The Polymerization of α-Methylstyrene by Iodine Catalyst

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Although it is well known that iodine is an inhibitor for radical polymerization, its power of polymerizing some vinyl monomers has been reported by several investigators[1-4]. We have also found that iodine plays a role as an initiator for the polymerization of α-methylstyrene (αMS) at room temperature. Since it seems interesting that the reaction proceeds under the presence of lower concentration of iodine (0.1~0.3%) as compared with the case of polymerization of styrene by iodine (10~20%) recently reported[4], preliminary results are reported as follows.

It was found that the reaction proceeded even in the atmosphere but reproducible results were not obtained. The sample, therefore, was dehydrated in vacuo with metallic sodium or calcium hydride and was distilled into a reaction vessel without exposing to the air. The extent of polymerization of the monomer for a week reached maximum when the concentration of iodine added was ca. 0.1~0.3%. When more iodine than 1% was added to the monomer, the temperature of the reactant rose markedly high, as soon as iodine was allowed to contact wiih the monomer. In such cases the reactant became very viscous but the high polymers could not be obtained.

In Fig. 1, the yield of polymer for the reaction at 25°C vs. time are plotted. All the samples were enclosed at the same time and polymerized for different intervals of time, and the polymers were precipitated with excess of methanol. It is shown that the initial rate of polymerization in higher concentration of iodine (0.2%) is larger than that in lower one (0.1%), but in the former case the conversion did not become more than about 25%, while it increased up to more than 50% for an interval of 160 hr. in the latter case.

The color of iodine disappeared in both cases after a long period of reaction. The intrinsic viscosity of the polymers was independent of the time of polymerization, i. e., ca. 0.1** dl./g. and slightly larger in the case of lower concentration of iodine.

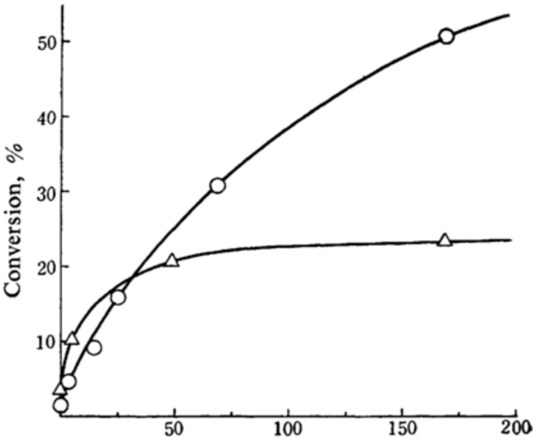

Fig. 1. Conversion of αMS vs. time.
Concn. of iodine: ○ 0.1%; △ 0.2%.

It is clear from the inhibitory power of iodine for polymerization by free radical mechanisms that this polymerization must be of non-radical and presumably of ionic character. It may be natural to assume that this reaction proceeds by a cationic mechanism as concluded in the polymerization of vinyloctylether[2] and of styrene[4] by iodine in view of the following experimental fact:—The polymer which is obtained from the mixture of αMS and methyl methacrylate (1 : 1 in volume ratio) in the presence of iodine showed essentially the same infrared absorption spectra as that of the polymer obtained from the similar mixture by stannic chloride.

Details of the experiment will be published in *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*.

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** This intrinsic viscosity corresponds to the molecular weight of ca. 3,000 (cf. C. P. Brown and A. R. Matheson, *J. Chem. Soc.*, 1958, 3507).