Polymerization of Styrene in Liquid Sulfur Dioxide Initiated by Alkyl or Aralkyl Chloride

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Alkyl chloride catalyzed polymerization has never hitherto been reported in the literature. Triphenylmethyl chloride has been shown to be a catalyst for a cationic polymerization of vinyl ether in cresol[1]; no detailed information, however, on the mechanism has been indicated. The role of alkyl chloride such as methyl chloride, ethyl chloride or ethyl bromide as a cocatalyst in a cationic polymerization with a Lewis acid catalyst has been the subject of controversy in recent years. While Plesch and his collaborators[2] have indicated in several experiments that alkyl halides are no more an effective cocatalyst for polymerization of isobutene with titanium(IV) chloride, Kennedy et al.[3] have suggested methyl chloride could be a cocatalyst in the same polymerization with aluminum chloride.

In this article, the present authors would like to report on the alkyl or aralkyl chloride catalyzed polymerization (without any Lewis acid) of styrene in liquid sulfur dioxide. It was found that ethyl, *n*-propyl, isopropyl, *n*-butyl, *t*-butyl, α-phenethyl, and benzyl chlorides are all effective catalysts for the cationic polymerization of styrene. No Lewis acid catalyst has been used with the alkyl chloride in the polymerization.

Initial over-all rates were estimated. The viscosity of the polymer was measured in ethyl methyl ketone and the number average molecular weight was calculated from the viscosity using Outer, Carr and Zimm's equation[4],

$$[\eta]_{\text{dl./g.}} = 3.9 \times 10^{-4}\ [\text{M}]^{0.58}$$

The polymerization may be of cationic nature, since (1), no styrene-polysulfone was found in the polymer and (2) any anionic polymerization may be inhibited in liquid sulfur dioxide

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TABLE I. ALKYL CHLORIDE INITIATED POLYMERIATION IN LIQUID SULFUR DIOXIDE

Chloride	Initial rate $-dM/dt$ $\times 10^4$ mol. l^{-1} sec^{-1}	$[\eta]$ dl/g. in ethyl methyl ketone	$\bar{P}_n \times 10^{-2}$	Conversion % (150 min.)
Benzyl	3.95	0.118	1.82	13.5
α-Phenethyl	1.84	0.132	2.20	14
n-Propyl	1.70	0.151	2.78	13
Isopropyl	1.45	0.165	3.24	9
t-Butyl	0.99	0.088	1.10	4
Ethyl	0.82	0.152	2.80	9
n-Butyl	0.44	0.132	2.20	10
Triphenylmethyl	Trace			
HCl	0			

$[\text{styrene}]_0 = 1.32$ mol./l. $[\text{RCl}]_0 = 0.366$ mol./l.
Total volume = 100 ml. Reaction temp. 25°C

because of its acid nature. The elementary analysis and the infrared[5] spectrum of the polymer indicated that the polymer was a polystyrene.

As is listed in Table I, the initial rates of the polymerization initiated by various chlorides seem to follow neither the order of the inductive effect of the respective alkyl groups nor the order of the ionization tendency of the alkyl chloride in liquid sulfur dioxide. Triphenylmethyl chloride has been said to be a good electrolyte in the solvent[6], and an extensive ionization is to be expected in the solvent, but no reproducible result on the polymerization was obtained and the rate was approximately zero. A steric inhibition of the triphenylmethyl carbonium ion may perhaps be partly responsible for the restriction of polymerization. An alternative explanation for the failure of polymerization by triphenylmethyl carbonium ion may exist in the fact that this ion is too stable in liquid sulfur dioxide to initiate the cationic polymerization.

The attempted polymerization with hydrogen chloride as catalyst failed to suggest that the formation of α-phenethyl cation is impossible in liquid sulfur dioxide, since the addition of a proton to styrene, as the following,

$$C_6H_5CH{=}CH_2 + H^+ \rightarrow C_6H_5\underset{+}{CH}{-}CH_3$$

α-Phenethyl cation

should yield an α-phenethyl cation which might be able to initiate the polymerization as is the case in α-phenethyl chloride. It should be also reminded that α-phenethyl cation[7] has been shown as an acting species for the initiation of the ordinary cationic polymerization of styrene. Inadequacy of hydrogen chloride as a catalyst may be verified by a few studies in our laboratory. The association of hydrogen chloride in liquid sulfur dioxide has already been suggested by one of the present authors[8]. No deuterium exchange in liquid sulfur dioxide between a growing polymer cation and heavy water has also been reported earlier[9]. These facts are well consistent with the protophobic nature of liquid sulfur dioxide.

The fastest rate is attained by benzyl chloride catalysis, however the authors have no appropriate explanation for such a phenomenon at present. As is seen in the table, the polymerization has also been conducted by ethyl, *n*-propyl or *n*-butyl chloride. The production of free carbonium ions of them is not conceivable in ordinary solvent, but a strong solvation of chloride anion with liquid sulfur dioxide may be operative during the polymerization in liquid sulfur dioxide. The ionized carbonium ion may initiate and conduct the polymerization, however, the mechanism of initiation needs a further study.

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