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Cationic polymerization in iodine/liquid sulfur dioxide system

II. The long-lived polymerization of alpha-methylstyrene in homogeneous medium

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Summary

Poly(alpha-methylstyrene) with narrow molecular weight distribution (MWD) was obtained by cationic polymerization initiated by iodine in methylene chloride/liquid SO_2 (80/20 vol.%) or toluene/liquid SO_2 (45/55 vol.%) mixed solvent at -60°C. The average number molecular weights of the product polymers increased with monomer conversion but the dependence was not linear because of the low initiation efficiency at the beginning of the reaction. On addition of a fresh feed of monomer at the end of the polymerization, the added feed was polymerized at the same rate with an increase of molecular weight. The low dispersity was kept after the second monomer addition. The initiation efficiency increased during the polymerization.

Introduction

In preceding paper, we have reported the presence of long-lived propagating species during the cationic polymerization of alpha-methylstyrene (a-MeSty) initiated by iodine in liquid SO_2 solvent (1). The polymerization is faster than in the absence of SO_2 with an average number of polymer chains less than theoretical. Although the number average molecular weight (Mn) of the polymers is proportional to monomer conversion and increases with monomer addition, the molecular weight distribution is broad. Poly(alpha-methylstyrene) is insoluble in this system and this heterogeneity can affect propagation and MWD.

In this paper, the polymerizations were performed at -60°C to suppress transfer and in a homogeneous medium by changing the SO_2/CH_2Cl_2 ratio, or by the use of an appropriate SO_2/toluene ratio.

Experimental

Materials.

Alpha-methylstyrene (free of inhibitor), iodine, methylene chloride (CH_2Cl_2) and SO_2 were purified as described (1). Toluene was distilled over sodium and then over calcium hydride.

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Procedures.

Polymerization was carried out under dry nitrogen in flamed apparatus as described (1,2). The following addition sequence was established: organic solvent/SO_2/1 mL of iodine solution in CH_2Cl_2 or toluene/monomer (1 mL). The reactions were performed at $-60^\circ C$ and quenched by injecting 1 mL of prechilled methanol. The monomer conversion was determined from insoluble material after precipitation in methanol. The MWD and the molecular weights of the polymers were determined by size-exclusion chromatography (SEC) in toluene at room temperature on a Toyo-Soda HLC-803A chromatograph equipped with three ultrastyragel columns (two linear and one 500A) and a refractive index detector. The Mn and Mw/Mn values were calculated from SEC eluograms on the basis of a polystyrene calibration.

Results and Discussion

Alpha-methylstyrene was polymerized by the I_2/ liquid SO_2 system at $-60^\circ C$, using CH_2Cl_2 or toluene as co-solvent. Using CH_2Cl_2 as the solvent, the polymer remains soluble only when the CH_2Cl_2/SO_2 ratio is 80/20 (vol.%). With toluene, the necessary amount of the organic solvent to keep the formed polymer soluble is smaller. The dielectric constant of the solvent mixtures can be considered similar. The results are presented in Table I. The conversion - time plots of polymerizations performed at different SO_2 concentrations are compared in Figure 1. The polymerization rates are high and similar in all situations when SO_2 is present, even in small proportion. In addition, we did not observe an induction period such as reported by Giusti in the styrene polymerization by I_2 in dichloroethane at $30^\circ C$ (3). The addition of fresh monomer (0.77M, equivalent to the first charge) to the mixture after the first monomer charge was completely consumed, resulted in an increase of conversion at nearly the same rate as the first charge.

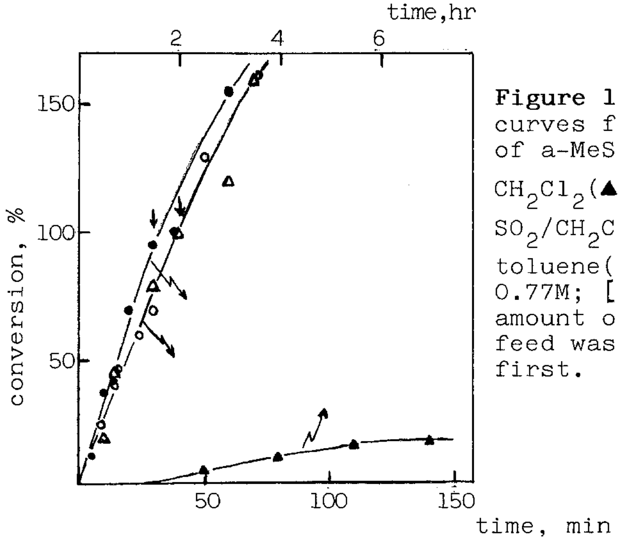

Figure 1. Time - conversion curves for the polymerization of a-MeSty by I_2 at $-60^\circ C$ in CH_2Cl_2(▲), SO_2/CH_2Cl_2(9/1)(●), SO_2/CH_2Cl_2 (2/8)(○) and SO_2/toluene(55/45) (△); [a-MeSty]= 0.77M; $[I]_o$= 5.9mM; The molar amount of the second a-MeSty feed was the same as in the first.

TABLE I

Polymerization of a-MeSty in different polar media using liquid SO_2 as co-solvent. [a]

Exp.nº	SO_2 (mL)	CH_2Cl_2 (mL)	toluene (mL)	time (min)	conv.[b] (%)	Mn[c] x 10^{-3}	Mw/Mn[c]	P (mM)	I_{eff}[d] (%)
SA165	2.0	7.0	-	10	24	30.6	1.28	0.7	24
SA246	2.0	7.0	-	15	40	28.2	1.33	1.3	44
SA267	2.0	7.0	-	25	60	41.8	1.52	1.3	44
SA167	2.0	7.0	-	30	70	46.1	1.34	1.4	47
SA266	2.0	7.0	-	40	100	59.2	1.36	1.5	52
SA269[e]	2.0	7.0	-	50	130	66.7	1.17	1.8	60
SA194[e]	2.0	7.0	-	70	160	72.3	1.27	2.0	68
SA234	5.0	-	4.0	10	20	13.8	1.54	1.3	44
SA134	5.0	-	4.0	15	45	33.5	1.30	1.2	41
SA136	5.0	-	4.0	30	80	50.6	1.19	1.4	48
SA276	5.0	-	4.0	40	100	52.0	1.14	1.7	59
SA279[e]	5.0	-	4.0	60	120	53.8	1.24	2.0	68
SA280[e]	5.0	-	4.0	70	160	57.8	1.30	2.5	85

a) $[I]_o$= 5.9mM; temp.= -60°C; $[\text{a-MeSty}]_o$= 0.77M.

b) conversion determined from methanol insoluble material.

c) Mn and Mw/Mn determined by SEC.

d) I_{eff} determined by assuming bimolecular initiation.

e) sequencial addition of 1 mL (0.77M) of a-MeSty after 40 min of reaction.

Under both conditions an increase of Mn was observed with conversion even after the addition of fresh monomer, as illustrated in Figure 2. This behavior is more accentuated in experiments carried out in CH_2Cl_2/SO_2 mixed solvents, and indicates a living or long-lived process. Although the average number of polymer chain, P, is less than the theoretical one even after the second monomer addition, the dependence of Mn on conversion is not linear for reactions performed in homogeneous media,that is, with less SO_2. These facts seem to indicate that transfer to monomer is not important and the nonlinear dependence can be explained by the increase of initiation efficiency during reaction (see Table I).

P can be calculated by $P = [M]_o - [M] / DP_n$

where DP_n is the number average degree of polymerization and

$[M]_o - [M]$ is the monomer converted to polymer (in mol/L).

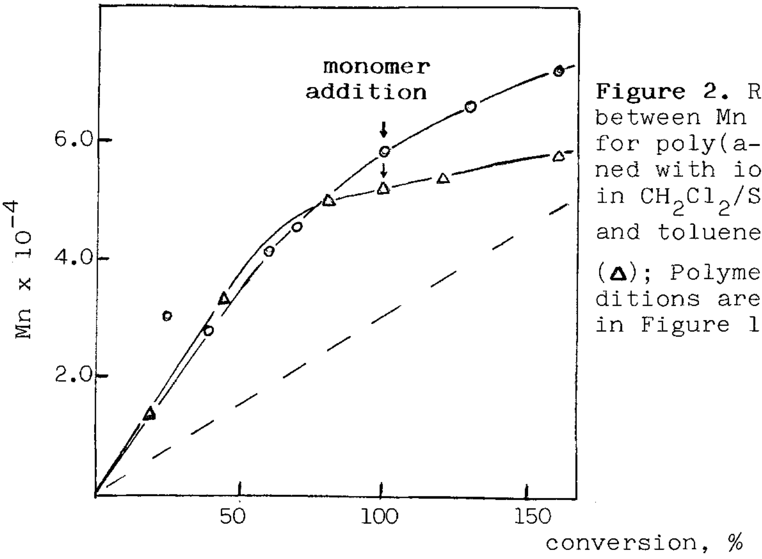

Figure 2. Relationship between Mn and conversion for poly(a-MeSty) obtained with iodine at -60°C in CH_2Cl_2/SO_2(8/2) (○) and toluene/SO_2 (45/55) (△); Polymerization conditions are the same as in Figure 1.

Figure 3 shows the dependence of P on conversion in homogeneous media (CH_2Cl_2/SO_2 = 80/20 and toluene/SO_2 = 45/55) together with the reported results in heterogeneous medium (CH_2Cl_2/SO_2 = 10/90) (1). The mechanism of initiation of a-MeSty in I_2/liquid SO_2 system has not been clarified yet. Nevertheless, if we assume bimolecular initiation by iodine in polar media (4), a living polymerization should result with P = 2.95 mM, since the initiator concentration is 5.9 mM. Therefore, the P values obtained at several SO_2 concentrations show that the initiation efficiency in heterogeneous medium, where SO_2 is employed in larger proportion is near to the theoretical, while in homogeneous media, the efficiency is low but increases with time.

In heterogeneous medium, the charge becomes yellow as soon as the monomer is added, while in homogeneous media, the color remains wine-red all the time, indicating the presence of free iodine complexed with aromatic compounds (5).

Figure 4 compares the MWD of the polymers obtained at different SO_2 ratios, including for comparison the heterogeneous system (CH_2Cl_2/SO_2 = 10/90) reported (1). It should be noted that the MWD curves shifted toward higher molecular weights even after the second monomer addition. In homogeneous media, the MWD curves did not show broadening and were of fairly low dispersities (Mw/Mn= 1.1-1.4) at any conversions even after the second monomer addition. The small tail toward lower molecular weights is in agreement with slow initiation.

These series of experiments indicate once more the possibility of having active carbocationic propagating species in polar media if an appropriate choice of monomer and initiation system is used. a-MeSty gives rise to a carbocation of moderate

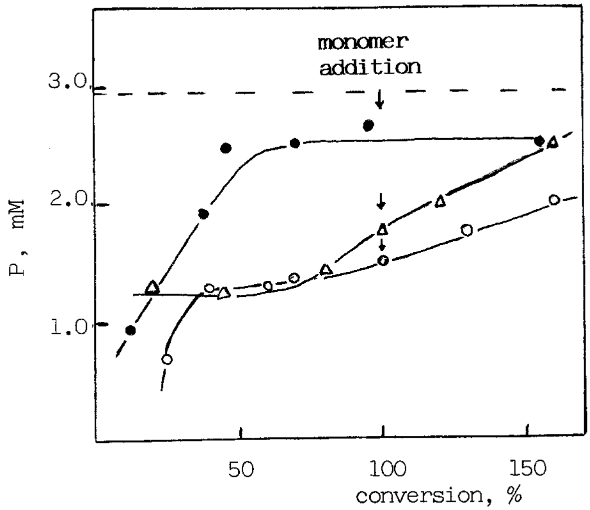

Figure 3. Relationship between the number of polymer chain (P) and the conversion in SO_2/CH_2Cl_2 (9/1) (●), SO_2/CH_2Cl_2 (2/8) (○) and toluene/SO_2 (45/55) (△). Polymerization conditions are the same as in Figure 1.

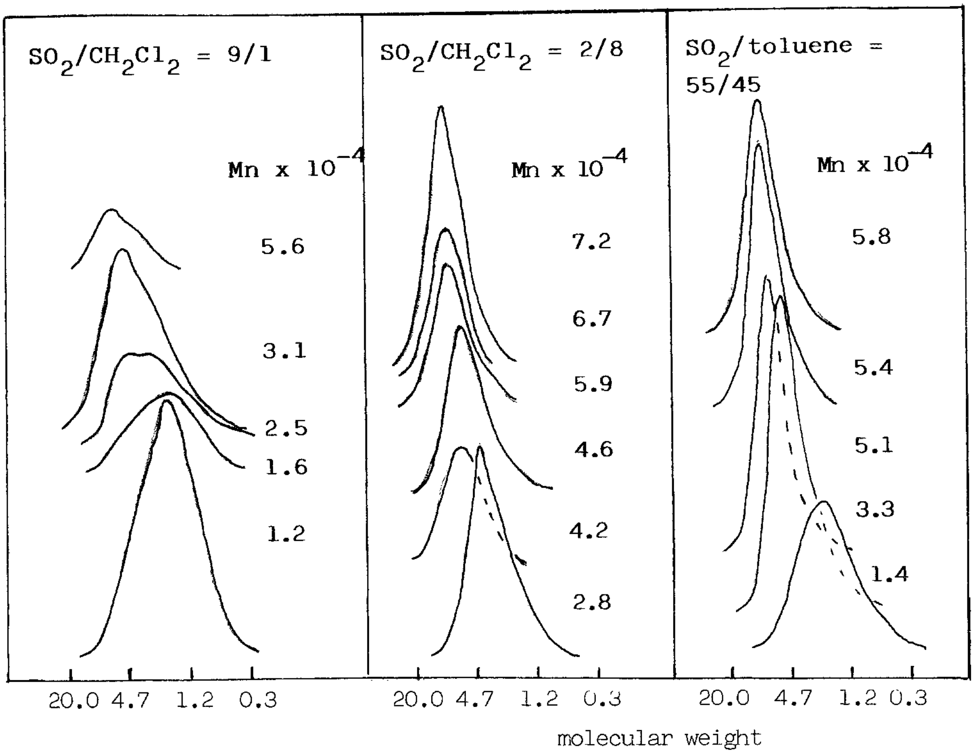

Figure 4. SEC curves of poly(a-MeSty) obtained at -60°C in different polar media, using liquid SO_2 as co-solvent.

stability and with a great tendency to transfer. The use of an initiation system which provides a counteranion of moderate nucleophilicity can avoid transfer. Without SO_2, the polymerization of a-MeSty initiated by I_2 is too slow, with the possibility of termination by collapsing the propagating end with the counteranion. With SO_2, termination can be avoided because of solvation of the counteranion. Since its Lewis acid characteristics is low, the I^- or I_3^- counteranion maintains enough nucleophilic character to protect the carbocationic propagating chainend thus, transfer can be reduced or even supressed.

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