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Cationic polymerization in iodine/liquid sulfur dioxide system

I. The polymerization of alpha-methylstyrene

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Abstract

The cationic polymerization of alpha-methylstyrene initiated by iodine was investigated in dichloromethane and liquid SO_2. Reactions carried out in SO_2 were faster with an increase of molecular weight at higher iodine concentration at -60°C. The increase of molecular weight with conversion and the values of average number of polymer chains less than theoretical suggest the presence of living or long-lived propagation species.

Introduction

Iodine has been reported as initiator in cationic polymerization of monomers like styrene, p-methoxy-styrene or N-vinyl carbazole. The polymerization of styrene was possible in ethylene dichloride at 30°C (1). The living character of the propagating species was not observed or discussed. Living polymerization was observed with monomers which have strongly electron-donating substituents that stabilize the propagating carbocations derived from them like p-methoxy-styrene in carbon tetrachloride at 0°C (2), isobutyl-vinyl ether in toluene at -15°C (3) or N-vinylcarbazole in dichloromethane or dichloromethane - carbon tetrachloride (1:1) at -50°C (4).

During the last few years, we have been studying the cationic polymerization and copolymerization of indene, styrene and alpha-methylstyrene initiated by percompounds using liquid SO_2 as the solvent (5,6) and trifluormethanesulfonic acid (7). These initiators can be considered protonic acids. Liquid SO_2 is protonphobic and has a high ionizing power which prevents chain transfer to the counteranion and solvent.

The present work examines the behavior of iodine as initiator in cationic polymerization of alpha-methylstyrene at low temperatures (-60°C and -20°C) using liquid SO_2 as the solvent.

Experimental

Materials.

Alpha-methylstyrene (a-MeSty) (free of an inhibitor) was distilled over calcium hydride and, over fluorenyl lithium just before the polymerization (8). Iodine was sublimed with

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potassium iodide (KI) several times. SO_2 was dried by passing the gas through sulfuric acid and phosphorus pentoxide. Methylene chloride was treated with concentrated sulfuric acid and then dried by refluxing over P_2O_5.

Procedures.

Polymerization was carried out under dry nitrogen in flamed apparatus as described (6). The reaction was initiated by monomer addition to an initiator solution (SO_2/CH_2Cl_2=8:1). After a certain period, the polymerization was quenched by injecting 1 µL of prechilled methanol. Monomer conversion was determined from insoluble material after precipitation in methanol. The polymers were washed with methanol and vacuum dried. 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

Polymerization of alpha-methylstyrene by iodine in CH_2Cl_2.

Since the literature does not contain results concerning the polymerization of a-MeSty initiated by iodine, we decided first to study this reaction in CH_2Cl_2 and to compare the results with those obtained by the iodine/SO_2 system. The results, summarized in Table I, indicate a very slow reaction even at -20°C and an absence of polymer in reactions carried out at low iodine concentration ($[I]_0$= 0.59mM). Giusti et al. obtained 40% styrene conversion after 180 min at room temperature with iodine concentrations higher than those used in our experiments (1).

The average number of polymer chains (P) suggests the presence of chain transfer at -20°C. These side reactions may be responsible for the low conversions at -20°C, since these values are related to methanol insoluble material. At -60°C, chain transfer is suppressed but the initiation efficiency is very low and increases a little with the time. The reason for low initiator efficiencies (I_{eff}= $P/[I]_0$) and relatively broad molecular weight distribution at -60°C may be poor interaction between iodine and the monomer. The color of the charge remains violet during the reaction indicating the presence of free iodine.

Polymerization of alpha-methylstyrene by iodine in liquid sulfur dioxide.

The reactions presented in Table II were carried out by the use of liquid SO_2/CH_2Cl_2 8/1 (v/v). The CH_2Cl_2 was used only to dissolve iodine, and then to permit the addition of iodine to the reactor as a solution. Although the dielectric constants of SO_2 (ϵ = 14.1 at 20°C) and CH_2Cl_2 (ϵ = 9.08 at 20°C) are similar, the former gives high conversions in a short time even at an

Table I

Polymerization of a-MeSty by iodine in CH_2Cl_2 [a]

Exp.nº	I_2 (mM)	temp. (^oC)	time (min)	conversion (%)	Mn x 10^{-3}	Mw/Mn	P [b] (mM)	I_{eff} [c] (%)
SS-1	0.59	-20	240	-	-	-	-	-
SS-2	0.59	-20	1440	-	-	-	-	-
SS-3	0.59	-20	9780	-	-	-	-	-
SS-7	5.91	-20	30	-	-	-	-	-
SS-16	5.91	-20	240	16	1.0	1.36	14.5	246
SS-8	5.91	-20	960	34	1.0	1.34	32.5	550
SS-9	5.91	-20	1440	33	1.0	1.30	30.6	690
SS-13	0.59	-60	30	-	-	-	-	-
SS-14	0.59	-60	420	-	-	-	-	-
SS-17	5.91	-60	30	-	-	-	-	-
SS-18	5.91	-60	150	6	39.9	1.25	0.14	2.4
SS-19	5.91	-60	240	11	18.1	2.03	0.55	9.3
SS-20	5.91	-60	330	16	17.6	2.01	0.82	13.9
SS-21	5.91	-60	420	18	19.2	1.87	0.85	14.4

a) a-MeSty= 0.77M; CH_2Cl_2= 9mL.
b) the average number of polymer chains calculated by
$P = [M]_o - [M]/ DP_n$
c) initiator efficiency calculated by $I_{eff} = [M]_o - [M]/DP_n[I]_o$

iodine concentration of 0.59 mM. At this initiator concentration, no polymerization occurs in the absence of SO_2 (see Table I). In SO_2, the charge became yellow as soon as the monomer was added indicating the absence of free iodine. This intense yellow color may be due to charge-transfer in the anion-SO_2 complex(9) and suggests the formation of cationic species plus I^- or I_3^- counteranions (10).

The use of ten times higher iodine concentration (5.91 mM) and a lower temperature (-60°C) gave higher conversions and molecular weights and an increase of molecular weight with conversion. This behavior suggests that higher iodine concentrations increase the polymerization rate and the interaction between the propagating carbocation and counteranion. The average number of polymer chains, P, is less than theoretical and remains practically constant suggesting little chain transfer or termination.

To confirm the probable living or long-lived character of the propagating species, a fresh amount of monomer was added after 90-95% conversion. After 30 minutes, increasing conversions and molecular weights were observed, indicating the presence of

Table II

Polymerization of a-MeSty by iodine in SO_2[a]

Exp.nº	I_2 (mM)	temp. (°C)	time (min)	conversion[b] (%)	Mn $\times 10^{-3}$	Mw/Mn	P[c] (mM)	I_{eff}[c] (%)
SA9	0.59	-20	5	30	1.3	1.55	20.90	3542
SA83	0.59	-20	15	50	2.3	1.75	19.70	3339
SA73	0.59	-20	30	50	2.0	1.84	22.70	3847
SA24	0.59	-40	5	30	3.5	1.33	7.80	1322
SA28	0.59	-40	15	70	4.2	1.23	15.10	2559
SA61	0.59	-40	30	95	5.2	1.28	16.60	2813
SA36	0.59	-60	15	5	-	-	-	-
SA94	0.59	-60	60	20	10.4	1.37	1.74	295
SA95	0.59	-60	180	70	14.3	1.86	4.45	754
SA123	5.91	-60	5	12	11.8	1.59	0.90	15
SA196	5.91	-60	10	37	17.1	1.67	1.96	33
SA197	5.91	-60	15	45	16.3	1.61	2.50	42
SA198	5.91	-60	20	70	25.2	1.65	2.52	43
SA108	5.91	-60	30	95	31.0	1.82	2.77	47
SA209[d]	5.91	-60	60	155	56.1	1.62	2.51	42

a) a-MeSty= 0.77M; SO_2= 8mL; CH_2Cl_2= 1mL.
b) conversion determined from methanol insoluble material.
c) P and I_{eff} as in Table I.
d) sequencial addition of 1mL of a-MeSty after 30 min reaction.

living propagating species (see Exp. nº SA209 in Table II). The Mn versus conversion plot, shown in Figure 1, illustrates this. The broad molecular weight distribution observed may be due to slow initiation. The SEC curves presented in Figure 2 confirm this suggestion. In fact, we can observe not only a shift to higher molecular weights with higher conversions but also an increase in the higher molecular weight fraction. It is important to emphasize that poly(alpha-methylstyrene) is insoluble in liquid SO_2 even at low conversion. Therefore, the system is heterogeneous which can also explain the broad MWD.

Additional experiments, including block copolymerizations, will be performed to substantiate the proposition of living or long-lived species. Living or long-lived carbocationic propagating species can exist even in a highly ionizing and heterogeneous medium and in the presence of a-MeSty. This monomer is known to exhibit strong chain transfer in conventional polymerizations. The results of homogeneous polymerization achieved by decreasing the SO_2:CH_2Cl_2 ratio, will be the subject of a subsequent paper.

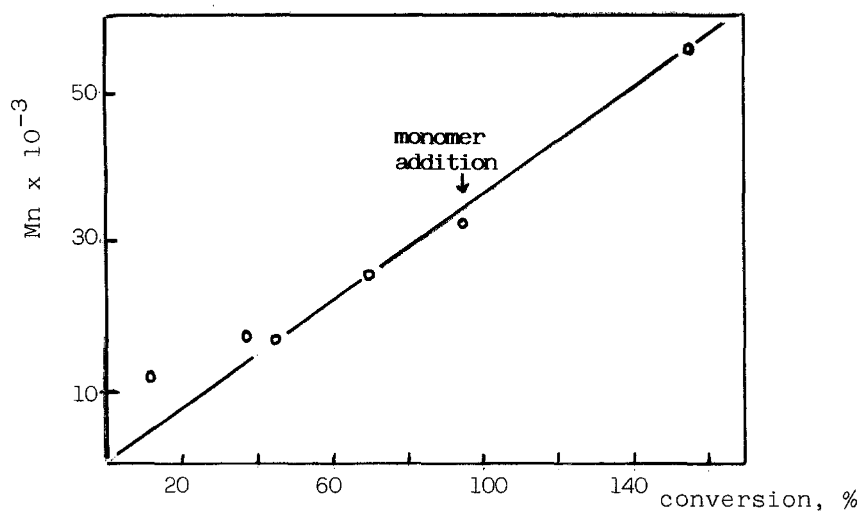

Figure 1. Conversion - Mn plot of poly(a-MeSty) obtained at -60°C in liquid SO_2. [a-MeSty]$_o$ = 0.77M; [I]$_o$= 5.91mM.

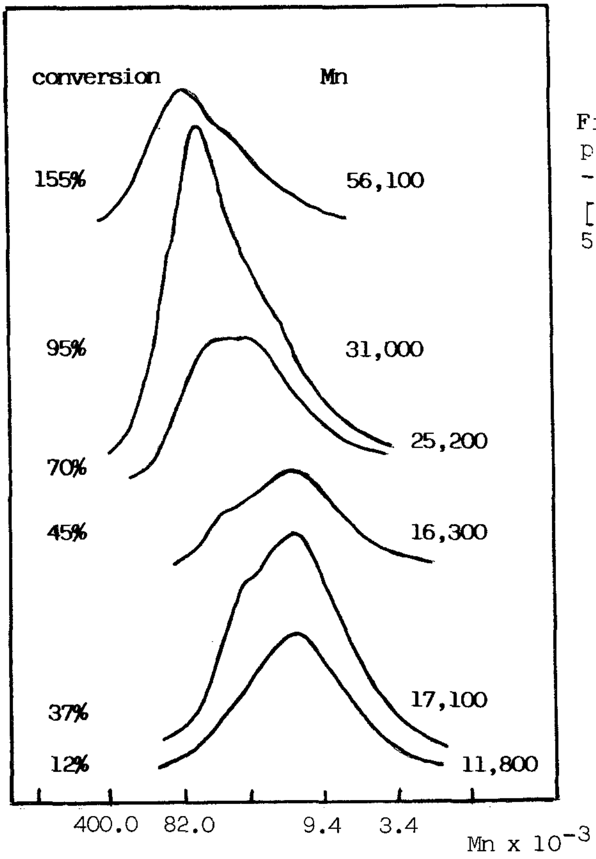

Figure 2. SEC curves of poly(a-MeSty) obtained at -60°C in liquid SO_2. [a-MeSty]$_o$= 0.77M; [I]$_o$ = 5.91mM.

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