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Living cationic polymerization of styrene by the methanesulfonic acid/tin tetrachloride initiating system in the presence of tetra-n-butylammonium chloride

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Summary

Living cationic polymerization of styrene was achieved by the methanesulfonic acid/tin tetrachloride ($CH_3SO_3H/SnCl_4$) initiating system in the presence of tetra-n-butylammonium chloride (nBu_4NCl) in methylene chloride solvent below 0 °C. The typical reagent concentrations of this initiating system were as follows: $CH_3SO_3H/SnCl_4/nBu_4NCl$ = 20/100/40 mM; $[Styrene]_0$ = 1.0 M. The number-average molecular weights of the product polymers increased in direct proportion to monomer conversion, and their molecular weight distributions (MWDs) were fairly narrow ($\bar{M}_w/\bar{M}_n \leq 1.2$) throughout the reaction. On addition of a fresh feed of styrene at the end of the polymerization, the added feed was smoothly polymerized at the same rate as in the first stage; the polymer molecular weight further increased in direct proportion to monomer conversion; and their molecular weight distributions stayed narrow ($\bar{M}_w/\bar{M}_n$ = 1.2-1.3). On the other hand, in the absence of nBu_4NCl, the polymerization initiated by $CH_3SO_3H/SnCl_4$ in CH_2Cl_2 at -15 °C led to non-living polymers with a broad molecular weight distribution. This indicates that nBu_4NCl is essential to this living system.

Introduction

Since the heralding discoveries for vinyl ethers (1) and isobutene (2), living cationic polymerization is now feasible for a variety of vinyl monomers. For styrene, however, such a living process has been considered difficult to occur, because of the low cationic polymerizability of the monomer and the low stability of the growing carbocation generated therefrom. Recently, two research groups (3,4) have independently studied the cationic polymerizations of styrene initiated by an aryl acetate in conjunction with boron trichloride. Kennedy's systems (3) have been reported to be living, where the number-average molecular weight ($\bar{M}_n$) of the polymer increases in direct proportion to monomer conversion, however, the molecular weight distribution (MWD) is broad. Matyjaszewsky's systems (4) indeed lead to polystyrene with a fairly narrow MWD but apparently involve termination.

This study is concerned with a truly living cationic polymerization of styrene by the methanesulfonic acid/tin tetrachloride ($CH_3SO_3H/SnCl_4$) initiating system, where a narrow MWD and a controlled polymer molecular weight can be achieved in methylene chloride (CH_2Cl_2) at 0 °C or below in the presence of an added salt, tetra-n-butylammonium chloride (nBu_4NCl).

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Results and Discussion

Polymerization of Styrene by $CH_3SO_3H/SnCl_4$ in the Presence of nBu_4NCl

Styrene was polymerized with a mixture of CH_3SO_3H and $SnCl_4$ in the presence of nBu_4NCl in CH_2Cl_2 at -15 and 0 °C (Figure 1). The tin and ammonium salts were in molar excess over the protonic acid;i.e., in typical runs, CH_3SO_3H, 10-20 mM; $SnCl_4$, 100 mM; nBu_4NCl, 40 mM; styrene, 1.0 M. CH_3SO_3H and $SnCl_4$ were mixed in CH_2Cl_2 at room temperature immediately before added to a solution of styrene and nBu_4NCl. Under these conditions, quantitative polymerizations invariably occurred without an induction phase and were completed after 1-4 hr, being faster at a higher CH_3SO_3H concentration (Figure 1, ○ vs. ●) or at a higher temperature (◑ vs. ○). The reaction mixtures were homogeneous and colorless throughout.

The MWDs of the polymers, thus obtained in the presence of nBu_4NCl, were all narrow ($\bar{M}_w/\bar{M}_n \sim 1.2$), independent of monomer conversion and reaction temperature, as shown in Figure 2. The $\bar{M}_n$ values increased in direct proportion to monomer conversion, indicating the polymerization is living (see below). At a constant CH_3SO_3H concentration and monomer conversion,

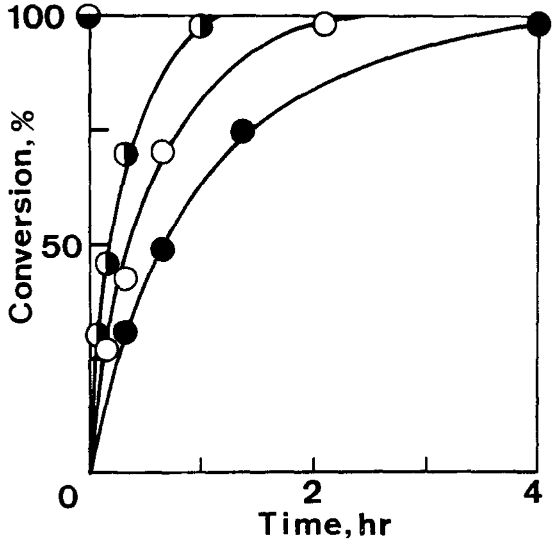

Figure 1. Time-conversion curves for the polymerization of styrene with $CH_3SO_3H/SnCl_4$ in CH_2Cl_2 in the presence and absence of nBu_4NCl: $[\text{styrene}]_0 = 1.0$ M. The polymerization temperature and reagent concentrations (in mM) as shown below.

Symbol	Temp. (°C)	$[CH_3SO_3H]_0$	$[SnCl_4]_0$	$[nBu_4NCl]_0$
◒	-15	20	100	0
◑	0	20	100	40
○	-15	20	100	40
●	-15	10	100	40

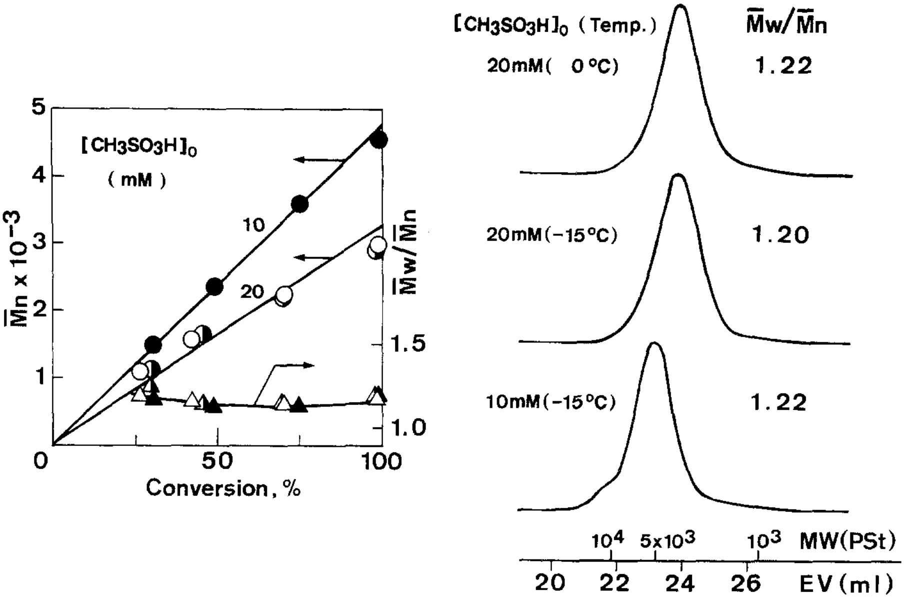

Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of polystyrene obtained with $CH_3SO_3H/SnCl_4$ in CH_2Cl_2 in the presence of nBu_4NCl: $[styrene]_0 = 1.0$ M. MWD was measured on polymers obtained at conversion ca. 100 %; the polymerization temperature and reagent concentrations (in mM) as shown below.

Symbol	Temp. (°C)	$[CH_3SO_3H]_0$	$[SnCl_4]_0$	$[nBu_4NCl]_0$
● , ▲	-15	10	100	40
○ , △	-15	20	100	40
◑ , ◮	0	20	100	40

polymer molecular weights were independent of polymerization temperature (Figure 2, ○ and ◑), but they were higher at a lower CH_3SO_3H concentration, though not inversely proportional to it (Figure 2, ● and ○). It is therefore possible to control the $\bar{M}_n$ of the polymers by regulating the initial CH_3SO_3H concentration or monomer conversion.

The observed $\bar{M}_n$'s, however, turned out smaller than the calculated values assuming that one polymer chain forms per CH_3SO_3H molecule; e.g., at 100 % monomer conversion, $\bar{M}_n = 4600$ (obd) vs. 10000 (calcd) and $\bar{M}_n = 3000$ (obd) vs. 5000 (calcd) for $[CH_3SO_3H]_0 = 10$ and 20 mM, respectively. At present, we are unable to offer any explanation to thus discrepancy, which should be related to the initiation and propagation mechanisms by the $CH_3SO_3H/SnCl_4/nBu_4NCl$ system.

In the absence of nBu_4NCl but otherwise under the same conditions, in contrast, the polymerization was almost instantaneous and completed within 1 minute (Figure 1, ◒). The produced polymers had very broad MWDs ($\bar{M}_w/\bar{M}_n$ = 6-7) and were not living.

Monomer-Addition Experiment

The living nature of the styrene polymerization by the $CH_3SO_3H/SnCl_4/nBu_4NCl$ system was further demonstrated by a so-called "monomer-addition" experiment in CH_2Cl_2 at -15 °C. A fresh feed of styrene (1.0 M, equivalent to the first charge) was added to the reaction mixture when the initial supply of the monomer was completely depleted. The added styrene feed was smoothly polymerized at nearly the same rate as the first charge was. As shown in Figure 3, after the monomer addition, polymer molecular weight further increased in direct proportion to monomer conversion as it did in the first stage. Though slightly broadening, the MWDs of the polymers in the second-stage polymerization were narrow ($\bar{M}_w/\bar{M}_n$ = 1.2 - 1.3).

In conclusion, living cationic polymerization of styrene was achieved by using the $CH_3SO_3H/SnCl_4$ initiating system in CH_2Cl_2 below 0 °C in the presence of nBu_4NCl. This initiating system formally resembles the hydrogen iodide-based systems previously reported (HI/I_2, HI/ZnI_2, etc.) (1) in that it consists of a protonic acid (CH_3SO_3H) and a Lewis acid ($SnCl_4$), but it clearly differs from them in the following aspects: (i) a relatively strong Lewis acid ($SnCl_4$) is employed; (ii) nBu_4NCl is needed to achieve the living polymerization; (iii) the Lewis acid (100 mM) and nBu_4NCl (40 mM) are molar excess over the protonic acid (20 mM).

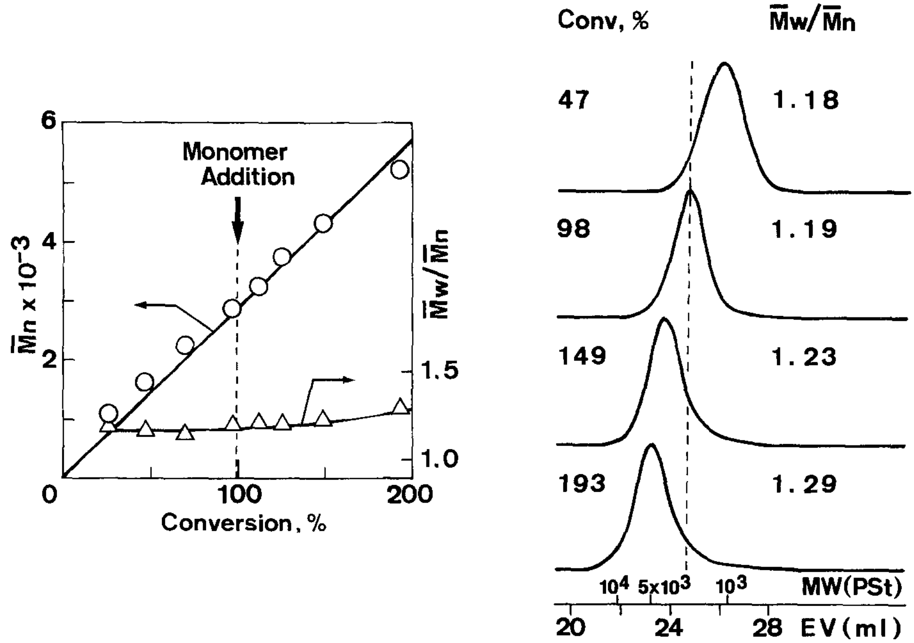

Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of polystyrene obtained with $CH_3SO_3H/SnCl_4$ in a monomer-addition experiment in CH_2Cl_2 at -15 °C in the presence of nBu_4NCl: $[styrene]_0$ = 1.0 M; $[CH_3SO_3H]_0$ = 20 mM; $[SnCl_4]_0$ = 100 mM; $[nBu_4NCl]_0$ = 40 mM. The molar amount of the second styrene feed was the same as in the first.

Among these features, the use of nBu_4NCl is unique and of particular importance in the living styrene polymerization by $CH_3SO_3H/SnCl_4$. Thus, the ammonium salt retards the polymerization (Figure 1) and is essential to give rise to a narrowly distributed living polystyrene (Figures 2 and 3). Although nBu_4NCl and related alkylammonium salts have already been employed for living cationic polymerizations of p-methylstyrene (5), N-vinylcarbazole (6), and isobutyl vinyl ether (7,8), their role therein is still obscure. In some cases (5,6), its function is attributed to a common ion salt effect, but this is probably not the case for the $CH_3SO_3H/SnCl_4$-mediated living polymerization, where the counteranion of the growing species is apparently not the chloride anion. There remains, however, a possibility that the chloride anion of nBu_4NCl alters the nature of the counteranion that is derived from $CH_3SO_3H/SnCl_4$.

Alternatively, nBu_4NCl may function as a nucleophile that stabilizes the growing carbocation generated by the $CH_3SO_3H/SnCl_4$ initiating system. In fact, the observed effects of this ammonium salt (Figures 1-3) are phenomenologically similar to those of externally added bases (like esters and ethers) on the polymerization of isobutyl vinyl ether with the cationogen/ethylaluminum dichloride initiating system (1b,9,10). These added bases indeed decelerate the vinyl ether polymerization and are essential to attain the livingness of the vinyl ether polymerization. It has been proposed (1b) that the externally added bases stabilize the growing carbocation via a nucleophilic interaction to give a living species.

With these possibilities in mind, we are currently studying the role of each component of the $CH_3SO_3H/SnCl_4/nBu_4NCl$ initiating system and the mechanism of the living polymerization thereby, which will be among the subjects of our forthcoming publications.

Experimental

Materials

nBu_4NCl (Tokyo Kasei, purity > 98 %) was used as recieved after drying in vacuo. $SnCl_4$ (Wako, purity > 97 %) was distilled under reduced pressure over phosphorus pentoxide. CH_3SO_3H (Wako, purity > 98 %) was used as received. Styrene, bromobenzene as an internal standard for gas chromatography, and methylene chloride were distilled at least twice over calcium hydride.

Procedures

Polymerization was carried out under dry nitrogen in baked glass tubes each equipped with a three-way stopcock. The reaction was initiated by addition of an initiator solution ($CH_3SO_3H/SnCl_4$ in CH_2Cl_2; 1 ml) into a monomer solution (in CH_2Cl_2; 4 ml) containing nBu_4NCl and bromobenzene, the latter being an internal standard for gas chromatography. After a certain period, the polymerization was terminated with prechilled ammoniacal methanol (2.0 ml). Monomer conversion was determined from its residual concentration measured by gas chromatography.

The quenched reaction mixtures were washed with dilute hydrochloric acid and then with water to remove the initiator residues, evaporated under reduced pressure, and vacuum dried to give the produced polymers. The MWD of the polymers was measured by size-exclusion chromatography (SEC) in chloroform at room temperature on a JASCO 880-PU chromatograph equipped with three polystyrene gel columns (Shodex K-802, K-803, and K-804) and refractive index/ultraviolet dual detector. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the polymers were calculated from SEC eluograms on the basis of a polystyrene calibration.

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