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The Polymerization of 1,3-Dioxolane Catalyzed by Ion Exchange Resin (Polystyrene Sulfonic Acid)

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ABSTRACT

Polystyrene sulfonic acid resin (Amberlyst 15) was found to initiate the cationic polymerization of 1,3-dioxolane easily in bulk at 0 to 50°C, and polymers with a reduced viscosity of 0.1 were obtained. However, this resin showed only low initiator activity for the polymerizations of 2-methyl-1,3-dioxolane and trioxane.

1,3-Dioxolane has been reported to polymerize with various acid catalysts, such as mineral acids [1], Friedel-Crafts catalysts [1, 2], the binary systems of perchloric acid/acetic anhydride [3], perchloric acid/phosphorus pentafluoride [4], and ferric acetylacetonate/acetyl chloride [5]. However, sulfonic acid, p-toluenesulfonic acid, and polyphosphoric acid were shown to have only low catalytic activity [2].

In a previous paper [6], polystyrene sulfonic acid as an ion exchange resin (Amberlite 200) was reported to initiate the cationic polymerizations of styrene, α -methylstyrene, and isobutyl vinyl ether.

We have recently found that a similar polystyrene sulfonic acid resin, Amberlyst 15 (Rohm and Haas Co.), can act as an effective initiator for the polymerization of 1,3-dioxolane. The present paper will describe the results obtained.

1,3-Dioxolane and its 2-methyl derivative were prepared according to the method described by Astle et al. [7]. They were purified by fractional distillation, and then redistilled on calcium hydride just before use. Amberlyst 15, which is a macroreticular-type ion exchange resin composed of polystyrene sulfonic acid, was treated with dilute hydrochloric acid to convert it to the acid form, washed with water, and then dried in vacuo. The polymerizations, in which Amberlyst 15 catalyst was insoluble in the polymerizing mixture, were carried out in a sealed tube under shaking. The reduced viscosities of the polymers obtained from 1,3-dioxolane were measured in a 1% aqueous solution at 30°C.

Table 1 summarized the results of the polymerization of 1,3-dioxolane and its methyl derivative. As shown, polystyrene sulfonic acid was found to show remarkable activity for the polymerization of 1,3-dioxolane. However, very low activity was observed for 2-methyl-1,3-dioxolane.

The curves of time vs polymer yield and time vs reduced viscosity for the polymerization of 1,3-dioxolane with this polystyrene sulfonic acid at 0, 30, and 50°C are shown in Fig. 1. As shown in this figure, the polymerization at 0°C was performed linearly with time, but that at 50°C was induced rapidly in its initial stage. This

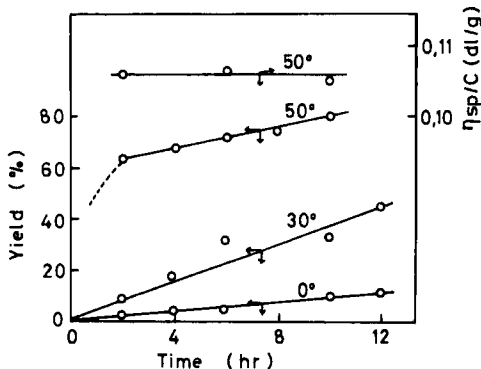


FIG. 1. Time-polymer yield and time-reduced viscosity curves for the polymerization of 1,3-dioxolane. 1,3-Dioxolane = 4 ml, catalyst resin = 100 mg.

TABLE 1. Polymerization of 1,3-Dioxolane and Other Cyclic Ethers Catalyzed by Polystyrene Sulfonic Acids^a

Monomer	Reaction temp (°C)	Reaction time (hr)	Polymer yield (%)
1,3-Dioxolane	0	24	42.4
1,3-Dioxolane	30	24	70.9
1,3-Dioxolane	50	10	80.4
2-Methyl-1,3-dioxolane	30	46	1.3
Trioxane	70	6	0.7 ^b

^a Monomer = 4 ml., Resin = 100 mg., Polymerized in bulk.

^b Monomer = 4 g., Resin = 100 mg., Polymerized in solution (4 ml of CH₂Cl₂).

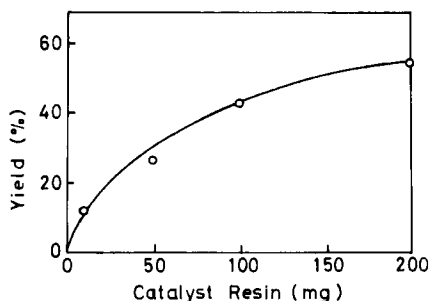


FIG. 2. Relationship between catalyst resin and polymer yield for the polymerization of 1,3-dioxolane (4 ml at 30°C for 12 hr).

behavior is almost similar to that observed in the polymerization of isobutyl vinyl ether [6]. The reduced viscosity of the resulting polymers was independent of the polymerization time at 50°C.

The polymer yield was found to increase with the weight of polystyrene sulfonic acid used, as shown in Fig. 2. Accordingly, it is assumed that polystyrene sulfonic acid can also catalyze the cationic polymerization of some cyclic ethers (see Table 1). However, tetrahydrofuran and propylene oxide did not polymerize with this acid.

From the IR spectrum of poly(1,3-dioxolane) thus obtained, the absorption bands based on polyoxymethylene and polyethylene oxide were observed, and they indicate that this polymer consists of a copolymer of formaldehyde and ethylene oxide.

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