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The cationic polymerization of α-methylstyrene in liquid sulfur dioxide initiated by the HI/I_2 system

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Abstract

The polymerization of α-methylstyrene (αMeSty) initiated by HI/I_2 or HI in the presence of liquid sulfur dioxide has been investigated. The number-average molecular weight increased with the monomer concentration for reactions initiated by the HI/I_2 system. I_2 also participates in the initiation process, increasing the number-average polymer chain at higher monomer concentration. HI alone is also able to initiate the polymerization of αMeSty in the presence of SO_2. With this initiator, transfer reaction can be minimized in systems containing low amount of SO_2.

Introduction

The cationic polymerization of α-methylstyrene (αMeSty) in liquid sulfur dioxide (SO_2) initiated by iodine (I_2) has been recently investigated.[1,2] The process was characterized by an increase of the molecular weight with conversion and an average number of polymer chains (*P*) less than the initial I_2 concentration. In addition, the introduction of a second feed of monomer resulted in an increase of the M_n and an unimodal distribution of the molecular weight, suggesting the presence of living or long-lived propagating species. The analysis of the nonpolymeric materials present in the methanolic layer indicated HI formation which may participate or be responsible for initiation.[3] The broadening of the molecular weight distribution (MWD) and a low molecular weight tail in these polymerization systems may be explained by slow HI formation. Initiation by HI was also reported by Giusti et al. in the iodine-initiated polymerization of styrene.[4-6]

In this communication we investigate the action of HI and HI/I_2 initiating system in the polymerization of αMeSty in liquid SO_2. The purpose of these experiments is to provide faster initiation which could give better-controlled cationic polymerization in liquid SO_2.

Experimental

Materials and Procedure. αMeSty, I_2, CH_2Cl_2 and SO_2 were purified as described.[1,2] HI was dehydrated over P_2O_5 and dissolved in dry CH_2Cl_2. The solution was stored under nitrogen at -20°C for one week. The concentrations of both I_2 and HI solutions were determined just prior to polymerizations.

Polymerizations were performed at -60°C under dry nitrogen in vacuum flamed two-necked flasks. The solvents, SO_2 and/or CH_2Cl_2, were introduced in the flask via capillary vial. Then, the initiator solutions were added. The reaction was started with

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the addition of the monomer and stopped with pre-chilled methanol containing small amounts of ammonium hydroxide. The reaction mixture was precipitated into methanol, the polymer was filtered and vacuum-dried at 50°C. The conversion was determined gravimetrically.

Measurements. The molecular weight distribution (MWD) of the polymers was measured by size-exclusion chromatography (SEC) in THF at room temperature on a Water 600 chromatograph equipped with four polystyrene gel columns (500, 10^3, 10^4 and 10^5 Å porosity). The M_n and M_w/M_n values of the polymers were calculated from SEC on basis of a polystyrene calibration. ^1H NMR spectra were recorded in $CDCl_3$ at 30°C on a Brucker 300MHz spectrometer.

Results and Discussion

The polymerization initiated by HI/I_2

The polymerization of αMeSty in liquid SO_2 was carried out at different HI/I_2 molar ratios. The results shown in Table 1 revealed that the *P* values are in agreement with the HI concentration, except for reactions performed at high $[I_2]_o/[HI]_o$ molar ratio (Exp. nº 2 and 6) where *P* values higher than the HI concentration were found. These results indicate the simultaneous participation of HI and I_2 in the initiation process, as expected, contributing also for the broadening in the MWD.

Table 1. HI/I_2-initiated polymerization of αMeSty in liquid SO_2 as a function of HI and I_2 concentration[a]

Exp. nº	HI x 10^5 mol	I_2 x 10^5 mol	M_n	Mw/Mn	P^b x 10^5 mol
1	0	6.0	31000	1.82	2.8
2	3.3	6.0	19000	2.23	4.8
3	6.0	6.0	16300	1.63	5.6
4	10.0	6.0	10300	1.55	8.8
5	6.0	2.5	14900	1.91	6.1
3	6.0	6.0	16300	1.63	5.6
6	6.0	10.0	9000	2.47	10.1

a) SO_2 = 8 ml; CH_2Cl_2 = 2 ml; αMeSty = 0.91g (0.78 mmol); time reaction = 30 min: temperature = -60°C; conversion ≈ 100%.

b) *P* =average number of polymer chain, calculated from M_n obtained by SEC measurements.

Table 2 presents the results concerning the effect of the monomer concentration for reactions performed at two SO_2/CH_2Cl_2 proportions. SO_2-rich system displays an increase of the molecular weight with the monomer concentration. With low amount of monomer, *P* values lower than the initial HI concentration were achieved. By increasing the $[M]_o$, the *P* values also increase, becoming a little higher than $[HI]_o$ at higher $[M]_o$. This behavior seems to indicate that initiation by I_2 becomes important as the $[M]_o/[HI]_o$ increases. The initiating action of I_2 seems to be higher in the medium containing lower amounts of SO_2. Indeed, higher *P* values and a substantial broadening of the MWD were observed for polymerizations performed at higher amounts of αMeSty. In addition to the simultaneous initiation by HI and I_2, transfer to the monomer must be contributing to the higher *P* values at higher $[M]_o$. In spite of the heterogeneity in the SO_2/CH_2Cl_2 (80:20 vol%) system, the polydispersities of the polymers are narrower than in the homogeneous system. According to the literature, the rapid exchange between active and dormant propagating species, influenced by the high ionizing power of SO_2, may be responsible for the narrower MWD. [7]

Table 2. The effect of the monomer concentration on the HI/I_2-initiated polymerization of αMeSty[a]

Exp. n°	SO_2 ml	CH_2Cl_2 ml	αMeSty g	αMeSty mmol	M_n mol/g	M_w/M_n	P[b] x 10^5 mol
7	8	2	0.35	2.97	12200	1.96	2.9
8	8	2	0.45	3.81	14800	1.90	3.0
9	8	2	0.65	5.51	14000	1.91	4.6
3	8	2	0.91	7.71	16300	1.63	5.6
11	8	2	1.30	11.0	17000	1.63	7.6
12	2	8	0.45	3.81	10200	2.05	4.3
13	2	8	0.81	6.86	12600	2.41	6.4
14	2	8	1.19	10.1	12600	2.73	9.4

a) [HI] = 6.0×10^{-5} mol; $[I_2] = 6.0 \times 10^{-5}$ mol; time = 30 min; temperature = -60°C; conversion ≈ 100%
b) P = average number of polymer chains calculated from SEC data.

Experiments involving sequential monomer addition were also performed. Figure 1 displays SEC eluograms of the polymers isolated before and after the addition of a second feed of monomer. The reactions were carried out by polymerizing 0.45g of αMeSty during 30 min (first polymerization stage) followed by the addition of another 0.45g of the monomer and subsequent polymerization for 30 min. Although the *P* values remain still lower or a little higher than the initial [HI] (in the case of SO_2/CH_2Cl_2 = 20:70 vol%) after the second polymerization stage, there is an increase of these values. The MWD profiles remain practically constant after the second feed of monomer. Considering that the initiation efficiency of HI for the first stage is less than 100%, the polymerization of incoming monomer should occur by the HI and I_2 present in the system.

The polymerization initiated by HI

The HI-initiated polymerization of αMeSty did not proceed in pure CH_2Cl_2 after 3 hours at -60°C. When the experiments were carried out in the presence of SO_2, fast polymerizations have been achieved. Table 3 presents the effect of the reaction time for reactions performed at two different proportions of SO_2/CH_2Cl_2 systems. The polymerizations performed in SO_2/CH_2Cl_2 = 80:20 vol% were characterized by transfer reactions as indicated by the average number of polymer chain (*P*) higher than the initial $[HI]_o$. For reactions performed at lower amounts of SO_2 (SO_2/CH_2Cl_2 = 20:80 vol%), the *P* values remained practically constant and a little higher than theoretical values. Here also the polymers obtained at high SO_2 concentration display narrower MWD than those obtained in the homogeneous medium indicating a fast equilibrium between dissociated and nondissociated propagating species, as discussed in the literature. [7]

The effect of the monomer concentration on the molecular weight for both solvent systems is illustrated in Fig. 2. The dotted line represents the theoretical dependence. Reactions performed at lower amounts of SO_2 display a linear relationship fairly close to the theoretical one. The deviation from linearity increases at higher monomer concentrations. Higher amounts of SO_2 increase transfer reactions as indicated by the lower M_n values.

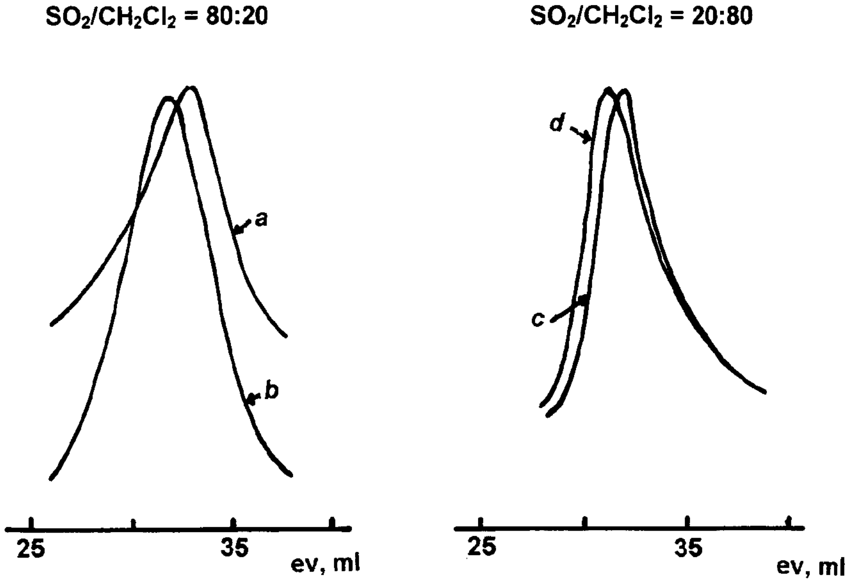

Fig. 1. SEC eluograms of poly(αMeSty) obtained by the HI/I_2 initiating system; (a,c) first polymerization stage and (b,d) after the addition of a second monomer feed; see Table below for the reaction conditions.

Exp. nº	SO_2 ml	CH_2Cl_2 ml	αMeSty g	time min	M_n mol/g	M_w/M_n	P x 10^5 mol
a	8	2	0.45	30	14800	1.90	3.0
b	8	2	0.45 + 0.45	30 + 30	17100	1.96	4.7
c	2	8	0.45	30	10200	2.05	4.3
d	2	8	0.45 + 0.45	30 + 30	11700	2.07	7.4

Table 3. Polymerization of αMeSty initiated by HI as a function of time and SO_2 concentration[a]

Exp. nº	SO_2 ml	CH_2Cl_2 ml	time min	conv. %	M_n mol/g	Mw/Mn	P x 10^5 mol
15	8	2	15	70	3600	1.2	17.5
16	8	2	30	80	3800	1.3	19.1
17	8	2	45	90	4200	1.2	19.5
18	8	2	60	100	5000	1.2	18.2
19	2	8	15	66	7100	2.0	8.5
20	2	8	30	82	9200	2.0	8.0
21	2	8	45	90	9500	2.0	8.5
22	2	8	60	100	12000	2.3	7.5

a) αMeSty = 0.91g (0.78 mmol); [HI] = 6.0 x 10^{-5} mol; temperature = -60°C;

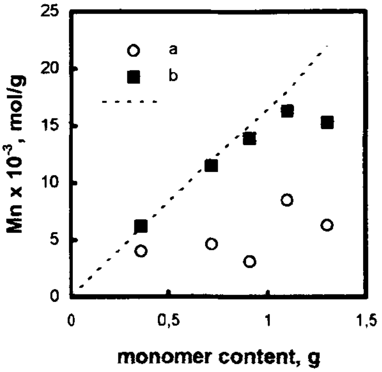

Fig.2. Effect of the monomer concentration on the M_n of poly (αMeSty) initiated by HI, as a function of the solvent system. [HI] = 6.0 x 10^{-5} mol; temperature = -60°C; time = 60min. (a) SO_2/CH_2Cl_2 = 80:20vol%; (b) SO_2/CH_2Cl_2=20:80 vol%.

The possibility of living or long-lived propagation in the HI-initiated polymerization in SO_2/CH_2Cl_2 = 20:80 vol% was also investigated by adding a second feed of monomer. The first polymerization step was performed with 0.91g of αMeSty. After complete polymerization (60 min), a second 0.45g feed of αMeSty was added and the process was continued for 60 min. The eluograms are illustrated in Fig. 3. It is interesting to note the shift of the MWD curve toward higher molecular weights after the second monomer addition. The *P* value remains practically constant after the second polymerization stage indicating the presence of living or long-lived propagating species. The low molecular weight tail contributes to the broadening of the MWD and is an indication of slow initiation.

Recently Sawamoto et al. reported the living cationic polymerization of αMeSty in CH_2Cl_2.[8] They employed the adduct of HCl and 2-chloroethyl vinyl ether coupled with $SnBr_4$ as the initiating system. The cumyl chloride/$SnBr_4$ initiating system gave rise to polymers with M_n higher than the calculated values indicating lower reactivity of this system. [8] In our system, the initiation by HI may be compared to the cumyl iodide initiation activated by SO_2 as the Lewis acid. The results observed in this paper indicate that the ionizing power of SO_2 increases the reactivity of this initiating system. In spite of the high nucleophilicity of the counterion, the propagating species are not enough protected to avoid transfer.

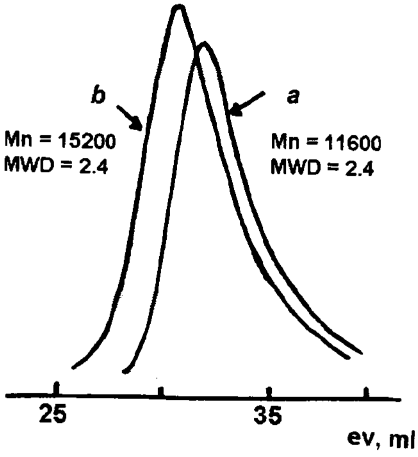

Fig. 3. SEC eluograms of poly(αMeSty) initiated by HI, in the SO_2/CH_2Cl_2 = 20:80 vol% as solvent. (a) first polymerization stage and (b) after the addition of a second feed of monomer. [HI] = 6.0 x 10^{-5} mol; temperature = -60°C.

The terminal structure of the polymers obtained with HI as initiator was analyzed by ^{1}H NMR spectroscopy. Figure 4 shows the spectra of poly(αMeSty) obtained in the two solvent systems. As expected for most cationic systems, the poly(αMeSty)'s obtained are practically syndiotactic.[9] Besides the signals related to the repeat unit, the small peaks at 4.6 and 5.0 ppm (peaks *a* and *b*) are observed in both spectra. These absorptions are attributed to the methylene proton of the olefin at the end group. Such groups may be generated from transfer reactions or during the workup of the product. In spite of the polar medium, it is possible that some terminal C-I bond would be formed because of the nucleophilic character of the counterion. The C-I end may eliminate HI thus giving rise to olefin. In addition, substitution reactions may occur during the quenching of the polymerization with methanol yielding metoxy end groups which appear as a small peak at 3.5 - 4.0 ppm (peak c). The two peaks in this region for the polymer obtained in the SO_2/CH_2Cl_2 (20:80) solvent system (Figure 4b) may be due to stereoisomers.

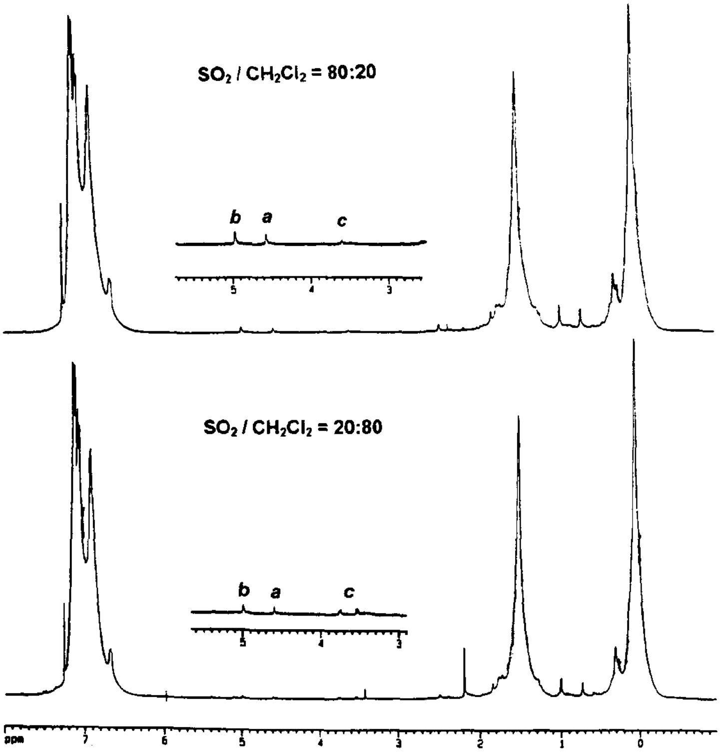

Fig. 4. ^{1}H NMR spectra of poly(αMeSty) initiated by HI in the SO_2/CH_2Cl_2 (a) 80:20 and (b) 20:80 vol% solvent systems. (αMeSty = 0.91g (0.78 mmol); [HI] = 6.0×10^{-5} mol; temperature = -60°C; time = 60 min)

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References

1. Soares BG, Silva A, Gomes AS (1992) Polym. Bull. 29:253
2. Silva A, Gomes AS, Soares BG (1992) Polym. Bull. 29:509
3. Silva A, Gomes AS, Soares BG (1993) Polym. Bull. 30:133
4. Giusti P, Andruzzi F (1968) J. Polym. Sci., Part C 16: 379.
5. Maschio G, Cerrai P, Giusti P (1982) Polym. Bull. 8: 147.
6. Maschio G, Cerrai P, Giusti P (1983) Polym. Bull. 10: 321.
7. Matyjaszewski K (1992) Makromol. Chem., Macromol. Symp. 54/55: 51
8. Higashimura T, Kamigaito M, Kato M, Hasebe T, Sawamoto M (1993) Macromolecules 26: 2670
9. Elgert KF, Seiler E, Puschendorf G, Ziemann W, Cantow HJ (1971) Makromol. Chem. 144: 73