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AND STABILIZATION OF POLYOXYMETHYLENE**

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## ABSTRACT

Gamma ray induced polymerization of trioxane from an indigenous source (M/s. Nuchem Plastics, Faridabad) has been investigated by both in-source and post polymerization techniques. Impurity levels in the trioxane sample are determined and compared with those in an imported material. Critical evaluation of the results of its purification by different methods, viz. treatment with molecular sieves, crystallization from solvents and their variations, has been carried out prior to optimising the conditions of polymerization. A novel but simple purification procedure has been arrived at during the course of this investigation employing benzene as the solvent which is found to form a ternary azeotrope with trioxane and water, a crucial cationic polymerization inhibiting impurity. The effect of these purification methods on the polymerization efficiency and their dependence on the molecular weight of the polymer formed are also discussed.

Experimental details of polymerizing trioxane in 10 Kg scale are also described. To improve upon the thermal stability of the polyoxymethylene thus formed, protection of the free hydroxyl end groups (end-capping) has been achieved by an acetylation procedure using acetic anhydride in presence of catalytic amounts of sodium acetate.

# RADIATION INITIATED POLYMERIZATION OF TRIOXANE AND STABILIZATION OF POLYOXYMETHYLENE

M.H. Rao, G. Ramanan, Joy T. Kunjappu and K.N. Rao

## I. Introduction

Radiation initiated polymerization has been studied in detail by various investigators.<sup>(1-4)</sup> At Takasaki, Japan, a pilot plant of 25 Kg scale was operated with a conversion of ~65% using an electron accelerator.<sup>(5)</sup> However, the results obtained by earlier investigators had shown a limiting conversion of the monomer to the polymer. In our laboratories, small scale experiments on super dry trioxane prepared by the method developed here making use of trioxane distilled over regenerated molecular sieve 5A, yielded very interesting results for the in-source and post polymerizations.<sup>(6-9)</sup> Typical results obtained for in-source polymerization including the molecular weights of the polymers thus obtained are shown in Figures 1 and 2, which indicate that polymerization goes to completion. The results obtained on the post polymerization of trioxane irradiated under vacuum for 1 Mrad at dry ice temperature and annealed at various temperatures revealed that maximum conversion efficiency was at 55°C. Figure-3 which represents the extent of conversion of super dry trioxane in a typical post polymerization study at an optimum annealing temperature of 55°C, indicates that the polymerization goes to 80% for an annealing time of 5 hrs. The molecular weights of the polymer obtained by post irradiation annealing averaged to  $\sim 3 \times 10^5$ .

## II. Purification and Polymerization

The feasibility of using locally produced trioxane was also examined. Nuchem plastics, Faridabad, supplied trioxane manufactured by them. The two grades of trioxane supplied by them were analysed for the impurities present and compared with an imported standard (Fluka, purum). Results are summarised in Table -1.

Table-1

Material	* HCHO (ppm)	** HCOOH (ppm)	*** MeOH (ppm)	*** Methylene dichloride (ppm)	**** Water (ppm)
Unpurified (Nuchem)	1150	113	530	85	1750
Purified (Nuchem)	12	14	16	640	1650
Imported (Fluka)	11	4	16	<40	1550

\*Bisulphite method  
\*\*Titrimetry  
\*\*\*Gas Chromatography  
\*\*\*\*Karl Fischer method

The results of conversion of the as-received monomer to the polymer are tabulated in Table-2

Table-2

<u>Material</u>	<u>% Conversion</u>
Unpurified (Nuchem)	10.9; 19.0; 46.4
Purified (Nuchem)	6.3; 52.0; 49.0
Imported (Fluka)	60.0; 60.0

Reproducibility is normally poor in this system in the absence of rigorous purification.

Now, we describe the experimental procedures adopted for the purification of trioxane on a large scale. The chief methods employed involve either the treatment of the impure substance with molecular sieves or its crystallization from solvents. Sometimes, combination of the above processes are also adopted.

#### A. Treatment with molecular sieves

Molecular sieve 5A was regenerated in a furnace maintained at 400°C under nitrogen flow for 2 hrs. The regenerated molecular sieve was stored in a desiccator and was later used.

The molten trioxane was mixed with molecular sieves at a ratio of 10:1 and heated at 70°C in a closed vessel for 4.5 hrs with occasional shaking. It was filtered through a dry cloth and the filtered trioxane was allowed to crystallize. This material



was used for polymerization (In one of the experiments this led to sudden depolymerization of trioxane to formaldehyde). Typical results obtained on polymerizing such a material are given in table 3.

Table-3

Dose rate (Mrads/hr)	Time (hrs)	Conversion (%)
0.78	1.5	71.3
0.78	2.0	91.7

B. Crystallization from solvents

(i) Methylene dichloride:

Since radiation polymerization of trioxane is through an insitu produced cation, it was felt that even traces of methylene dichloride present after crystallization would stabilise the cationic species due to its anion scavenging property. Moreover, methylene dichloride is having good solvent characteristics.

Trioxane (13.5 g) was dissolved in methylene dichloride (6 ml) by heating on a warm water bath and allowed to crystallize by cooling first to room temperature and then to ice point. The crystallized material was used for irradiation and the results are tabulated as follows in Table-4.

Table-4

History of crystallized samples	% crystallized	% conversion for 1 Mrad at 55°C
Room temperature crystallization	34.3	44.0
Ice temperature crystallization	51.0	4.3

From the results it is evident that simple crystallization procedure does not remove the impurities and they get trapped in trioxane crystals.

In a second approach, a non-solvent was used for precipitating trioxane from methylene dichloride solution. Accordingly, n-heptane was added to precipitate trioxane. Though complete recovery was achieved, the conversion efficiency was poor. Typical results are depicted in table-5.

Table-5

Sample No.	Dose rate (Krad/hr)	Time of irradiation (hrs)	% conversion
1	40	8	48.0
2	44	8	9.3; 9.0

From the above results it follows that the precipitation procedure is also not superior to the simple crystallization procedure.

The next batch was processed in methylene dichloride solution treated with fresh molecular sieves without regeneration under shaking for 2 hrs, prior to filtration. The filtrate was allowed to crystallize and the crystals were dried in vacuum. The conversion of this monomer to the polymer was ~29% for 1 Mrad indicating that impurities were not completely removed. The method was, then, modified to use both dry methylene dichloride and regenerated molecular sieves. Methylene dichloride was dried by sodium wire and the molecular sieves were regenerated at 400°C for 2 hrs under nitrogen flow. Trioxane solution in methylene dichloride was treated with molecular sieves, shaken for 8 hrs, filtered and allowed to crystallize. The amount of material taken in each batch was as follows: 310 g of trioxane, 120 ml of methylene dichloride and 25 g of molecular sieve. The percentage of crystallized material recovered was 69.8 and 64.8 for two batches. These samples were irradiated and the results are given in Table-6.

Table-6

Dose rate:  $4.2 \times 10^4$  rad/hr

Irradiation time (hrs)	% conversion of purified sample	% conversion of unpurified sample
12	54.2	38.9
16	74.3	66.6
20	80.0	61.0

These results indicate an improvement over that of simple crystallization. However, polymerization to completion was not achieved.

(ii) Benzene:

During the processing of irradiated polyoxymethylene for the recovery of trioxane from the polymer-monomer mixture, it was observed that trioxane forms a ternary azeotrope with water and benzene distilling at 68.5°C. Hence attempts were made to purify trioxane using benzene. Trioxane and benzene were taken in a 1:1 ratio. The mixture was distilled, first to remove the azeotrope and then to collect excess benzene. When most of the benzene was distilled off, the solution was allowed to crystallize. Experimental details for the two batches of 10 Kg level are given below.

First Batch:

Total weight of trioxane taken	....	13,118 g
Weight of crystallized material	....	11,643 g
% Recovery	....	88.8

Second Batch:

Total weight of trioxane taken	....	10,000 g
Weight of crystallised material	....	8863 g
% Recovery	....	88.63

Experimental details of distillation for a 10 Kg batch are given below in table-7 which include the amounts of solvent recovered and reused, and of trioxane crystallized and collected.

Table-7

Particulars	I	II	III	IV	V
1. Wt. of trioxane initially taken(g)	1994	2200	2017	2013	2085
2. Volume of benzene added(fresh and distillate from the previous batch) in ml	2000	500+ 1690	300+ 1870	330+ 1670	410+ 1675
3. Volume of benzene distilled (ml)	1690	1870	1670	1675	1730
4. Volume of mother liquor after crystallisation(ml)	625	500		745	
5. Wt. of trioxane crystallised(g)	1175	3518		3505	
<hr/>					
Total volume of mother liquor and the benzene distilled in the 5th cycle				....	3600 ml
Volume of benzene distilled in this fraction				....	2475 ml
Weight of trioxane crystallized				....	914 g
Volume of mother liquor				....	390 ml
Volume of benzene solution of mother liquor from the last fraction and the distillate				....	2865 ml
Total weight of trioxane collected and dried				....	8.863 Kg
% recovery				....	<u>88.63</u>
Total amount of benzene used				....	3745 ml

Repetition of the above process once again can yield ~810 g of trioxane crystals and ~2100 ml of benzene. On the basis of the above results the recovery of trioxane approaches ~97%. Benzene loss during distillation for processing 10 Kg comes to ~1900 ml.

The samples thus obtained were polymerized at  $52 \pm 2^\circ\text{C}$  for different durations at a dose rate of 48 K rads/hr. The results are shown in Fig.4. The molecular weights of some representative samples are shown in table-8.

Table-8

Dose rate ... 48 K rads/hr

Time of Irradiation (hrs)	% conversion	Molecular wt $\bar{M}_n$
7	51.8	51,520
11	82.3	33,250

When the bulk sample was irradiated for 20 hrs for a total dose of 1 Mrad at a dose rate of 48 Krads/hr, the amount of monomer converted to the polymer was ~98.2%. The average molecular weight of the polymer thus obtained was ~35,000. Samples of this polyoxymethylene polymer (POM) was used for bulk acetylations.

### III. Acetylation Procedures

Capping of end hydroxyl group was attempted using acetic anhydride as the acetylating agent and pyridine or sodium acetate

as catalysts. Results of some of the experiments are given in table 9 and 10.

Further experiments were carried for Acetylation with anhydrous sodium acetate as catalyst. The results obtained are given in Table-11.

The details of experimental procedure adopted for the above was as follows : one part of POM (by weight) was taken in a perfectly dry glass reactor and was mixed with 8 parts of acetic anhydride and 0.016 parts of anhydrous sodium acetate (i.e. in a typical experiment, 9 g of POM +70 ml of acetic anhydride +140 mg of sodium acetate in a glass vessel of total volume of 140 ml). The resulting mixture was deoxygenated by passing dry nitrogen for about 15 to 20 min and sealed in nitrogen. The sealed glass reactor was placed in a constant temperature bath at 150°C and was attached to a mechanical stirrer to ensure good stirring during the acetylation. The reaction mixture took about 15 min to reach 150°C. The bath temperature was raised to 162°C over a period of 15 min and then the bath was allowed to cool to 126°C in about an hour and a half with the glass reactor continuously stirring all the time [At 162°C the reaction mixture becomes homogeneous, i.e. single liquid phase. The solid separates as fine granules when the temperature is lowered].

Table-9

Acetylation of POM with sodium acetate as catalyst  
Molecular wt. of sample ..35,000 (98% yield) Temp. of Irradiation:52±2°C

Temp & time	Composition			Catalyst (mg)	Atmosphere	yield (%)	Thermal stability: wt.% loss in 30 min at 222°C in N <sub>2</sub>
	POM (g)	Ac <sub>2</sub> O (ml)	Toluene (ml)				
158°C 3 hrs	2	8	8	3	AIR (sealed)	62	9.6
160°C 3 hrs	2.2	8	8	3	Vac	76	8.1
160°C 2 hrs	2	12	-	10	Vac	75	9.0
150°C 40 min	2	20	-	20	AIR	87	26
180°C 1 hr	2.5	25	-	50	Vac	78	16
145°C Refluxed 3 hrs	3.6	35	-	50	N <sub>2</sub>	86	36
180°C 3 hrs	2.7	25	-	20	Vac	75	11.4
180°C 3 hrs	3	30	-	dried	Vac	70	4.2
145°C Refluxed	9.8	50	-	20	AIR	-	54
145°C Refluxed 3 hrs	10	50	25 (C <sub>6</sub> H <sub>6</sub> )	30	AIR	87	30
165°C 12 hrs	3.4	30	-	30	Vac	69	0.8
165°C 7 hrs	3.9	35	-	-	Vac	50	0.6



Table-10

Acetylation of POM with pyridine as catalyst

Molecular wt of sample ...35,000

Irradiation temperature =  $52 \pm 2^\circ\text{C}$

Temp & time of Acetylation	Ratio of POM to AC <sub>2</sub> O	Composition		Atmos-phere	Yield (%)	wt. % loss in 30 min at 222°C in N <sub>2</sub>
		Toluene (ml)	Catalyst (ml)			
160°C, 3 hrs	1:4	8	1	Vac	68	3.2
"	1:5	-	25ul	"	70	0.93
140°C, 3 hrs	1:5	-	25ul	"	75	11.4
160°C, 3 hrs	1:5	-	50ul	"	71	5.1
180°C, 0.5 hr	1:5	-	125ul	"	69	3.0
180°C, 1 hr	1:5	-	125ul	"	80	2.4
145°C, 0.5 hr refluxed	1:10	-	1	air	87	18
"	1:8	-	1	air	88	23
145°C 3 hrs refluxed	1:10	-	1	N <sub>2</sub>	84	12.3
"	1:5	25ml (C <sub>6</sub> H <sub>6</sub> )	0.5	N <sub>2</sub>	87	26
" 4 hrs	1:5	25ml (C <sub>6</sub> H <sub>6</sub> )	-	N <sub>2</sub>	80	26
"	1:7	100ml DMF	1	air	61	1.2
Slowly added AC <sub>2</sub> O to POM at 139°C 4 hrs reflux	1:7	-	1	air	76	6
165°C 3 hrs	1:10	-	0.3	Vac	74	0.4
121°C 17 hrs	1:10	-	0.1	"	66	8.1
130°C 3 hrs						
100+20°C 2 hrs +1Mrad dose	1:5	-	1	air	94	16.2
150°C 2 hrs	1:12	-	0.1	Vac	84	2.7
165°C 1 hr						

Table-11

Catalyst concn. with respect to $Ac_2O$	POM: $Ac_2O$	Yield of stabilised polymer (%)	Thermal stability at $222^{\circ}C$ in $N_2$ wt.loss% min
0.2%	1:8	88	0.09%
0.2%	1:5	78.5	-
0.2%	1:3	90.0	0.24%
0.2% + 0.5% of Diphenylamine	1:8	90.0	0.1%
0.6%	1:8	89.5	0.26%
1.0%	1:8	88.2	0.1%
0.1%	1:8	90.1	0.1%

The contents of the vessel were cooled to about  $20^{\circ}C$  and then one part of benzene was added to the mixture. The solid was washed twice with benzene (2 parts), thrice with acetone (2 parts), thrice with water (6 parts) and six times with acetone containing 0.1% by weight of diphenylamine. The product was dried at  $45^{\circ}C$  under vacuum for 24 hrs.

The thermal stability of the product was determined in a nitrogen atmosphere at  $220 \pm 2^{\circ}C$  and was found to be 0.089% loss per minute during a period of 30 min.

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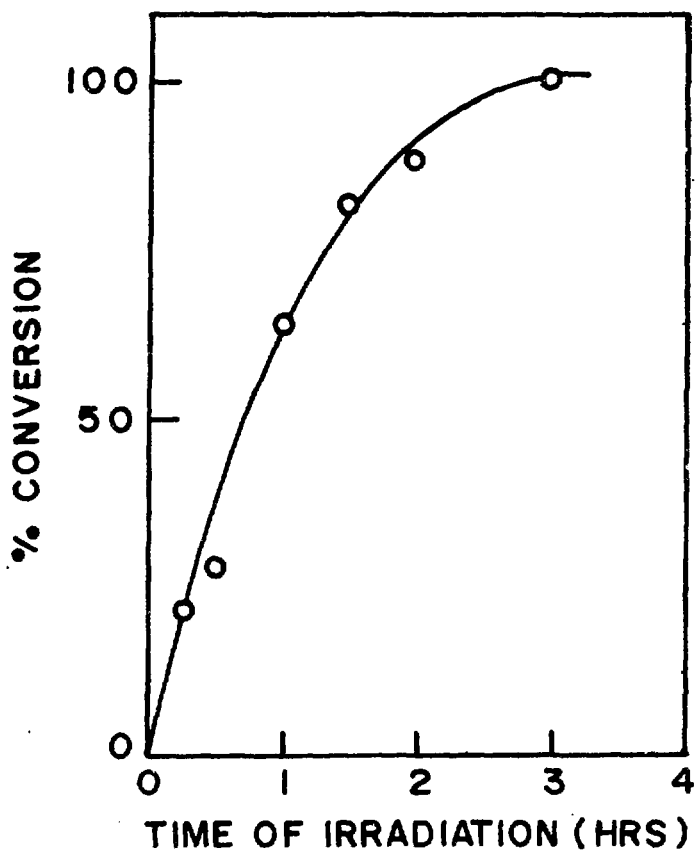


FIG. 1 INSOURCE POLYMERIZATION  
OF SUPER DRY TRIOXANE :  
PLOT OF CONVERSION AGAINST  
DOSE AT 51°C (DOSE RATE :  
 $3.13 \times 10^5$  Rads / Hr.)

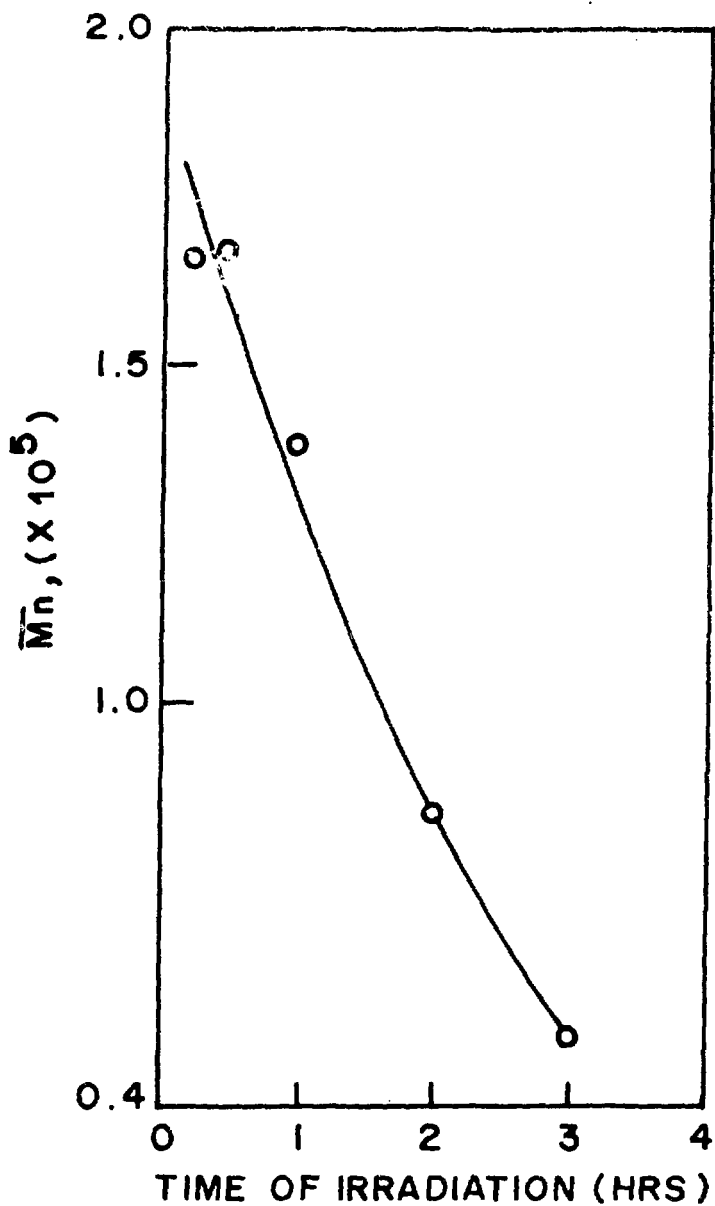


FIG. 2 INSOURCE POLYMERIZATION OF SUPER DRY TRIOXANE : PLOT OF MOLECULAR WEIGHT AGAINST RADIATION DOSE AT 51°C (DOSE RATE :  $3.13 \times 10^5$  Rads/Hr.)

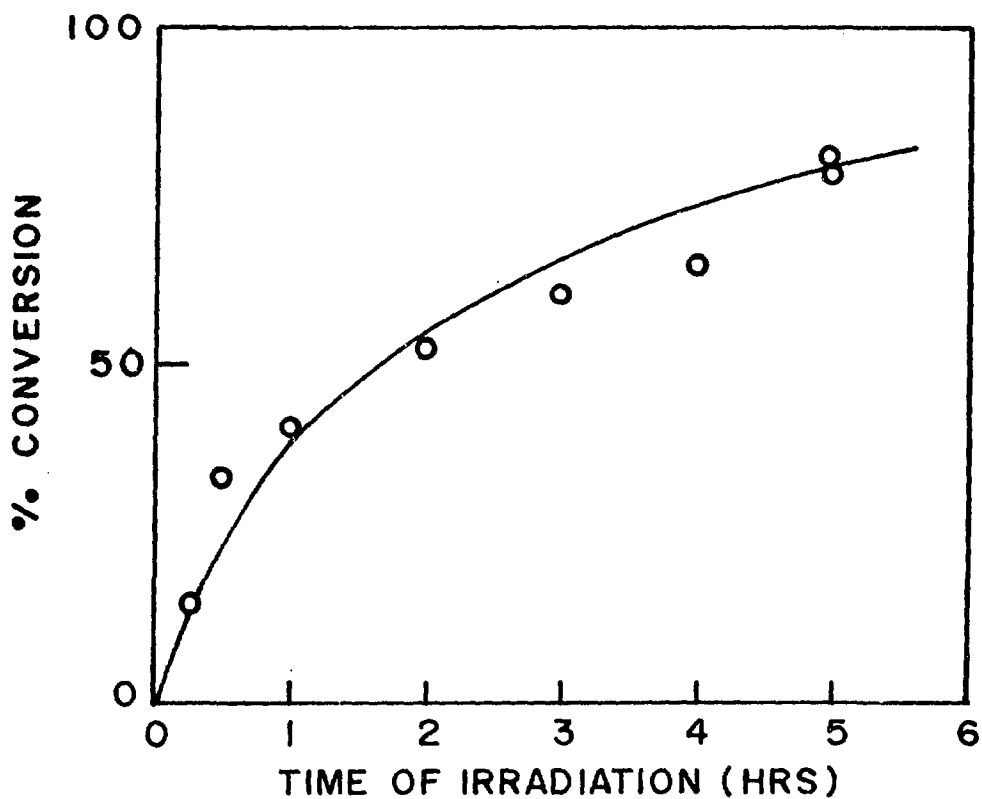


FIG.3 POST POLYMERIZATION OF SUPER DRY TRIOXANE: PLOT OF CONVERSION AGAINST TIME OF ANNEALING AT 55 °C

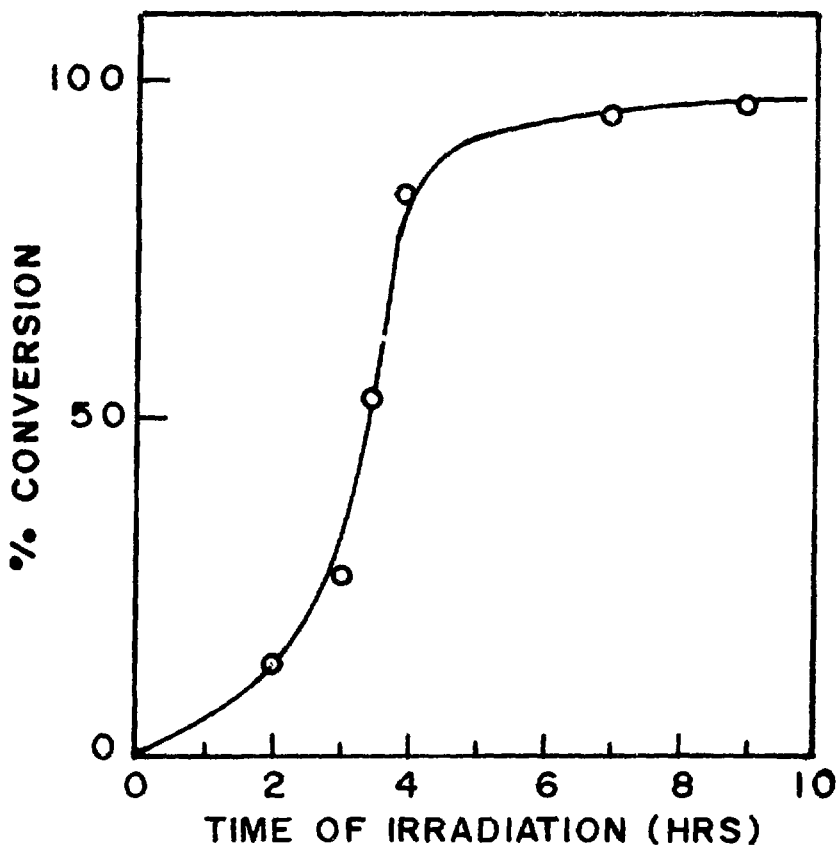


FIG. 4 INSOURCE POLYMERIZATION OF  
TRIOXANE PURIFIED BY BENZENE  
METHOD: PLOT OF CONVERSION  
AGAINST DOSE AT 51 °C  
(DOSE RATE : 0.055 Mrads/Hr.)

