

Examination of Variables in the Radiation-Induced Solid-State Polymerization of Trioxane

NELSON S. MARANS and FORREST A. WESSELLS, *Washington
Research Center, W. R. Grace and Co., Clarksville, Maryland*

Synopsis

Additional studies have been conducted on the radiation-induced, solid-state polymerization of trioxane. The out-of-source polymerization rate has been investigated as a function of radiation dose and of temperature and time of polymerization. The empirical relationship of $\log \text{time} \propto Y$ (where Y is the polymerization percentage) was found to be satisfactory over wide ranges of conversion, of dose, and of polymerization time. At a given dose, the yield was directly proportional to the $\text{RSV}^{1.33}$ (where RSV is the reduced specific viscosity). Either increasing the dose or decreasing the particle size gave lower RSV values at the same conversions.

INTRODUCTION

A number of papers and patents have appeared within the last few years on the solid-state, radiation-induced polymerization of trioxane.¹⁻¹⁴ However, none of these papers has given detailed relationships between the percentage conversion, particle size, and temperature or conditions of polymerization and the molecular weight. The effect of these variables on the molecular weight is of interest in understanding the mechanism of polymerization.

EXPERIMENTAL

Starting Materials

Trioxane was obtained from Celanese Corporation of America and was purified by fractionation from calcium hydride in the presence of a nitrogen stream. The material distilling at 114-115°C. was collected directly into 10-mm. O.D., 8-mm. I.D. glass tubes. The tube contents were melted and then allowed to resolidify. Finally the tube was sealed at pressures below 0.5 mm. of mercury. In a number of cases, the trioxane was used in flake form as received from Celanese. The trioxane purity, particle size, and tube loading were found to be important variables in the polymerization, and these were controlled as carefully as possible.

γ -Butyrolactone was obtained from Eastman Kodak and was used without distillation.

Radiation Technique

All samples were irradiated with 2-M.e.v. electrons from a 2-M.e.v. Van de Graaff electron accelerator. Dosimetry was accomplished by a modification of the method of Dragonic¹⁵ using oxalic acid. Confirmation of the dose values was obtained by using the blue cellophane method of Henley.¹⁶ With our accelerator, a dose of approximately 1.0 Mrad was obtained in a single pass at a pass rate of 18.4 in./min., a scan width of 12 in., and a beam current of 155 μ amp. for the tube samples and of 195 μ amp. for the monomer directly under the beam. However with electrons, nonuniform energy absorption is found as a function of depth of penetration. For this reason, thicknesses of monomer samples were kept as constant as possible in each series of comparison runs. Dose variations were made possible by changing the beam current.

For irradiation at ambient temperature, the glass tube or the monomer was placed directly on a styrofoam board inserted into an aluminum tray, 20 in. long by 12 in. wide. The tray was then passed back and forth under the beam until the requisite dose was achieved. For irradiation at elevated temperatures, a special aluminum plate was constructed which contained channels into which glass tubes could be fitted. The temperature of the plate was controlled by an aluminum base plate containing coils for circulating water from a constant temperature bath. The temperature of the aluminum plate could be controlled within 1°C.

Polymerization and Isolation Techniques

The sample after irradiation was usually placed immediately into a constant temperature bath maintained at $\pm 0.1^\circ\text{C}$. of the specified temperature. Temperature measurements in larger samples indicated that the monomer temperature during the polymerization might exceed the temperature of the bath by as much as 3°C . However for the smaller samples, in 8-mm. I.D. glass tubes, the difference between bath temperature and sample temperature was probably much less.

After the desired time of aging, the tubes were cooled in air, then broken open and the contents added to tared glass vials. The weighed samples were treated with water for 16 hr. and the residual polymer filtered into tared, glass-sintered crucibles. This polymer was washed with acetone and air-dried for 2 days to give constant weight.

Reduced Specific Viscosity (RSV)

The radiation-produced polyoxymethylene was ground in a Wiley mill to pass through a 20 mesh screen. An accurately weighed sample, about 0.05 g., was added to sufficient stabilized γ -butyrolactone to give a final concentration of 0.1000 g. of polymer in 150.9 g. of solvent; the viscosity solvent contained 1% weight of diphenylamine and 0.5% by weight of dilaurylthiodipropionate. Solution was accomplished with a Mag-mix stirrer within 15 min. at the minimum temperature possible. For solution, the

required temperature varied from 155 to 170°C. When solution was complete, the sample was added immediately to a Stabin viscometer in a constant temperature bath at $135.0 \pm 0.1^\circ\text{C}$. The solution was sufficiently stabilized so that replicable flow times could be obtained over a period of 15 min. In addition, duplicate samples gave average viscosity differences of only 0.01 at 1.0 dl./g. and of 0.05 at 2.0 dl./g.

EXPERIMENTAL RESULTS

Effect of Polymerization Temperature

Distilled samples of trioxane in tubes were irradiated at 25°C . to a dose of 0.3 Mrad in one pass. These samples were then polymerized after irradiation for a series of times at temperatures of 25–55°C. The results at 35, 45, 50, and 55°C. are presented in Figures 1 and 2: the empirically found relationship that $\log t \propto Y$ being used.¹⁷ No polymerization was obtained by this technique when samples were stored at 25°C . after irradiation at

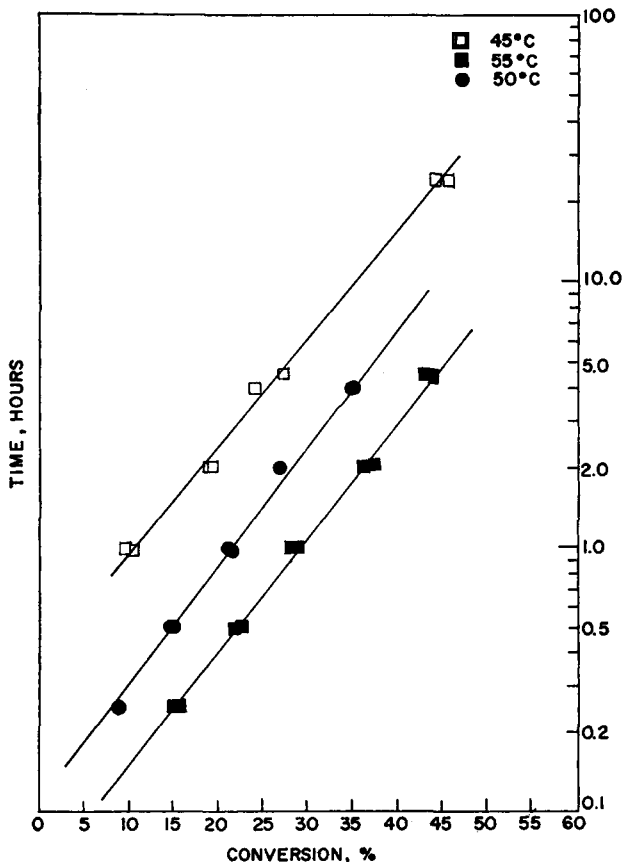


Fig. 1. Percentage polymerization as a function of polymerization time: (□) 45°C.; (●) 50°C.; (■) 55°C.

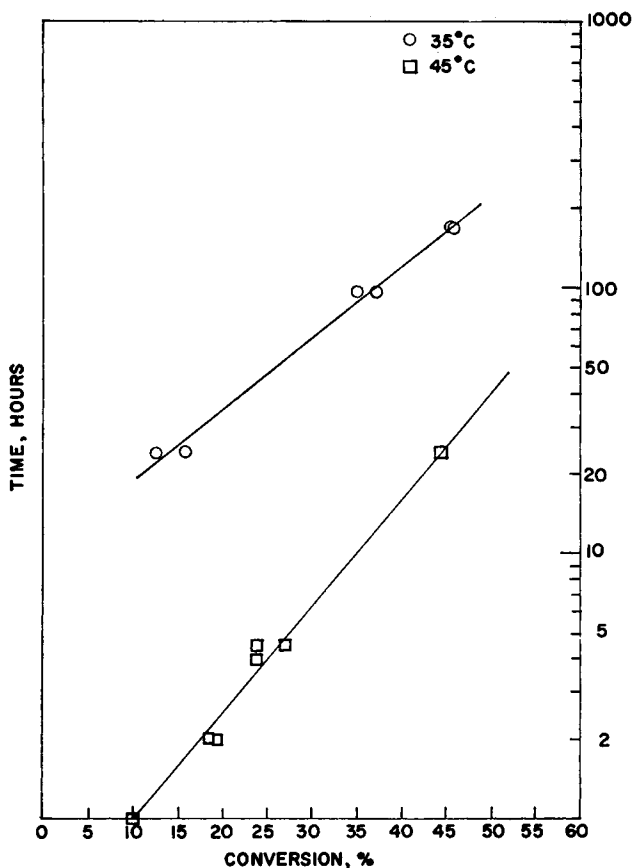


Fig. 2. Percentage polymerization as a function of polymerization time: (○) 35°C. (□) 45°C.

25°C. For the same samples, the curve relating RSV and percentage conversion is given in Figure 3.

Effect of Dose

The effect of dose was studied in two series of experiments. In one series, samples were irradiated at 0.3 and 0.8 Mrad and then polymerized afterwards at 55°C. for varying periods of time. The percentage polymerization as a function of log of time of polymerization is shown in Figure 4. The percentage polymerization as a function of RSV for the same samples is shown in Figure 5.

In the second series, the percentage polymerization and RSV were determined for a range of doses but for only one polymerization period. The data are shown in Figure 6 for the relationship between percentage conversion and dose over the dose range of 0.05–0.5 Mrad for a 4-hr. aging period. In Figure 7, the log of dose is plotted against conversion/RSV^{1.33} for the

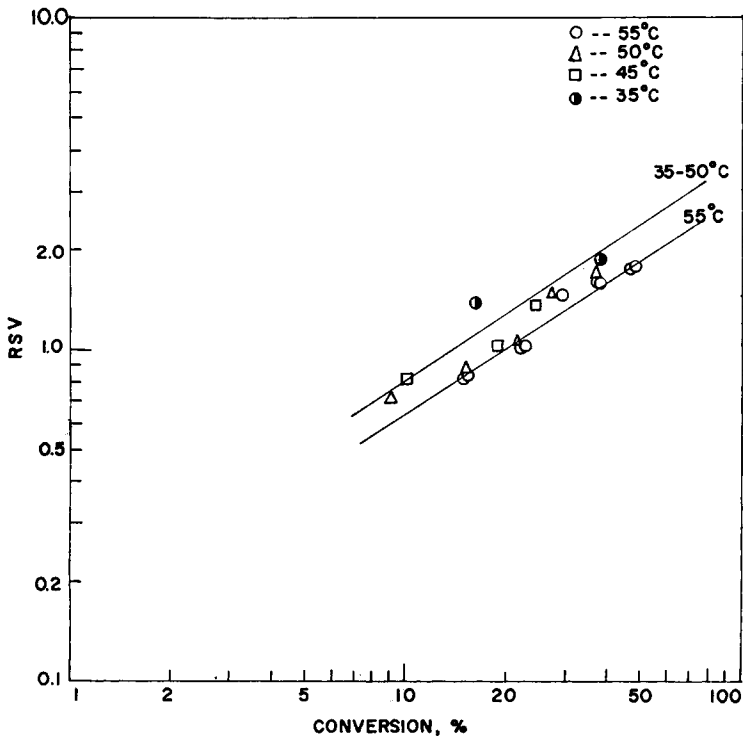


Fig. 3. RSV as a function of percentage conversion: (○) 55°C.; (△) 50°C.; (□) 45°C. (●) 35°C.

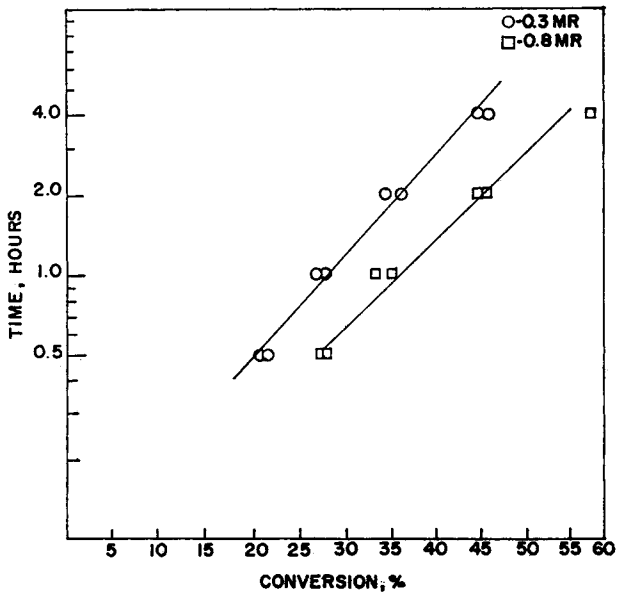


fig. 4. Conversion as a function of dose: (○) 0.3 Mrad; (□) 0.8 Mrad.

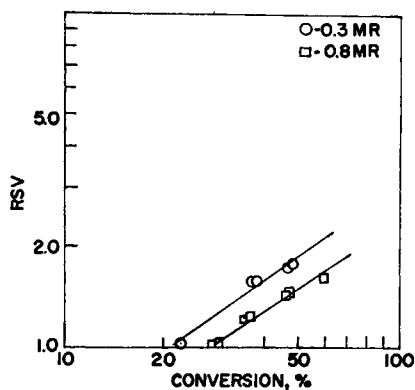


Fig. 5. RSV as a function of conversion: (○) 0.3 Mrad; (◻) 0.8 Mrad.

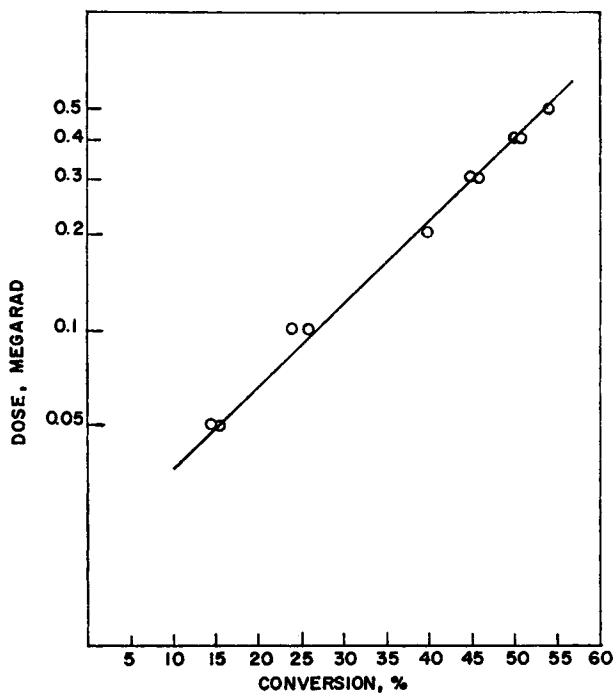


Fig. 6. Percentage conversion as a function of dose (4 hr. at 55°C.).

same samples as well as for samples irradiated at higher doses but polymerized for only 0.5 hr. at 55°C.

Effect of Purity

The polymerization of granular trioxane (as received from Celanese) was compared after melting and resolidification to that of the same trioxane after purification by distillation and then melting and resolidification. The

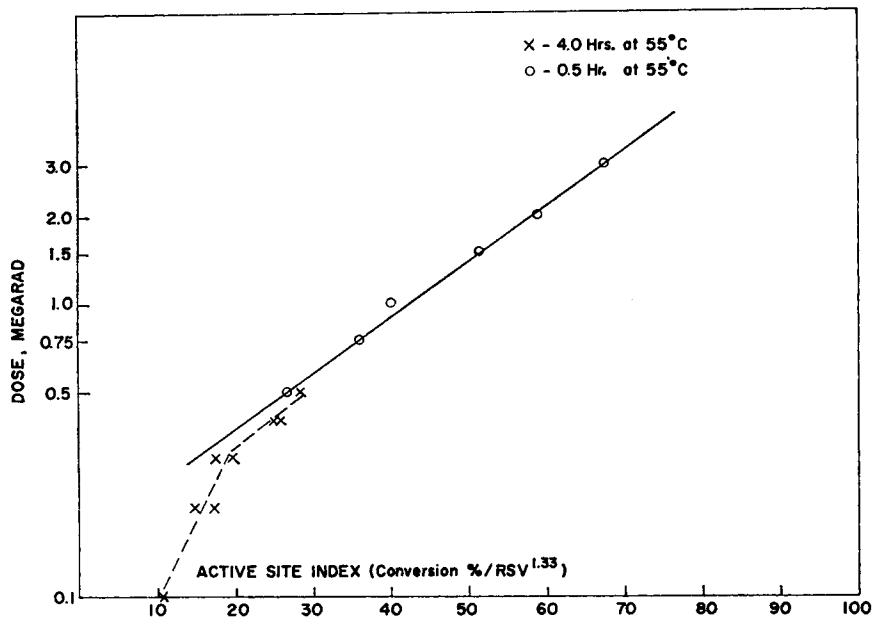


Fig. 7. Dose as a function of active site index: (X) active site index derived from irradiation at 25°C. and aging for 4 hr. at 55°C.; (O) active site index derived from irradiation at 25°C. and aging for 0.5 hr. at 55°C.

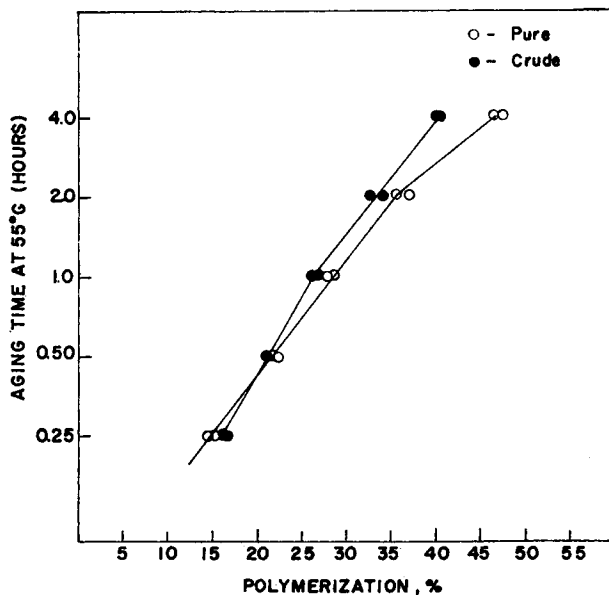


Fig. 8. Effect of purity on polymerization: (O) pure; (●) crude.

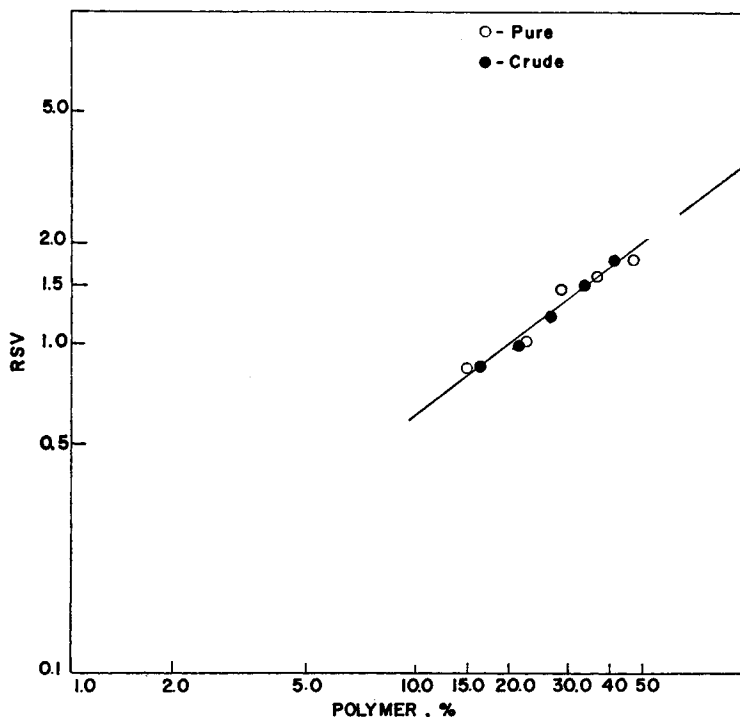


Fig. 9. Effect of purity of trioxane on RSV as a function of conversion percentage: (○) pure; (●) crude.

samples in sealed tubes were irradiated to 0.3 Mrad and then polymerized at 55°C. for varying periods of time. The values for percentage polymerization and RSV as a function of time are given in Figure 8. In Figure 9, the RSV values as a function of percentage polymerization are shown. Despite differences in purification, the above samples gave almost equivalent values for percentage polymerization and RSV. However, for other samples where the measured water content of the trioxane ranged from more than 100 to 400 ppm, the percentage conversion and RSV were 50–100% of the values for purified trioxane. When the water content exceeded 400 ppm, conversions ranged from 0 to 50% of those obtained for the purified trioxane.

Effect of Air

A limited number of experiments were conducted with the irradiation in air and the polymerization afterwards in vacuum. Both the percentage conversion values and the RSV determinations indicated that the effect of air was negligible for the radiation dose and the times of polymerization used. The values are collected in Table I. The atmospheric conditions are both for the irradiation and for the polymerization afterwards at elevated temperatures.

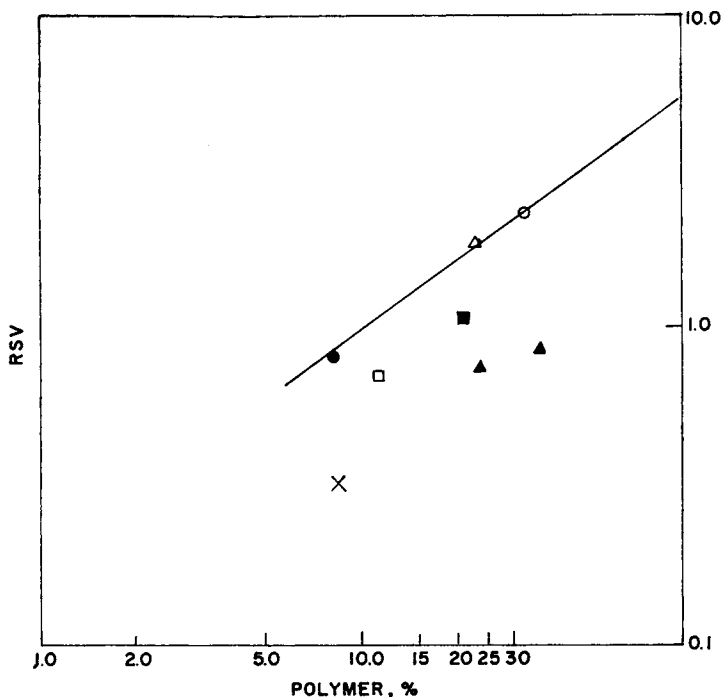


Fig. 10. Effect of comonomer of RSV and percentage polymerization of trioxane; (○) no comonomer; (□) β -propiolactone; (Δ) hexamethylcyclotrisiloxane; (●) epichlorohydrin; (■) 3,3-bis(chloromethyl)oxetane; (\blacktriangle) styrene oxide; (×) *n*-heptaldehyde.

TABLE I
Effect of Air on Percentage Polymerization (Dose 0.1 Mrad)

Atmosphere	Irradiation temp., °C.	Aging temp., °C.	Aging time, hr.	Polymerization, %	Polymer sample for RSV, %	RSV
Vacuum	25	55	6	31.6 \pm 0.2	31.4	2.34
Air	25	55	6	31.0 \pm 0.9	30.1	2.10
Vacuum	55	—	—	4.02 \pm 0.07	4.09	0.49
Air	55	—	—	4.01 \pm 0.14	4.15	0.49

Effect of Comonomer Composition

A number of potential comonomers were added in the melt to trioxane and then the samples allowed to resolidify. No effort was made to determine changes in the crystal structure of trioxane as a function of the addition of a second monomer. For most of the monomers used, there was a reduction in percentage polymerization and RSV. However, a few comonomers did give anomalous results. The results are collected in Table II and are also shown in Figure 10. Figure 10 indicates that certain monomers

probably gave termination of polymerization, other monomers gave both chain termination and chain transfer, and finally one monomer gave chain transfer without premature termination.

Effect of Particle Size

Other investigators² have reported the effect of particle size on percentage conversion to be decreasing conversion with decreasing particle size. We were unable to show such a relationship except with very fine particle size monomer. However, our experiments have indicated that the particle size of the polymer under certain specific conditions is related to the RSV of the polymer.

TABLE II
Effect of Comonomers on Solid-State Polymerization^a

Monomer	Additive, %	Polymerization, %	RSV
—	0	29.5 32.5	2.35
3,3-Bis(chloromethyl)oxetane	4.15 4.24	21.0 20.5	1.07 —
β -Propiolactone	4.70 4.61	11.6 11.9	0.71 —
Hexamethylcyclotrisiloxane	4.41 4.39	22.9 26.1	1.87
3-Chloro-1,2-epoxypropane (epichlorohydrin)	4.39 4.74	8.2 6.3	0.82
1,2-Epoxyethylbenzene (styrene oxide)	4.73 4.87	24.0 36.2	0.76 0.85
1,2-Epoxy-3-phenoxypropane	4.59 4.72	43.1 37.9	0.32 ^b
<i>n</i> -Heptaldehyde	4.91 4.60	8.5 6.7	0.33

^a Irradiation at 25°C. to 0.1 Mrad and aging for 6 hr. at 55°C.

^b Insolubles present in this sample.

For our study, the granular trioxane was used as received, the monomer irradiated in air to a dose of 0.3 Mrad and then placed into 250-cc. screw-cap bottles at various loadings of monomer. The samples were then polymerized in a constant temperature bath at 55°C. for 5 hr. The percentage polymerization was determined and the final product sieved through standard sieves to give the distributions and RSVs shown in Table III. The polymer yield was shown to decrease with increased loading while the RSV increased. Analysis of the RSV showed that the molecular weight decreased with decreasing of polymer particle size. When melted and then resolidified monomer was polymerized, the same increase in RSV with increasing particle size was noted, as shown in Table IV.

TABLE III
Relationship of Polymer Particle Size to RSV^a

Wt. of monomer, g.	Yield, %	Particle size range, μ	Fraction of total	RSV
160	35.6	2000+	Trace	
		840+	0.120	1.48
		500+	0.435	1.28
		420+	0.122	1.16
		250+	0.242	1.10
		250-	0.058	0.99
Summation of products of RSV and fraction of total 1.18				
80	39.1	2000+	Trace	
		840+	0.182	1.20
		500+	0.348	1.01
		350+	0.205	0.84
		250+	0.155	0.78
		250-	0.110	0.68
Summation of products of RSV and fraction of total 0.94				
40	44.5	2000+	Trace	
		840+	0.163	1.14
		500+	0.334	0.89
		350+	0.214	0.78
		250+	0.163	0.71
		250-	0.126	0.62
Summation of products of RSV and fraction of total 0.84				

^a Radiation dose, 0.3 Mrad; aging 4 hr. at 55°C.

TABLE IV
Variation of RSV with Polymer Size^a

Particle size, μ	Fraction of Total	RSV
4000+	0.500	1.64
2000+	0.340	1.37
840+	0.117	0.92
500+	0.030	0.80
350+	0.005	0.64
250+	0.004	0.64
250-	0.005	0.61
Summation of products of RSV and fraction of total 1.43		

^a Radiation dose, 0.3 Mrad; aging 4 hr. at 55°C.

Effect of Radiation on the RSV of Radiation-Polymerized Polyoxymethylene

Radiation-prepared polyoxymethylene primarily gives scission on electron irradiation. The shape of the curve of RSV related to radiation dose should be a function both of the molecular weight distribution and of the labile or "weak" bonds in the final polyoxymethylene. Thus a study of

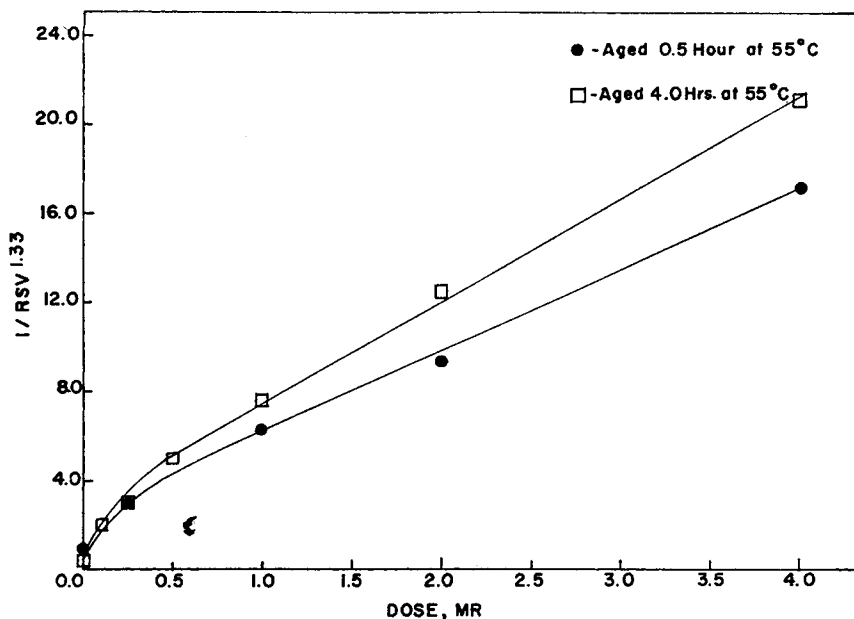


Fig. 11. Radiation scission of polyoxymethylene (melted and resolidified): (□) aged 4.0 hr. at 55°C.; (●) aged 0.5 hr. at 55°C.

the change in RSV as a function of radiation dose might give clues both to molecular weight distribution changes as a function of polymerization conditions and also to the presence of weak bonds in the radiation-induced, solid-state, polymerized polyoxymethylene. The results are shown in Figure 11. Based on the previous data, we have chosen to use the value of $1/\text{RSV}^{1.33}$ as being proportional to $1/\bar{M}_w^{18}$. The data are then presented in the standard fashion for polymer scissioning, namely $1/\text{RSV}^{1.33}$ plotted against radiation dose. The curves obtained indicated a relatively broad molecular weight distribution or weak bonds in these two samples of radiation-prepared polyoxymethylene.

In addition to the normal size crystals prepared above, large crystals of trioxane averaging 2–6 in. in length were irradiated at 25°C. and then aged for varying periods of time at 55°C. The percentage of conversion as a function of polymerization time is compared in Figure 12 to that for melted and resolidified trioxane. As can be seen, the substantial difference in crystal size had relatively little effect on the conversion. The relationship between polymer scission and radiation dose for the large crystal polymer is shown in Figures 13 and 14. Again, either a broad molecular weight distribution or weak bonds in the polyoxymethylene is indicated.

Effect of Compacting on RSV

Since we had indicated previously that the particle size of the polymer did not substantially influence the degree of conversion of trioxane to polyoxy-

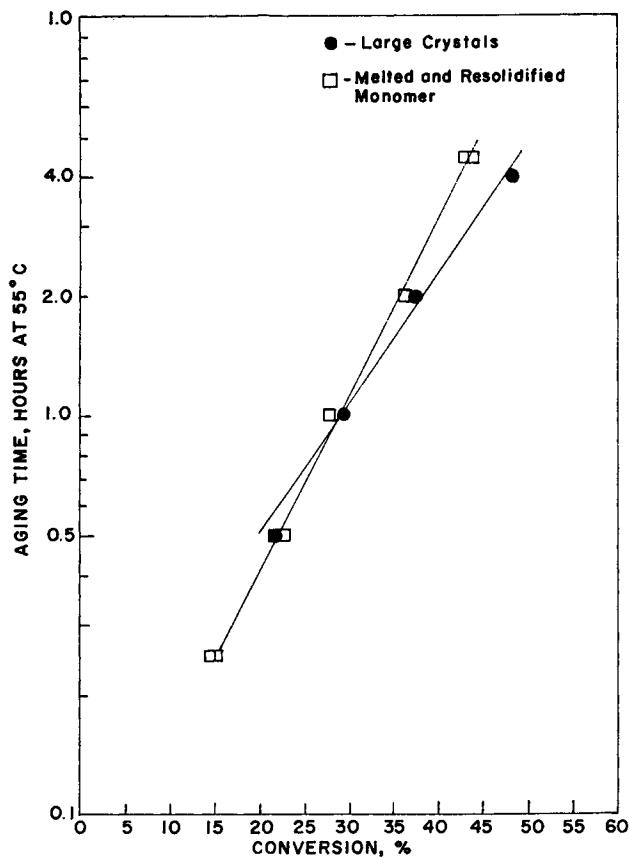


Fig. 12. Percentage conversion as a function of time for large crystals of trioxane (0.3 Mrad): (●) large crystals; (□) melted and resolidified monomer.

TABLE V
Effect of Compacting on Polymerization

Compacting pressure, psi	Bulk density, g./cc.	Conversion, %	Avg. conversion, %	RSV	Avg. RSV
—	0.70	39.2	40.6	0.92	0.88
		42.1		0.85	
225	1.03	44.3	43.5	0.79	0.79
		42.7		0.79	
Melted	1.26	44.0	41.4	1.28	1.45
		40.1		1.45	
1,300	1.35	42.7	43.1	1.59	1.56
		44.4		1.54	
10,200	1.39	41.8	41.3	1.63	1.57
		44.4		1.58	
31,800	1.40	41.2	41.3	1.51	1.57
		41.3		1.58	
50,900	1.40	41.5	42.0	1.51	1.58
		42.1		1.60	
		41.9		1.53	

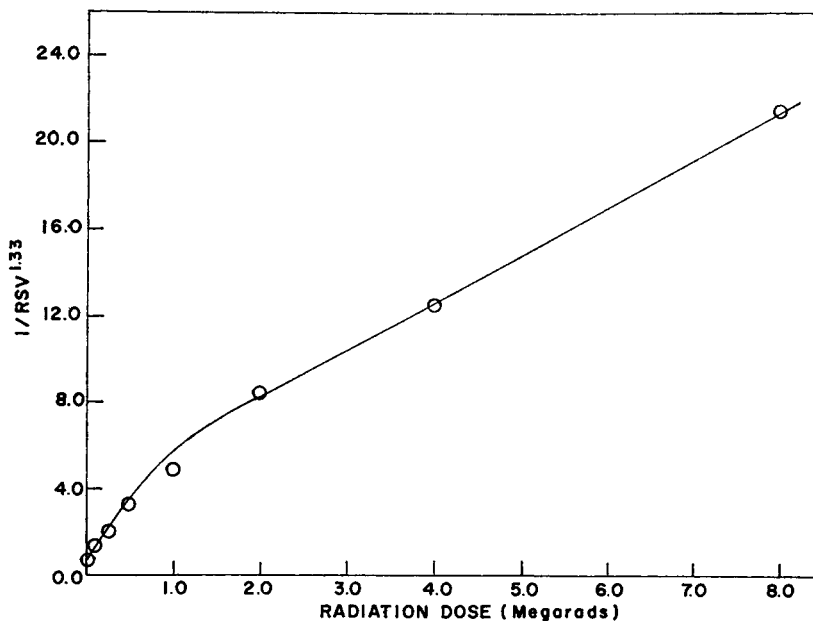


Fig. 13. Radiation scission of large polyoxymethylene crystals with 0.5 hr. aging.

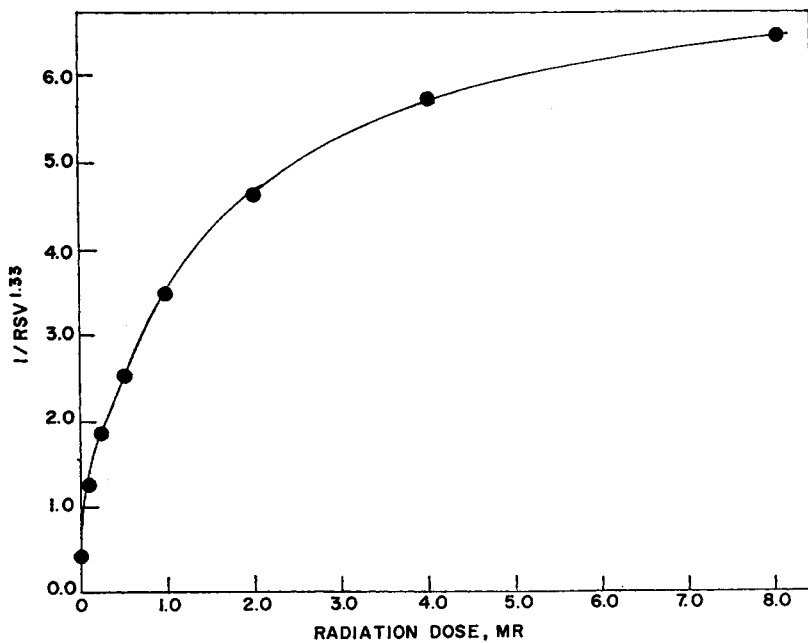


Fig. 14. Radiation scission of large polyoxymethylene crystals with 4 hr. aging at 55°C.

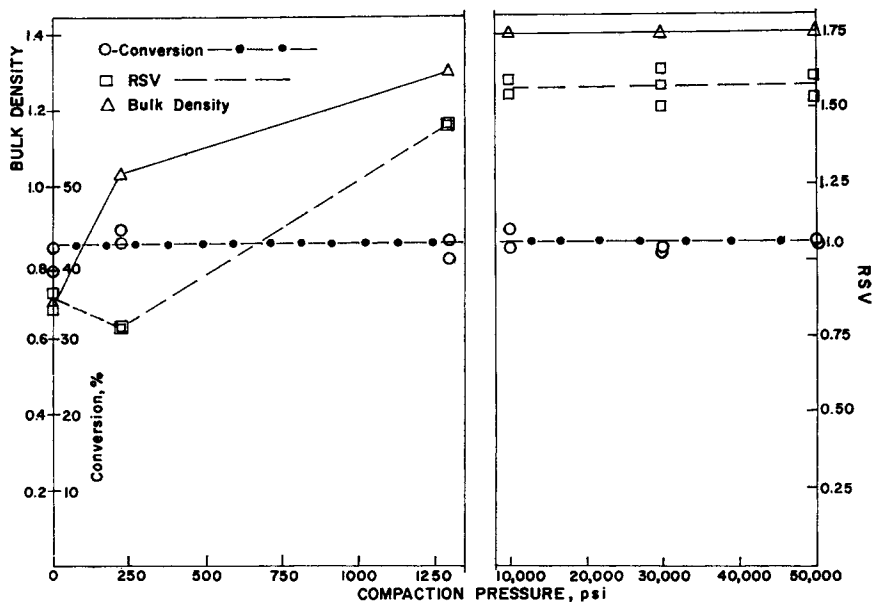


Fig. 15. Bulk density, RSV, and conversion as functions of compaction pressure of trioxane: (\odot) conversion; (\square) RSV; (Δ) bulk density.

methylene, we did not expect that compaction of monomer would affect conversion to polymer. However, the RSV of the final polymer might be modified by the degree of compaction.

Pellets were prepared by compacting 4.5 ± 0.1 g. samples in the standard KBr press for preparing samples for infrared spectroscopy. For these samples, the approximate density was determined by measuring the volume and then weighing the sample accurately. Irradiation was conducted to give equal radiation doses irregardless of density. The irradiated monomer, 50 g., was then transferred to a 73-cc. volume screw-cap bottle for polymerization. Polymerization conditions were 55°C . for 5 hr. As shown in Table V and Figure 15, only the RSV changed as a function of compacting pressure.

DISCUSSION

Although previous investigators³ have presented data on the polymerization of trioxane as a function of temperature, there has been no systematic effort to study the polymerization fully from the standpoint of dose, temperature of polymerization, and time of polymerization in relationship to the molecular weight and molecular weight distribution. The data given in the experimental results section serves to expand our picture of the out-of-source, radiation-induced, solid-state polymerization of trioxane.

During our investigations, a number of variables that might be of importance in obtaining replicable results were found. These are listed below: (1) the percentage of water present in the trioxane—replication can be ob-

tained in polymerization as long as this value is below 0.01%; (2) heat transfer during the polymerization—the exotherm of the polymerization, although small, is significant because of the large temperature dependence of the rate of polymerization; (3) the particle size of the monomer—sublimation and condensation of the monomer becomes important because of the high monomer vapor pressure at 60°C., namely >150 mm. Hg pressure.

To avoid the interference of these variables, the trioxane was usually distilled from a drying agent, collected in small-diameter tubes, and then melted and resolidified into a compact mass before radiation-induced polymerization. With these conditions, replicate results were readily obtained. However, when the percentage of water was allowed to exceed the stated amount, when the polymerization was accomplished under poor conditions of heat transfer, or when the particle size of the monomer was allowed to decrease, difficulty was found in obtaining replicate results. Methods of modifying the reaction conditions to give consistent results are covered in a series of patents.⁴

Using these preferred, controlled conditions, we have shown the following: (1) the solid-state polymerization of trioxane follows previously shown kinetics for solid-state polymerizations; (2) the reduced specific viscosity to an experimentally determined power, 1.33, is directly proportional to the percentage conversion for a given dose; (3) the radiation dose can be related to the percentage conversion/RSV^{1,33} over a wide range of dose; (4) the introduction of another monomer into trioxane modifies the polymerization in a systematic and explicable manner; (5) the radiation-induced scission of polyoxymethylene, prepared by solid-state polymerization, is indicative of either a broad molecular weight distribution or of weak links in the polyoxymethylene; (6) the reduced specific viscosity of polyoxymethylene is a function of the final polymer particle size under certain conditions; (7) the degree of "aggregation" of the monomer, obtained by melting or compaction, is one of the determining variables in the final molecular weight of the polyoxymethylene.

Now we shall examine each of these statements separately and show the experimental evidence to support these views. First, the solid-state polymerization of trioxane was shown to follow previously demonstrated kinetics for solid state polymerization. Figures 1 and 2 show the linear relationship between the log time and percentage conversion with the curve fitting the general equation $Y = A(1 + B \log t)$. This relationship was shown for the full range of useful polymerization temperatures, namely 35–55°C. However at 35°C., the slope of the line was markedly different from those at 45, 50, and 55°C. The change in the mechanism of the polymerization from 35 to 45°C. can be explained by the change in configuration of the trioxane molecule over this temperature range. NMR data to support this view is found in the literature.¹⁹ Although activation energies for solid-state polymerization can be calculated from our data, the temperature range of 45–55°C. appears inadequate. For the record, the calculated value is 30 kcal./mole.

Second, the reduced specific viscosity to the 1.33 power has been shown to be directly proportional to the percentage conversion for a given irradiation dose. Such a relationship would be in accord with the obtaining of a monodisperse system of molecular weights from the solid-state polymerization of trioxane, with the α in the Mark-Houwink equation, $\eta = KM^\alpha$, being equal to 0.75. Although this view is attractive because of its inherent simplicity, we do not feel that it is tenable. Two major objections are (1) the found dependence of molecular weight of polyoxymethylene on particle size and (2) the curve for polymer chain scission of polyoxymethylene on irradiation.

Third, the log of radiation dose is directly proportional to the percentage conversion/ $RSV^{1.33}$ over a wide range of dose. Again, if we use the naive assumption that the molecular weight is proportional to $RSV^{1.33}$, the ratio of the percentage conversion to $RSV^{1.33}$ would represent a value for the number of molecules present, or, in the absence of chain transfer, the number of sites. Thus a linear relationship might be postulated between the log of dose and the number of polymer molecules formed. Although this relationship does not give us any insight into the kinetics of the polymerization nor into the termination reaction, it does present a clue as to the formation of active sites. The found correlation is in accord with the random activation of a limited number of sites distributed throughout the solid matrix. The nature of these sites, that might be activated by radiation, is not known. However as a tenuous approximation, we might consider them to be lattice defects already existing in the trioxane crystal.

Fourth, we found that the introduction of another monomer into the trioxane modifies the polymerization in an understandable manner. Based on our known relationship for pure trioxane between the RSV and percentage conversion at a specific dose, we can indicate the possible mechanisms for modification both of the percentage conversion and the RSV. For example, any percentage polymerization and RSV found for a comonomer system that lies on the master line for the homomonomer trioxane polymerization (drawn in Fig. 10) would indicate that very little chain transfer occurred during the polymerization. Thus in Figure 10, we see that the percentage conversion and RSV for the additives, hexamethylcyclotrisiloxane and epichlorohydrin, fall on the line characteristic of trioxane homopolymerization. From this, we can surmise that the hexamethylcyclotrisiloxane and epichlorohydrin probably terminate the polymerization of trioxane. At the same time, these two additives do not participate in a chain transfer mechanism of polymerization, since such a chain transfer would result in lower RSV at the designated percentage polymerization than those values found for trioxane homopolymerization. On the other hand, the other additives in the system were shown not only to chain terminate but also to chain transfer based on the points falling below the master curve for RSV versus percentage polymerization for the homopolymer.

Fifth, the radiation scission of polyoxymethylene prepared by solid-state

polymerization is indicative of either a fairly broad distribution of molecular weight or of weak links in the polyoxymethylene. Radiation scissioning studies of polymers have been used as a method²⁰ for determining molecular weight distributions. However, the possibility always exists that so-called weak links are present in the polymer that is being scissioned. For example, in the case of polyoxymethylene, such weak links could result from head-to-head polymerization to yield peroxidic main chain bonds or from the action of oxygen on the system to give conversion of the methylene grouping to a peroxide or hydroperoxide.

Unfortunately, the direct determination of molecular weight distribution by fractionation of polyoxymethylene could not be performed because of the poor thermal stability and low solubility of the unstabilized material. In the absence of a standard fractionation, preliminary separations with the use of selective solvents indicated that the polymer had a broad distribution of molecular weights. Such a finding is in accord with the relationship between polymer particle size and RSV. However, this finding is not reconciled readily with the described relationship between percentage conversion and RSV.

Sixth, the reduced specific viscosity of polyoxymethylene is a function of the final polymer particle size. As the particle size decreases, the RSV or the molecular weight decreases. However, other experiments show that under controlled conditions, the percentage conversion does not decrease appreciably with monomer particle size. The problem then is whether the final molecular weight of the polyoxymethylene is caused by the monomer particle size or whether the final polymer particle size is caused by the degree of polymerization achieved with the monomer.

The only pertinent information was derived from a study (not presented here) of polymer particle size as related to monomer particle size where we have shown that the monomer and polymer particle size distribution was approximately the same. This finding indicated that the monomer particle size was important in determining the final molecular weight of the polymer. At the same time since the percentage polymerization was not drastically reduced, we must conclude that the number of active sites is greater per unit weight in the small particle monomer or that chain transfer may occur more readily in the small particle monomer. Such questions could only be answered by a more exhaustive study including such problems as the following. (1) Is the purity of the small particle size monomer different than that of the larger particle size monomer? (2) Are more lattice defects present per unit weight in the small particle size monomer than in the large particle size monomer? (3) Is there any difference in the ESR signal derived from small particle size monomer compared to the large size? (However, ESR measurements may not relate necessarily to number of active sites.) (4) What role does the sublimation and recondensation of the monomer molecule play in the propagation steps, and can such disordering be traced back quantitatively to the particle size of the monomer?

Finally, seventh, the "degree of aggregation" of the monomer is one of the

determining variables in the final molecular weight of the polyoxymethylene produced by solid-state irradiation. The carefully controlled series of experiments collected in Figure 15 and Table V show that although the state of compaction or "degree of aggregation" does not alter the conversion, the RSV is modified greatly by the amount of compaction used. Thus, when the sample is compacted by pressure or by melting and resolidifying before irradiation, the RSV is shown to have a much larger value than for granular, noncompact trioxane. Again, we are probably seeing the effect of a sublimation and recondensation of fine particle monomer at the polymerization temperature of 55°C. Other experiments in which the atmosphere was changed during sample preparation or during polymerization yielded lower molecular weight material. This finding is in accord with a sublimation disordering phenomenon reducing the molecular weight. However, this solid-state disordering should not be confused with the major disordering that is sometimes found when polymerization is effected close to the melting point. For example, at 60°C. early termination of polymerization is found when the polymerization exotherm causes localized melting.

SUMMARY

Although we have reported only partially a large body of experimental data obtained on the radiation-induced solid-state polymerization of trioxane, we note a number of anomalies. We have a very ordered polymerization as indicated by x-ray studies on the final polymer and by kinetic data. On the other hand, we have a system which can only be replicated under rather precise conditions with variables of major importance being particle size, degree of compaction, size of reaction vessel, etc. We then conclude that any condition that will contribute to disordering of the monomer will increase the difficulty of replication of results, and contrariwise any method of retaining the original order of the monomer will aid in duplication of results.

We thank Dr. F. W. Mitchell for a number of fruitful discussions as well as for his suggestion on compacting trioxane. We thank Mr. S. Olfky for the irradiations described in this paper and for the dosimetry measurements. Finally, we are grateful to W. R. Grace and Co. for permission to publish this investigation.

References

1. Okamura, S., K. Hayashi, and Y. Nakamura, *Isotopes Radiation*, **3**, 416 (1960).
2. Hayashi, K., and S. Okamura, *Makromol. Chem.*, **47**, 230, 237 (1961).
3. Hayashi, K., H. Ochi, and S. Okamura, *J. Polymer Sci.*, **A2**, 2929 (1964).
4. W. R. Grace Co., French Pats. 1,310,141; 1,350,349; 1,351,326; 1,348,294; 1,352,671; 1,386,213; Brit. Pats. 983,075; 983,673; 984,097; 984,322; 984,394.
5. Houilleres du Bassin du Nord et Pas de Calais, French Pats. 1,292,224; 1,352,998; 1,352,999; Belg. Pats. 641,714; 637,434; Brit. Pats. 939,498; 984,874.
6. Japanese Assoc. for Radiation Research, Brit. Pat. 923,154.
7. Toyo Rayon, French Pat. 1,330,650.
8. Kanegafuchi Spinning Co. Ltd., Brit. Pat. 939,475.
9. Van der Heijde, H. B., *Nature*, **199**, 798 (1963).

10. Lando, J., N. Morosoff, H. Morawetz, and B. Post, *J. Polymer Sci.*, **60**, S24 (1962).
11. Okamura, S., K. Hayashi, and M. Nishii, *J. Polymer Sci.*, **60**, S26 (1962).
12. Carazzolo, G., S. Leghissa and M. Mammi, *Makromol. Chem.*, **60**, 171 (1963).
13. Tupikov, V. I., and S. Ya. Pshezhetskii, *Zh. Fiz. Khim.*, **38**, 2430 (1964).
14. Okamura, S., T. Higashimura, and K. Takeda, *Makromol. Chem.*, **51**, 217 (1962).
15. Dragonic, I., *Nucleonics*, **21**, 33 (Feb. 1963).
16. Henley, E. J., and D. Richman, *Anal. Chem.*, **28**, 1580 (1956).
17. Morawetz, H., *J. Polymer Sci.*, **A1**, 65 (1963).
18. Nakajima, N., unpublished work.
19. Komaki, A., and T. Matsumoto, *J. Polymer Sci.*, **B1**, 671 (1963).
20. Bovey, F. A., *The Effects of Ionizing Radiation on Natural and Synthetic High Polymers*, Interscience, New York, 1958.

Résumé

Des études complémentaires ont été faites sur la polymérisation en phase solide du trioxane, initiée par irradiation. La vitesse de la polymérisation en dehors de la source a été examinée en fonction de la dose d'irradiation et en fonction de la température et de la durée de polymérisation. La relation empirique entre le log du temps et Y (Y indiquant le pourcentage de polymérisation) est satisfaisante dans un large domaine de conversion, de dose et de durée de polymérisation. Pour une dose donnée, le rendement est directement proportionnel à $RSV^{1,32}$ (RSV indiquant la viscosité spécifique réduite). L'augmentation de la dose ou la diminution des dimensions des particules donnent des valeurs de RSV plus basses pour des conversions équivalentes.

Zusammenfassung

Weitere Untersuchungen über die strahlungsinduzierte Polymerisation von Trioxan in festem Zustand wurden ausgeführt. Die Polymerisations-geschwindigkeit nach Entfernung der Quelle wurde als Funktion der Strahlungs-dosis sowie der Polymerisations-temperatur und -dauer untersucht. Die empirische Beziehung $\log \text{Zeit} \propto Y$ (wo Y der Polymerisationsumsatz ist) erwies sich über weite Umsatz-, Dosis- und Polymerisations-dauerbereiche als befriedigend. Bei gegebener Dosis war die Ausbeute direkt proportional zu $RSV^{1,32}$ (wo RSV die reduzierte spezifische Viskosität ist). Sowohl Erhöhung der Dosis als auch Herabsetzung der Teilchengröße lieferte beim gleichen Umsatz niedrigere RSV -Werte.

Received August 3, 1965

Prod. No. 1264