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Cationic polymerization in iodine/liquid sulfur dioxide system

III. Investigation about elementary steps in α-methylstyrene polymerization

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Abstract

Investigations concerning the initiation step in cationic polymerization of alpha-methylstyrene in liquid SO_2 initiated by iodine have been made, based on the analysis of the low molecular weight components soluble in methanol by gas chromatography coupled with mass spectrometry. The results suggest that the formation of the alpha-methylstyrene diiodide is not possible, probably due to steric hindrance. HI formed from the carbocation (generated by the attack of iodine on the monomer at -60°) may initiate the polymerization.

Introduction

In preceeding papers we have reported on the cationic polymerization of alpha-methylstyrene (a-MeSty) initiated by iodine in the presence of liquid SO_2 (1,2). The facts that the average number of polymer chain was less than theoretical at -60°C and the molecular weights increased with conversion suggested the presence of living propagating species. At -20°C the reactions yields were very low indicating chain transfer. These side reactions could yielded low molecular weight materials (dimers and trimers) which remain soluble after the precipitation of polymer in methanol.

In addition, a curious fact was observed concerning the color of the reaction media. While reactions performed in the absence of SO_2 remained violet all the time, in presence of a large amount of SO_2, the solution changed from violet to yellow as soon as the monomer was added. Several authors have proposed some explanations for this initiation system in organic solvents (3-6). First, it was proposed that initiation could be unimolecular or bimolecular depending on the polarity of the solvent (3).

$$I_2 \quad + \quad CH_2{=}CHR \xrightarrow{CCl_4} I{-}CH_2{-}\overset{+}{C}HR \ldots I^-$$

$$2\ I_2 \quad + \quad CH_2{=}CHR \xrightarrow{CH_2Cl_2} I{-}CH_2{-}\overset{+}{C}HR \ldots I_3^-$$

Recently, it was suggested that with vinyl ethers (4) or styrene derivatives (5,6), the first step of initiation in-

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volves the formation of monomer-iodine adducts and that propaga- is nonionic. In the case of styrene, the adduct decomposes as follows (5,6):

$$I\text{-}CH_2\text{-}CH(C_6H_5)I \longrightarrow ICH{=}CH(C_6H_5) \quad + \quad HI$$

and HI is the actual initiator.

This communication concerns the identification of the nature of the initiation involving such a polymerization system using gas chromatography coupled with mass spectrometry analyses of the nonpolymeric material soluble in methanol.

Experimental

materials.

a-MeSty, dichloromethane, iodine and SO_2 were purified as described (1). HI was first dehydrated over P_2O_5, then stored in n-hexane solution in the dark at -40°C (4).

procedures.

Polymerizations were initiated by iodine as previously described and are summarized in Table I (1). Polymerizations initiated by HI or HI/I_2 were carried out in a similar way. The reaction was initiated by monomer addition to the initiator solution. For the analysis of the soluble material in methanol, the reaction was quenched with 1 mL chilled methanol. Then 4 mL of CH_2Cl_2 were added to solubilize the polymer (for reactions in SO_2) and the solution was poured into 40 mL methanol. The precipitated polymer was filtered and the filtrate was analysed by gas chromatography-mass spectrometry (HRGC-MS-C).These analyses were performed on a high resolution gas chromatograph CG-master (HRGC) on SE-54 glass capillary column (25m x 0.30 mm, d_f=0.25um) using hydrogen as carrier gas and temperature programming from 60 to 300°C at 10°C/min. The same chromatographic conditions were used for HRGC-MS-C analyses (He as carrier) on an HP-5987A instrument using linear scanning 50-500 daltons, electron impact (70ev) ionization.

Results and Discussion

For the proposed study , the polymerization reactions of a-MeSty initiated by iodine were performed in the presence or absence of liquid SO_2. The conditions are summarized in Table I. As described in the Experimental, after the precipitation of the polymers in methanol, the methanolic layer was analysed by HRGC and HRGC-MS to identify the nature of the components present in the solution . Figure 1 shows the gas chromatograms of the filtrates of some of these reactions. After comparing some of these chromatograms with those obtained after HRGC-MS, we have been able to identify some components present in solution. The mass spectra of these components are illustrated in Figure 2

retention time	component
7.0	alpha-methylstyrene
12.2	(1-methoxy-1-methylethyl)benzene
23.6	1,1'-(1,1,2,2-tetramethyl-1,2-ethanediyl)benzene
24.6	2,3-dihydro-1,1,3-trimethyl-3-phenyl-indane

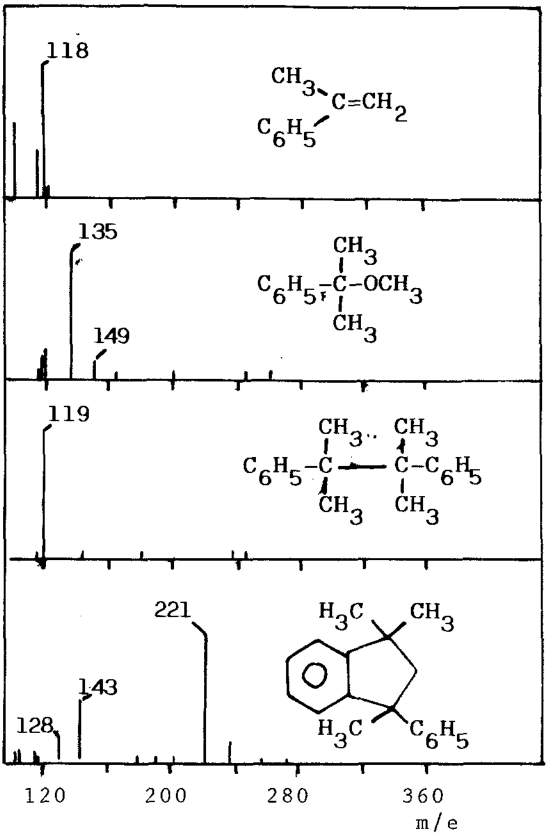


Figure 2.mass spectra of the soluble components in methanol.

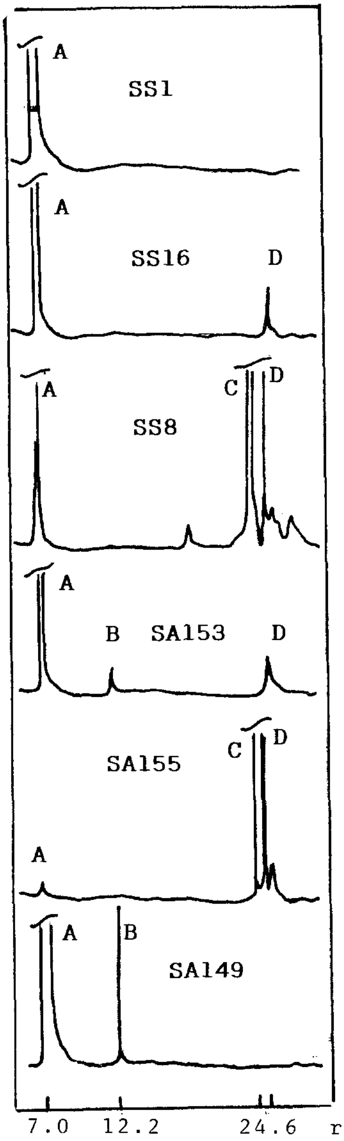


Figure 1 . gas chromatograms of methanolic layer after precipitation and filtration of the polymers. Reactions conditions are described in Table I

TABLE I

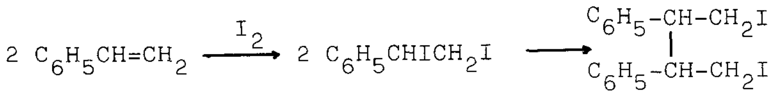
Polymerization of a-MeSty initiated by iodine: data from components soluble in methanol

Exp.nº	SO_2 (mL)	CH_2Cl_2 (mL)	I_2 (mM)	time (min)	temp. (°C)	conv. (%)	Mn $\times 10^{-3}$	comp. in methanol A (%)	B (%)	C (%)	D (%)
SS1	-	9.0	0.6	240	-20	-	-	100.0	-	-	-
SS16	-	9.0	5.9	240	-20	16	1.0	82.0	0.3	-	-
SS8	-	9.0	5.9	960	-20	34	1.0	28.0	-	17	20
SA153	8.0	1.0	0.6	5	-20	30	1.4	67.0	0.4	-	3
SA155	8.0	1.0	5.9	5	-20	30	1.2	1.0	-	21	48
SS13	-	9.0	0.6	30	-60	0	-	99.9	0.07	-	-
SS17	-	9.0	5.9	30	-60	0	-	99.9	0.08	-	-
SS19	-	9.0	5.9	240	-60	11	18.0	88.8	0.18	-	-
SA149	8.0	1.0	0.6	5	-60	0	-	99.0	0.7	-	-
SA152	8.0	1.0	5.9	5	-60	15	11.0	84.0	0.8	-	-
SA158	8.0	1.0	5.9	10	-60	37	16.0	63.0	-	-	-

components present in solution after precipitation of polymer in methanol:(A) a-MeSty;(B) (1-methoxy-1-methyl-ethyl)benzene; (C) 1,1'-(1,1,2,2-tetramethyl-1,2-ethanediyl)bis-benzene and (D) 2,3-dihydro-1,1,3-trimethyl-3-phenylindane

Reactions performed at -20°C give rise to cyclic dimer (compound D) indicating, as expected, irreversible chain transfer. In liquid SO_2, its formation is more significant (see Exp. n° SA155). The low conversion under these conditions is mainly due to transfer and not to termination or slow propagation.

The formation of compound B is explained by protic initiation . This substance could be formed from the carbocation E or the halogenated product F after the reaction with methanol.These reactions are illustrated in Scheme 1.The presence of cumyl iodide (compound F) is more probable since it could also explain the formation of compound C through the homolytic scission of the C-I bond. A similar reaction has been proposed a long time ago by Trifan and Bartlett (7). In that paper, the authors have isolated 1,4-diiodo-2,3-diphenyl-butane as one of the product of reaction between styrene and iodine :



$$2\ C_6H_5CH{=}CH_2 \xrightarrow{I_2} 2\ C_6H_5CHICH_2I \longrightarrow \begin{array}{c} C_6H_5\text{-}CH\text{-}CH_2I \\ | \\ C_6H_5\text{-}CH\text{-}CH_2I \end{array}$$

It seems that both free radical and ionic processes are ocurring at -20°C. The formation of polymer is a cationic process while the coupling of alpha-methylstyryl is a free radical process. The later is suppressed by decreasing the temperature since reactions performed at -60°C do not yield products which could indicate a free radical process.

None of the samples showed a diiodo-dimer of a-MeSty, similar to that found by Trifan and Bartlett. Evidently the formation of alpha-methylstyrene diiodide is not possible for a-MeSty, probably due to steric hindrance.

As previously discussed, the formation of (1-methoxy-1-methylethyl)benzene (compound B) is explained by protic initiation (see Scheme 1). Since only a-MeSty, iodine and liquid SO_2 were employed the origin of the proton should be explained.

The possibility which first comes to mind is chain transfer. It can be noted in Table I that reactions at -60°C in the presence or absence of liquid SO_2 give rise to compound B. We have previously reported that reactions performed at -60°C do not contain considerable chain transfer (1). These reactions carried out in liquid SO_2 show an increase of the molecular weight with conversion and the average number of polymer chains is less than the theoretical, which suggest absence of chain transfer. Since the amount of compound B in the methanolic phase obtained at -20 is higher than at -60°C this explanation may not be the best one.

The second possibility is the adventitious presence of a small quantity of protic impurity, like water. It is well known that iodine reacts with SO_2 in the presence of water to give HI (Karl-Fischer test). The formed HI could be responsible for the formation of compound B and consequently for that of compound C. The appearance of compound C in reactions carried out in the absence of SO_2 does not support this hypothesis.

Giusti and co-workers (5,6) and Bartlett (7) have proposed a mechanism for the polymerization of styrene with iodine. They suggested that initiation involves the formation of a diiodo styrene adduct followed by its decomposition to HI and 1-iodo- 2-phenyl-ethene at 30°C. They believe that HI is the actual initiator. Adapting their theory for a-MeSty, we propose the formation of compound B and C as described in Scheme 1. This later possibility seems to be the best one. However, we have not detecteded 1-iodo-2-phenyl-1-propene ($C_6H_5-C(CH_3)=CHI$) in the methanolic layer, or some other product which could originate from it.

The ability of HI in initiating the polymerization of a-MeSty in liquid SO_2 has been proved by some preliminary reactions. Table II presents some results concerning polymerizations initiated by HI,HI/I_2 or I_2.

SCHEME 1

The proposed mechanism of initiation

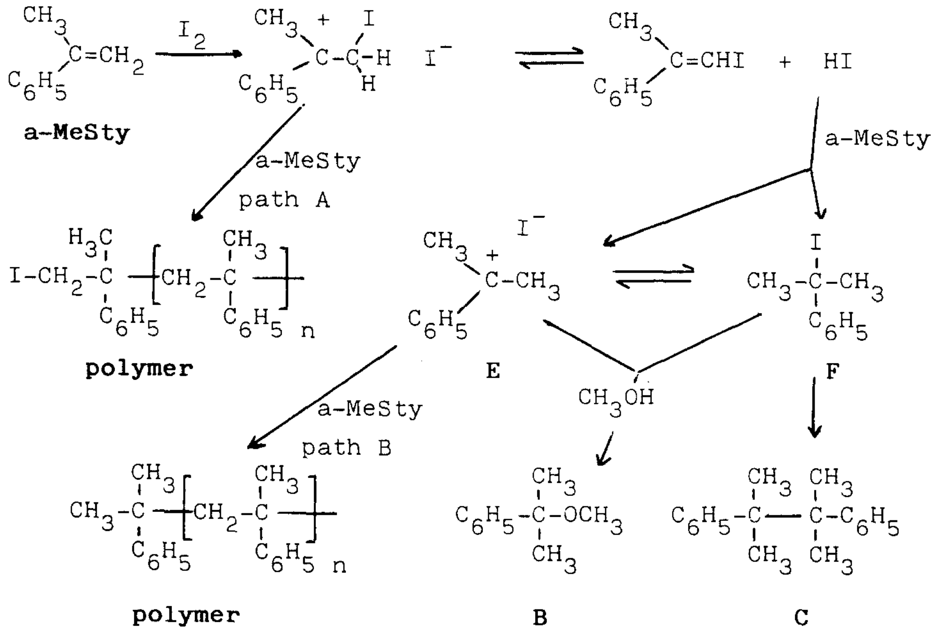


TABLE II

Polymerization of a-MeSty initiated by HI, HI/I_2 in liquid SO_2[a]

Exp.nº	HI (mM)	I_2 (mM)	time (min)	conversion (%)	Mn x 10^{-3}	Mw/Mn	P (mM)
SA197	-	5.9	15	45	16.3	1.61	2.5
SA108	-	5.9	30	95	31.0	1.82	2.8
HI18	5.9	-	15	30	7.8	1.40	3.5
HI20	5.9	-	30	75	17.5	1.70	3.9
HI21	5.9	5.9	15	100	16.3	1.63	5.8

a) a-MeSty: 0.77M; SO_2: 8.0 mL; CH_2Cl_2: 1.0 mL; temp.: -60°C.

HI alone is able to initiate the polymerization of a-MeSty in liquid SO_2 at -60°C. Although the reaction is slower than with iodine, the initiation is more efficient. These results are in agreement with a previous hypothesis concerning the bimolecular nature of initiation by iodine in polar media (3). Reactions performed by the HI/I_2 initiating system are faster and the initiation efficiency is nearly 100% as compared to HI alone.

Based on these results, we suggest that polymerizations initiated by iodine, the HI may also take part in the initiation. HI formation was evidencied even at -60°C and may be responsible for the slow initiation observed previouly (1). We cannot be sure however, that initiation is only due to HI. We propose the presence of two kinds of initiations as shown in Scheme 1,both of them being influenced by the temperature. The high percentage of compound C in reactions at -20°C in liquid SO_2 indicates that (Exp.n° SA155)initiation is predominantly by HI at this temperature.

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