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Living cationic polymerization of *p*-methoxystyrene by hydrogen iodide/zinc iodide at room temperature

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SUMMARY

Cationic polymerization of *p*-methoxystyrene initiated by HI/ZnI_2 in toluene afforded living polymers not only at low temperature (-15°C) but at room temperature (+25°C) as well. The number-average molecular weight of the polymers was directly proportional to monomer conversion and in excellent agreement with the calculated value assuming that one polymer chain forms per unit hydrogen iodide. On addition of a fresh feed of monomer at the end of the first-stage polymerization, the added feed was smoothly polymerized at nearly the same rate as in the first stage; the polymer molecular weight further increased in direct proportion to monomer conversion and was close to the calculated value for living polymer. Throughout these reactions, the molecular weight distribution of the polymers stayed very narrow ($\bar{M}_w/\bar{M}_n < 1.1$). This is the first example of living cationic polymerizations of styrene derivatives that proceed even at room temperature.

INTRODUCTION

Living cationic polymerization of styrene derivatives has so far failed of such unambiguous success that has been achieved for vinyl ethers (1,2) and isobutylene (3). Previous attempts have been only partly successful, yielding not perfectly living but long-lived (or "quasi-living") polymers of *p*-methoxystyrene (4,5), α-methylstyrene (6), *p*-methylstyrene (7), styrene (8,9), and other derivatives (10,11). The common disadvantages of these systems include the less precise control of polymer molecular weight and the low polymerization temperatures (-15 to -78°C) that are required to suppress chain transfer and other side reactions. Polymers of a monodisperse molecular weight distribution (MWD) have not been prepared from styrenic monomers by cationic mechanisms.

Quite recently, we found that an initiating system (HI/ZnI_2) consisting of hydrogen iodide and zinc iodide induces living cationic polymerization of vinyl ethers even above room temperature (12). The HI/ZnI_2 system surpasses the hydrogen iodide/iodine combination, another initiating system for living cationic processes (1,2), in activity (higher polymerization rate) and in maximum temperature ($\geq$ +40°C) for living polymerization.

These features prompted us to employ HI/ZnI_2 for styrene derivatives, which are less reactive than alkyl vinyl ethers. This preliminary report concerns living cationic polymerization of *p*-methoxystyrene (*p*MOS) initiated by the zinc-based system that proved to occur even at room temperature.

RESULTS AND DISCUSSION

Living Cationic Polymerization of pMOS at +25°C and -15°C

*p*MOS was polymerized by the HI/ZnI_2 system (2:1 molar ratio) in toluene at +25°C and -15°C. Figure 1 shows the time-conversion curves. At both temperatures, a quantitative polymerization occurred smoothly without an induction phase. Under the conditions of Figure 1, the reaction was completed in 10 min at +25°C and in 90 min at -15°C. The polymerization mixtures were slightly yellow and homogeneous throughout; ZnI_2 alone did not polymerize *p*MOS at all under these conditions.

Figure 2 plots the number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) of the polymers thus obtained at +25°C and -15°C. The $\bar{M}_n$ values for both temperatures increased in direct proportion to monomer conversion to give a single straight line passing through the origin, which indicates that the polymer molecular weights are independent of polymerization temperature. These $\bar{M}_n$ values, though based on a polystyrene calibration, are in excellent agreement with the calculated values assuming that one polymer chain forms per unit hydrogen iodide (the solid line in Figure 2). As also shown in Figure 2, all of the obtained polymers exhibited very narrow molecular weight distributions (MWD), maintaining the $\bar{M}_w/\bar{M}_n$ ratio well below 1.1 over the whole conversion range. These facts show that the polymerization of *p*MOS by HI/ZnI_2 is living not only at low temperature (-15°C) but at room temperature (+25°C) as well.

Comparison of Figure 1 with our previous data (12) reveals that the overall rate of the *p*MOS polymerization at +25°C with $[HI]_0$ = 10 mM and $[ZnI_2]_0$ = 5.0 mM is roughly the same as that of the corresponding polymerization of isobutyl vinyl ether with $[HI]_0$ = 5.0 mM and $[ZnI_2]_0$ = 0.20 mM. Namely, to obtain the same polymerization rate, less reactive *p*MOS needs a higher amount of ZnI_2 relative to HI. The mechanistic implication of this fact and the kinetics of the HI/ZnI_2-mediated polymerization of *p*MOS will be discussed further in our forthcoming paper.

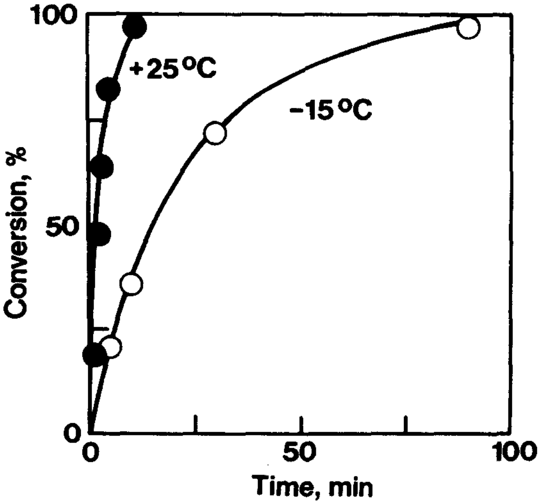

Figure 1. Time-conversion curves for the polymerization of *p*MOS with HI/ZnI_2 in toluene at -15 (o) and +25°C (•): $[p\text{MOS}]_0$ = 0.50 M; $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 5.0 mM.

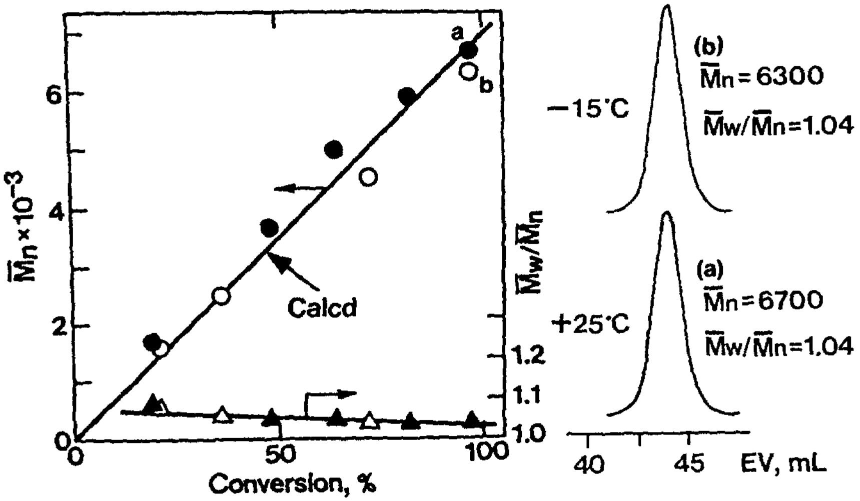

Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(*p*MOS) obtained with HI/ZnI$_2$ in toluene at -15 (o,Δ) and +25°C (•,▲): [*p*MOS]$_0$ = 0.50 M; [HI]$_0$ = 10 mM; [ZnI$_2$]$_0$ = 5.0 mM: The same experiments as for Figure 1. MWD curves a and b are for the samples corresponding to points a and b in the $\bar{M}_n$-conversion profile, respectively.

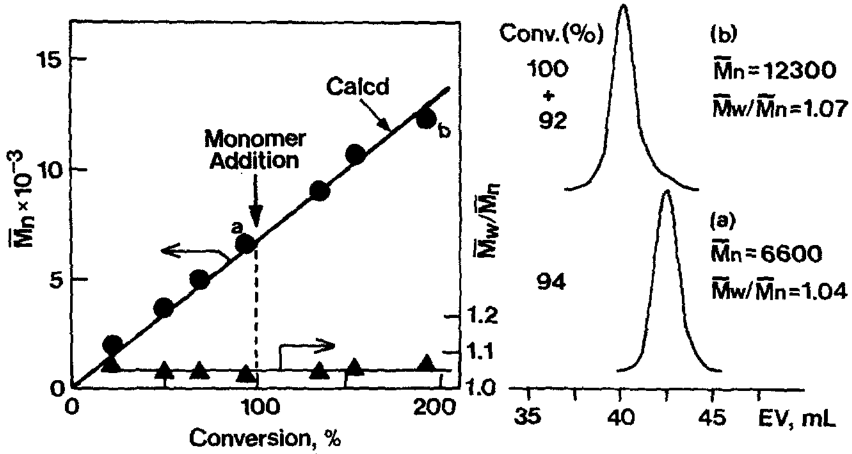

Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(*p*MOS) obtained in a monomer-addition experiment in the polymerization by HI/ZnI$_2$ in toluene at +25°C: [*p*MOS]$_0$ = 0.50 M; [HI]$_0$ = 10 mM; [ZnI$_2$]$_0$ = 5.0 mM. The molar amount of the second *p*MOS feed was the same as in the first. MWD curves a and b are for the samples corresponding to points a and b in the $\bar{M}_n$-conversion profile, respectively.

Monomer-Addition Experiment at +25^{o}C

The living nature of the polymerization at +25^{o}C was further demonstrated by a so-called "monomer-addition" experiment where a fresh feed of *p*MOS (0.50 M) was added to the reaction mixture when the initial charge (0.50 M) of the monomer was polymerized completely (Figure 3). The added *p*MOS feed was smoothly polymerized at nearly the same rate as in the first stage. The polymer molecular weight further increased in direct proportion to monomer conversion and was very close to the calculated value for living polymers (one polymer chain per unit hydrogen iodide). The MWD of the polymers stayed very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) even after the monomer addition, and no tailing appeared at all in the low molecular weight region. These facts show that the polymerization of *p*MOS by HI/ZnI_2 in toluene is perfectly living even at +25^{o}C; i.e., *all* polymer chains are active and can resume propagation when an additional monomer feed is supplied.

In conclusion, this study has demonstrated that the HI/ZnI_2 system effectively polymerizes not only vinyl ethers (12) but also less reactive *p*MOS, and equally important, it has provided the first example of perfectly living cationic polymerizations of styrene derivatives that proceed even at room temperature (+25^{o}C).

EXPERIMENTAL

Materials

*p*MOS was prepared from *p*-methoxyacetophenone by the literature method (13) and purified by double distillation over calcium hydride under reduced pressure. The gas-chromatographic purity of the monomer exceeded 99.8%. Anhydrous hydrogen iodide was prepared as an *n*-hexane solution as already reported (1). ZnI_2 (Aldrich, purity > 99.99%) was used as received; it was vacuum dried at least overnight just before use and handled in the dark under dry nitrogen. Toluene, *n*-hexane, and diethyl ether as solvents and tetrahydronaphthalene as an internal standard for gas chromatography were purified by the usual method (1) and doubly distilled over calcium hydride just before use.

Procedures

Polymerizations were carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. The reactions were initiated by adding, via dry syringes, prechilled solutions of hydrogen iodide (in *n*-hexane; 0.50 ml) and ZnI_2 (in diethyl ether; 0.50 ml), sequentially in this order, into a monomer solution (in toluene; 4.0 ml) kept at the polymerization temperature (12). After a certain period, the polymerization was terminated with prechilled ammoniacal methanol. Monomer conversion was determined from its residual concentration measured by gas chromatography with tetrahydronaphthalene as an internal standard (ca. 7 vol%).

The quenched reaction mixtures were washed with 10% aqueous sodium thiosulfate solution and then with water to remove initiator residues, evaporated to dryness under reduced pressure below 40^{o}C, and vacuum dried to give the product polymers. The MWD of the polymers was measured by size-exclusion chromatography (SEC) in chloroform at room temperature on a JASCO Trirotar-II chromatograph equipped with three polystyrene gel columns (Shodex AC-802 and A-804 x 2) and refractive index/ultraviolet dual detectors. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ ratio of the polymers were calculated from SEC eluograms on the basis of a polystyrene calibration.

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