SHORT COMMUNICATIONS

Liquid Sulfur Dioxide Catalyzed Polymerization of Styrene Derivatives and Formaldehyde

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It has been recently shown that liquid sulfur dioxide is an excellent medium for cationic polymerization[1] with Lewis acid as catalyst. Moreover, there have been reported several cases where the polymerizations were carried out only by the medium (sulfur dioxide) without any catalyst[2,3]. Vinyl ethers are known as belonging to this class[3].

The present authors have found some additional monomers which are capable of carrying out such a liquid sulfur dioxide catalyzed polymerization. It has been found by the present authors that alkyl substituted styrenes are easily polymerized by liquid sulfur dioxide itself. Especially, *p*-methylstyrene will be mentioned here as an example. *p*-Methylstyrene, b. p. 58.5°C/12 mmHg, was dissolved in liquid sulfur dioxide with a trace of hydroquinone and allowed to stand at 50°C in a thermostat. The polymer obtained was separated and purified by the usual procedure (precipitation by methanol from benzene solution of the polymer). The product (5.67 wt.% conversion at 90 min.) was an amorphous powder and melted at 159~162°C (Found: C, 91.23; H, 8.58. Calcd. for poly-*p*-methylstyrene: C, 91.47; H, 8.35%, $[\eta]_{\text{dl./g.}}$ (in DMF), 0.04).

That the polymerization is of cationic mechanism is proved by the facts (a) the radical polymerization of the *p*-methylstyrene in liquid sulfur dioxide must result in the formation of of polysulfone[4], (b) the polymerization by sulfur dioxide was inhibited by electron-donors such as dimethylformamide (DMF), dioxane or amine into the mixture and (c) the reaction was not inhibited by hydroquinone or else which were recognized as radical inhibitor. When the monomer was subjected to a condition of a radical polymerization at 50°C with azobisisobutyronitrile (AIBN), as a catalyst, the product obtained was a mixture of poly-*p*-methylstyrene and *p*-methylstyrene polysulfone, the constitution of the latter being *p*-methylstyrene : SO_2 = 2 : 1 in its mole ratio. The polymer melted at 149~151°C. Analysis of the polysulfone, (Found: C, 71.30; H, 6.61; S, 10.23. Calcd. for 2 : 1 polysulfone; C, 72.00; H, 6.67; S, 10.67%, $[\eta]_{\text{dl./g.}}$, (DMF), 0.4).

Thus a cationic polymerization arose competitvely in liquid sulfur dioxide with an AIBN catalyzed radical polymerization. The product produced by the simultaneous cationic and radical polymerization could be separated by the extraction of poly-*p*-methylstyrene with cyclohexane in a Soxhlet apparatus, the yield of the poly-*p*-methylstyrene being 13~15% of the total.

α-Methylstyrene was polymerized readily by liquid sulfur dioxide. However, in contrast to the result of *p*-methylstyrene, an attempted radical polymerization with AIBN was not successful and gave only poly-α-methylstyrene as a result of a cationic polymerization. The detail of the simultaneous polymerization will be reported elesewhere in the near future.

The present authors have also observed that formaldehyde was polymerized by liquid sulfur dioxide or by sulfur dioxide vapor to yield polyoxymethylene. When liquid sulfur dioxide was maintained at a constant temperature between −70 to −10°C and formaldehyde vapor was streamed into this medium, semitransparent films were obtained on the surface of the solution or on the wall of the glass vessel. The films produced at −70°C were colorless and melted at 169~172°C, containing no sulfur atom (Found: C, 39.37; H, 6.37. Calcd. for $(-CH_2O-)_n$: C, 40.0; H, 6.67%). $[\eta]_{\text{dl./g.}}$ (acetylated polymer in *p*-chlorophenol with 2% α-pinene) was 0.6. The infrared spectrum of the specimen was in close resemblance to that of polyformaldehyde prepared by Novak et al.[5], at low temperature. IR, 2990

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4) a) N. Tokura and M. Matsuda, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 501 (1961); b) N. Tokura, M. Matsuda and F. Yazaki, ibid., **64**, 713 (1961); c) N. Tokura, R. Asami, M. Matsuda and H. Negishi, ibid., **64**, 717 (1961).
5) A. Novak and E. Whall, *Trans. Faraday Soc.*, **55**, 1490 (1959).

(m, ν-CH), 1492, 1472, 1435, 1387(m), 1290, 1220, 1240(s), (CH_2 bending), 1100 (v. s. –C–O–) and 910~970(s) (KBr). From the evaporation residue of the sulfur dioxide solution, a powdery polymer was also obtained, which was identified as lower molecular weight polyoxymethylene from elementary analysis, infrared spectrum and viscosity, [η], 0.1, the sulfur test was negative. The total yield of the film and the powder was almost quantitative.

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