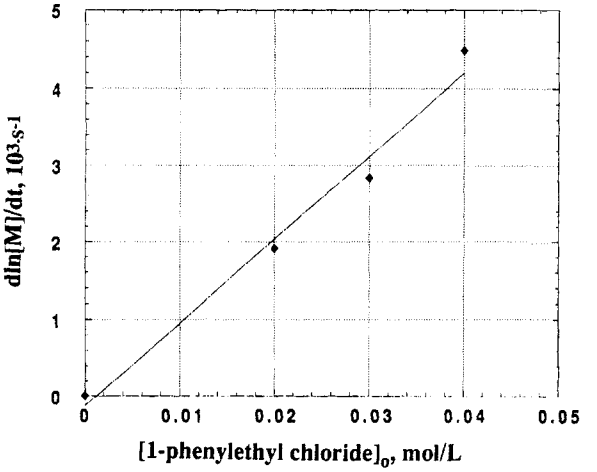



**Figure 2.** Effect of [1-phenylethyl chloride]$_0$ on polymerization rate for polymerization of styrene initiated by 1-phenylethyl chloride/$SnCl_4$ in the presence of tetrabutylammonium chloride in $CD_2Cl_2$ at 20 °C ([styrene]$_0$ = 1 mol/L, $[SnCl_4]_0$ = 0.1 mol/L, $[Bu_4NCl]_0$ = 0.04 M).

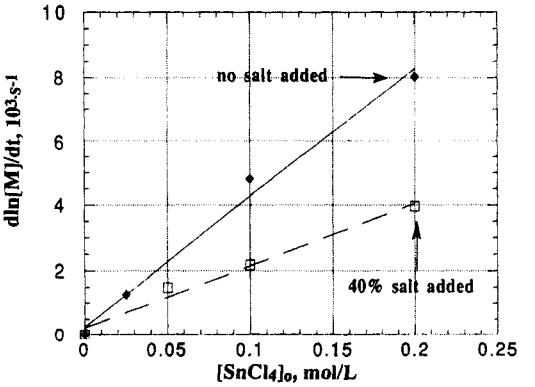



**Figure 3.** Effect of $[SnCl_4]_0$ on polymerization rate in systems with and without added salt in $CD_2Cl_2$ at 20 °C ([styrene]$_0$ = 1 mol/L, [1-phenylethyl chloride]$_0$ = 0.02 mol/L, $[Bu_4NCl]_0$ = 0 or 0.04 M).

between ion pairs and free ions ($K_D^1$) are quite small, the amount of ion pairs is approximately constant in the system, and free ions are converted to a large reservoir of dormant covalent species. The addition of only a small amount of the salt is sufficient to reduce the rates and polydispersities.

Chloride anion from added tetrabutylammonium chloride traps $SnCl_4$ to form tetrabutylammonium pentachlo-

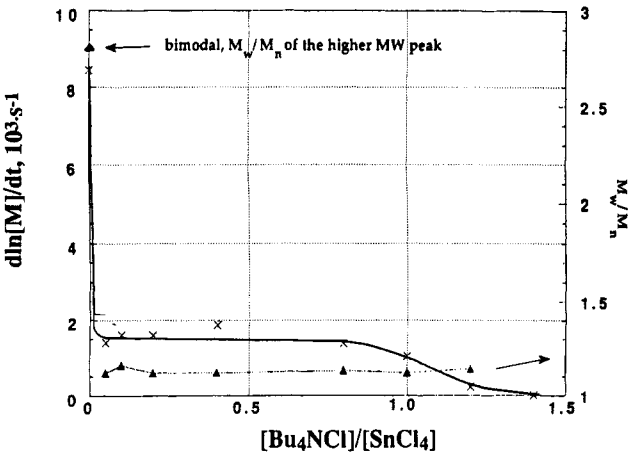



**Figure 4.** Effect of salt on the polymerization rate and polydispersity in $CD_2Cl_2$ at 20 °C ([styrene]$_0$ = 1 mol/L, [1-phenylethyl chloride]$_0$ = 0.02 mol/L, [$SnCl_4$]$_0$ = 0.1 mol/L, [$Bu_4NCl$]$_0$ = 0.005–0.14 mol/L).

**Scheme II. First Set of Equilibria**

$$NR_4^+, Cl^- + SnCl_4 \underset{}{\overset{K_s^1}{\rightleftharpoons}} NR_4^+, SnCl_5^-$$

$$R\text{-}Cl + SnCl_4 \overset{K_i^1}{\rightleftharpoons} R^+, SnCl_5^-$$

$$R^+, SnCl_5^- \overset{K_D^1}{\rightleftharpoons} R^+ + SnCl_5^-$$

rostannate. Thus, further addition of the salt was expected to reduce the polymerization rate by simply removing $SnCl_4$ from the system via complexation with $NR_4^+Cl^-$. This should lead to the complete inhibition of polymerization at 100% salt added. However, further addition of up to 100% salt reduces the polymerization rate by only 20–30%. This indicates that $SnCl_5^-$ may also ionize alkyl halides, although slightly less efficiently than $SnCl_4$. However, the polymerization rate is dramatically reduced when the salt concentration becomes higher than [$SnCl_4$]$_0$ (about a 1000 times rate decrease at 120% of salt added) (Figure 4). The reason for this behavior may be the formation of oligomerized anions, explained in subsequent sections.

**2. Molecular Weights and Molecular Weight Distribution.** Although the molecular weight distribution is very broad and bimodal in the absence of salt, it is dramatically reduced in the presence of less than 10% added salt (based on Lewis acid) as shown in Figures 4 and 5. Polydispersity and molecular weight do not change with further addition of salt up to 100%. This indicates that the added salt is sufficiently dry since moisture would act as an initiator and the concentration of active sites should therefore be higher than expected, leading to lower molecular weights. No polymerization was observed with salt but without initiator, in contrast to polymerization of vinyl ethers with $Bu_4NTiCl_5$.[22]

The resulting molecular weights obey the classic relation for living systems in which the degree of polymerization equals the ratio of the concentration of monomer reacted to the initial initiator concentration ([1-phenylethyl chloride]$_0$):

$$DP_n = \Delta[M]/[I]_0 \qquad (1)$$

The polymerization of styrene initiated by 1-phenylethyl chloride/$SnCl_4$ in the presence of tetrabutylammonium chloride obeys this relation for molecular weights up to 5000 ($DP_n \approx 50$) for polymerizations conducted at 20 °C. At lower initiator concentrations the molecular weight levels off because of transfer reactions. This will be discussed in the next paper on the effect of solvent and temperature on transfer reactions.

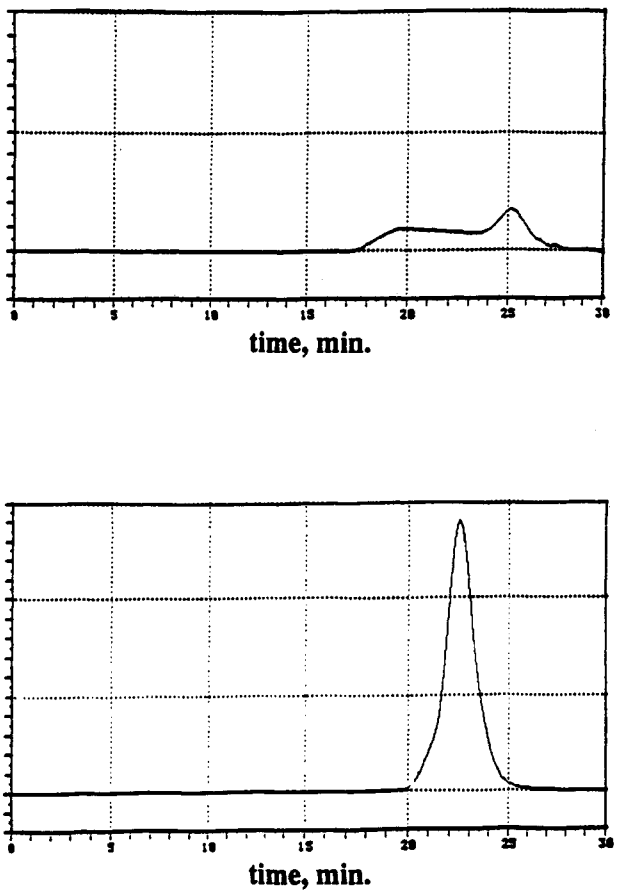



**Figure 5.** GPC traces of polystyrene obtained from polymerization of styrene initiated by 1-phenylethyl chloride/$SnCl_4$ without and with tetrabutylammonium chloride in $CD_2Cl_2$ at 20 °C at complete conversion (upper, without salt; lower, with added salt; [styrene]$_0$ = 1 mol/L, [1-phenylethyl chloride]$_0$ = 0.02 mol/L, [$SnCl_4$]$_0$ = 0.1 mol/L, [$Bu_4NCl$]$_0$ = 0 or 0.04 mol/L).

**3. $^{119}$Sn NMR Studies.** Tin tetrachloride can coordinate up to two chloride anions to form hexachlorostannate dianion via pentachlorostannate anion. The chemical shifts for $SnCl_4$, $SnCl_5^-$, and $SnCl_6^{2-}$ were reported to be −148, −480, and −732 ppm, respectively.[23] The addition of the salt at concentrations lower than or equal to [$SnCl_4$] results in one sharp signal that is approximately the mole average of $SnCl_5^-$ and $SnCl_4$ resonances (Figures 6 and 7). This indicates that the chloride ligands are rapidly exchanging between these species. However, when the added salt is in excess, the signal suddenly becomes very broad with a half-width >3000 Hz. When [$Bu_4NCl$]/[$SnCl_4$] is greater than 200%, a sharp signal at −732 ppm corresponding to $SnCl_6^{2-}$ is observed.

The changes in the NMR spectra correlate with changes in the polymerization kinetics as a function of salt concentration. There is a rapid drop in the polymerization rate when the salt concentration exceeds that of $SnCl_4$. The reaction mixture develops a slightly yellow color at lower salt concentrations due to the formation of $SnCl_5^-$ anion. The absorption spectrum of the solution with [$Bu_4NCl$]/[$SnCl_4$] = 0.6 displays a shoulder on the peak at 250 nm which extends to 500 nm. This shoulder disappears at [$Bu_4NCl$]/[$SnCl_4$] ≥ 1.0. At higher salt and $SnCl_4$ concentrations, a small precipitate appears which may be due to the formation of aggregated oligomeric or polymeric anionic species.

**4. Formation of Oligomeric Tin Species.** The present study indicates that a second set of equilibria

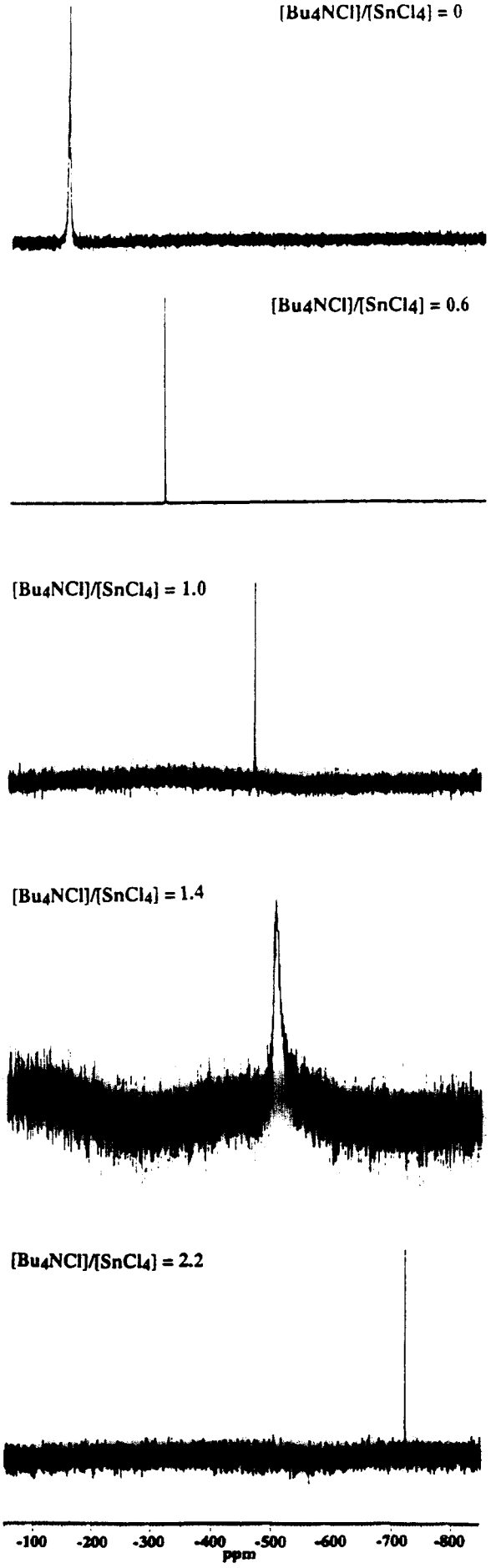



**Figure 6.** $^{119}Sn$ NMR spectra at various $[Bu_4NCl]_0/[SnCl_4]_0$ ratios in $CD_2Cl_2$ at 20 °C ($[SnCl_4]$ = 0.7 mol/L).

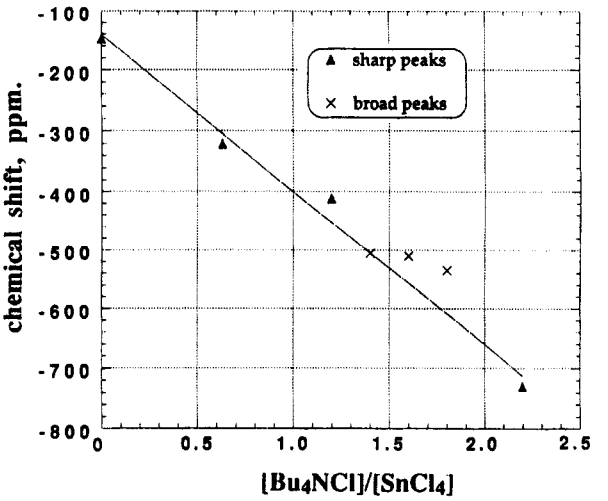



**Figure 7.** Effect of the $[Bu_4NCl]/[SnCl_4]$ ratio on $^{119}Sn$ NMR chemical shifts in $CD_2Cl_2$ at 20 °C ($[SnCl_4]$ = 0.7 mol/L).

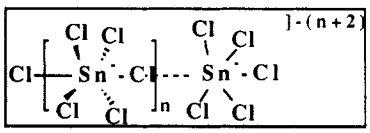
**Scheme III. Second Set of Equilibria**

$$NR_4^+,Cl^- + NR_4^+,SnCl_5^- \underset{}{\overset{K_s^2}{\rightleftharpoons}} (NR_4^+)_2,SnCl_6^{2-}$$

$$R\text{-}Cl + NR_4^+,SnCl_5^- \underset{}{\overset{K_i^2}{\rightleftharpoons}} R^+,SnCl_6^{2-},NR_4^+$$

$$Cl^- + n\ SnCl_5^- \underset{}{\overset{K_A^2}{\rightleftharpoons}} Cl\text{-}[(SnCl_4^-)Cl]_{n-1}\text{-}SnCl_5^-\text{-}Cl$$

**Chart II. Structure of Oligomeric Tin Species**



(Scheme III) involving coordination of a second chloride anion may be involved in the polymerization in addition to the equilibria described in Scheme II. Although the negative charge on $SnCl_5^-$ may strongly repel an additional chloride anion, tin tends to form hexacoordinated species which are more stable than pentacoordinated species and the ability of $SnCl_5^-$ to coordinate chloride anions is only slightly weaker than that of $SnCl_4$.[24] Thus, $SnCl_5^-$ is capable of ionizing alkyl halides and $K_s^1 > K_s^2$ but $K_i^1 \approx K_i^2$. This may explain the small drop in the polymerization rate upon going from 5 to 100% added salt, but it does not explain the sudden drop in the rate at >100% salt, as well as the corresponding change in the $^{119}Sn$ NMR spectra. Both phenomena may be due to a nearly quantitative removal of $SnCl_4$ and $SnCl_5^-$ from the system, which could be associated with oligomerization of $SnCl_5^-$ anions to form linear chains by –Cl– bridges (Chart II). Similar "oligomers" have been reported for other tin compounds[25,26] and are well-known for other elements such as antimony.[27]

In this case, the broadening of the NMR signals in the presence of 120–140% salt would be due to equilibration and reshuffling of the internal and terminal tin atoms which have different chemical shifts and to Sn–Sn coupling. Although the signal becomes sharp again at 200% salt, the system is inactive for polymerization due to the hexacoordinated structure of the anion. Pentacoordinated tin anions may have a spontaneous tendency to form oligomeric chains with the preferred hexacoordinated structure. However, at salt concentrations <100% there is free $SnCl_4$ in the system which may prevent the oligomerization by consuming any available chloride anions. Once $SnCl_4$ is consumed, hexacoordinated oligomers can be formed. Since all six valencies are occupied in oligomeric species, they are catalytically inactive.

**5. Estimation of the Proportions and Reactivities of Various Species. Dissociation Equilibria.** Covalent species are inactive in the cationic polymerization and serve as a source of the reactive carbocations. Therefore, the apparent rate constant of propagation depends on the proportion and reactivities of the carbenium ions: $k_p^{app} = k_p^i([C^+] + [C^\pm])/[I]_0$ The rate constant of ionic propagation, $k_p^i$, may still be a composite value if reactivities of free ions and ion pairs are different.

$$\begin{array}{ccc} C^+,A^- & \overset{K_D}{\rightleftharpoons} & C^+ + A^- \\ M \downarrow k_p^\pm & & M \downarrow k_p^+ \\ \text{polymer} & & \text{polymer} \end{array} \qquad (2)$$

$$K_D = [C^+][A^-]/[C^+,A^-] = \alpha^2/(1-\alpha)$$
$$k_p^i = \alpha k_p^+ + (1-\alpha)k_p^\pm$$

The rate constants of propagation in the cationic polymerizations of styrene initiated by the protonic acids were estimated to be in the range of $k_p \approx 10^5$–$10^6$ mol$^{-1}$·L·s$^{-1}$ at 25 °C by stopped-flow experiments.[10,11,28] In cationic systems, the reactivities of ion pair and free ions are similar.[29] Reactivities of free ions and ion pairs are identical for onium species[30] as well as in the addition of benzhydryl cations to alkenes.[31] In addition, reactivities of ion pairs do not change with the counterion. This was ascribed to the large size of onium and carbenium species which are strongly solvated regardless of the stage of association.[29] This is a big contrast to anionic systems in which counterions and not active species are solvated. In the polymerization of styrene initiated with triflic acid, ions are less than 7 times more reactive than ion pairs.[10] Assuming that the reactivities of growing polystyryl cations are not greatly affected by the nature of counterions, the concentration of active sites in the polymerization of styrene initiated by 1-phenylethyl chloride and activated by $SnCl_4$ can be estimated from a semilogarithmic plot of monomer conversion vs time. The slope of this plot is equal to the product of the rate constant of propagation and the momentary concentration of the growing carbenium ions (eq 3). In the absence of salt, the slope is

$$-d[M]/dt = k_p^i[M]([C^+] + [C^+,SnCl_5^-])$$

$$-d\ln[M]/dt = k_p^i([C^+] + [C^+,SnCl_5^-]) \qquad (3)$$

$-d\ln[M]/dt = 10^{-2}$ s$^{-1}$ at 25 °C in $CH_2Cl_2$, using $[M]_0 =$ 1 mol/L, $[R–Cl]_0 = 0.02$ mol/L, and $[SnCl_4]_0 = 0.1$ mol/L. Assuming $k_p^i \approx 10^5$ mol$^{-1}$·L·s$^{-1}$ (refs 10 and 11), this polymerization rate corresponds to the total concentration of ions and ion pairs ($[C^+] + [C^+,SnCl_5^-]$) $\approx 10^{-7}$ mol/L.

The polymerization rate is reduced approximately by a factor of 5 in the presence of a small amount of $Bu_4N^+Cl^-$. A 5 times reduction of the rate in the presence of salt corresponds to conversion of 80% of carbocations to covalent species, assuming similar reactivities of ion pairs and free ions. Thus, the dissociation constant can be estimated (eq 4 and 5)

$$K_D = ([C^+][SnCl_5^-])/[C^+,SnCl_5^-] \approx (8 \times 10^{-8}\ \text{mol/L})^2/2 \times 10^{-8}\ \text{mol/L} \qquad (4)$$

$$K_D \approx 3 \times 10^{-7}\ \text{mol/L} \qquad (5)$$

This dissociation constant is quite low when compared with that for trityl and benzhydryl salts which are in the range of $K_D \approx 10^{-5}$ mol/L under similar conditions.[31,32] To fit the observed rate decrease, the propagation rate constants on ions $k_p^+ \approx 10^5$ mol$^{-1}$·L·s$^{-1}$ and the dissociation constant in the range $K_D \approx 10^{-5}$ mol/L, it is necessary to assume reactivities of ion pairs 30 times higher than ions (very unlikely). It is, however, possible that $SnCl_4$ forms with impurities (e.g., water) ionic species such as hydronium pentachlorostannate or tetrachlorohydroxystannate. In such a case, even, in the absence of added salt the common ion effect may partially operate with the "advantitious" impurities. It is enough to have $10^{-5}$ mol/L of such species (ppm of $H_2O$) to fit a 5 times rate decrease and $K_D \approx 10^{-5}$ mol/L. This level of protonic impurities has no effect on molecular weights, since they are at concentrations 1000 times lower than initiator.

**Ionization Equilibria.** Alkyl esters and halides are reversibly ionized by Lewis acids. The equilibrium constant $K_i$ describes the ratio of the rate constants of ionization ($k_i$) and collapse of the ion pair (deactivation, $k_d$ in eq 6). The previously discussed calculations of the

$$...–CH_2CHPhCl + SnCl_4 \underset{k_d}{\overset{k_i}{\rightleftharpoons}} ...–CH_2C^+HPh,SnCl_5 \qquad (6)$$

concentration of ion pairs enables one to estimate the value of $K_i$.

$$K_i = [C^+,SnCl_5^-]/[R–Cl][SnCl_4] \approx 10^{-5}\ \text{mol}^{-1}\cdot\text{L} \qquad (7)$$

The ionization of 1-phenylethyl chloride by $SnCl_4$ has been previously studied in less polar solvents such as $CHCl_3$,[33] $C_6H_6$,[34] and $CCl_4$.[21] Ionization must be even more effective in more polar $CH_2Cl_2$. Rate constants of racemization (twice lower than that of ionization if the probabilities of inversion and retention are similar) are $k_{rac} = 0.015$ mol$^{-1}$·L·s$^{-1}$ in $CCl_4$ and $k_{rac} = 1.3$ mol$^{-1}$·L·s$^{-1}$ in $C_6H_6$ and should be even faster in $CH_2Cl_2$. Assuming the rate constant of ionization to be at least in the range of that found in benzene and knowing the equilibrium constant ($K_i = k_i/k_d \approx 10^{-5}$ mol$^{-1}$·L), we can estimate the lower limit of the rate constant of recombination of the counterions in the ion pair and formation of dormant covalent species $k_d > 10^5$ s$^{-1}$. This rate constant is in the same range as the propagation rate constant. The rapid recombination (lifetime of the ion pair $\tau_{ip} < 10^{-5}$ s) indicates that the ion pair converts to a dormant state after addition of (average) one monomer molecule. Thus, all chains will grow at approximately the same rate and polymers with narrow molecular weight distribution should be formed with ion pairs as chain carriers.

On the other hand, the lifetime of free carbocation will be determined by the rate constant of association of ions ($k_a \approx 10^9$ mol$^{-1}$·L·s$^{-1}$) and by the concentration of anions (eq 8). During this time, 0.01 s, a free ion can react 1000

$$\tau_i = 1/\{k_a[A^-]\} = 1/(10^9\ \text{mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1} \times 8 \times 10^{-8}\ \text{mol/L}) \approx 10^{-2}\ \text{s} \qquad (8)$$

times with monomer molecules (assuming $k_p = 10^5$ mol$^{-1}$·L·s$^{-1}$ and $[M]_0 = 1$ mol/L). However, molecular weights of the fraction suppressed by a common ion are in the range of $M_n \leq 20\,000$ rather than 100 000. This means that either this fraction is transfer dominated (formation of indan, terminal unsaturation) or scavenged by anions already present in the system (transfer to counterion), for example, hydronium tetrachlorohydroxystannate. At lower temepratures higher molecular

weights were found for this fraction, which indicates transfer as the main reason for low molecular weight.[17]

Salts such as tetrabutylammonium bromide form a mixed $SnCl_4Br^-$ anion which is not the same as the one produced from the initiator ($SnCl_5^-$). However, they have the similar effect on rates and polydispersities as tetrabutylammonium chloride.[17] This indicates the complete dissociation of the C–Cl bond during propagation and equivalence of all halide atoms in the counterion. Similar observations have been reported before in solvolysis studies[35,36] and recently in model studies in the polymerization of vinyl ethers.[37]

Thus, the polymerization of styrene initiated by the 1-phenylethyl chloride/$SnCl_4$ system with and without a tetrabutylammonium chloride additive in $CH_2Cl_2$ occurs through simple ionization of polymeric styryl chloride end groups by either a $SnCl_4$ or $SnCl_5^-$ anion and addition of carbocations to styrene. The lifetime of an ion pair is very short; it rapidly collapses to dormant covalent species. Less than one styrene molecule can be added during each ionization period. This leads to the formation of a polymer with a narrow molecular weight distribution. On the other hand, once the ion pair is dissociated, the lifetime of the free cation is much longer and higher polymer can be formed. The molecular weight of this fraction is probably transfer controlled. This fraction can be suppressed by addition of salts with common ions and salts with other anions capable of reversible formation of covalent species.

Thus, the new living system is basically working in the same way as classic systems initiated by $SnCl_4$. However, molecular weights are much lower and controlled by the amount of added initiator. Additionally, the dissociation of carbocationic ion pairs is suppressed by salts with common ions. Molecular weights are usually low, transfer cannot be easily detected, and polymers with low polydispersities are formed.

In subsequent papers we will discuss the contribution of transfer reactions in this system at various temperatures and various solvents as well as the effect of the structure of Lewis acid on the kinetics and polydispersities.

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