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Cationic polymerization of styrene and indene in iodine/liquid sulfur dioxide system

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Abstract

The cationic polymerizations of indene (Ind) and styrene (Sty) initiated by iodine (I_2) in liquid sulfur dioxide (SO_2) were investigated. Reactions involving Ind were characterized by termination by neutralization between the growing carbocationic species and the nucleophilic counteranion, at low temperature. Sty polymerization is also termination-dominated and gives low conversion at -20°C. High resolution gas chromatography coupled with mass spectrometry (HGC-MS) analysis of non polymeric material in the Sty polymerization suggested that initiation of Sty polymerization involves the formation of 1,2 diiodide adduct prior to initiation with HI.

Introduction

The ability of iodine in induce cationic polymerizations in common organic solvents has been reported for several monomers including styrene (Sty),[1-6] α-methylstyrene (αMeSty),[7] p-methoxystyrene (pMOSty),[8-9] N-vinylcarbazole (NVC)[10-12] and vinyl ethers.[13-18] The initiation of Sty was suggested to involve the "in situ" generation of hydrogen iodide (HI) by the following reactions:[1, 4-6]

$$C_6H_5CH{=}CH_2 + I_2 \rightarrow C_6H_5CHICH_2I \rightarrow C_6H_5CH{=}CHI + HI$$

In contrast, the initiation of vinyl ethers seems to involve the 1,2-diiodide adduct.[17-18] The stability of the carbocationic growing species and the counteranion nucleophilicity contribute to a propagation through polarized covalent species rather than full positive charge and consequently living or long-lived cationic polymerizations.[12,19]

Recently, I_2 was employed as initiator in cationic polymerization of α-MeSty using SO_2 as solvent.[20-22] In this system, the reaction is faster than in usual solvents with an increase of the molecular weight with the conversion. The initiation process was suggested to involve HI formation which may be responsible for the initiation.[22] This communication examines the characteristics of the cationic polymerization of Sty and Ind using the I_2/SO_2 system. The nature of the initiation system was also investigated by gas chromatography - mass spectrometry analyses of non polymeric material present in the methanolic layer after the polymer precipitation.

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Experimental part

materials. Sty was treated with 10 wt.% aqueous NaOH, washed with distilled water, dried overnight over $CaCl_2$ and distilled from CaH_2 under vacuum. Just before the polymerization it was distilled from fluorenyl lithium under vacuum. Ind was stirred with 6N HCl aqueous solution overnight, washed with distilled water, dried over $CaCl_2$ and distilled twice from CaH_2 under vacuum. Just prior the polymerization, it was once again distilled from CaH_2 under vacuum. SO_2, methylene chloride (CH_2Cl_2) and I_2 were purified as reported.[20-21]

polymerizations. Polymerization was carried out under nitrogen in a 100 cm^3 two-neck flask equipped with stirrer, rubber septum and a stop-cock for vacuum or nitrogen inlet. Dried SO_2 was introduced into the cold flask using a flamed capillary. The reaction was then initiated by adding, via dry syringes, iodine (1 mL of CH_2Cl_2 solution) and the monomer sequentially in this order, into the liquid SO_2 maintained at the polymerization temperature. After an established time, the polymerization was stopped by adding 1 mL of pre-chilled methanol to the reaction mixture. Conversions were determined gravimetrically after precipitation into methanol.

characterization. The number-average molecular weight (Mn) and molecular weight distribution (MWD) were obtained from size exclusion chromatography (SEC) on a Waters high pressure SEC assembly (Model 600E pump) equipped with four ultrastyragel columns (10^5, 10^4, 10^3 and 500 Å) and photo diode array UV and RI detectors. Molecular weights were calculated from a calibration curve obtained with polystyrene standards. Tetrahydrofuran solutions were used and the flow rate was 1 mL/min.

^{1}H-NMR spectra were recorded in $CDCl_3$ at 30°C on a Varian XL-300 spectrometer.

For the analysis of the non polymeric compounds soluble in methanol, the reaction was quenched with 1 mL chilled methanol. Then 4 mL of CH_2Cl_2 were added to solubilize the polymer and the solution was poured into 40 mL methanol. After precipitation, the CH_2Cl_2/methanolic layer was analyzed by high resolution gas chromatography-mass spectrometry (HRGC-MS-C), performed on a HP-5987A instrument, with linear scanning 50-500 daltons, electron impact (70 ev) ionization, on SE-54 glass capillary column (25m x 0.30mm, $d_f = 0.25$ μm) using hydrogen as carrier gas and temperature programming from 60 to 300°C at 10°C/min.

Results and Discussion

Polymerization of Indene.

Ind was polymerized with I_2 as initiator in liquid SO_2 as solvent and in the temperature range from -20 to -60°C. The experimental conditions and results are described in Table 1. Reactions performed at -20°C are characterized by chain transfer reactions as indicated by initiation efficiency higher than 100%. At -60°C the reaction seems to achieve an equilibrium at low conversion indicating termination-dominated reaction in spite of the high ionizing power of SO_2 and its high ability of solvating the counteranion. Indeed, the reaction medium showed a violet color throughout the polymerization suggesting the presence of free I_2. These features are in agreement with the low initiation efficiency. Concerning the α-MeSty polymerization, a strong yellow color appeared when the monomer was added.[20] This phenomenon was attributed to charge-transfer in the anion-SO_2 complex,[23] indicating the presence of cationic species plus the counteranion (I^- or I_3^-).[12] Ind polymerizations performed at -40°C and at lower I_2 concentration (5.91mM) are characterized by an initiation efficiency almost quantitative after 120 min but the conversion is not high. In this case, the solution changes from violet into yellow during the polymerization. The increase of I_2 concentration results in an increase of conversion but a decrease of initiation efficiency. Similar results have been found in the polymerization of αMeSty by the I_2/SO_2 system.[20]

The analysis of methanolic layer by HRGC-MS indicated only the presence of unreacted monomer. Therefore, no speculation concerning the nature of initiation by this method could be made. Fig. 1 shows the ^1H NMR spectrum of polyindene prepared in the I_2/SO_2 system at -40°C. The absence of olefinic protons suggests chain transferless polymerization. The absorptions around 3.5 ppm may be attributed to the methoxy and methyne initial and terminal groups originated from substitution of iodide group during the workup of the product. It is curious to observe the relatively narrow molecular weight distribution of all samples, including those obtained at -20°C where transfer reactions are important.

Table 1. Cationic polymerization of indene by iodine in liquid sulfur dioxide [a]

Exp. n°	$[I_2]_o$ mM	temp. (°C)	time (min)	conversion (%)	Mn x 10^{-3}	Mw/Mn	P [b] mM	I_{eff} [c] (%)
AV31	5.91	-20	15	45	6,0	1.5	7.12	120
AV32	5.91	-20	30	60	6.7	1.4	8.49	144
AV33	5.91	-20	45	70	7.3	1.46	8.80	149
AV81	5.91	-20	60	75	7.4	1.40	9.56	162
AV83	5.91	-20	120	90	7.6	1.48	11.18	189
AV91	5.91	-40	30	25	6.8	1.31	3.49	59
AV93	5.91	-40	60	35	8.4	1.23	3.95	67
AV95	5.91	-40	90	42	7.0	1.29	4.72	80
AV97	5.91	-40	120	45	7.3	1.34	5.81	98
AV139	29.5	-40	15	22	6.4	1.35	3.24	11
AV140	29.5	-40	30	40	6.3	1.35	6.00	20
AV143	29.5	-40	60	56	6.5	1.37	8.13	27
AV145	29.5	-40	90	70	5.9	1.48	11.20	38
AV155	29.5	-40	120	76	6.4	1.25	11.21	38
AV49	5.91	-60	30	5	5.3	1.45	0.89	15
AV50	5.91	-60	60	11	6.2	1.41	1.67	28
AV51	5.91	-60	120	11	6.5	1.41	1.59	27
AV99	29.5	-60	30	5	3.9	1.38	1.21	4
AV101	29.5	-60	60	10	5.8	1.43	1.63	5
AV105	29.5	-60	120	25	5.6	1.35	4.21	14
AV102	29.5	-60	240	30	7.2	1.37	3.93	13

a) reaction conditions: In = 0.8M; SO_2 = 8 mL; CH_2Cl_2 = 1 mL;

b) number-average polymer chain calculated by $P = ([M]_o - [M]) \div DP_n$

c) initiator efficiency calculated by $I_{eff} = \{([M]_o - [M]) \div DP_n [I_2]_o\} \times 100$

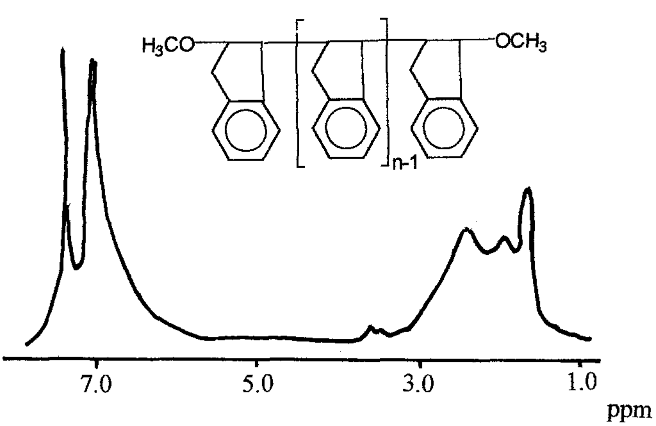

Fig. 1. ^1H NMR spectrum of polyindene obtained in I_2/SO_2 system. Reaction conditions: temperature = -40°C; time = 60 min; $[I_2]_o$ = 5.91mM; $[M]_o$ = 0.80M; SO_2 = 8 mL.

The relatively narrow MWD and the absence of olefinic proton in the ^1H NMR spectrum of polyindene obtained at -40°C led us to investigate the living or "long-lived" character of this system by adding a second feed of monomer after the first one has been consumed. The chromatograms of the polymers obtained at a I_2 concentration of 29.5 mM are shown in Fig. 2. In fact, an increase of Mn was observed after the second step. Nevertheless the MWD has broadened and the average number of polymer chains have increased indicating initiation of new chains by the free I_2 present in the system.

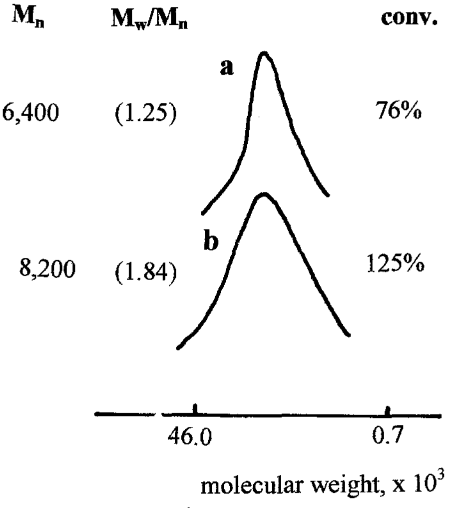

Fig.2. SEC curves of polyindene samples (a) before and (b) after the second monomer addition. Ind = 0.8M; SO_2 = 8 mL; I_2 = 29.5 mM -40°C

Polymerization of styrene.

Sty was able to polymerize in this system only at -20°C. Table 2 presents the results concerning the polymerization using different I_2 concentrations. In contrast to αMeSty and Ind polymerizations at -20°C, Sty polymerizes with low conversion and a number-average polymer chain less than the initial I_2 concentration, suggesting absence of chain transfer and a strong tendency for termination. The charge turns pale pink indicating the formation of carbon - iodide terminal bond.

Fig. 3 displays the ^1H NMR spectrum of polystyrene prepared by the I_2/SO_2 system at -20°C. Similarly to polyindene spectrum, no chemical shift related to olefinic protons was observed, indicating also chain transferless polymerization. The absorption around 3.2ppm may also be attributed to methoxy initial and/or end groups.

Table 2 . Cationic polymerization of styrene by iodine in liquid sulfur dioxide [a]

Exp. N°	$[I_2]_o$ (mM)	time (min)	conversion (%)	Mn x 10^{-3}	Mw/Mn	P [b] (mM)	I_{eff} [b] (%)
AAS1	5.91	30	1	3.5	1.34	0.26	4.4
AAS2	5.91	60	2	4.9	1.65	0.37	6.2
AAS3	5.91	90	3	5.1	1.54	0.53	8.9
AAS4	5.91	120	8	8.5	1.79	0.85	14.4
AAS9	29.5	60	4	4.3	1.51	0.84	2.8
AAS11	29.5	120	23	6.3	1.81	3.30	11.2
AAS14	29.5	180	25	5.2	1.46	4.35	14.7
AAS16	29.5	240	29	8.4	1.50	3.12	10.6

a) reaction conditions: Sty = 0.8M; SO_2 = 8 mL; CH_2Cl_2 = 1 mL; temperature = -20°C.
b) P and I as in Table 1.

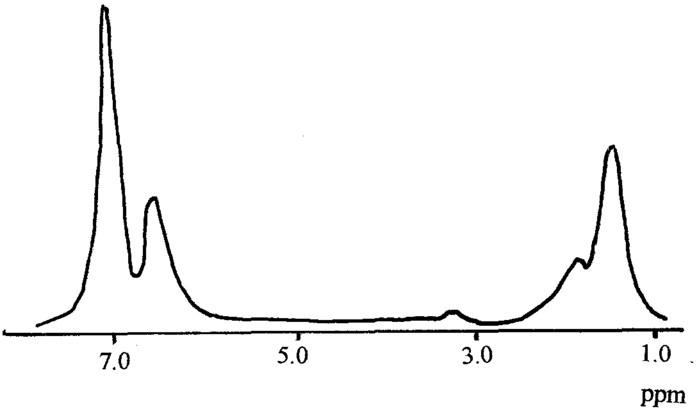

Fig. 3. ^1H NMR spectrum of polystyrene obtained in I_2/SO_2 system. Reaction conditions: temperature = -20°C; time = 180 min; $[I_2]_o$ = 29.5 mM; $[M]_o$ = 0.8 M; SO_2 = 8 mL.

The methanolic layer was also analyzed by HRGC-MS to identify the nature of the components present in the solution. Besides unreacted Sty, a compound was found, identified as (1,2-dimethoxy-ethyl)-benzene, as presented in Fig. 4. This substance probably derives from the 1,2-diiodide adduct of Sty after quenching and precipitation with methanol, as follows:

$$C_6H_5CH{=}CH_2 + I_2 \rightarrow C_6H_5CHICH_2I \rightarrow C_6H_5CH(OCH_3)CH_2(OCH_3)$$

Surprisingly product which could indicate initiation by HI was not observed, as previously detected in the αMeSty/I_2/SO_2 system.[22] As reported in the literature [1, 4-6] the initiation of Sty by I_2 in common organic solvent is characterized by the prior formation of HI, the actual initiator. Those studies were performed at high temperature (30°C). Probably, the low temperature used in our experiments does not favor the decomposition of the stable 1,2 diiodide adduct of Sty into HI. In the case of αMeSty, decomposition could be favored even at lower temperature because of steric factors.

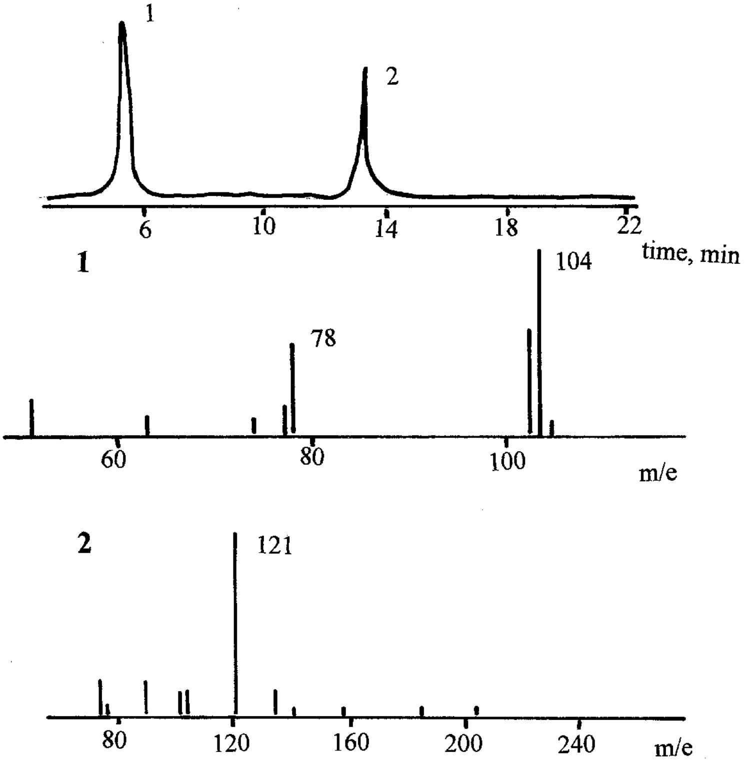

Fig. 4. (A) Gas chromatogram of methanolic layer after precipitation and filtration of polystyrene (Exp. n° AAS9 in Table II).; mass spectra of component 1(styrene) **(B)** and component **2** (1,2-dimethoxy-ethyl)-benzene) **(C)**.

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