The Acyl Halide-initiated Polymerization of Styrene in Liquid Sulfur Dioxide

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The polymerization of styrene in liquid sulfur dioxide initiated by various alkyl and aralkyl chlorides has recently been reported by two of the present authors[1]. We have now examined polymerization of styrene in liquid sulfur dioxide initiated by acyl halides and have found that various acyl halides, such as acetyl, chloroacetyl, propionyl, *n*-butyryl, isobutyryl and benzoyl chlorides, and acetyl and isobutyryl bromides are all effective initiators of the cationic polymerization of styrene in liquid sulfur dioxide. *p*-Toluenesulfonyl chloride is also an excellent initiator.

The polymerizations were performed at 25°C in liquid sulfur dioxide with 0.698 mol./l. of styrene and 0.004∼0.34 mol./l. of an acyl halide in a total volume of 175 ml. The initial overall rates of polymerization, the average degrees of polymerization of the polymer, and the conversion in 3 hr. are listed in Table I. The average molecular weight of the polymer was calculated from the intrinsic viscosity in benzene by Pepper's equation[2] to be:

$$[\eta] = 2.7 \times 10^{-4} M^{0.66}$$

The polymer produced by acyl halides was polystyrene, as was expected; it was identified by the infrared spectra. Sulfur analysis showed the product was not contaminated by polysulfone ruling out a radical nature of this polymerization process.

The results mentioned above and listed in Table I suggest that the polymerization is initiated by an acylium cation, $R\overset{+}{C}O$. which may be derived by the ionization of an acyl halide in liquid sulfur dioxide:

$$RCOCl \rightleftarrows RCO^{+} + Cl^{-}$$

or by an associated ion, such as $RCO^{+}Cl^{-}$-RCO^{+}, which may likely be present in a medium with a low dielectric constant[3]. The characteristic feature of this polymerization is that the over-all rate of polymerization seems to depend on the initiation, because the species of the initiator has a strong influence on the rate of the polymerization, while the counter anion (Cl^{-} or Br^{-}) is unchanged throughout the reaction and the nature of the propagation of the polymer chain remains the same.

The evidence for such an assertion is that: (a) Chloroacetyl chloride is a weaker initiator than acetyl chloride; (b) *p*-toluenesulfonyl chloride is an excellent initiator; (c) *p*-nitrobenzoyl chloride cannot initiate the polymerization, whereas benzoyl chloride can initiate the polymerization; (d) the acyl bromide is more reactive than the corresponding chloride; (e) the polymerizations are terminated by the addition of such substances as tetramethylammonium chloride or triphenylmethyl chloride, and (f) the time-conversion curve of the polymerization is flattened as time elapses, the polymerization being terminated at a lower conversion when an initiation is not so strong. These phenomena may partly be elucidated by the mass-law effect[4] on both the ionization of

TABLE I. ACYL HALIDE-INITIATED POLYMERIZATIONS IN LIQUID SULFUR DIOXIDE

Acyl halide, 0.34 mol./l.	Initial rate $-dM/dt \times 10^5$ mol./l. sec. at 25°C	$[\eta]$ dl./g. in benzene	$\overline{P}$	Conversion in 3 hr. %
Isobutyryl bromide	Very large	0.149	136	9.4
Isobutyryl chloride	Very large	0.445	746	9.6
Acetyl bromide	Very large	0.189	197	11.2*
p-Toluenesulfonyl chloride	11.92	0.114	94	84.2*
Acetyl chloride	6.29	0.195	206	18.8
Propionyl chloride	4.46	0.172	170	18.5
Chloroacetyl chloride	0.93	0.161	150	4.7
Benzoyl chloride	0.93	0.205	220	3.9
n-Butyryl chloride	0.56	0.207	226	1.1
p-Nitrobenzoyl chloride	0			0

* Conversion at 2 hr.

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[1] N. Tokura and T. Kawahara, This Bulletin, 35, 1902 (1962).

[2] D. C. Pepper, *J. Polymer Sci.*, 7, 345 (1951).

[3] D. E. Hughes, C. K. Ingold, S. Patai and Y. Pocker, *J. Chem. Soc.*, 1957, 1206.

[4] C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell Univ. Press, Ithaca, New York (1953), p. 360.

the acyl halide and the growing ion pair in liquid sulfur dioxide. *p*-Toluenesulfonyl chloride is an excellent initiator in the sense that this halide initiates a polymerization which proceeds to over an 80% conversion within 2 hr.

We have not yet been able to identify the terminal acyl group or the carbonyl group in the polymer end; however, the inclusion of a sulfur atom in the polymer initiated by *p*-toluenesulfonyl chloride was verified by elementary analysis. No correlation has been found between the average degrees of polymerization and the initial rates of polymerization. The mechanism of the polymerization will be scrutinized again in a further study.

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