Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Ishigaki, Isao , Watanabe, Yuhei , Ito, Akihiko and Hayashi, Koichiro(1977) 'Radiation-Induced, Solid-State Copolymerization of Tetraoxane with 1,3-Dioxolane', Journal of Macromolecular Science, Part A, 11: 1, 149 — 170
To link to this Article: DOI: 10.1080/00222337708061259
URL: http://dx.doi.org/10.1080/00222337708061259

J. MACROMOL. SCI.–CHEM., A11(1), pp. 149-170 (1977)

Radiation-Induced, Solid-State Copolymerization of Tetraoxane with 1,3-Dioxolane

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ABSTRACT

The radiation-induced, solid-state copolymerization of tetraoxane with 1,3-dioxolane has been investigated. The results were discussed in comparison with those of trioxane-1,3-dioxolane copolymerization reported previously. In the copolymerization in vacuo, it was found that the thermal stability of the copolymer increases with increasing polymerization temperature, time, and the preirradiation dose, although that of trioxane-1,3-dioxolane copolymer decreases with increasing preirradiation dose and is nearly constant irrespective of polymerization temperature and time. The yield and intrinsic viscosity behavior of the copolymer are similar to those found in trioxane-1,3-dioxolane copolymerization. The copolymerization in air, however, was found to be very complicated. Trioxane formation in this system was also investigated in detail.

INTRODUCTION

Cyclic oligomers of formaldehyde, such as trioxane (trimer), tetraoxane (tetramer), pentoxane (pentamer), etc., are known to be polymerized by ionizing radiation in the solid state. Especially, the radiation-induced copolymerization of trioxane, which can be prepared easily, has been studied extensively by Rösinger et al. [1], Sakamoto et al. [2], and Ishigaki et al. [3]. On the other hand, few studies on the polymerization of tetraoxane and pentoxane have been reported because these monomers had not been commercially produced. (Today, however, tetraoxane can be obtained commercially.) No studies on the radiation-induced copolymerization of these monomers have yet been reported. The present authors reported previously [3] that trioxane is copolymerized with 1,3-dioxolane by ionizing radiation to give a copolymer having excellent thermal stability and a high molecular weight only when the rigorously purified monomers are used.

In the present study, the radiation-induced, solid-state copolymerization of tetraoxane with 1,3-dioxolane was investigated.

EXPERIMENTAL

Commericail tetraoxane (produced by Mitsui Toatsu Chemical Co. Ltd.) was purified by sublimation under reduced pressure (10-15 Torr) at 50° C just before use. 1,3-Dioxolane was refluxed for a few hours over sodium metal and then distilled over new sodium metal under a stream of nitrogen. The purified tetraoxane (2 g) was introduced into a glass ampoule (external diameter, 10 mm; internal diameter, 8 mm; length, 150 mm) and then degassed for about 30 min under 10^{-6} Torr at room temperature.

A vessel containing purified 1,3-dioxolane was connected previously to a vacuum line and degassed thoroughly by repeated freezing and melting under vacuum. 1,3-Dioxolane thus obtained was vaporized and introduced to the reservoir through Na-K alloy. Subsequently, ampoules containing tetraoxane were kept at a liquid nitrogen temperature under 10^{-6} Torr, and a certain amount of 1,3-dioxolane was added from the reservoir to the ampoules by operation of the glass stopcocks. The ampoule was then sealed off. The sample thus obtained was allowed to stand in the dark overnight at room temperature so that 1,3-dioxolane was homogeneously dispersed into tetraoxane. Subsequently, it was placed in a Dry Ice-methanol bath and subjected to γ-ray irradiation from a cobalt-60 source, and then placed in a constant temperature bath. The reaction mixture in the ampoule was washed well with acetone in order to remove unreacted monomers and other soluble materials (which is formed during the polymerization) and the copolymer thus obtained was dried under vacuum at room temperature. The polymer yield was determined gravimetrically.

The residual amount of 1,3-dioxolane was measured as follows. The copolymerization was stopped by quenching the sample in a Dry Ice-methanol bath, and a certain amount of toluene was added to the reaction mixture. Subsequently, the unreacted monomers were extracted thoroughly with toluene at room temperature, and the extract was analyzed by gas chromatography.

The intrinsic viscosity $[\eta]$ of the copolymer was measured at 60° C in p-chlorophenol containing 2% α-pinene after the copolymer sample was dissolved at 115°C in 15 min. The molecular weight of the sample was calculated by using the equation [4]:

$$[\eta] = 5.43 \times 10^{-4} M_n^{0.66}$$

The thermal stability of the copolymer was determined by measurement of weight loss under a stream of nitrogen at 222° C by use of a thermobalance, and this value was quoted as R^{60}_{222}, i.e., percentage of the residual weight after 60 min heating at 222° C.

RESULTS AND DISCUSSION

The effects of 1,3-dioxolane concentration, preirradiation dose, copolymerization temperature, and atmosphere on the radiation-induced, solid-state copolymerization of tetraoxane with 1,3-dioxolane were studied.

The effect of 1,3-dioxolane concentration on the polymer yield, the intrinsic viscosity $[\eta]$, and the thermal stability R^{60}_{222}, of the copolymer are shown in Fig. 1. The results are good agreement with those found in the radiation-induced, solid-state copolymerization of trioxane with 1,3-dioxolane as described in the previous paper [3]. The copolymer yield and $[\eta]$ decrease with increasing 1,3-dioxolane concentration, and the latter does so markedly compared with the former. On the other hand, R^{60}_{222} of the copolymer increases with increasing 1,3-dioxolane concentration. R^{60}_{222} is, however, quite small compared with the case of the trioxane–1,3-dioxolane system. Nevertheless, tetraoxane seems to copolymerize with 1,3-dioxolane, because R^{60}_{222} of the polymer obtained in the presence of 1,3-dioxolane is higher than that of tetraoxane homopolymer.

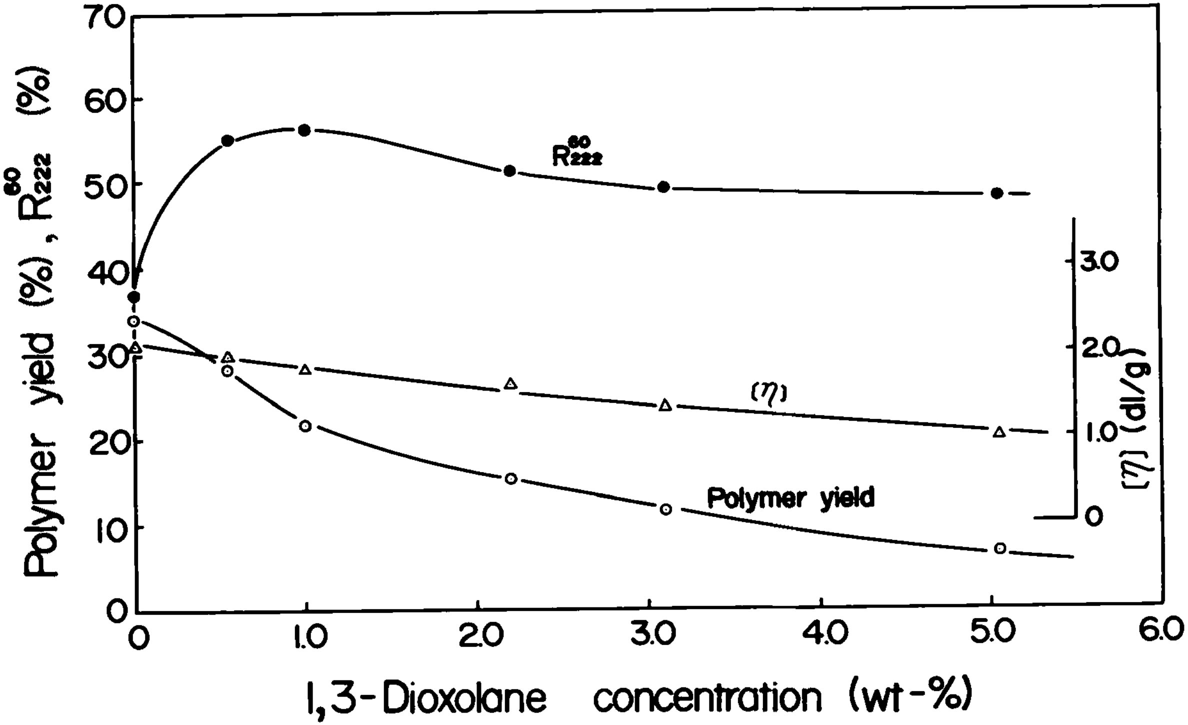

FIG. 1. Effects of 1,3-dioxolane concentration on the yield, intrinsic viscosity, and thermal stability of the copolymer. Preirradiation, 1 × 10^6 rad at -78° C; polymerization 5 hr at 105° C; in vacuo.

As clarified by x-ray analysis of the radiation-induced, solid-state polymerization of trioxane and tetraoxane, the reaction proceeds along the crystal lattice of monomer, i.e., it is characterized by so-called topotactic reaction [5]. Therefore, the polymerization rate is influenced by defects and distortion of the monomer crystal. As the tetraoxane crystal is influenced by addition of 1,3-dioxolane into this system, the polymerization rate and the yield decrease with increasing 1,3-dioxolane concentration.

Figure 2 shows that a plot of the reciprocal of the polymer yield against the degree of polymerization gives a straight line passing through the origin. As can be deduced from Fig. 2, chain transfer scarcely occurs in this system [6].

Figure 3 gives the relationships between preirradiation dose and the yield, [η], and R_{222}^{60} of the copolymer at 1% 1,3-dioxolane. The copolymerization was carried out at 105° C for 24 hr. The polymer yield increases monotonously, and the molecular weight of the copolymer decreases with increasing preirradiation dose. This tendency is similar to that found in the trioxane–1,3-dioxolane system [3]. On the other hand, the thermal stability of the copolymer increases with increasing preirradiation dose and goes up to its highest value (R_{222}^{60} = 63%) at 5×10^6 rad, though, in the case of trioxane–1,3-dioxolane system, it has been found to decrease with increasing preirradiation dose.

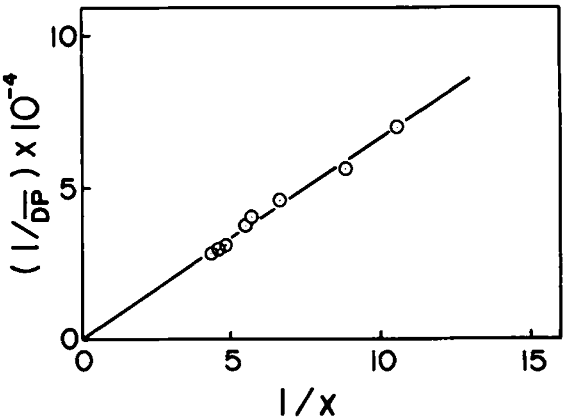

FIG. 2. Reciprocal of the degree of polymerization vs. reciprocal of polymer yield. Preirradiation, 1×10^6 rad at -78° C; polymerization at 105° C; in vacuo.

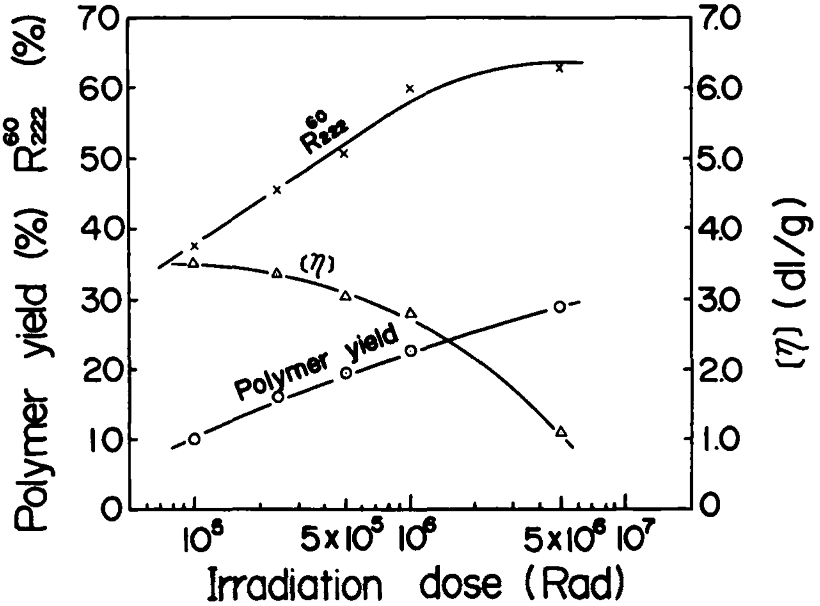

FIG. 3. Effects of preirradiation dose on (o) yield, (△) intrinsic viscosity, and (×) thermal stability of the copolymer. 1,3-Dioxolane, 1 wt %; polymerization 24 hr at 105° C; in vacuo.

In the trioxane–1,3-dioxolane system, it has been found that more than 90% of 1,3-dioxolane added is consumed in the early stage of copolymerization, since the reactivity of 1,3-dioxolane with active ends of polymer is much higher than that of trioxane [7]. In the tetraoxane-1,3-dioxolane system, on the contrary, it was found by gas chromatography of the residual monomers that the reactivity of 1,3-dioxolane with active end is rather low compared with that of tetraoxane. The relationship between the amount of the 1,3-dioxolane consumed and copolymerization time is shown in Fig. 4, where the ordinate indicates the percentage of the consumed 1,3-dioxolane. In vacuo, only 1/5 of 1,3-dioxolane is consumed within 24 hr, at which time the polymer yield reaches a saturation value. The polymer yield in air is very large compared with that in vacuo and no less than 3/4 of 1,3-dioxolane was consumed within 24 hr. In any case, the unreacted 1,3-dioxolane remains more or less in the range of polymerization time examined in this study. This finding is largely different from that found in the trioxane-1,3-dioxolane system.

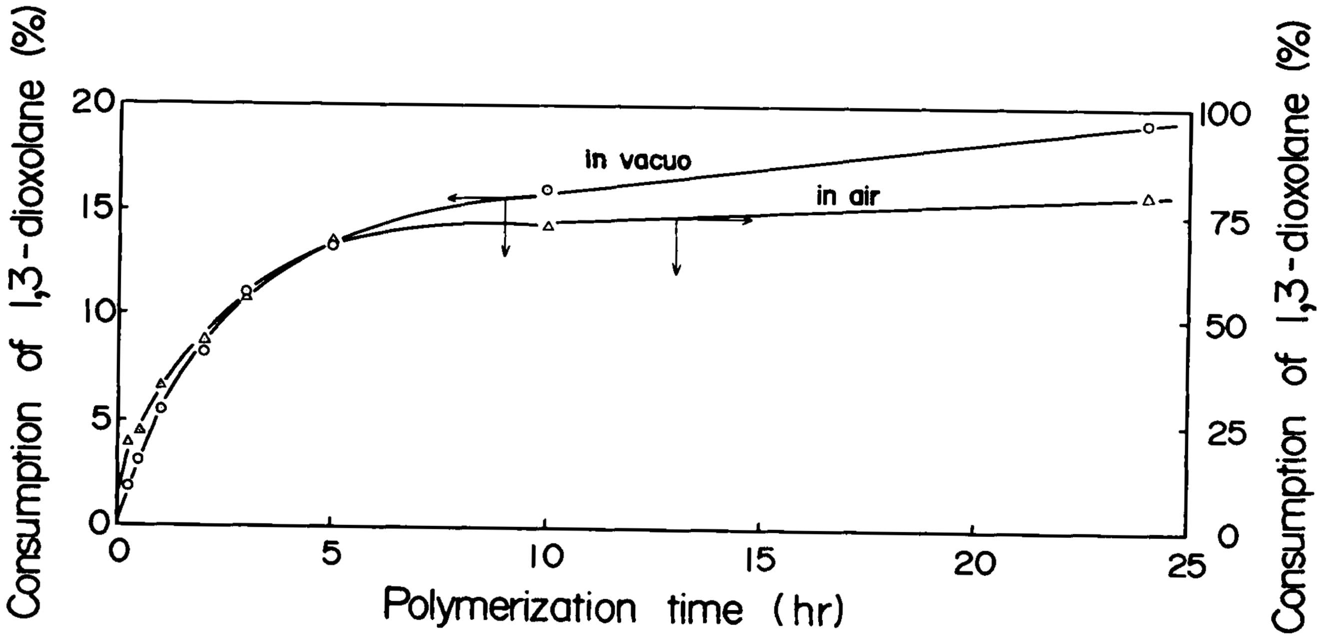

FIG. 4. Consumption of 1,3-dioxolane in the copolymerization as a function of polymerization time. 1,3-Dioxolane, 1 wt%; preirradiation, 1×10^6 rad; polymerization at 105° C.

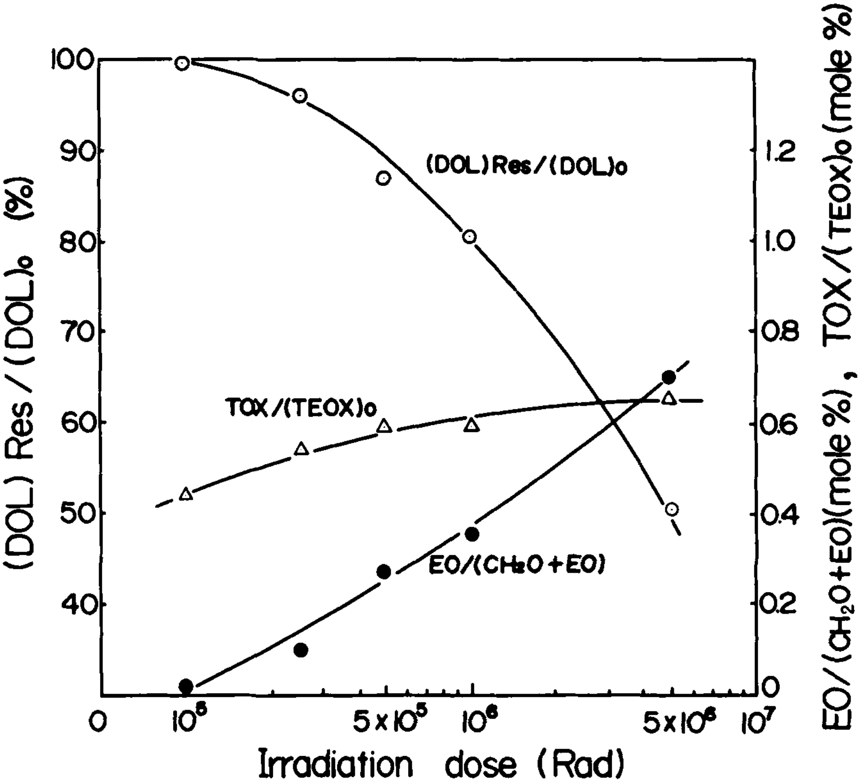

FIG. 5. Residual amount of (○) 1,3-dioxolane, (●) ethylene oxide unit content in the copolymer, and (△) trioxane formation as a function of preirradiation dose. 1,3-Dioxolane, 1 wt%; polymerization 24 hr at 105° C; in vacuo.

Figure 5 shows the effects of preirradiation dose on the residual 1,3-dioxolane, formation of trioxane, and the ethylene oxide unit content in the copolymer. The ethylene oxide unit content in the copolymer was calculated by subtracting the residual amount of 1,3-dioxolane from the added amount of it. At a small preirradiation dose, almost all of the added 1,3-dioxolane remains unreacted. However, the amount of consumed 1,3-dioxolane, i.e., the ethylene oxide unit content in the copolymer, increases with increasing dose. It is, therefore, reasonable that the thermal stability of the copolymer increases with increasing dose.

In the polymerization of trioxane or tetraoxane, it is well known that cyclic oligomers of formaldehyde are formed by the back-biting reaction of the propagating polymer chain [8]. In this system also, trioxane is formed and the amount of it is directly proportional to the polymer yield. As described later, from the comparison of the preirradiation dose dependence of the polymer yield (see Fig. 3) with that of trioxane formation (see Fig. 5), it is easily presumed that trioxane formation is closely related to the polymer yield.

The time dependences of the yield, R_{222}^{60}, and [η] of the copolymer at various preirradiation dose are shown in Figs. 6 and 7. In any preirradiation dose, the polymer yield, R_{222}^{60}, and [η] increase with increasing polymerization time and reach their saturation values. Although the behaviors of the polymer yield and [η] agree approximately with those found in the trioxane–1,3-dioxolane system [3], the polymerization time needed for the yield and [η] to reach their saturation values are found to be extremely short compared with those in the case of the trioxane–1,3-dioxolane system. The time dependence of R_{222}^{60} was found to be similar to that of polymer yield and to be different from that of R_{222}^{60} found for the trioxane–1,3-dioxolane system. In the copolymerization of trioxane with 1,3-dioxolane, it was found that the thermal stability of the copolymer is influenced by preirradiation dose, but scarcely by polymerization time. Since, as described above, the reactivity of 1,3-dioxolane with the propagating chain end is lower than that of tetraoxane in this system, the ethylene oxide unit content in the polymer formed at the early stage of the copolymerization should be low.

The fact that R_{222}^{60} of the copolymer increases with increasing polymerization time can be explained as follows. In the solid-state polymerization of trioxane and tetraoxane, as mentioned above, polymerization is largely influenced by the crystal structure of the monomer. It is known that the higher the crystallinity of monomer, the higher the polymerization rate, i.e., the polymerization rate found for the large crystal of monomer is quite high compared with that for small crystals [9]. It is reasonably considered that the apparent reactivity of the active end decreases gradually with increasing polymerization time, since monomer crystals which remain unreacted are disarranged by polymer formed in the course of polymerization. On the other hand, as the mobility of 1,3-dioxolane in the trioxane or tetraoxane crystal seems to be larger than that of trioxane or tetraoxane, the mobility of 1,3-dioxolane is not expected to be appreciably influenced by the copolymer formed. The reactivity of 1,3-dioxolane with the active end is accordingly constant irrespective of polymerization time. Therefore, the relative ethylene oxide unit content in the copolymer chain increases, and accordingly, the average ethylene oxide unit content increases with increasing polymerization time. The thermal

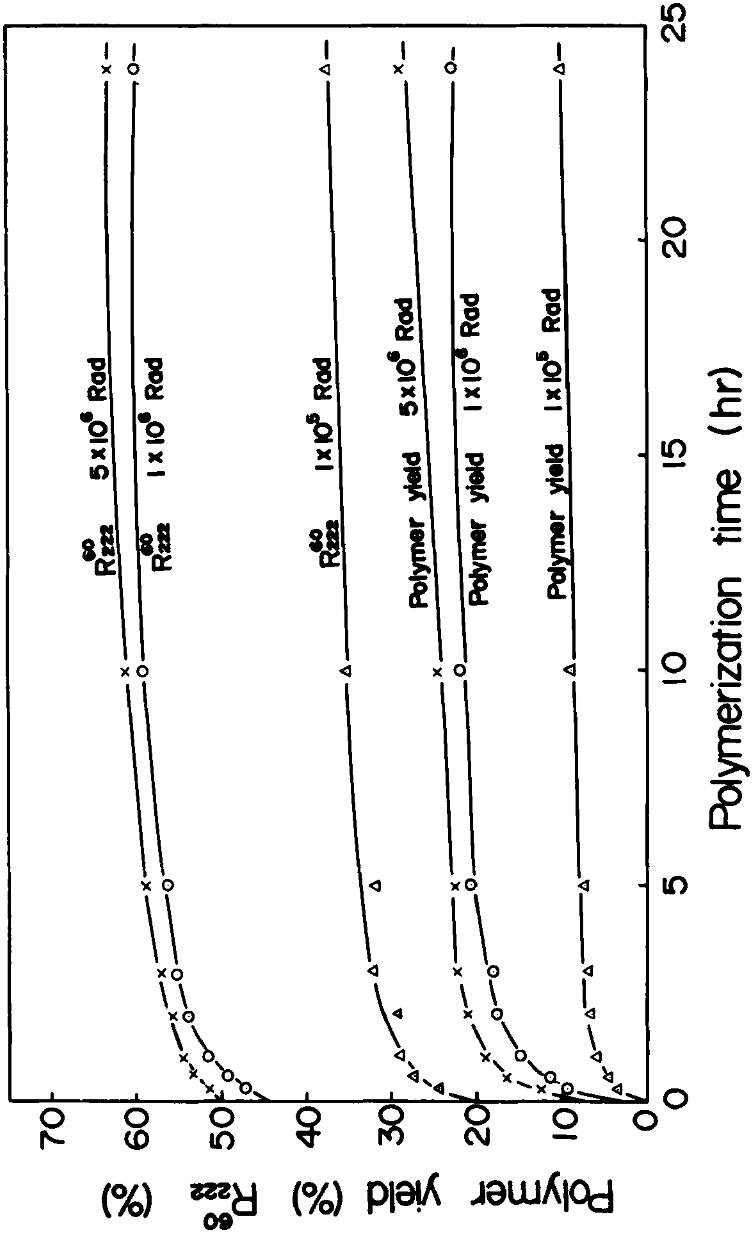

FIG. 6. Effects of preirradiation dose on the yield–time and R_{222}^{60}–time curves: (×) 5×10^6 rad; (○) 1×10^6 rad; (△) 1×10^5 rad. 1,3-Dioxolane, 1 wt%; polymerization at 105°C; in vacuo.

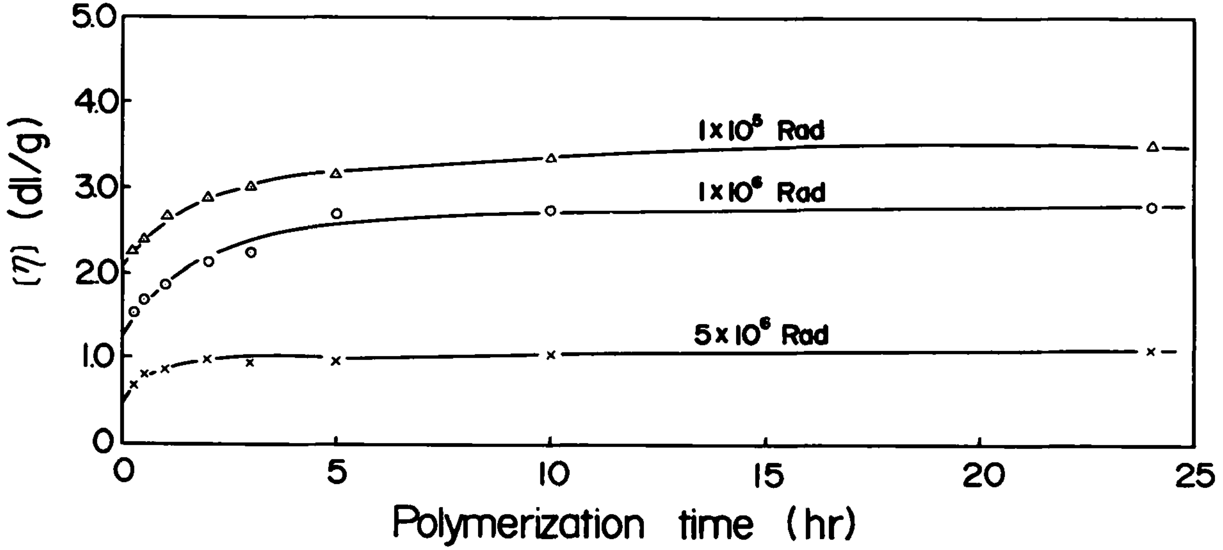

FIG. 7. Effect of preirradiation dose on the [η]–time curve: (△) 1×10^5 rad; (○) 1×10^6 rad; (×) 5×10^6 rad. 1,3-Dioxolane, 1 wt%; polymerization at 105° C; in vacuo.

stability of the copolymer, consequently, rises with polymerization time. The relationship between time and R_{222}^{60} shown in Fig. 6 can be reasonably understood on this basis.

The effect of polymerization temperature on the yield, $[\eta]$, and R_{222}^{60} of the copolymer in this copolymerization is shown in Figs. 8 and 9. The temperature dependence of the polymer yield-time curve is similar to that found in the radiation-induced, solid-state polymerization of trioxane [10]. The initial rate of polymerization and the saturation yield increase with increasing polymerization temperature. At 110°C, i.e., just below the melting point (112°C) of tetraoxane, a higher rate of polymerization was observed and the polymer yield was found rapidly to attain its saturation value, which is lower than any other one. These facts agree with the values found for trioxane polymerization ranging in temperature from 55 to 58°C. The thermal stability of the copolymer increases with increasing polymerization temperature in the range of 95-105°C. The thermal stability of the copolymer obtained at 110°C is, however, lower than that of the copolymer obtained at 105°C. In particular, the relationship between R_{222}^{60} of the copolymer obtained at 110°C and polymerization time indicates that R_{222}^{60} reaches its saturation value more rapidly than at any other polymerization temperature. The relationship between $[\eta]$ and polymerization time was also found to be very similar to those obtained in polymer yield and R_{222}^{60}.

An Arrhenius plot of the initial polymerization rate obtained from the polymer yield–time curves (shown in Fig. 8) is shown in Fig. 10. In this system an overall activation energy of ca. 20 kcal/mole was obtained. Munoz-Escalona et al. [11] studied the radiation-induced, solid-state homopolymerization of tetraoxane and obtained ca. 24 kcal/mole as the overall activation energy. The activation energy found in this system is very close to that value.

The effects of atmosphere and 1,3-dioxolane concentration on the polymer yield–time curves are shown in Fig. 11. The results obtained in vacuo can be easily anticipated from Fig. 1 which shows the relationship between polymer yield and 1,3-dioxolane concentration. The initial rate of polymerization decreases in the presence of 1,3-dioxolane. The shape of the polymer yield–time curve scarcely changes in the presence or absence of 1,3-dioxolane.

The initial rate of polymerization in air also was found to decrease with increasing 1,3-dioxolane concentration. It was found, however, that both the absolute value of the polymer yield and the shape of the polymer yield–time curve vary in a complex manner, depending on 1,3-dioxolane concentration. In air, the polymer yield–time curve in the early stage of polymerization (in 1 hr) is very similar to that

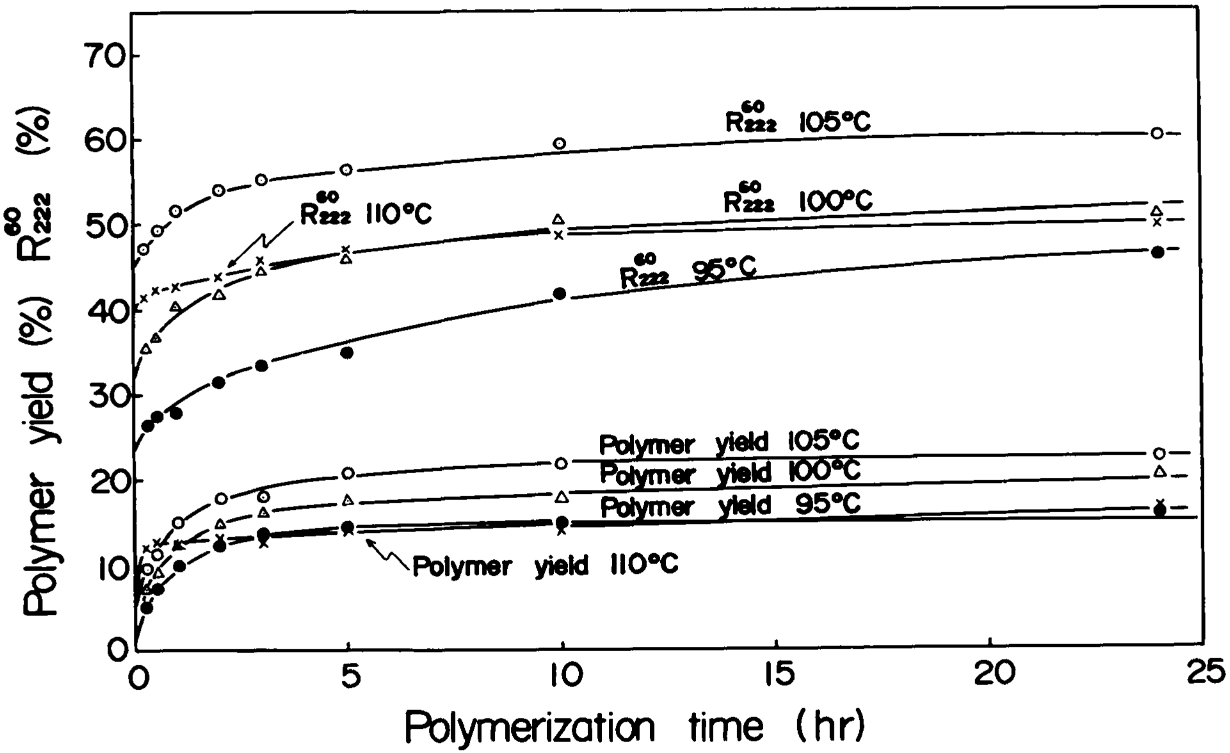

FIG. 8. Effects of polymerization temperature on the yield–time and R_{222}^{60}–time curves: (●) 95° C; (△) 100° C; (○) 105° C; (×) 110° C. 1,3-Dioxolane, 1 wt%; preirradiation, 1×10^6 rad at -78° C; in vacuo.

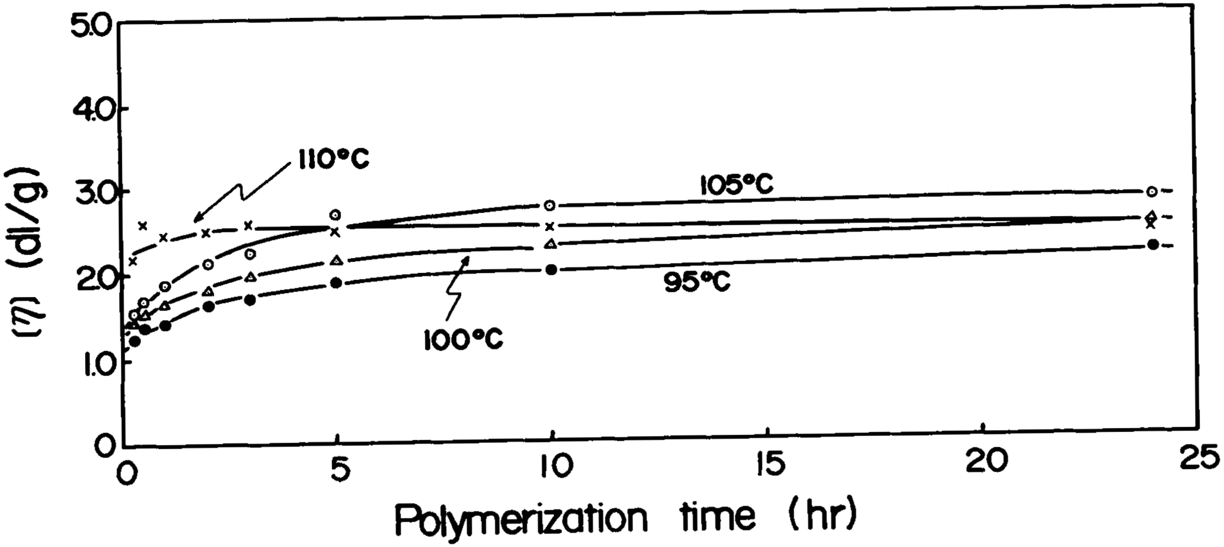

FIG. 9. Effect of polymerization temperature on the [η]–time curve: (●) 95° C; (△) 100° C; (○) 105° C; (×) 110° C. 1,3-Dioxolane, 1 wt%; preirradiation, 1×10^6 rad at -78° C, in vacuo.

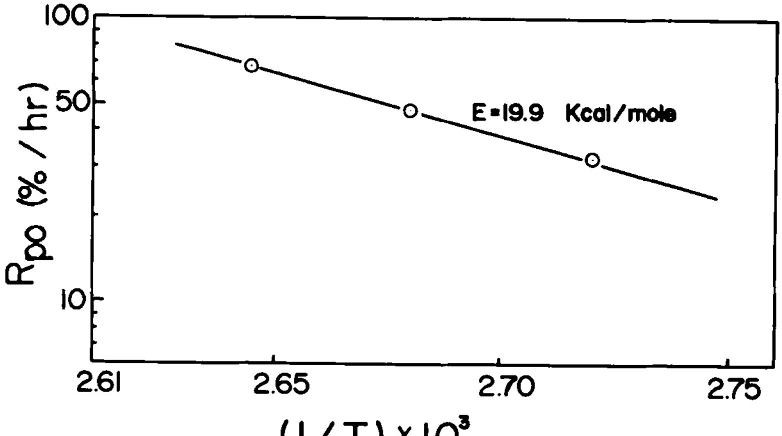

FIG. 10. Arrhenius plots of initial rate of copolymerization; 1,3-dioxolane, 1 wt%; preirradiation, 1 × 10^6 rad at -78° C; in vacuo.

in vacuo. However, the rate of polymerization in air was observed to be accelerated rapidly when the polymerization proceeded further. In order to clarify in detail this respect, the polymerization time dependences of [η], R_{222}^{60}, ethylene oxide unit content, and trioxane formation were determined as shown in Figs. 12 (in vacuo) and 13 (in air). Comparison of the results in vacuo with those in air shows a characteristic difference between them. In vacuo, the yield, [η], and R_{222}^{60} of the copolymer increase with increasing polymerization time. In air, on the contrary, [η] decreases monotonously with increasing polymerization time and R_{222}^{60} initially increases to reach a maximum value and then decreases as the polymerization further proceeds. The polymerization time at which R_{222}^{60} of the copolymer reaches a maximum value was found to occur approximately the same time as an acceleration on the polymer yield–time curve.

In vacuo, as mentioned above, [η] increases with increasing polymer yield, while [η] of the copolymer obtained in air decreases in spite of the steep increase in the polymer yield. These facts suggested that, in the presence of air, some radiolysis products initiate the polymerization of tetraoxane when the irradiated polymeric mixture is heated to the polymerization temperature. The polymerization of tetraoxane can take place with various kinds of initiators and the polymerization behavior seems to vary with method

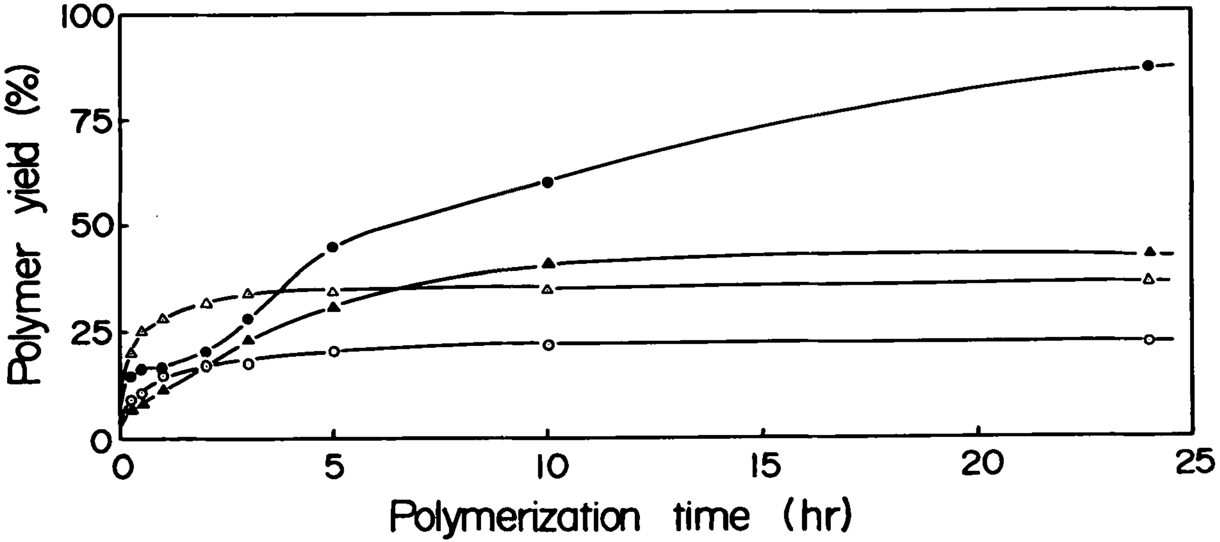

FIG. 11. Effects of 1,3-dioxolane and atmosphere on the yield–time curves: (△) no dioxolane, in vacuo; (○) 1 wt% dioxolane, in vacuo; (●) 1 wt% dioxolane, in air; (▲) 3 wt% dioxolane, in air. Preirradiation, 1 × 10^6 rad at -78° C; polymerization at 105° C.

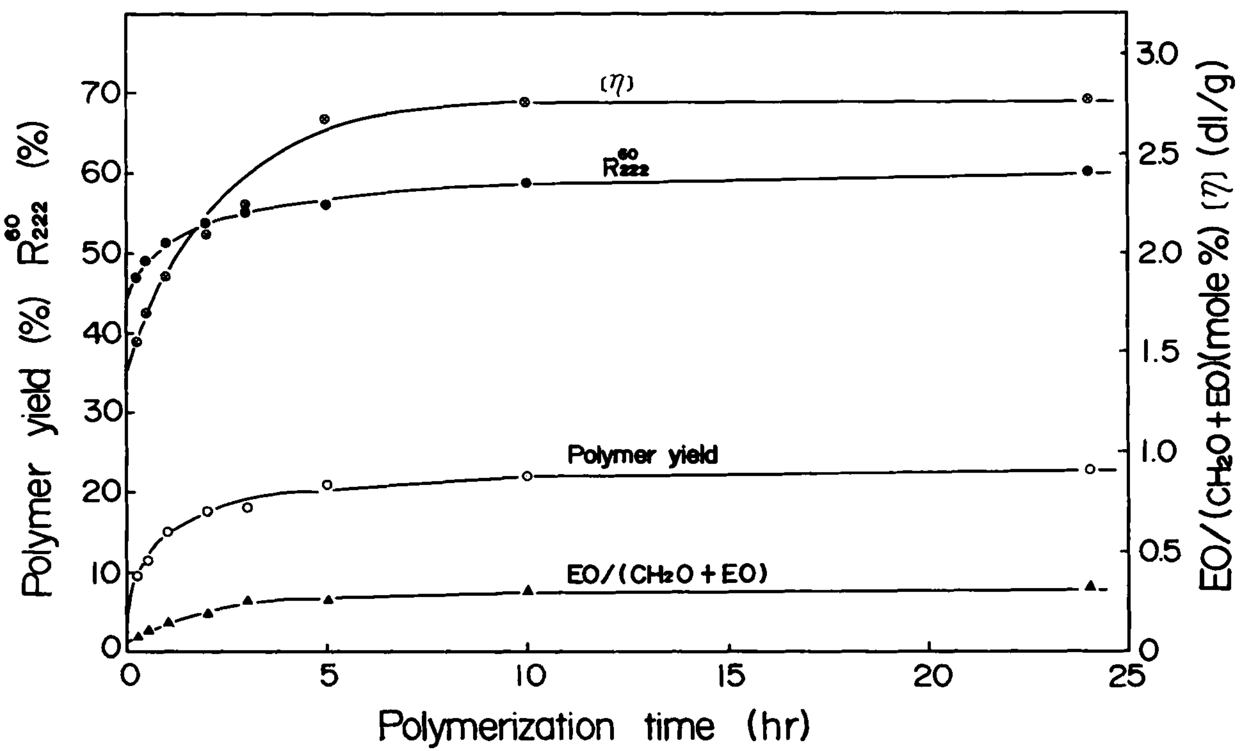

FIG. 12. Plots of (○) yield, (⊗) [η], (●) R_{222}^{60}, and (▲) ethylene oxide unit content of the copolymer as a function of polymerization time; 1,3-dioxolane, 1 wt%; preirradiation, 1×10^6 rad at -78° C; polymerization at 105° C; in vacuo.

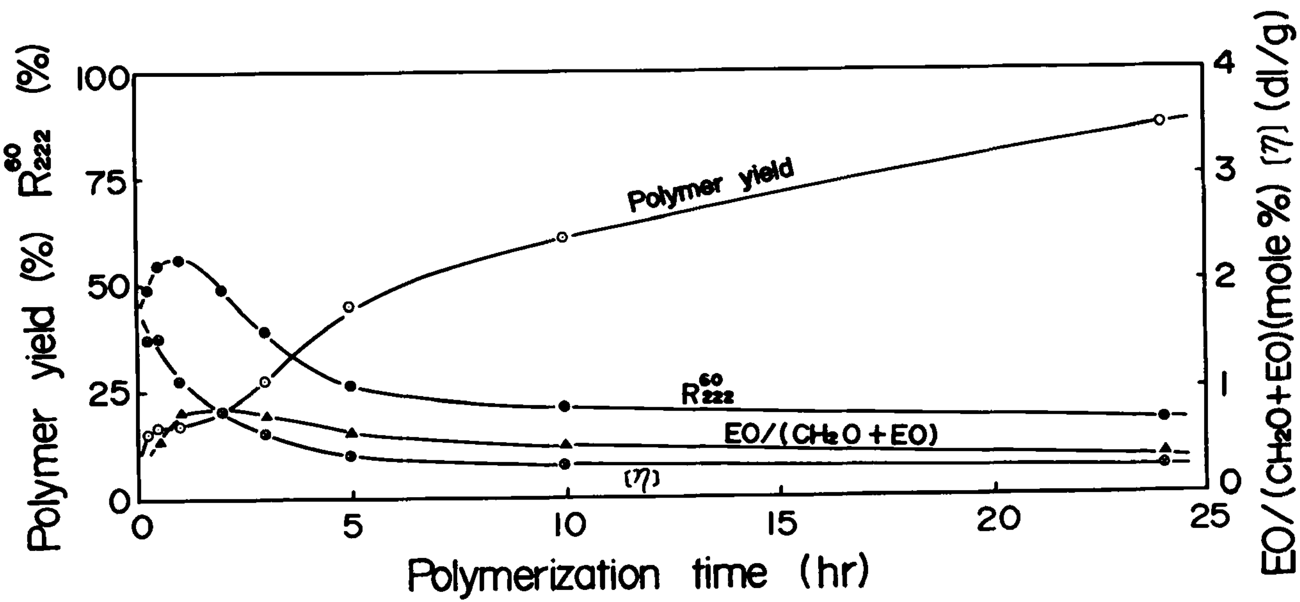

FIG. 13. Plots of (○) yield, (⊛) [η], (●) R^{60}_{222}, and (▲) ethylene oxide unit content of the copolymer as a function of polymerization time; 1,3-dioxolane, 1 wt%; preirradiation, 1 × 10^6 rad at -78° C; polymerization at 105° C; in air.

of initiation. In the radiation-induced, solid-state polymerization of tetraoxane, the rate of polymerization is very low at a temperature below 80° C, and even at a temperature higher than 100° C, the saturation value of the polymer yield is also low. It has been reported, however, that in the solid-state polymerization of tetraoxane initiated by BF_3OEt_2 [12], a typical cationic initiator, the polymerization rate is, even in the range of 60-80° C, higher than that of the radiation-induced polymerization at temperatures ranging from 95 to 105° C.

The polymerization of tetraoxane has been also known to be initiated by radical initiators, such as benzoyl peroxide and α,α'-azobisisobutyronitrile, although this polymerization is considered to proceed by cationic mechanism [13]. A copolymer with an excellent thermal stability is obtained by the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane [14]. 1,3-Dioxolane used in this copolymerization must be distilled in a stream of nitrogen and be stored under nitrogen in the dark [15]. It is known that the thermal stability of the copolymer obtained by using 1,3-dioxolane which is in contact with air during distillation or in storage, is quite low, although the polymerization rate is not appreciably influenced. From these facts and the results of Figs. 12 and 13, therefore, it is strongly suggested that the steep acceleration of the polymerization rate in air is attributed to the polymerization reaction owing to active species formed from 1,3-dioxolane by means of air and γ-rays.

The relationship between polymer yield and trioxane formation determined by gas chromatography is shown in Fig. 14. It can be seen that in the copolymerizations, both in vacuo and in air, the relationship between the amount of trioxane and the copolymer yield gives straight lines. In air, as already discussed above, the polymerization is not only induced by irradiation but also caused by the reaction between 1,3-dioxolane and air. Moreover, the latter reaction is considered to participate throughout except at the early stage of this copolymerization. Therefore, some differences in reaction mechanism between the solid-state copolymerization in air and that in vacuo are suggested. It is supposed that, in vacuo, the radiation-induced polymerization proceeds mainly by free-ion mechanism; even in air, at the early stage of the copolymerization, it proceeds by the same mechanism as in vacuo (see Fig. 11). However, after the early stage, where the copolymerization rate begins to be accelerated, the copolymerization initiated by active species attributable to a radiolysis product from 1,3-dioxolane formed in the presence of air proceeds. Further, provided that polymerization in air proceeds by a gegenion mechanism, the effect of atmosphere on the rate of formation of trioxane can be reasonably understood as follows. The

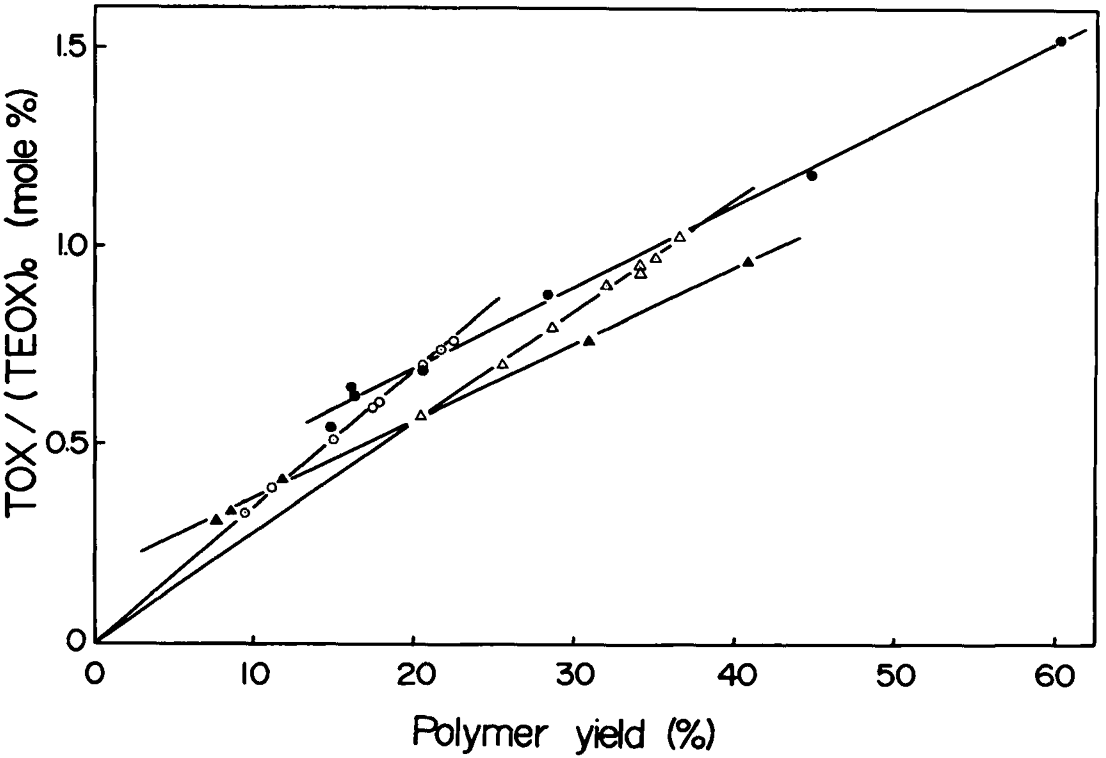

FIG. 14. Relationships between trioxane formation and polymer yield: (△) no dioxolane, in vacuo; (○) 1 wt% dioxolane, in air; (●) 1 wt% dioxolane, in air. (▲) 3 wt% dioxolane, in air. Preirradiation, 1 × 10^6 rad; polymerization at 105°C.

slope of the straight line shown in Fig. 14, which represents the ratio of the back-biting reaction rate to the propagation rate, indicates that the back-biting reaction occurs more easily in vacuo than in air. In the solid state, the back-biting reaction as well as the propagation reaction should be influenced by the mobility of the active end. The mobility of the active end which is a free ion must be larger than that of the active end which is a gegenion. Consequently, the formation rate of trioxane in vacuo is higher than that in air.

As will be reported in the near future [16], however, a study of the radiation-induced, solid-state homopolymerization of tetraoxane in the presence of the small amount of solvent which can not be copolymerized with tetraoxane showed that the effect of the solvent on trioxane formation is different from that in the case of the tetraoxane–1,3-dioxolane system, e.g., trioxane formation scarcely increases with increasing amount of solvents, such as cyclohexane, benzene, and 1,4-dioxane. Therefore, it is suggested that 1,3-dioxolane not only increases the mobility of the active end by distorting the monomer crystal, but also that 1,3-dioxolane acts as a comonomer to give a more mobile active end containing an ethylene oxide unit.

In vacuo, the difference in the trioxane formation between tetraoxane homopolymerization and copolymerization with 1,3-dioxolane is similar to that found for tetraoxane formation in the case of trioxane polymerization [7]. That is, the difference in trioxane formation can be explained by the mobility of the active end. However, investigation of further details, especially on the copolymerization in air and the polymerization of tetraoxane initiated by radical initiators, is required and is in progress.

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Accepted by editor March 1, 1976
Received for publication May 5, 1976