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Living cationic polymerization of styrene by the 1-phenylethyl chloride/tin tetrachloride initiating system in the presence of tetra-n-butylammonium chloride

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Summary

An initiating system, consisting of 1-phenylethyl chloride, tin tetrachloride, and tetra-*n*-butylammonium chloride [$CH_3CH(Ph)Cl/SnCl_4/nBu_4NCl$], led to living cationic polymerization of styrene in CH_2Cl_2 solvent at -15 °C; typically, $CH_3CH(Ph)Cl/SnCl_4/nBu_4NCl$ = 20/100/40 mM for 1.0 M of styrene. The living nature of the process was confirmed by an increase in the number-average molecular weight ($\bar{M}_n$) of the polymers in direct proportion to monomer conversion and its continuation on supplying a fresh feed of styrene after the polymerization; the observed $\bar{M}_n$ was close to the calculated value assuming that one molecule of $CH_3CH(Ph)Cl$ yields one living polymer. Throughout these reactions, the polymer's molecular weight distribution (MWD) stayed very narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$), though slightly broadening after the second monomer addition. In the absence of nBu_4NCl, the $CH_3CH(Ph)Cl/SnCl_4$ system yielded polystyrene with a bimodal MWD where the lower polymer fraction alone was apparently of a long lifetime. Styrene polymerization with the $H_2O/SnCl_4$ system was also examined, both with and without added nBu_4NCl, and a long-lived propagating species was obtained in the presence of nBu_4NCl.

Introduction

Quite recently, we have reported living cationic polymerization of styrene initiated by a combination of methanesulfonic acid and tin tetrachloride ($CH_3SO_3H/SnCl_4$) in methylene chloride (CH_2Cl_2) solvent in the presence of tetra-*n*-butylammonium chloride (nBu_4NCl) (1). In addition of the living nature of the polymerization, we have noticed two important facts therein: First is a vital role of added nBu_4NCl; namely, the reaction is living in the presence of the salt, whereas without it the CH_3SO_3H /$SnCl_4$ systems leads to a nonliving polymerization. This fact indicates that the chloride anion is indispensable in attaining this particular living process. Second, although the number average-molecular weight ($\bar{M}_n$) of the polymers is indeed proportional to monomer conversion and decreases at a higher concentration of CH_3SO_3H, $\bar{M}_n$ is clearly lower than the calculated value assuming that one CH_3SO_3H molecule forms one living chain. A rather complex initiation/propagation mechanism has been suggested.

In view of these observations, particularly the critical role of the chloride anion, we employed, in this study, another new initiating system that comprises 1-phenyethyl chloride [$CH_3CH(Ph)Cl$] and $SnCl_4$; and the $CH_3CH(Ph)Cl/SnCl_4$ system was applied to styrene in CH_2Cl_2 solvent either in the presence or absence of added nBu_4NCl. Because $CH_3CH(Ph)Cl$ is regarded

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*To whom offprint request should be addressed as the adduct of styrene and hydrogen chloride (HCl), the $CH_3CH(Ph)Cl/SnCl_4$ initiating system is formally equivalent to $HCl/SnCl_4$, in which the protonic acid component in the $CH_3SO_3H/SnCl_4$ counterpart is replaced with HCl.

We herein report that specifically in the presence of nBu_4NCl, the $CH_3CH(Ph)Cl/SnCl_4$ system induces a well-defined living cationic polymerization to give polystyrene with a controlled molecular weights and a very narrow molecular weight distributions (MWD).

Results and Discussion

Styrene Polymerization by $CH_3CH(Ph)Cl/SnCl_4$

Styrene was polymerized by the $CH_3CH(Ph)Cl/SnCl_4$ system in CH_2Cl_2 solvent at -15 °C, either in the presence or absence of added nBu_4NCl. The typical reagent concentrations were as follows: $[styrene]_0 = 1.0$ M; $[CH_3CH(Ph)Cl]_0 = 20$ mM; $[SnCl_4]_0 = 100$ mM; $[nBu_4NCl]_0 = 40$ mM. Under both conditions, quantitative polymerizations smoothly occurred, and the presence of nBu_4NCl clearly retarded the reaction; i.e., styrene conversion reached 88% in 0.5 h without nBu_4NCl and 83% in 1.5 hr with nBu_4NCl. Without $SnCl_4$, $CH_3CH(Ph)Cl$ alone could not polymerize styrene at all.

Figure 1, A and B, show the MWDs of the polymers thus obtained in the

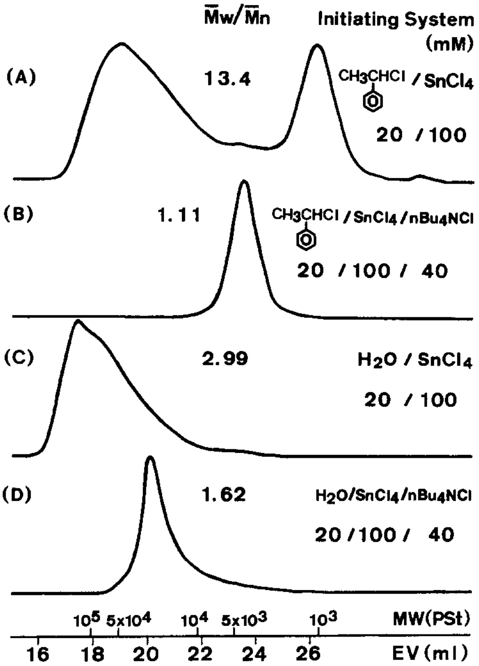

Figure 1. MWD of polystyrene obtained in CH_2Cl_2 at -15 °C: $[styrene]_0 = 1.0$ M; conversion ca. 80%. Initiating systems: (A and B) $CH_3CH(Ph)Cl/SnCl_4$; (C and D) $H_2O/SnCl_4$; reagent concentrations as indicated; B and D with added nBu_4NCl. All MWD curves were obtained on the column set (a) specified in the Experimental; thus, curves A and C are false-shaped for elution volume < 17 mL (beyond the exclusion limit).

absence and presence of nBu_4NCl, respectively. The salt-free system yielded polymers with a bimodal MWD (Figure 1A) in which the higher polymer fraction had a broad MWD whose peak molecular weight stayed virtually unchanged throughout the reaction, whereas the lower polymer part was of a much narrower distribution that shifted progressively toward higher molecular weight with increasing conversion.

In the presence of nBu_4NCl, in contrast, polymers with a unimodal and very narrow MWD ($\bar{M}_w/\bar{M}_n \lesssim 1.1$) were produced (Figure 1B). This distribution, in terms of narrowness and molecular weight range, was similar to that of the lower polymer fraction for the nBu_4NCl-free system; namely, the added ammonium salt apparently suppressed the formation of the higher polymer fraction. More important, the peak molecular weight similarly increased as the polymerization progressed, indicating the involvement of a living intermediate. It is also important that the MWD with $\bar{M}_w/\bar{M}_n \lesssim 1.1$ is perhaps the narrowest among the polystyrenes hitherto obtained in cationic polymerization.

Living Polymerization by $CH_3CH(Ph)Cl/SnCl_4/nBu_4NCl$

To clarify further the living nature of the polymerization by $CH_3CH(Ph)Cl/SnCl_4$ in the presence of nBu_4NCl, a fresh styrene feed was added to a reaction mixture in CH_2Cl_2 at -15 °C where the first-phase polymerization was almost completed (at 92-96% conversions). The added monomer was readily polymerized to quantitative conversion. Figure 2 shows the $\bar{M}_n$ values and MWDs of the product polymers, obtained before and after the

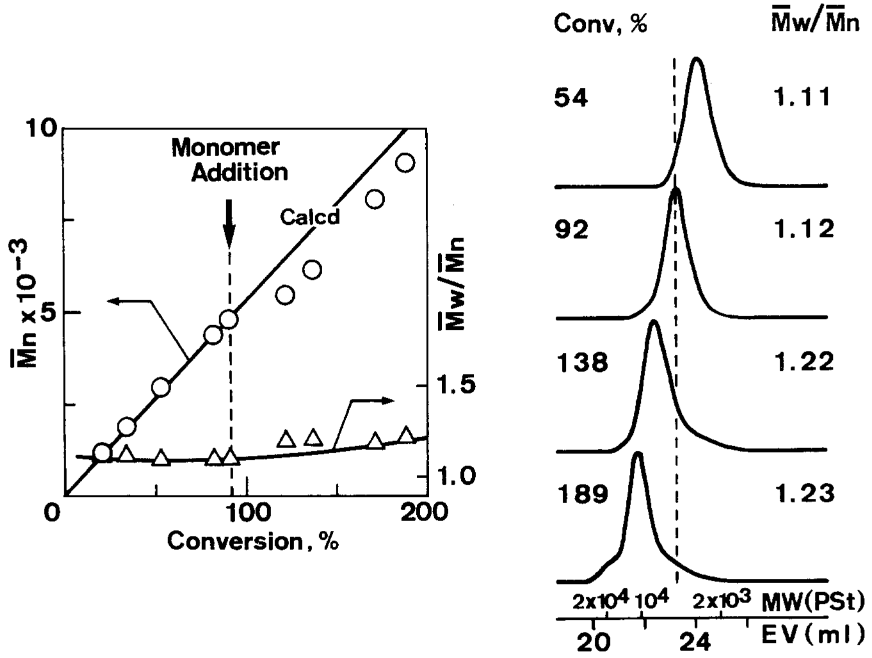

Figure 2. $\bar{M}_n$ and MWD of polystyrene obtained with $CH_3CH(Ph)Cl/SnCl_4$ in a monomer-addition experiment in CH_2Cl_2 at -15 °C in the presence of nBu_4NCl: $[\text{styrene}]_0$ = 1.0 M; $[CH_3CH(Ph)Cl]_0$ = 20 mM; $[SnCl_4]_0$ = 100 mM; $[nBu_4NCl]_0$ = 40 mM. The molar amount of the second styrene feed was the same as in the first.

second monomer addition, as a function of conversion. The $\bar{M}_n$ increased proportionally to conversion; the linear increase was smoothly continued in the second-stage polymerization; and the observed $\bar{M}_n$ values were in close agreement with those calculated with the assumption that one molecule of $CH_3CH(Ph)Cl$ forms one polymer chain. In addition, the narrow MWDs of the polymers ($\bar{M}_w/\bar{M}_n \leq 1.1$) were still maintained after the monomer addition, although a slight broading was observed ($\bar{M}_w/\bar{M}_n \leq 1.2$) and a small amount of higher polymers was formed at higher conversion.

All these facts demonstrate that living polymerization of styrene has been achieved with the $CH_3CH(Ph)Cl/SnCl_4$ system in conjunction with added nBu_4NCl. Particularly important, this new initiating system excels the $CH_3SO_3H/SnCl_4$ counterpart (1) in that the use of $CH_3CH(Ph)Cl$ in place of CH_3SO_3H leads to the near quantitative initiation efficiency from the chloride; accordingly, $\bar{M}_n$ = (weight of reacted styrene)/$[CH_3CH(Ph)Cl]_0$. The agreement between the observed and calculated $\bar{M}_n$ values further shows that $CH_3CH(Ph)Cl$ is herein an initiator that triggers styrene polymerization in the presence of $SnCl_4$, which serves as an acitivator (or coinitiator).

Styrene Polymerization by $H_2O/SnCl_4$

The above-described polymerization experiments were all carried out under a dry nitrogen atmosphere where the reaction mixtures contained ca. 0.5 mM of adventitious water. It has been well-documented that such water, as protogen, is able to initiate styrene polymerization in the presence of $SnCl_4$, and the initiation from water may occur parallel in the living polymerization by $CH_3CH(Ph)Cl/SnCl_4$. We thus examined styrene polymerization with purposefully added water in conjunction with $SnCl_4$, either in the presence and absence of nBu_4NCl. Except for the use of water instead of $CH_3CH(Ph)Cl$, all the other reagent concentrations were unchanged ($H_2O/SnCl_4/nBu_4NCl$ = 20/100/40 mM; styrene, 1.0 M).

Despite the use of a relatively high concentration of water, the polymerization by $H_2O/SnCl_4$ took place in a completely homogeneous state without an induction phase to quantitative conversion, but it was clearly slower than the corresponding reaction with $CH_3CH(Ph)Cl/SnCl_4$. In the absence of nBu_4NCl, for example, it needed 2 hr to give 83% conversion, which could be attained in 0.5 hr with the $CH_3CH(Ph)Cl/SnCl_4$ counterpart (see above). Interestingly, addition of nBu_4NCl to the polymerization system with $H_2O/SnCl_4$ resulted in a retardation (76% conversion after 8 hr); this reaction was even slower than that with $CH_3CH(Ph)Cl/SnCl_4/nBu_4NCl$ otherwise under the same conditions (83% after 1.5 hr).

Figure 1, C and D, illustrate the MWDs of the polymers produced with $H_2O/SnCl_4$. The MWD for the nBu_4NCl-free system (Figure 1C) was unimodal and broad, in sharp contrast to the bimodal distribution obtained with $CH_3CH(Ph)Cl/SnCl_4$ (Figure 1A). The overall polymer molecular weight for $H_2O/SnCl_4$ was even higher than that of the higher polymer fraction for the latter. These differences, both in rate and polymers' MWD, indicate that the polymerization reactions initiated by the H_2O- and $CH_3CH(Ph)Cl$-based systems proceed via different propagating species. In view of this conclusion, coupled with the low concentration of adventitious water in our systems (0.5 vs. 20 mM), a parallel initiation by this protogen may be neglected in the living polymerization by $CH_3CH(Ph)Cl/SnCl_4$ with nBu_4NCl.

In the presence of nBu_4NCl, the $H_2O/SnCl_4$ system yielded polymers with much narrower MWD (Figure 1D) and lower molecular weight than that without the ammonium salt (Figure 1C). Although this narrowed distribution was still broader than the MWD for the living polymer with $CH_3CH(Ph)Cl/SnCl_4/nBu_4NCl$ (Figure 1B; $\bar{M}_w/\bar{M}_n$ = 1.62 vs. 1.11), polymer molecular weight was found to increase with increasing conversion, as illustrated in Figure 3.

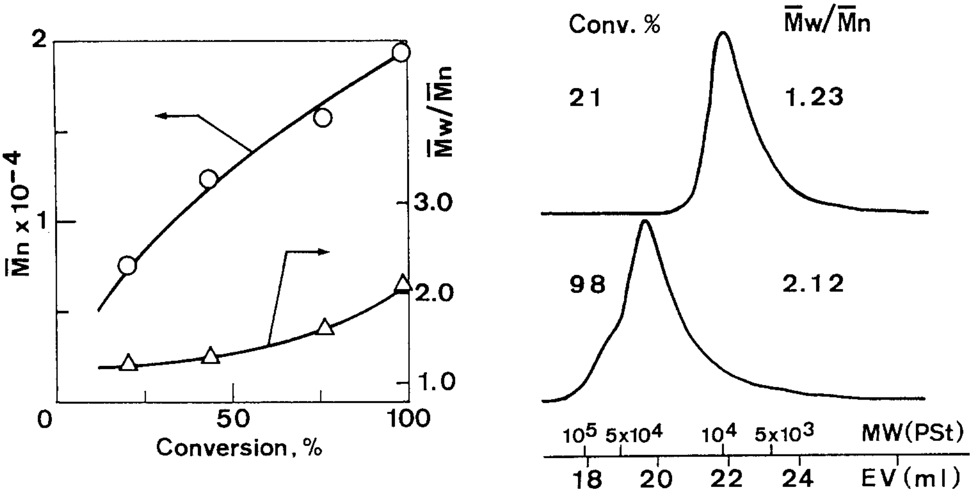

Figure 3. $\overline{M}_n$ and MWD of polystyrene obtained with $H_2O/SnCl_4$ in CH_2Cl_2 at -15 °C in the presence of nBu_4NCl: $[styrene]_0$ = 1.0 M; $[H_2O]_0$ = 20 mM; $[SnCl_4]_0$ = 100 mM; $[nBu_4NCl]_0$ = 40 mM.

However, in addition of the broader MWDs, the increase in $\overline{M}_n$ was not linear against conversion, and the observed molecular weights were about 4 times higher than the calculated values based on the initial concentration of added water; e.g., $\overline{M}_n$ = 19000 (obd) vs. 5000 (calcd) at 100% conversion. Nevertheless, it is important that, although not perfectly living, long-lived polystyrene was formed with $H_2O/SnCl_4$ in the presence of nBu_4NCl.

Conclusions

This paper has shown that the $CH_3CH(Ph)Cl/SnCl_4$ system with added nBu_4NCl can initiate a well-defined living cationic polymerization of styrene in CH_2Cl_2 solvent at -15 °C. This living process is superior to the similar reaction with $CH_3SO_3H/SnCl_4/nBu_4NCl$ (1) and others (2,3) previously reported, in that it gives very narrow polymer MWDs ($\overline{M}_w/\overline{M}_n \leq 1.1$), a perfect initiation efficiency from $CH_3CH(Ph)Cl$, and thereby a better regulation of polymer molecular weights (Figures 1 and 2). As noticed for the CH_3SO_3H-based system (1), the intervention of nBu_4NCl appears mandatory in achieving this living polymerization.

Phenomenologically, the bimodal MWD (Figure 1A) and its changes on addition of nBu_4NCl (Figure 1B) are strikingly similar to those observed in the styrene polymerizations by acetyl perchlorate (4,5), perchloric acid (6), and other related protonic acids (7). For these systems, the double-peaked distributions have been attributed to the existence of two independent propagating species in different ionic dissociation states (5,7), for which added common ion salts (e.g., nBu_4NClO_4 for acetyl perchlorate initiator) are known to suppress the formation of the ionically dissociated species. Although the observed effects of nBu_4NCl resemble those of common ion salts, further study is needed to clarify how nBu_4NCl and/or its chloride anion participates in the growing living site.

Experimental

Materials

$CH_3CH(Ph)Cl$ and $SnCl_4$ were of commercial source and distilled under reduced pressure (over phosphorus pentoxide for the latter), and stored in brown ampules under dry nitrogen. Styrene monomer (free of an inhibitor), CH_2Cl_2, and bromobenzene (internal standard for gas chromatography) were purified by the usual methods (5) and distilled twice over calcium hydride under reduced pressure except for CH_2Cl_2. The gas-chromatographic purity of $CH_3CH(Ph)Cl$ and styrene exceeded 99%. nBu_4NCl (Tokyo Kasei, purity > 98 %) was used as received after drying in vacuo.

Procedures

Polymerization was carried out in CH_2Cl_2 under dry nitrogen in baked glass tubes each equipped with a three-way stopcock. When the $CH_3CH(Ph)Cl/SnCl_4$ system was employed, a premixed solution (1.0 mL, aged at 25 °C for 30 min) of the two components was added to a monomer solution (4.0 mL) containing 0.1 mL bromobenzene at -15 °C, and the mixture was vigrously stirred manually to initiate the reaction; in some runs, nBu_4NCl was added to the monomer solution in advance. The polymerization with $H_2O/SnCl_4$ was initiated by adding a solution (1.0 mL) of $SnCl_4$ into a monomer solution (4.0 mL), which contained styrene, deionized water, and bromobenzene (0.1 mL) (plus nBu_4NCl when required). On preparation of the monomer solution, a known amount of deionized water was dissolved in dry and distilled CH_2Cl_2 before the other ingredients were mixed. For both initiating systems, the polymerizations were 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 tin-containing residues, evaporated to dryness under reduced pressure, and finally dried overnight in vacuo to give the product polymers. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios were determined relative to standard polystyrene samples by size-exclusion chromatography as reported (1); depending on polymer molecular weight, the following two sets of polystyrene gel columns were employed: (a) Shodex K-802, K-803, and K-804, exclusion limit ca. 3×10^5; (b) Shodex K-803, K-804, and K-805, exclusion limit ca. 2×10^6.

References

1. Y. Ishihama, M. Sawamoto, and T. Higashimura, Polym. Bull., **23**, 361 (1990).
2. R. Faust and J. P. Kennedy, Polym. Bull., **19**, 21 (1988).
3. (a) C. H. Lin and K. Matyjaszewski, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., **29**(2), 67 (1988); (b) K. Matyjaszewski, Makromol. Chem., Macromol. Symp., **13/14**, 433 (1988).
4. T. Masuda and T. Higashimura, J. Polym. Sci., Part B, **9**, 783 (1971).
5. T. Higashimura and O. Kishiro, J. Polym. Sci., Polym. Chem. Ed., **12**, 967 (1974).
6. D. C. Pepper, Makromol. Chem., **175**, 1077 (1974).
7. For a review, see: T. Higashimura, J. Polym. Sci., Polym. Symp., **56**, 71 (1976).

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