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Radiation-Induced Copolymerization of Trioxane with 1,3-Dioxolane

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ABSTRACT

Copolymerization of 1,3-dioxolane (DOX) with trioxane in the solid state was studied by radiation. The effects of radiation dose, DOX concentration, postpolymerization temperature and duration on the copolymer yield, and DOX incorporation were investigated and compared with published data.

INTRODUCTION

Recently the radiation-induced copolymerization of trioxane (TOX) in the solid state was studied using styrene oxide [1] penta-acetyl glucose [2] and tetrahydrofuran [3] by Sagu and Bhattacharyya as comonomers. Several authors [4-6] studied the radiation-induced polymerization of trioxane with 1,3-dioxolane (DOX) as comonomer. As an extension of these copolymerization studies, investigations were also carried out with DOX as comonomer. The results obtained, although showing trends similar to those of the earlier authors, indicated higher yields of the copolymer. These results are presented here.

The low thermal stability of polyoxymethylene is expected to improve through introduction of C-C bonds through incorporation of a copolymer. Cyclic ethers have some structural similarities with TOX,

and hence copolymerization of TOX with cyclic ethers has attracted the attention of researchers.

EXPERIMENTAL

TOX was purified to 99.99% by repeated crystallization. DOX was purified by treatment with sodium metal followed by distillation. Weighed quantities of DOX and TOX were placed in a stoppered flask, heated gently until the mixture melted, and then thoroughly mixed by shaking. Samples of this melt, about 2 g each, were transferred into 10 mm diameter test tubes and cooled. These TOX-DOX blends were irradiated with gamma rays from a cobalt-60 chamber at a temperature of 25-30°C, followed by postpolymerization heating at 43, 48, and 53°C in a thermostatic bath. The temperature in the bath was controlled within $\pm 0.1^\circ\text{C}$. After heating for specified time periods, the tubes were taken out of the bath and quickly quenched by dipping in an ice-common salt mixture. The unreacted monomers were washed out of the polymer product by toluene and analyzed by gas-liquid chromatography. The weight of dried polymer indicated the yield. The difference of the weights of the comonomer charged and recovered indicated the comonomer incorporation in the polymer.

RESULTS AND DISCUSSIONS

TOX-DOX blends containing 1% DOX were irradiated with 0.1, 0.2, 0.4, and 1.0 Mrd radiation doses and postpolymerized for 6 h at 53°C. The polymer yields obtained are shown in Fig. 1. A separate curve shows the homopolymer yields under similar conditions. The polymer yield increased with the radiation dose, reaching the optimum level at 0.4 to 0.5 Mrd. The trend of the results is somewhat similar to those published by Ishigaki et al. [6]; their data have also been plotted in Fig. 1 for comparison. The yield obtained by Ishigaki et al. was lower in spite of the fact that the postpolymerization time was longer (24 h) than in this study (6 h). Their results further showed that the yields continue to rise with the radiation dose up to 1.0 Mrd.

To study the effect of DOX concentrations, TOX-DOX blends containing 1 to 5% of DOX were irradiated with a 0.4 Mrd dose and postpolymerized at 53°C for 6 h. The copolymer yields with increasing DOX concentration in the feed are shown in Fig. 2. The data of Ishigaki et al. [6] and Sakamoto et al. [5] are also plotted in this figure. Ishigaki et al. reported that the copolymer yield was the same as that of the homopolymer with 1% DOX in the feed, but with 2 to 3% DOX the yield decreased sharply. In this work it was also found that with 1% DOX in the charge, the copolymer yield was practically the same as that of homopolymer. With increasing DOX content in the charge, the copolymer yield decreased slowly and not as steeply as

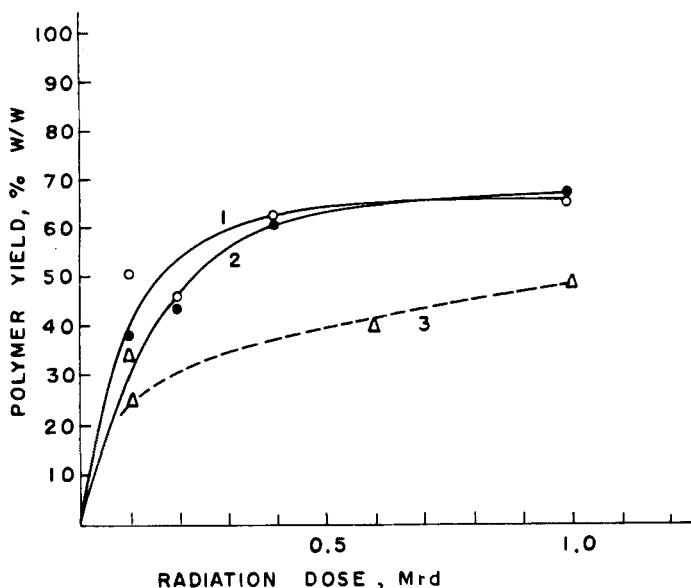


FIG. 1. Effect of radiation dose on polymer yield. DOX, 1%. Post-polymerization at 53°C for 6 h. (1) Copolymer of TOX with DOX. (2) Homopolymer of TOX. (3) Data of Ishigaki (DOX, 1% w/w; polymerization, 24 h at 55°C).

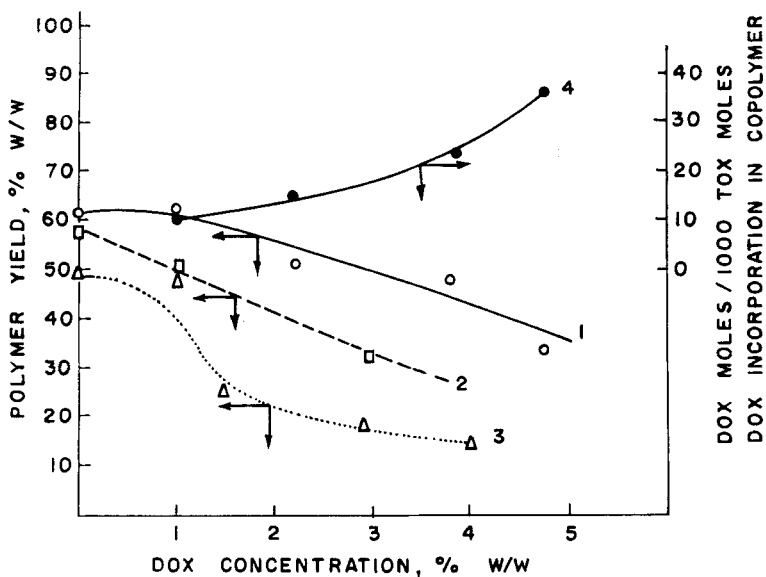


FIG. 2. Effect of DOX concentration on polymer yield. Dose, 0.4 Mrd. Postpolymerization at 53°C for 6 h. (1) This work. (2) Data of Sakamoto (1.0 Mrd; polymerization, 3 h at 55°C). (3) Data of Ishigaki (0.1 Mrd; polymerization, 5 h at 55°C). (4) This work (DOX incorporation).

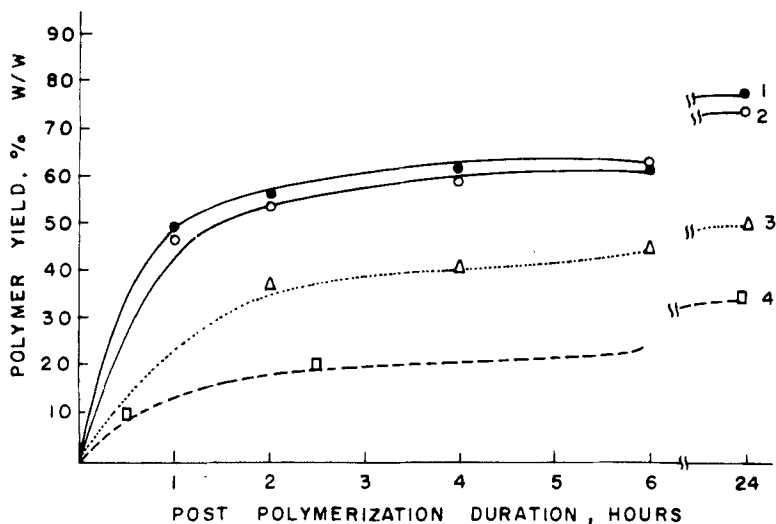


FIG. 3. Effect of postpolymerization duration on polymer yield. DOX, 1%; dose, 0.4 Mrd. Postpolymerization temperature, 53°C. (1) Homopolymer of TOX. (2) Copolymer of TOX with DOX. (3) Data of Ishigaki (1.0 Mrd; polymerization, 50°C; DOX, 1% w/w). (4) Data of Sakamoto (0.1 Mrd; polymerization, 55°C; DOX, 1% w/w).

observed by Ishigaki et al. Sakamoto et al. [5] also reported a slow decrease of yield with increasing DOX concentration in the feed; of course, the copolymer yields they obtained were always lower. Rosinger et al. [4] used an in-source polymerization method and found that the copolymer yield increased with increasing DOX concentrations in the feed; the results of Rosinger et al., therefore, cannot be exactly compared with the results obtained by the postpolymerization method. However, the results confirm that the copolymer yields decrease with increasing amounts of DOX in the monomer charged by the postpolymerization method.

Although the yield decreased, the DOX content in the copolymer was found to increase with increasing DOX concentration in the feed. This is shown in Fig. 2. Ishigaki et al. [6] reported a similar trend.

The copolymer yield somewhat improved with longer postpolymerization periods. This is shown in Fig. 3. TOX-DOX blends containing 1% DOX were irradiated with a 0.4 Mrd dose and postpolymerized at 53°C for 1, 2, 4, 6, and 24 h. Initially, the yield rose sharply; it was 47% after 1 h and 54% after 2 h of postpolymerization. Thereafter, the rise was slow and very similar to that of TOX homopolymer. In the case of homopolymer, the yield was slightly higher. The copolymer yields reported by Ishigaki et al. [6] and Sakamoto et al. [5], although lower, showed a similar trend (Curves 3 and 4). Ishigaki used lower

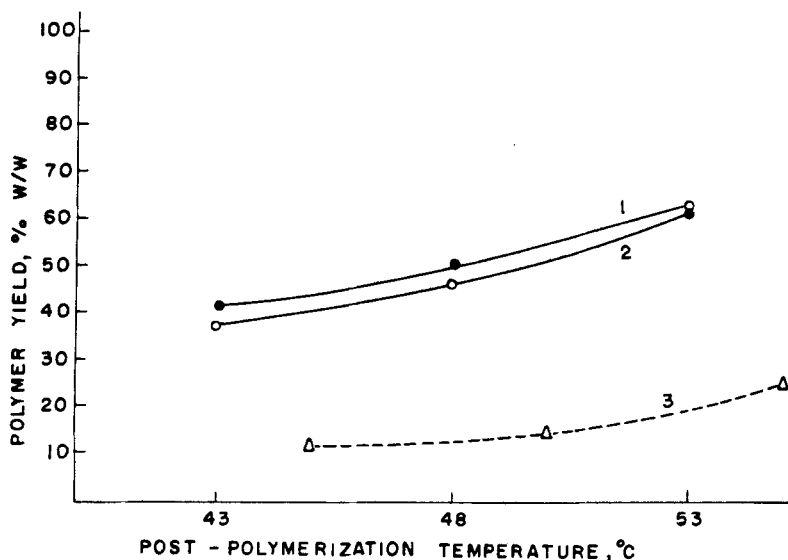


FIG. 4. Effect of postpolymerization temperature on polymer yield. (1) Homopolymer of TOX (0.4 Mrd, 6 h). (2) Copolymer of TOX with DOX (0.4 Mrd; 1% DOX; polymerization 6 h). (3) Data of Ishigaki (0.1 Mrd; 1% DOX; polymerization, 5 h).

radiation doses. The higher yields obtained in our work in comparison with those of Ishigaki et al. and Sakamoto et al. could be principally due to the higher purities of the TOX and the comonomer used.

Postpolymerization temperature also influences copolymer yield. Monomer charges containing 1% DOX were irradiated with 0.4 Mrd and postpolymerized for 6 h at 43, 48, and 53°C. The copolymer yield was found to increase with an increase of the postpolymerization temperature; a similar trend was reported by Ishigaki et al. [6] (Fig. 4, Curve 3).

The thermal stabilities of the TOX-DOX copolymer samples were also examined. Samples with different DOX contents were first stabilized by the method reported by Rosinger et al. [4]. One gram of copolymer was dissolved in 10 mL benzyl alcohol containing 2% triethanolamine at 150°C and heated for 30 min to remove the unstable parts of the copolymer. The weight losses of the copolymer samples during this treatment are shown in Curve 1 of Fig. 5. The weight loss was around 40% for all the samples containing 10 to 36 DOX mol/1000 TOX mol. This is, however, in contrast to the observations of Rosinger et al. [4] who reported that the polymer loss decreased with DOX content for copolymers prepared by in-source polymerization. They reported losses decreasing from 38 to 12% for a DOX content increase of 1 to 5%. In the case of homopolymer, they observed a loss of 82%

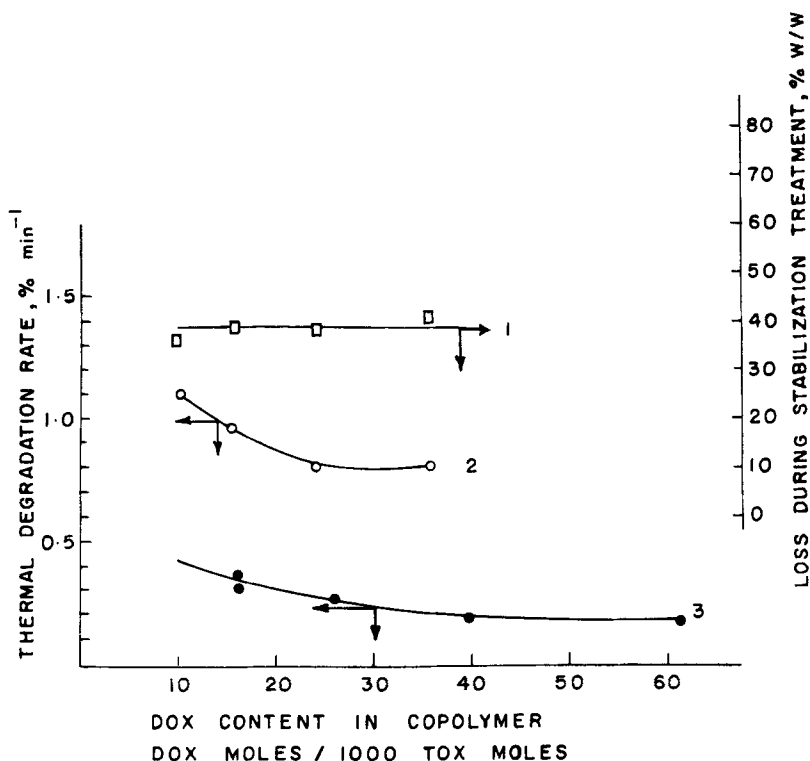


FIG. 5. Effect of DOX content in copolymer and stabilization on thermal degradation rate. (1) Loss during stabilization. (2) Thermal degradation before stabilization. (3) Thermal degradation after stabilization.

with the same stabilization treatment; a loss of 65 to 70% was observed in this work.

The thermal degradation rates of the stabilized copolymer samples were then determined by heating at 222°C for 60 min in a nitrogen atmosphere. The thermal degradation rate in terms of wt% loss/min was found to be markedly lower than in the cases of unstabilized samples; it was only 0.22% min⁻¹ compared with 0.8% min⁻¹ for the unstabilized copolymer containing 30 mol DOX/1000 mol TOX. The rate decreased with increasing DOX content in both cases. Similar findings were also reported by Rosinger et al. [4], Sakamoto et al. [5], and Ishigaki et al. [6]. The thermal degradation rate was significantly lower after stabilization treatment. Ishigaki et al. found copolymer weight losses of 5.4% in 60 min for their samples, whereas Sakamoto et al. found weight losses of 67.0% in 60 min; both of their samples

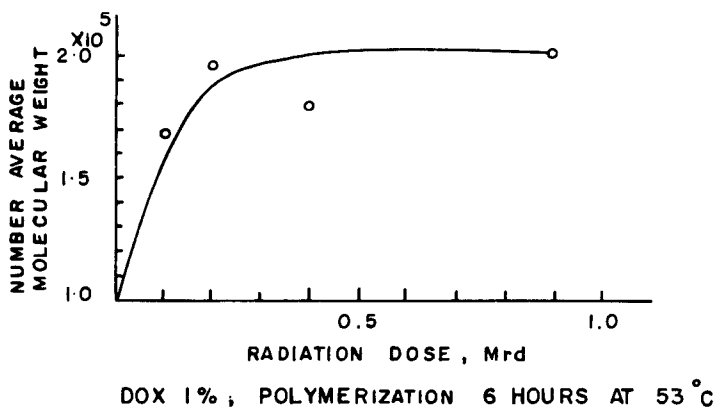


FIG. 6. Effect of radiation dose in copolymer on molecular weight. DOX, 1%; polymerization, 6 h at 53°C.

were prepared under the same reaction conditions. Ishigaki et al. felt that this was due to the higher purity of the monomers used by them. The weight losses in the case of our copolymer are close to that of Ishigaki et al.

The molecular weight (\bar{M}_n) of the copolymer samples prepared by using different radiation doses are shown in Fig. 6. The molecular weight increases initially with increasing radiation dose up to 0.2 Mrd and thereafter remains almost unchanged. This result is not in agreement with the data of Ishigaki et al. [6] who reported that the molecular weight decreased with increasing radiation doses.

With DOX incorporation in the range studied (prepared at 0.4 Mrd), the \bar{M}_n was found to remain almost constant. This is in agreement with the results of Rosinger et al. [4] but in disagreement with those of Ishigaki et al. who reported a decrease of molecular weight with increasing DOX content.

The melting points of the TOX-DOX copolymers, shown in Fig. 7, decreased from 182°C for the homopolymer to about 173°C when the copolymer contained 35 mol DOX/1000 TOX mol. Rosinger et al. [4] reported the melting point of homopolymer as 175°C, which decreased to 166°C with an increase of DOX content up to 5.6% w/w in the copolymer. Sakamoto et al. [5] found the melting point of homopolymer to be 187°C, and for the copolymer it decreased to 164°C for a DOX content up to 3% w/w. These data by earlier authors differ considerably from our results.

The density of the TOX-DOX copolymer also decreased with the DOX content. It can be seen from Fig. 7 that the density decreased from 1.460 g/mL for the homopolymer to 1.445 g/mL for the copolymer containing 35 DOX mol/1000 TOX mol. Droscher and Wegner [7]

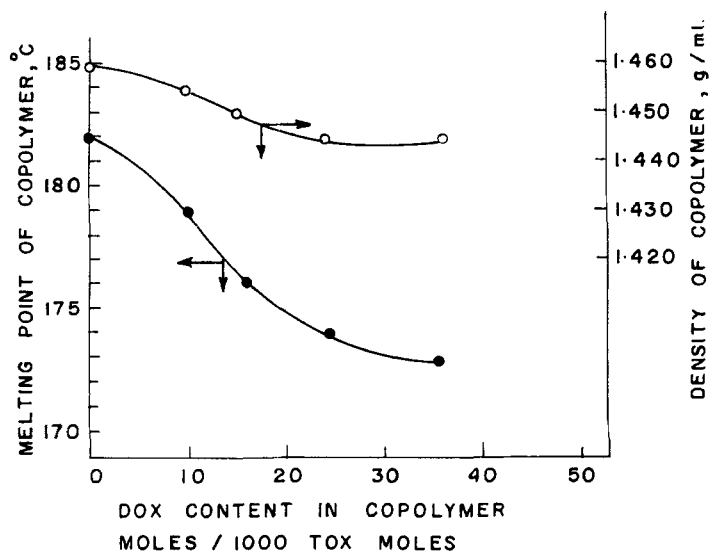


FIG. 7. Effect of DOX content in copolymer on its melting point (●) and density (○).

also reported a decrease in density, as well as in melting point, with increasing DOX content in the copolymer.

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