Radiation-induced copolymerization of trioxane with tetrahydrofuran

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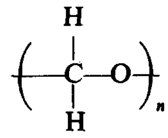
Radiation-initiated copolymerization of solid trioxane (TOX) with tetrahydrofuran (THF) was investigated. The effects of radiation dose, THF concentration, and post-polymerization temperature and duration on copolymer yield and THF incorporation were studied. These results are compared with the results of TOX homopolymerization under identical conditions. Copolymer yield was lower than that of homopolymer. Only a fraction of charged THF entered into the polymer chain. THF content and radiation dose also altered the *MW* of the copolymer but it showed better thermal stability. The initial reaction rates of the copolymerization were determined and from these the activation energy was found to be 36.2 kcal mol^{-1}.

(Keywords: trioxane; tetrahydrofuran; copolymerization; radiation; solid-state-reaction; thermal stability)

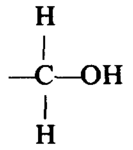
INTRODUCTION

Polyoxymethylene homopolymer made from trioxane, consists of



$$\left(\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - O \right)_n$$

chains containing C—O bonds. Though possessing very good mechanical properties, these bonds induce thermal instability; the hemiacetal groups



$$-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-OH$$

at the chain ends undergo degradation at temperatures above 160°C, thus continuing an 'unzippering' of formaldehyde units. The key property of this polymer is its thermal stability which can be determined through weight loss on heating to 222°C. Thermal degradation is generally controlled by end-capping through acetylation which introduces the C—C bonds. Alternatively, C—C bonds are introduced in the polymer chain by copolymerization with a cyclic ether comonomer containing at least one C—C bond.

Copolymerization has certain advantages over homopolymerization followed by end capping. It can be achieved in a single step, and the copolymer is stable to alkali while the homopolymer is unstable. However, because the comonomer incorporation is small (and not ensured to be at the chain ends), a considerable part of the chain may remain unstable and consequently the yield of stable polymer may be low.

Copolymerization of trioxane (TOX) with pentaacetylglucose (which has a six membered ring) has been reported earlier[1]; polymerization of TOX with tetrahydrofuran (THF) (which has a 5 membered oxycyclic ring), induced by gamma radiation, is described here. Price and McAndrew have reported[2] that TOX and THF can be copolymerized by using a strong acidic catalyst; the possibility of solid state copolymerization by irradiation and heating without any catalyst was, therefore, investigated.

EXPERIMENTAL

THF was purified by treatment with solid sodium hydroxide and sodium metal followed by distillation. TOX was purified by repeated crystallization. Weighed quantities of THF and TOX were placed in a stoppered flask and heated gently and when the mixture melted it was thoroughly mixed by shaking. Samples of this melt (about 2 g) were transferred into 10 mm diameter test tubes and cooled. These TOX–THF blends were irradiated with gamma rays from a cobalt-60 chamber at room temperature of 25°–30°C followed by post-polymerization by heating at 43°, 48° and 53°C in a thermostatically controlled bath. (The temperature in the bath was controlled within ±0.1°C). After heating for specified periods, the tubes were removed and quickly quenched by dipping in an ice–common salt mixture. The unreacted monomers were washed out of the polymer product with toluene and analysed by gas liquid chromatography (g.l.c.). The weight of the dried polymer indicated the yield, and the difference between the weights of the comonomer charged and recovered, indicated the comonomer incorporation in the polymer. The general reproducibility of the results were checked for the initial samples (the statistical error was only 1.6%).

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RESULTS AND DISCUSSION

THF–TOX blends containing 1% w/w THF was irradiated at various doses and post-polymerized at 53°C for 6 h and 24 h. The copolymer yields under these experimental conditions are shown in *Figure 1*. For comparison, the yields of homopolymer of TOX under identical conditions are also shown. The yields of homopolymer and copolymer increased with increasing dosages and reached the maximum level at 0.4 to 0.5 mrad. Thereafter it remained constant up to a radiation dose of 1.0 mrad. The copolymer yield was substantially lower than the yield of the homopolymer (40% compared with 66% for the homopolymer).

An interesting point in the copolymer yield curve was that the yield first increased slowly at low doses and then showed a fast rise giving an S-type curve. This suggests that an 'induction period' was required for the copolymerization. At low doses, the active centres generated in the THF–TOX blend were probably not sufficient in number to give good yields. It is possible that hinderances or deactivation due to the presence of THF might occur at low levels of radiation. The copolymer yield curves for 6 h as well as 24 h post-polymerization at 53°C coincided above 0.5 mrad doses. This showed that when the charge contained 1% THF the active species were depleted and attained saturation within 6 h.

TOX–THF blends containing higher amounts of THF (5.5% w/w) were irradiated at higher radiation doses up to 4.5 and 10 mrad in presence of air, as well is in vacuum. The irradiated samples were post-polymerized at 53°C for 6 h. The yields of the copolymer and homopolymer are shown in *Figure 2*. The polymer yields decreased at doses above 1 mrad in all cases). Higher doses above 1 mrad might have caused radiolysis resulting in the lowering of polymer yields. The curves in *Figure 2* show that the presence of air during irradiation affected the yield of the homo- and copolymer in opposite ways. In the case of homopolymer, the yield was higher in the presence of air than in vacuum. For the copolymer, the reverse was found. (Two stray points at 0.5 mrad are due to experimental error). The effect of nitrogen in the air, vacuum conditions or higher amounts of moisture have also been observed by other authors[9–11]. It is possible that activated oxygen atoms (formed by radiation in the presence of air) helped in the homopolymerization of pure TOX and increased the yield. In the presence of THF, the oxygen might form an intermediate of THF which could cause a chain termination and thus reduce the polymer yield. With 5.5% THF, the yield was lower than with 1% THF in the charge. To investigate how the THF contents in the charge, affect the copolymer yield and THF incorporation in the product, THF–TOX blends containing 1–5% THF were irradiated (0.5 mrad) and post-polymerized at 53°C for 6 h. The results are presented in *Figure 3*. For the homopolymer, the yields decreased from 62.2% to 40% at 1% THF and to 30% at 3% THF.

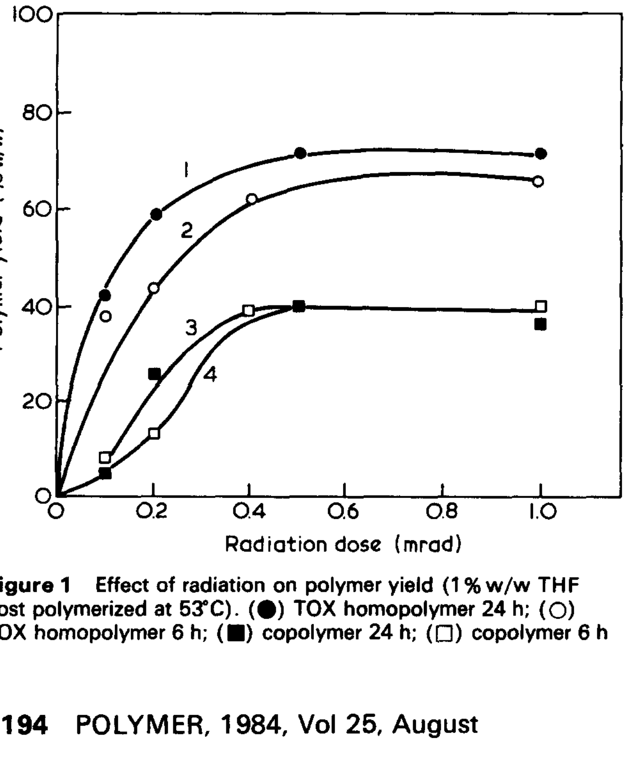

Figure 1 Effect of radiation on polymer yield (1% w/w THF post polymerized at 53°C). (●) TOX homopolymer 24 h; (○) TOX homopolymer 6 h; (■) copolymer 24 h; (□) copolymer 6 h

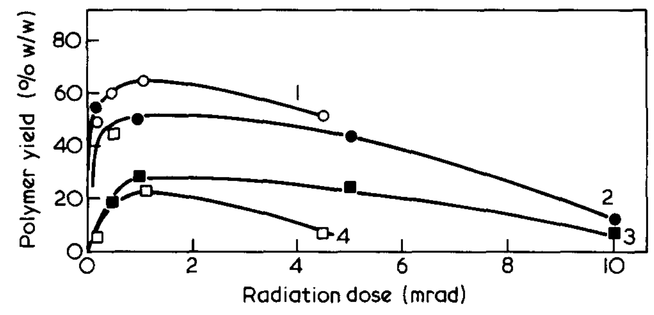

Figure 2 Effect of extended radiation and environment on polymer yield (5.5% w/w post polymerized for 6 h at 53°C). (○) TOX homopolymer in air; (●) TOX homopolymer in vacuum; (■) copolymer in vacuum; (□) copolymer in air

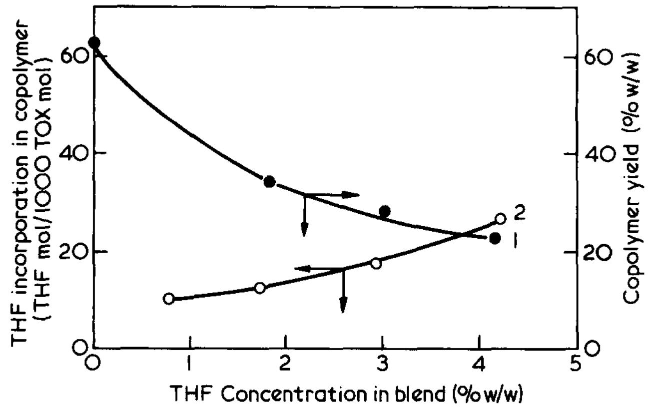

Figure 3 Incorporation of THF into the copolymer (post polymerized at 53°C for 5 h, 0.5 mrad). (●) copolymer yield; (○) THF incorporation

But the incorporation of THF in the polymer increased with increasing THF content. It rose from 10 mol/1000 mol TOX at 1 wt % THF to 25 mol THF per 1000 mol TOX at 4 wt % THF. The incorporation of THF was observed to decrease with increasing radiation doses. A 5.4% THF + TOX blend on irradiation at 0.2, 0.5, 1.0 and 4.5 mrad showed a yield curve similar to *Figure 2* but the THF content in the polymer showed a gradual decrease with a maximum of 29.6 mol/1000 TOX mol at 0.2 mrad and 12 mol/1000 TOX mol at 4.5 mrad.

The comonomer THF is a liquid at room temperature, but when it is mixed with 95–99 parts of TOX (which is a crystalline solid), the THF either remained as a liquid adsorbed on the TOX crystals or entered the TOX crystal lattices and created imperfections. It may have remained partly inside and outside the crystal. THF which has a 5 membered epoxide ring, has very little strain in the bonds and is difficult to activate for polymerization. The polymerization of THF has been achieved by using strong acid catalysts, in the presence of a chain carrier[3]. The polymerization occurs through ring opening at the C—O bond, with the formation of an oxonium ion.

As seen in *Figure 1*, at low radiation levels the monomer conversion was much lower in the case of copolymer than for the homopolymer. On increasing the radiation dose, the yield increased with an S-shape curve. The initial low increase may possibly be due to the retarding effect of THF in the outer adsorbed layers. The overall lower yields of the copolymer may be due to crystal imperfections and the lower activation of the THF under the moderate conditions used in these cases.

The results obtained for the variation of the THF content showed that as more THF entered the copolymer, the TOX conversion decreased. This indicates that the THF probably hindered the reaction, possibly by decreasing the TOX activation; or some chain transfer activity of THF; or an intermediate formed from THF.

THF–TOX blends containing 5.4% THF were irradiated at 0.5 mrad and post-polymerized at 48° and 53°C for 1–5 h. The THF incorporation and polymer yields under these conditions are shown in *Figure 4*. The polymer yield and the THF content in the polymer increased with post-polymerization times up to 5 h. The curves show, however, that the saturation level was attained after 5–6 h. The nature of the curves indicates that the rate of polymer build up was slow in the presence of THF.

However, it is interesting to note that the yield of the copolymer was higher at 53°C than at 48°C, but the incorporation of THF was lower at the higher temperature. At a higher temperature of 5°, the THF content decreased from 29 to 18 mol/1000 mol TOX. This could be due to a deactivation of the THF molecules which would occur with rise in the temperature. The polymerization of THF is known to be an equilibrium polymerization; the equilibrium values were determined by studying this polymerization using a very strong acid catalyst. It was found to decrease sharply at temperatures above 45°C reaching a maximum at a temperature of 83°C. Although the amount of THF converted to copolymer in this study was much lower than the equilibrium value, the observation of decrease of THF conversion at higher temperatures is similar.

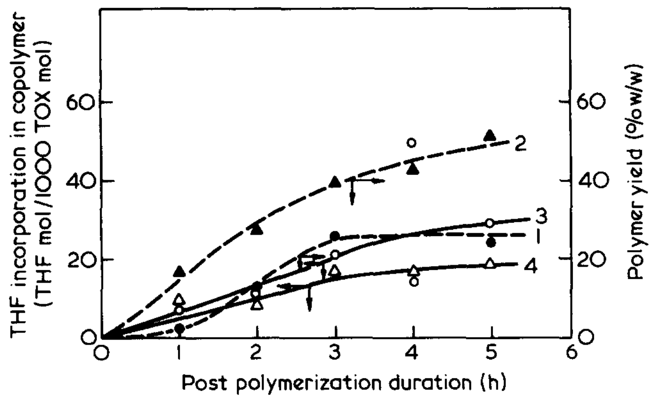

Figure 4 Effect of post-polymerization duration and temperature on THE incorporation into the copolymer (5.4% w/w THF, 0.5 mrad). (●) yield at 48°C; (▲) yield at 58°C; (○) THF incorporation at 48°C; (△) THF incorporation at 53°C

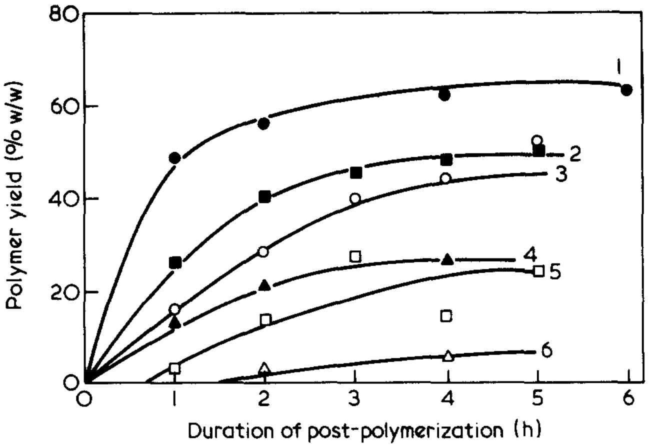

Figure 5 Effect of post-polymerization temperature and duration on the polymer yield (5.4% w/w THF, 0.5 mrad).

1	●	53°C	homo TOX
2	■	48°C	
3	▲	43°C	
4	○	53°C	5.4 THF in blend
5	□	48°C	
6	△	43°C	

Kinetics of THF–TOX copolymerization

The polymerization reaction actually occurs when the irradiated monomer blend is heated for post-polymerization. The yields of the copolymer from TOX–THF blends containing 5.4% THF (on post-polymerization at three temperatures for 1–6 h) are shown in *Figure 5*. The yields of TOX homopolymer under the same conditions are also shown. The homopolymer yields were always more than that of the copolymer at the same temperatures. The curves showing the copolymer yields at 43° and 48°C indicate that the polymerization started after an induction period of about 3/4 h at 48°C and $1\frac{1}{2}$ h at 43°C. This is clearly due to the presence of 5.4% THF. The saturation yields for the homopolymer were also attained earlier than for copolymer. Evidently, under these polymerization conditions, it is difficult to activate THF and the copolymerization proceeds at a slower rate.

To determine the initial reaction rates avoiding the induction period, the polymerization was carried out with 1% THF in the blend. The radiation dose was also varied (at 0.1 mrad and 1.0 mrad). These data are plotted in *Figure 6*. The initial reaction rates R_p (% h^{-1}) were then determined from the tangent of the yield curves. Arrhenius plots of these data against the inverse of the absolute temperature is shown in *Figure 7*. The activation energy was found to be 36.2 kcal mol^{-1} which is very close to the activation energy of 38.5 found for the homopolymer[1]. Thus the activation energies for the homopolymerization as well as copolymerization of TOX–THF can be taken to be the same; this indicates that the activation of TOX virtually controls the polymerization in these cases.

Stabilization of the copolymer

The copolymer of TOX–THF was treated with benzyl alcohol containing 2% triethanol amine at 150°C for 30 min to remove the unstable part[4] of the polymer chains.

Figure 8 shows the losses during stabilization of the copolymers containing increasing amounts of THF. The losses were lower for samples containing larger amounts of THF. These weight losses due to degradation may be either from the ends of the polymer chains if THF had not entered at the ends, or from the degradation of the homopolymer which might have been formed.

Thermal stability is an important criterion to assess the extent of incorporation of C—C bonds in the polymer chain. It was measured in terms of thermal degradation rate (% $\min^{-1}$) at 222°C under nitrogen atmosphere[5,6]. The lower the degradation rate, the better the thermal stability.

Figure 9 shows the thermal degradation rate of the copolymer as such and after the stabilization treatment. At THF contents of 11 and 30 THF mol/1000 TOX mol in the copolymer the thermal degradation rates of the untreated copolymer was 1.54 and 1.01% $\min^{-1}$. After stalization, the rates decreased substantially to a low value of about 0.30% $\min^{-1}$. This appeared to be the same for the copolymer containing 20 to 50 mol THF/1000 mol TOX. This higher thermal stability is a clear and positive indication of the formation of the copolymer and C—C bonds.

Molecular weight of copolymer

The number average molecular weight of the copolymer was determined by the viscosity method[7]. The molecular weights are plotted against the THF contents as shown in *Figure 10*. It was 1.5×10^5 when the

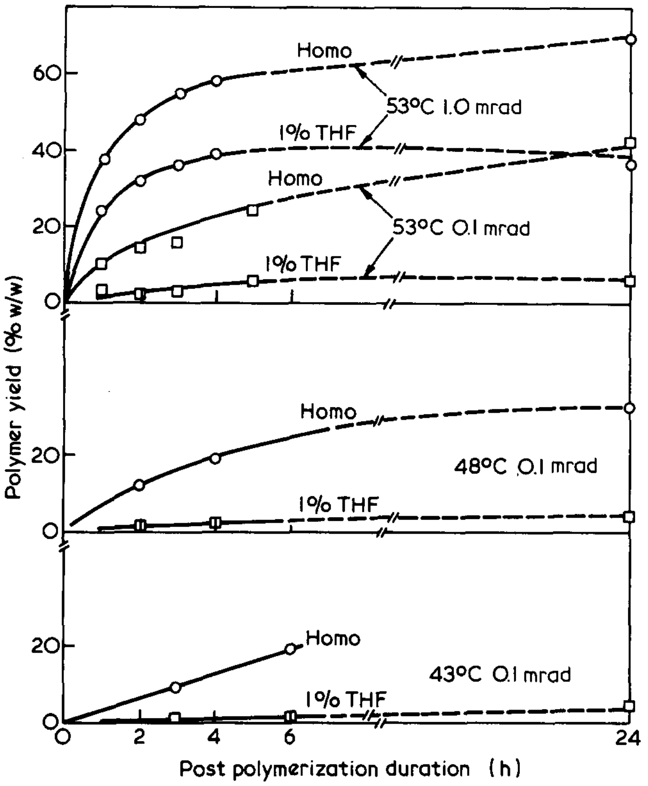

Figure 6 Effect of dose, temperature and duration on polymer yield

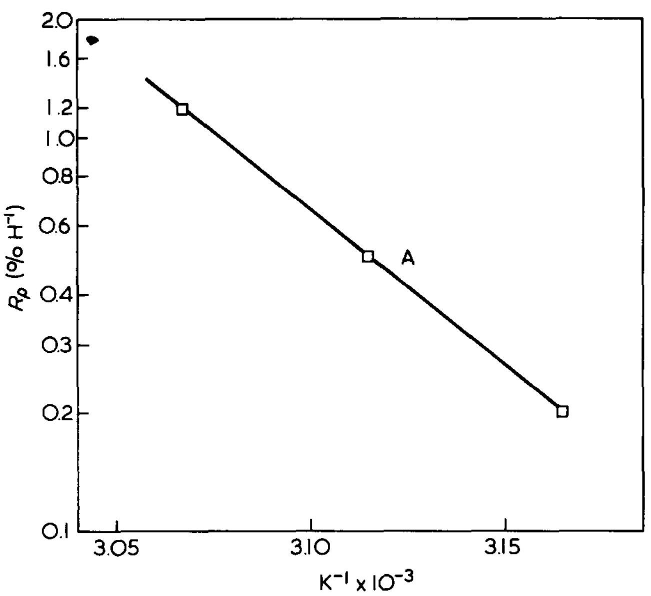

Figure 7 Activation energy of copolymerization of TOX with THF (0.1 mrad). $\Delta E = 36.2$ kcal mol^{-1}

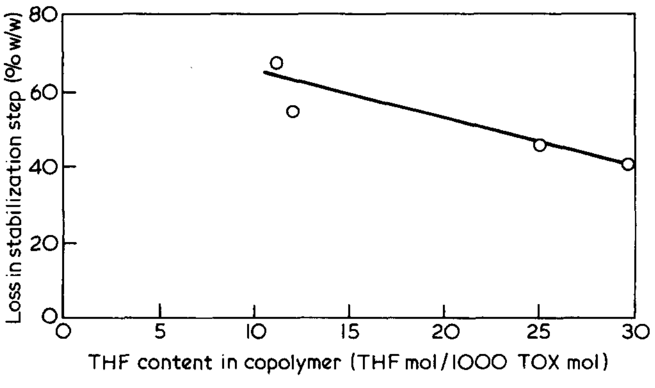

Figure 8 Copolymer composition *versus* degradation

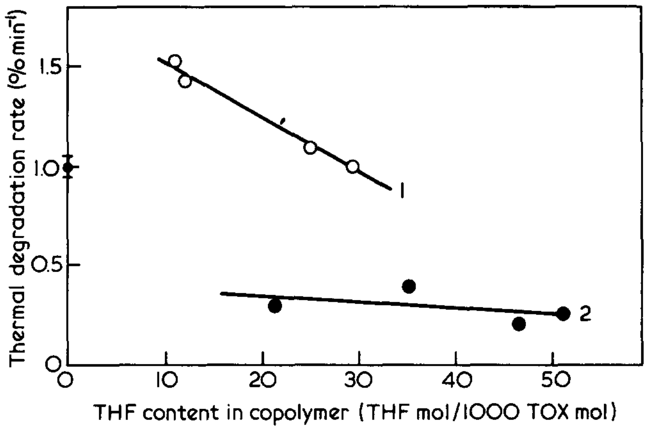

Figure 9 Effect of THF content and stabilization on thermal degradation rate (○) before stabilization; (●) after stabilization; ● TOX homopolymer

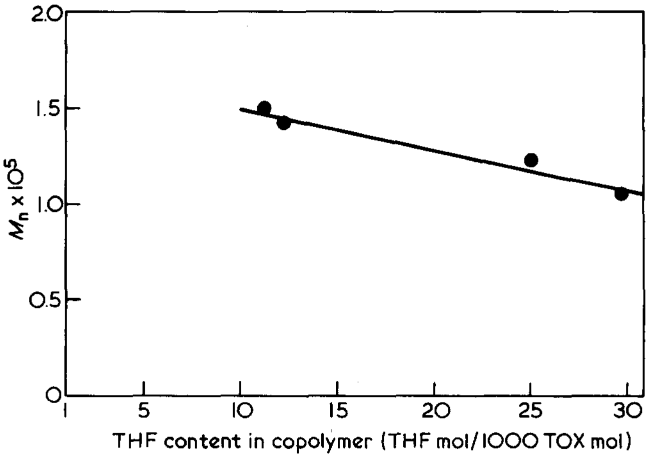

Figure 10 Effect of THF content on M_n of the copolymer

copolymer had 10 mol THF/1000 mol TOX, but it decreased to about 1.0×10^5 when the THF content was 30 mol. The polymer yield was also found to decrease with increasing incorporation of THF. These results indicate that the THF molecules probably act to some extent as chain transfer agents.

Radiation doses also affected the molecular weight of the copolymer (*Figure 11*). The molecular weight increased from 0.5×10^5 to 1.8×10^5 when the radiation dose was increased from 0.2 to 1.0 mrad (THF 1%, post-polymerization at 53°C for 6 h). The trend of molecular weight increase with radiation is similar to the increase of yields (as shown in *Figure 1*). The molecular weight was also found to rise with increasing conversions as the duration of the post-polymerization was extended from 1–5 h (*Figure 4*).

These increases (yields and molecular weights) lend strong support to the nuclei growth model of Avrami which has been found to agree well with the solid state polymerization of TOX[8].

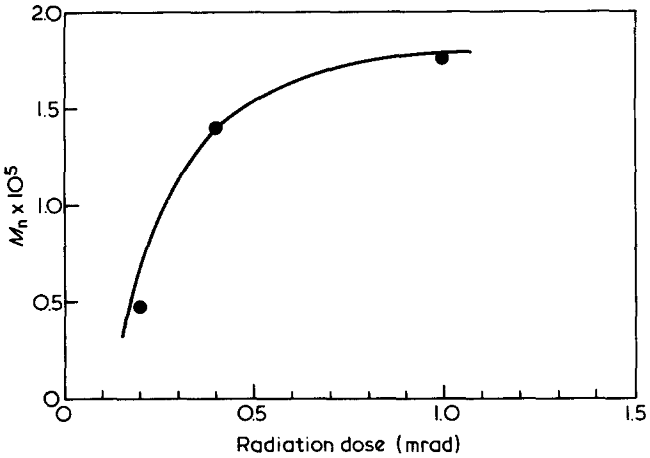

Figure 11 Effect of radiation dose on the *MW* of the copolymer (1% THF, post polymerized at 53°C for 6 h)

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