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Radiation-Induced Copolymerization of Trioxane with Styrene Oxide

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ABSTRACT

Copolymerization of trioxane (TOX) and styrene oxide (STO) induced by gamma radiation was studied under varying operating conditions to see the effects of radiation dose, STO concentration, postpolymerization temperature, and duration on the polymer yield. Charging 5% STO with TOX, STO conversion was 65% but yield was only 23% compared with 62% for the homopolymer. Molecular weight, melting point, density, and thermal stability of the copolymer samples were determined.

INTRODUCTION

Polyoxymethylene has very good mechanical properties and is used as engineering plastic [1]. However, the homopolymer is not stable at temperatures of around 200°C and above when it starts losing the $-\text{CH}_2\text{O}-$ units. It is made stable by capping the two end hydroxyl groups in the polymer chain by such reactions as acetylation [2-4]. Alternatively, introduction of C-C linkages in the polymer chain [5-7] by forming copolymer improves the stability. Such copolymer can be produced by incorporation of a small quantity of a compatible oxycyclic compound such as epoxides. Styrene oxide (STO) has a three-membered oxycyclic ring attached to the benzene ring, and has sufficient strain

for easy ring opening to react during polymerization. An investigation was therefore carried out for the copolymerization of trioxane (TOX) with STO which is reported here.

EXPERIMENTAL

TOX was purified to 99.99% purity by repeated crystallization; its melting point is 60.3°C but it starts sublimation at about 46°C. For melting, it has to be heated rapidly. STO is a liquid boiling at 194.1°C. Pure STO was prepared by double distillation. Weighed quantities of STO and TOX (moisture content below 300 ppm) were taken in a stoppered flask and heated gently; when the mixture melted, it was mixed thoroughly by shaking. Samples of this melt, about 2 g each, were transferred into 10-mm diameter test tubes and cooled. These TOX-STO blends were irradiated with gamma rays from a cobalt-60 chamber at ambient temperature, followed by postpolymerization by heating at 43, 48, and 53°C in a thermostatic bath. The temperature of the bath was controlled within $\pm 0.1^\circ\text{C}$. After heating for the specified period, the tubes were taken out and quickly quenched by dipping in an ice-salt mixture. The product was then treated with toluene six to seven times with thorough stirring to separate the unreacted STO and TOX from the polymer product; the unreacted components were analyzed by gas-liquid chromatography.

RESULTS AND DISCUSSION

The STO-TOX blends containing 1% w/w STO were irradiated with 0.1, 0.2, 0.4, and 1.0 MR doses and postpolymerized at 53°C for 6 h. The polymer yields at these radiation doses are shown in Fig. 1. The yields of TOX homopolymer under the same conditions are also shown in this graph for comparison. Without any radiation, there was no reaction. The yield of STO-TOX copolymer was substantial, 32.7% w/w, even with a small irradiation of 0.1 MR. Subsequently, the yield increased slowly with higher irradiation, reaching 40.6% at 0.2 MR and a maximum of 47% at 0.4 MR. Thereafter, a slight decrease of the copolymer yield was observed at 1.0 MR.

In the case of the homopolymer, on the other hand, the yield was always higher than the STO-TOX copolymer at the same radiation doses; it was above 60% at 0.4 MR and remained high at 1.0 MR.

The irradiation had created active centers in the TOX and STO molecules, which initiated their polymerization. The number of such active centers would normally depend on the radiation dose applied. A higher dose, up to a certain limit, would produce more active centers and result in increased polymer yield. This was true for the homopolymer here, but in the case of the TOX-STO copolymer the relative concentrations of the generated active species at 1.0 MR,

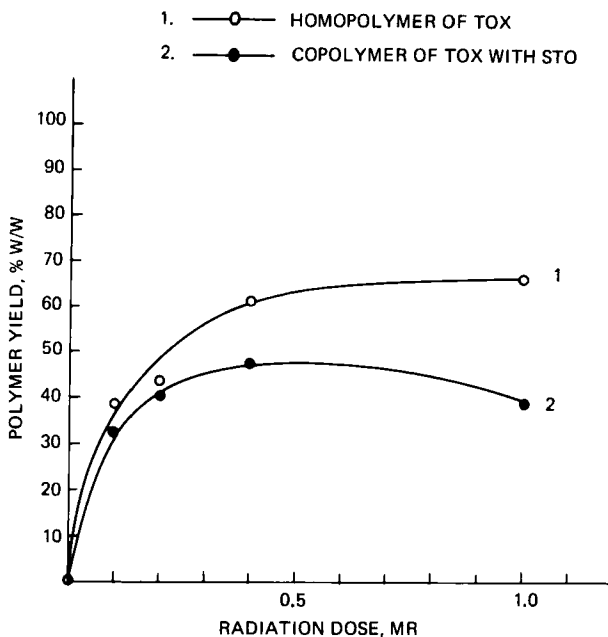


FIG. 1. Effect of radiation dose on polymer yield. STO concentration: 1% w/w. Polymerization at 53°C for 6 h.

and possibly above, seem to cause some radiolysis and reduce the copolymer yield. 0.4-0.5 MR seemed to be the optimum dosage for a maximum of 47-48% yield.

The copolymerization was then studied with higher amounts of STO. TOX-STO blends containing 1.0 to 5.4% w/w were irradiated with 0.4 MR dose and postpolymerized at 53°C for 6 h. Figure 2 shows that the polymer yield decreased with increasing STO content in the charge. The yields were 48% when the STO concentration was 1.0%; with 5% STO in the charge the yield decreased to 23%.

At the same radiation doses, however, the STO content in the copolymer rose with an increasing amount of STO in the feed. TOX-STO blends containing 1.00, 1.95, 3.75, and 5.34% STO were irradiated with 0.4 MR and postpolymerized at 53°C for 6 h. Figure 2 shows that the STO content in the copolymer rose from 4.6 to 12.4 mol/1000 TOX moles on increasing the STO content in the charge from 1.0 to 5.34 wt%; the corresponding conversions of STO were 20 and 65%. The latter is a high level of conversion in comparison with those of TOX and other monomers [8, 9]. On increasing the postpolymerization period, there was only a slight, though negligible, increase of STO incorporation in the polymer. TOX-STO blends, irradiated at 0.4 MR,

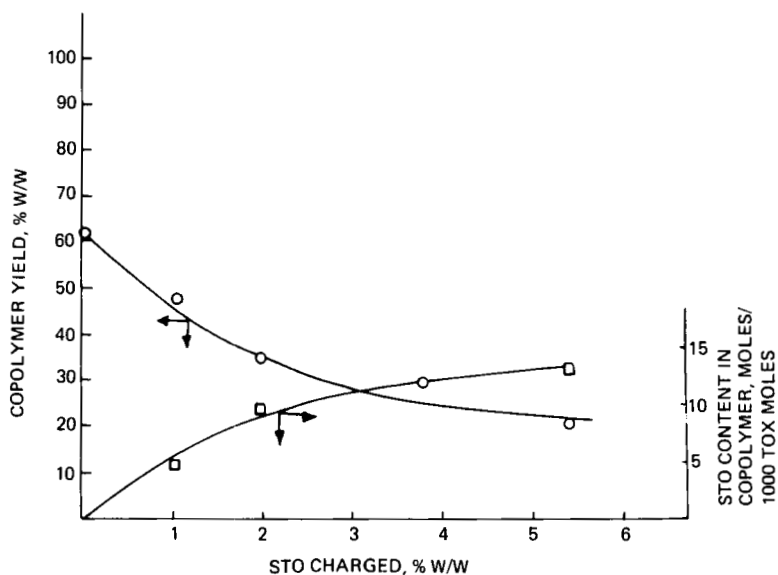


FIG. 2. Effect of STO concentration on its incorporation and copolymer yield. Dose: 0.4 MR postpolymerization at 53°C for 6 h.

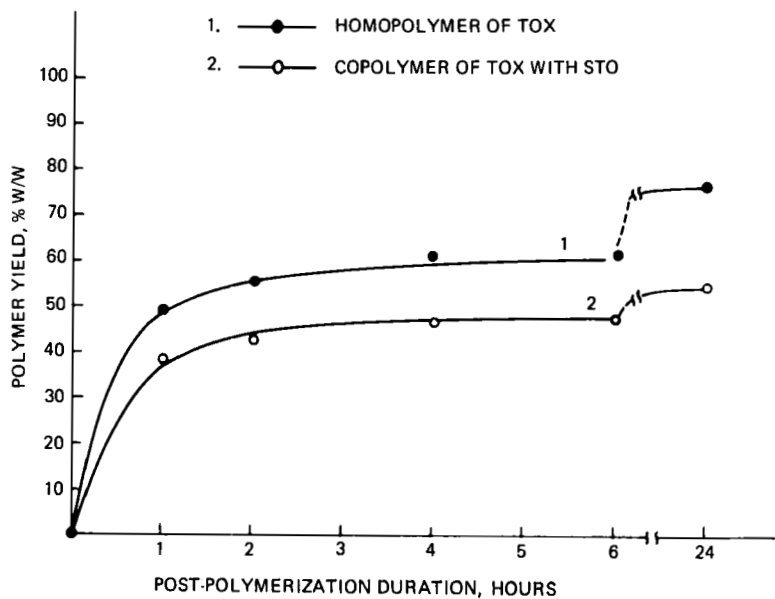


FIG. 3. Effect of postpolymerization duration on yield. Dose: 0.4 MR. STO: 1%. Postpolymerization temperature: 53°C.

were postpolymerized at 53°C for up to 24 h (Fig. 3); the yield increased from 47% at 6 h to 55% on heating for 24 h. The homopolymer yield was always about 12% higher than that of the corresponding copolymer.

The temperature of postpolymerization appeared to have a pronounced effect on the copolymer yield which is shown in Fig. 4. The copolymer yields were 27.0, 37.0, and 48.0% at 43, 48, and 53°C, respectively, showing an increase with a rise in postpolymerization temperature. The homopolymer yields were higher than that of the copolymer and showed a parallel rise. The frequency and amplitude of molecular vibrations in TOX crystals increases with a rise in temperature; this would increase the interaction between the neighboring molecules leading to higher yields. A similar trend was also observed in studies on other copolymers [8, 9] and the reaction was found to follow the Arrhenius law.

For examining the extent of copolymer formation and its stability, the copolymer samples were treated with benzyl alcohol containing 2% triethanolamine at 150°C for 30 min [5]. This removed the unstable part of the copolymer. The weight losses during this treatment of the copolymer samples containing 4.6 to 12.4 STO moles per 1000 TOX moles are shown in Fig. 5. The losses, supposedly of the homopolymer contents and/or of the uncapped homopolymer ends of the polymer chains, amounted to 65 to 70%.

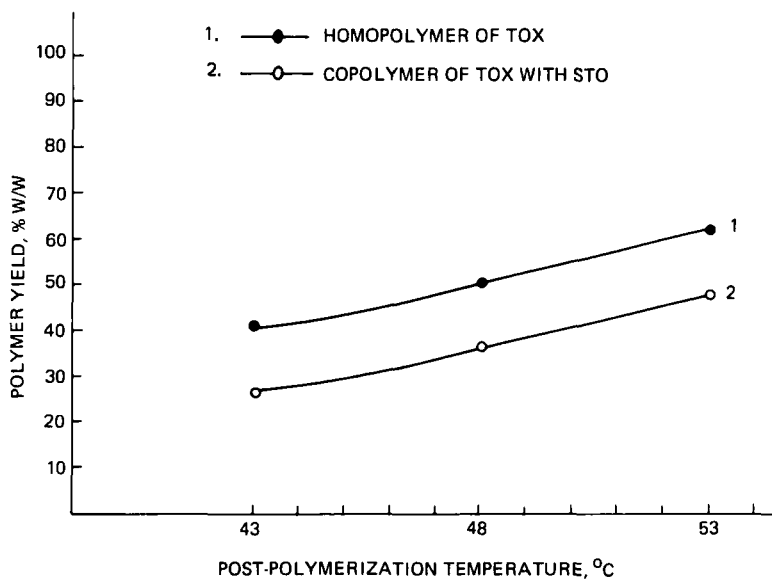


FIG. 4. Effect of postpolymerization temperature on polymer yield. Dose: 0.4 MR. STO: 1%. Postpolymerization duration: 6 h.

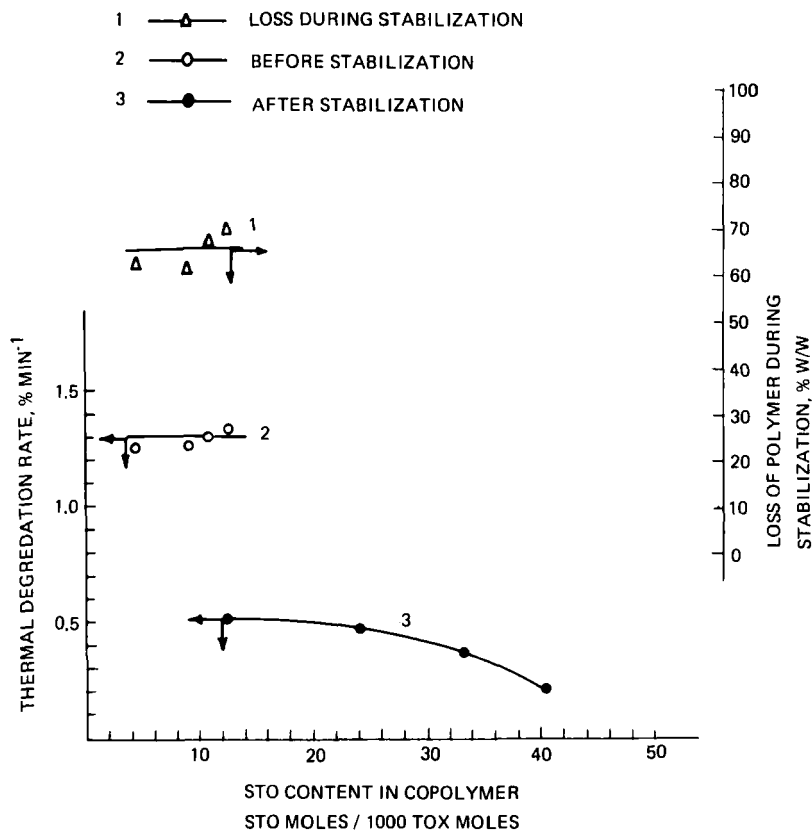


FIG. 5. Effect of STO content and stabilization on thermal degradation rate.

The original copolymer samples as well as those obtained after stabilization were studied for thermal degradation by the usual method of heating at 222°C under a nitrogen atmosphere for 60 min. The rate of weight loss in percent per minute was determined. The degradation rate of the untreated copolymer samples was quite high, ~1.3%/min (Fig. 5); this rate did not seem to vary with the STO contents in this small range. The stabilized copolymers showed appreciable improvement in thermal stability; the degradation was only about 0.5%/min, and this was found to decrease with the STO content in the copolymer.

The molecular weights of the STO-TOX copolymer samples obtained under different experimental conditions were determined by the viscosity method; the values, approximating the \bar{M}_n , are shown against three parameters in Fig. 6.

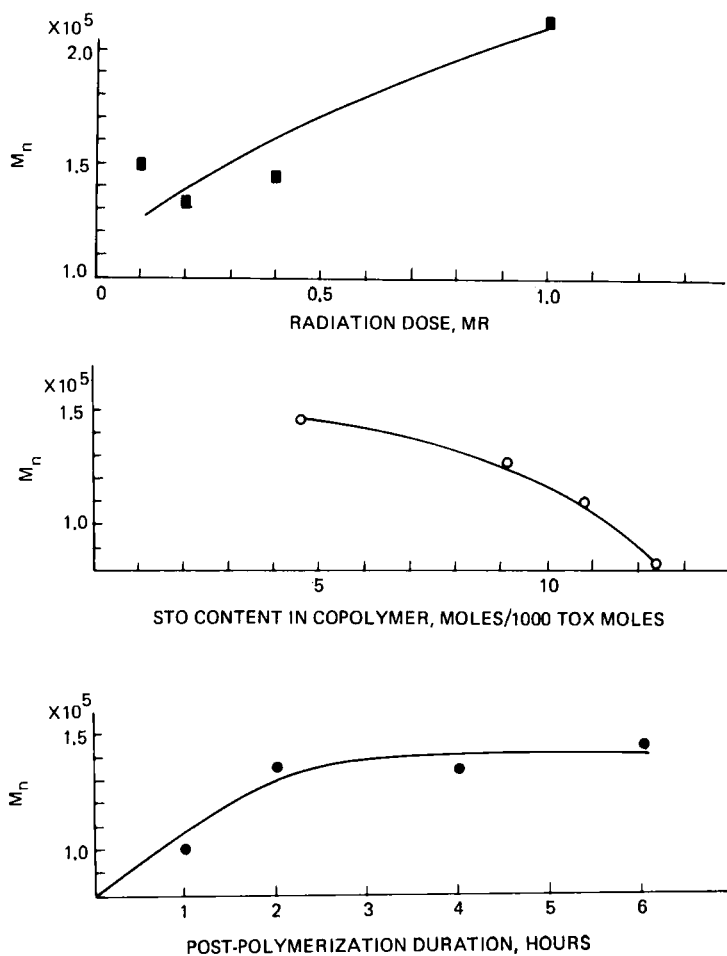


FIG. 6. Effect of radiation dose, STO content in polymer, and post-polymerization duration on number-average molecular weight.

The molecular weight of the copolymer was found to be higher, 2.15×10^5 , at a radiation dose of 1.0 MR in comparison with 1.51×10^5 at 0.4 MR. As already mentioned, the polymer yield was, however, slightly lower at 1.0 MR than at 0.4 MR.

On the other hand, with increasing STO content of the copolymer, the molecular weight was found to decrease; for the sample containing 12.4 mol of STO/1000 mol of TOX, the \bar{M}_n was 0.85×10^5 in compari-

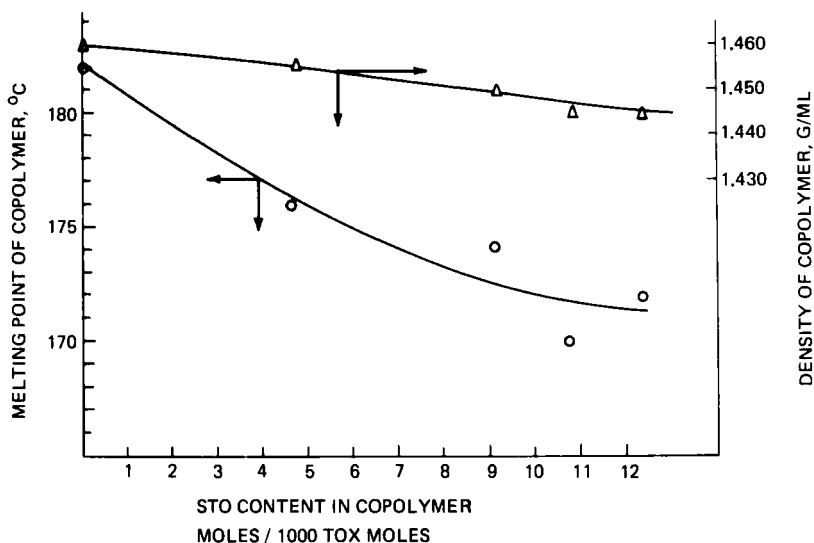


FIG. 7. Effect of STO content on melting point and density of copolymer.

son with 1.5×10^5 for the sample containing 4.7 mol/1000 mol of TOX. The duration of postpolymerization for 2 to 6 h had no effect on the \bar{M}_n ; the molecular weight remained almost the same.

As the STO monomer is a bulkier molecule than TOX, its introduction into the crystal lattice should produce more disorder, particularly due to the branching by an aromatic ring in the copolymer chain. This should result in a lower melting point of the copolymer than that of the TOX homopolymer. The lowering of the melting point was observed to be appreciable (Fig. 7). The melting point of the TOX homopolymer is 182°C. For the copolymer containing 12 mol/1000 TOX moles, it decreased to 172°C.

The density of the copolymer also decreased slightly with increasing STO content due to disturbances of the crystallinity of the polymer.

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