

SYNTHESIS STUDIES OF POLY-m-PHENOXYLENE\*

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ABSTRACT

Many of the variables affecting the synthesis of poly-m-phenoxyene via self-condensation of potassium m-halophenoxides have been studied. The most significant factors affecting the molecular weight are carbon-carbon rather than carbon-oxygen coupling and cyclization. Non-polar solvents reduce the ionization of the starting salt and so reduce carbon-carbon coupling. Cyclization is less at high concentration of starting materials relative to solvent and since bulk polymerization is not feasible due to the exothermic nature of the reaction, heterogeneous reaction in highly non-polar medium gives highest degree of polymerization yet attained.

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Basically there is little novelty in suggesting that polymers composed of alternating phenylene and oxygen units might have interesting thermal stability. Recent publications by Hay, et al<sup>1</sup>, Staffin and Price<sup>2</sup> in this country, and by Golden<sup>3</sup>, abroad, indicate the continuing interest in polymers of such structure. Interestingly the bulk of the published work in this field covers poly-p-phenoxyene (or poly-p-phenylene oxide) and substituted poly-p-phenoxyenes only. Indeed except for work on the "chain-stopped" oligomers of interest as lubricants<sup>4,5,6</sup>, poly-m-phenoxyene has received scant attention. The only mention of such a polymer, of which the authors are aware, is that of thermal stability data presented by Wright<sup>7</sup>. The fact is, that in addition to the obvious, attractive thermal stability possible in poly-m-phenoxyene, the "amorphous nature"<sup>4</sup> of the m-phenoxyene unit suggests interesting physical properties for such a polymer, including the possibility of elastomeric properties. Such was the basis for conducting the work herein reported.

Synthesis of the desired poly-m-phenoxyene, because of the desired configuration, obviously cannot be approached through the attractive oxidative and free-radical reactions developed by Hays and Price, respectively. The only alternative is a displacement reaction such as that of the Ullman ether synthesis, utilizing reaction of the alkali metal salt of a phenol with a halogenated compound under the influence of copper catalyst. For polymer formation two routes are theoretically feasible, condensation of a dihydroxy compound with a dihalo compound or self-condensation of a material having both hydroxyl and halogen in the same

\*Poly-m-phenylene oxide,  $(\text{m-C}_6\text{H}_4\text{O})_n$

compound. In earlier work on the synthesis of oligomers of poly-m-phenoxyene for lubricants it was shown that the only readily accessible dihydric compound, resorcinol, failed to undergo the desired reaction. This leaves only the second alternative, that of self-condensation of (salts of) m-halophenol, and higher analogs, as the sole available route (by straightforward reaction schemes) for preparation of poly-m-phenoxyene.

Limited self-condensation of alkali-metal salts of m-bromophenol had previously been used for the preparations of intermediates for lubricants with reasonable success. This only means, however, that the products of such reaction were not so grossly contaminated that they could not be adequately purified by conventional techniques. Since essentially zero per-cent is the limiting amount of side-reaction that can be tolerated in a polymer forming reaction, a series of studies involving investigation of homogeneous vs heterogeneous conditions, effect of solvent, catalyst, catalyst addition temperature, light, concentration and alkali metal were undertaken. The effects of some of these variables on the polymerization as indicated by effect on the molecular weight are discussed.

## EXPERIMENTAL

### A. "Homogeneous" Conditions

Homogeneity in a variety of solvents was sought by allowing water present in the starting 87% KOH, water of reaction and, in some cases, added water to remain in the reaction mixture. In general, the moist solvent so attained provided homogeneous reaction mixtures. Solvents used in these experiments included dimethylformamide, phenyl ether, pyridine, nitrobenzene, dimethyl sulfoxide, xylene, pyridine and diethyl carbitol. Reaction temperatures varied from 110°C for pyridine to 180°C for phenyl ether and for nitrobenzene. Two slightly different methods of performing the reactions were used; in the first 87% KOH pellets (0.5 mole), m-bromophenol (0.5 mole), 1 to 2 grams of copper powder catalyst, and solvent were charged together and allowed to react under N<sub>2</sub> flow with stirring. In the second reaction method, m-bromophenol, copper catalyst, and solvent were charged and heated to the reaction temperature and then an equimolar quantity of KOH in concentrated aqueous solution was added dropwise. Products were isolated by extraction or precipitation, as fitted the individual case, and were redissolved and reprecipitated before analyses. Determination of molecular weight by freezing point depression of p-dibromobenzene was performed where solubility was appropriate, and analyses for bromine and hydroxyl<sup>8</sup> were carried out.

Comparison of end group analyses, as confirmed by infrared spectra, indicated that none of the polymers so prepared was authentic poly-m-phenoxyene. Results for these preparations are exemplified by results for a run in phenyl ether and one in nitrobenzene as shown in Table I.

### B. Anhydrous Conditions

m-Bromophenol and m-chlorophenol (Eastman) were purified by passage of a 50% solution in one to one benzene/ether mixture through an alumina column, followed by removal of solvents by distillation and then distillation at reduced pressure. The anhydrous alkali metal salts of m-halophenols were prepared by azeotropic distillation of water with benzene from a concentrated aqueous salt solution under nitrogen. Benzene was displaced by addition of solvent with

concurrent distillation. Copper powder catalyst (originally 1 g. but in later experiments 3 g.) was added, preferably before the reaction mixture temperature reached 100°. Reaction times and temperatures were varied from 2 to 88 hours and from 120° to 250°C with preferred temperatures being 180° to 200°C.

In general, the reaction mixtures were cooled to room temperature, diluted with benzene and the benzene solution filtered and washed. The solution was then concentrated to 50-75 ml and the polymer precipitated by addition to 2-1/2 to 3 liters of methanol. The polymer was taken up in 50 to 100 ml of benzene, or in later experiments a 1 to 1 mixture of benzene/chloroform, chilled and filtered. At this point the precipitate was a mixture of small amounts of unidentified "trash" and in some cases low molecular weight cyclic oligomers. The filtrate was then added to methanol to precipitate polymer, which was recycled through the above steps before final freeze-drying from benzene solution. Polymers so prepared in general have flow points of 120 to 130°, except where cyclization has been extensive, in which case flow points may be as low as 65 to 75°C.

Microanalytical analyses for carbon, hydrogen and halogen were obtained from either Schwartzkopf Microanalytical Laboratories, Woodside, Long Island, N.Y. or Dr. Carol K. Fitz, Needham Heights, Mass. Analysis for active hydrogen was by Schwartzkopf Microanalytical Laboratories. Vapor pressure osmometric (VPO) molecular weight determinations were performed in this Laboratory using a Mechrolab Model 301 Vapor Pressure Osmometer. Determination of molecular weights by viscometry measurements were carried out in phenyl ether and/or benzene using the approximations  $a = 1$  and  $K = 2 \times 10^{-5}$  in the Staudinger equation,  $[\eta] = KM^a$ .

### C. Cyclic Oligomers

Small quantities of crystalline products were isolated from several of the polymer preparations by precipitation from a benzene or benzene/chloroform solution of poly-*m*-phenoxyene, or were collected as a sublimate in reactions run under reduced pressure. In general yields were 100 mg or less though in two cases yields were on the order of 250 mg. The crystalline products were separated into two components when sufficient quantities were on hand by recrystallization from benzene. Where yields were insufficient to allow separation, both fractions were nevertheless demonstrable by infrared spectra.

One of the larger batches was separated and analyzed as follows: the crystalline precipitate was recrystallized from benzene to afford two fractions. The larger first crop melted at 236°, while the second melted at 275°.

Microanalysis: Calculated for  $(C_6H_4O)_3$  : C, 78.25%; H, 4.38%.

Found\*: 275° fraction: C, 78.93%; H, 4.79%; Br, 0%, Active H, 0%; Mol. wt. 312.  
236° fraction: C, 78.51%; H, 4.33%; Br, 0%, Active H, Trace;  
Mol. wt. could not be determined due to insolubility.

Theoretical molecular weight for  $(C_6H_4O)_3$  is 276 and for  $(C_6H_4O)_4$  is 368.

\*By Schwartzkopf Microanalytical Laboratories

The analysis for another batch of material which was not separable because of the small sample size but which contained both components (by infrared spectra) was:

Found\*: C, 78.97%; H, 4.69%, Br, 0%; Active H, 0.05% and Mol. wt. 339.

## RESULTS AND DISCUSSION

The results for representative syntheses are shown in Tables 1 through 5 in which are tabulated significant experimental details together with results of various measures of the molecular weights of the resultant polymers.

Table 1 shows results for two runs made under "homogeneous", that is to say moist, conditions. In both of these, as well as in several more for which results are not presented, the equivalent weight based on hydroxyl content is significantly lower than that based on bromine content. This would serve to indicate that extensive carbon-carbon coupling occurred.

The importance of the use of copper as a catalyst is illustrated by the results given in Table 2. Without added catalyst the reaction proceeds only to a limited extent. Cuprous oxide apparently has some catalytic activity, but is obviously less efficient than powdered copper metal. These reactions illustrate an important further point. Both the cuprous oxide and the metallic copper catalyzed reactions yielded crystalline cyclic oligomers and the end group analyses for both polymers, as compared to the vapor pressure osmometry (VPO) values, indicate that these also contain (large) cyclic components.

Since many of the polymerizations were carried out over extensive periods of time, it was inevitable that attack on glassware would be evident. Such attack shows up in etching of the glassware itself (noticeable after several runs have been made in the same flask) and in ash content found on microanalysis. In an effort to avoid this factor several runs were made in Monel metal flasks (results not presented) in which it was found that reaction either did not take place at all or else was seriously inhibited. In an effort to differentiate between the possible causes of this inhibition, either inhibition by Monel or by lack of illumination of the reactants, a series of runs were set up using identical conditions except for the flask. These experiments are shown in Table 3 and tend to indicate a minor role for the effect of light.

The effect of concentration on the degree of polymerization is indicated in Table 4. Decreasing the amount of solvent tends to promote higher degree of polymerization. Several attempts to achieve bulk polymerization of potassium *m*-bromophenoxide gave only very low yields of polymer, however, due largely to decomposition engendered by uncontrollable exothermic heating. The closest approach to true bulk polymerization is that of beginning the reaction in a solvent followed by removal of solvent by reduced pressure distillation while holding constant temperature. This technique is represented in the table as 100 → None under the heading Vol. of Solvent and is shown by the analytical results as being no more effective than the use of high concentration of starting material relative to solvent.

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TABLE 1. ATTEMPTED SYNTHESIS OF POLY-m-PHENOXYLENE, "HOMOGENEOUS REACTION CONDITIONS"

Reagents: m-Bromophenol, aqueous KOH, copper catalyst

Time: 2 Hours @ 180°C

<u>SOLVENT</u>	<u>Cryoscopic</u>	<u>Bromine</u>	<u>Hydroxyl</u>
Phenyl Ether	--	16,500	265
Nitrobenzene	5400	3,300	800

TABLE 2. SYNTHESIS OF POLY-m-PHENOXYLENE, "EFFECT OF COPPER CATALYST"

<u>Catalyst</u>	<u>Time (hrs.)</u>	<u>Temp. °C</u>	<u>VPO*</u>	<u>Molecular Weight</u>		
				<u>Bromine</u>	<u>Active H</u>	<u>Active H</u>
None	60	175-180	930	1100	--	--
Cu <sub>2</sub> O	60	150	1400	3700	5000	5000
Cu	36	150	2000	7200	5000	5000

Reagents: Anhydrous potassium m-bromophenoxide

Solvent: Phenyl ether

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\*Vapor Pressure Osmometry

TABLE 3. SYNTHESIS OF POLY-m-PHENOXYLENE, "EFFECT OF LIGHT"

Reagents: Anhydrous potassium m-chlorophenoxide, copper catalyst  
Solvent: Phenyl ether  
Time: 40 Hours at 185°C

<u>Flask</u>	<u>Molecular Weight</u>			
	<u>VPO</u>	<u>Chlorine</u>	<u>Active H</u>	<u>Viscosity</u>
Copper	1500	7100	3300	3700
Amber Coated Pyrex	1500	7100	3300	3250
Regular Pyrex	1900	5900	2500	3500

TABLE 4. SYNTHESIS OF POLY-m-PHENOXYLENE, "EFFECT OF CONCENTRATION"

Reagents: One-quarter mole anhydrous potassium m-chlorophenoxide, copper catalyst  
Solvent: Phenyl ether  
Time: 40 Hours at 185°C

Vol. of Solvent ml	<u>Molecular Weight</u>		
	<u>VPO</u>	<u>Chloride</u>	<u>Active H</u>
200	2000	5900	2500
100	2400	5500	5000
50	2900	6500	3333
100 → None*	2800	7100	5000

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 \* Reaction started in 100 ml of phenyl ether, then solvent removed by reduced pressure distillation keeping temperature constant.



TABLE 5. SYNTHESIS OF POLY-m-PHENOXYLENE, "ANHYDROUS CONDITIONS"

Solvent	Time	Temp.	VPO	Molecular Weight			Visc.
				Halogen	Active H		
Reagents: Anhydrous Potassium <u>m</u> -Bromophenoxide, Copper Catalyst							
Phenyl Ether	5	180	2700	3000	3300	3100	
Diphenyl	6	170	3600	20,000	3300	-----	
Benzophenone	7	185-205	1600	29,000	--	1900	
Phenyl Ether → None*	80	155	3900	5,600	4000	8000	
Phenyl Ether	48+	120+	3100	20,000	>4000	6800	
	18	150					
Reagents: Anhydrous Potassium <u>m</u> -chlorophenoxide, copper catalyst							
Phenyl Ether → None*	88	175	5500	5,900	2500	--	
Eicosane	62	180	6900	--	--	9800	

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 \* Reaction started in phenyl ether, then solvent removed under reduced pressure.

# Contrails

Table 5 presents the results for a number of representative polymerizations conducted in various solvent media. The results indicate a higher degree of polymerization is attained the less polar is the solvent. Also, indicated is a higher degree of polymerization with higher temperature and longer reaction times. Noteworthy also is a tendency for the molecular weight as determined by viscometry vs that obtained by VPO to rise from a one to one relationship to as high as two to one with longer reaction times.

The results for the reaction conducted in eicosane were incomplete at the time of writing. They are of especial interest though in that the molecular weight as measured by both VPO and viscometry were the highest yet attained and since reaction in eicosane is the only instance of a completely heterogeneous reaction. All other solvent systems were found to give homogeneous reaction, either dissolving the starting metal halophenoxide (as in the case of benzophenone) or dissolving the oligomeric products at onset of polymerization.

At the beginning of this program, it was acknowledged that the probability of preparing high molecular weight poly-m-phenoxyene via the Ullmann reaction was poor unless all competing side reactions could be effectively suppressed. In this connection particular attention was given to the results of Kornblum and Lurie<sup>9</sup> who had shown that in the preparation of phenyl benzyl ethers carbon-carbon coupling was enhanced by heterogeneous reaction and was suppressed by homogeneous reaction conditions. These results led us to undertake experiments designed to give homogeneous reaction conditions, which were largely conditions such that water was present in the reaction mixture. The results for these reactions indicated that in the presence of water carbon-carbon coupling was high. Further, comparison of results for polymerizations run under anhydrous conditions show that for the preparation of poly-m-phenoxyene the more non-polar is the solvent, then the more heterogeneous is the reaction, and that under such conditions, the degree of polymerization reaches higher values. It is not possible to rigorously prove that the higher molecular weight polymers receive no contribution from carbon-carbon coupling since analyses for residual hydroxyl (or active hydrogen) are not sufficiently accurate by virtue of the very low percentage content of these groups. It bears noting, however, that the greater the polarity of the solvent, then the higher would be the degree of ionization of the metal halophenoxide, and as ionization increases, so should carbon-carbon coupling increase.

On the other hand, the higher degree of polymerization achievable under heterogeneous conditions may be due at least in part to still another factor. Cyclization is strongly evident under conditions leading to low reaction rates and under conditions of high dilution. Heterogeneity should provide more intimate contact between catalyst and reactant thus maximizing reaction rates at a given temperature and at the same time should remove the concentration effect. Thus, reaction under heterogeneous conditions would be expected to give higher degree of polymerization due to suppression of cyclization.

THERMOGRAVIMETRIC ANALYSIS OF POLY-m-PHENOXYLENE

Figures 1 and 2 show typical results of thermogravimetric analyses (TGA) of poly-m-phenoxyene in nitrogen and in air, respectively, at a heating rate of 180°C per hour. Except for the expected difference in final weight of residue, there is essentially no difference in the character of the plots or temperature of decomposition due to the atmosphere. These results tend to indicate that the oxidation of the polymer is a non-chain reaction and is the result of oxidative attack on the products of thermal decomposition of the polymer.

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# *Contrails*

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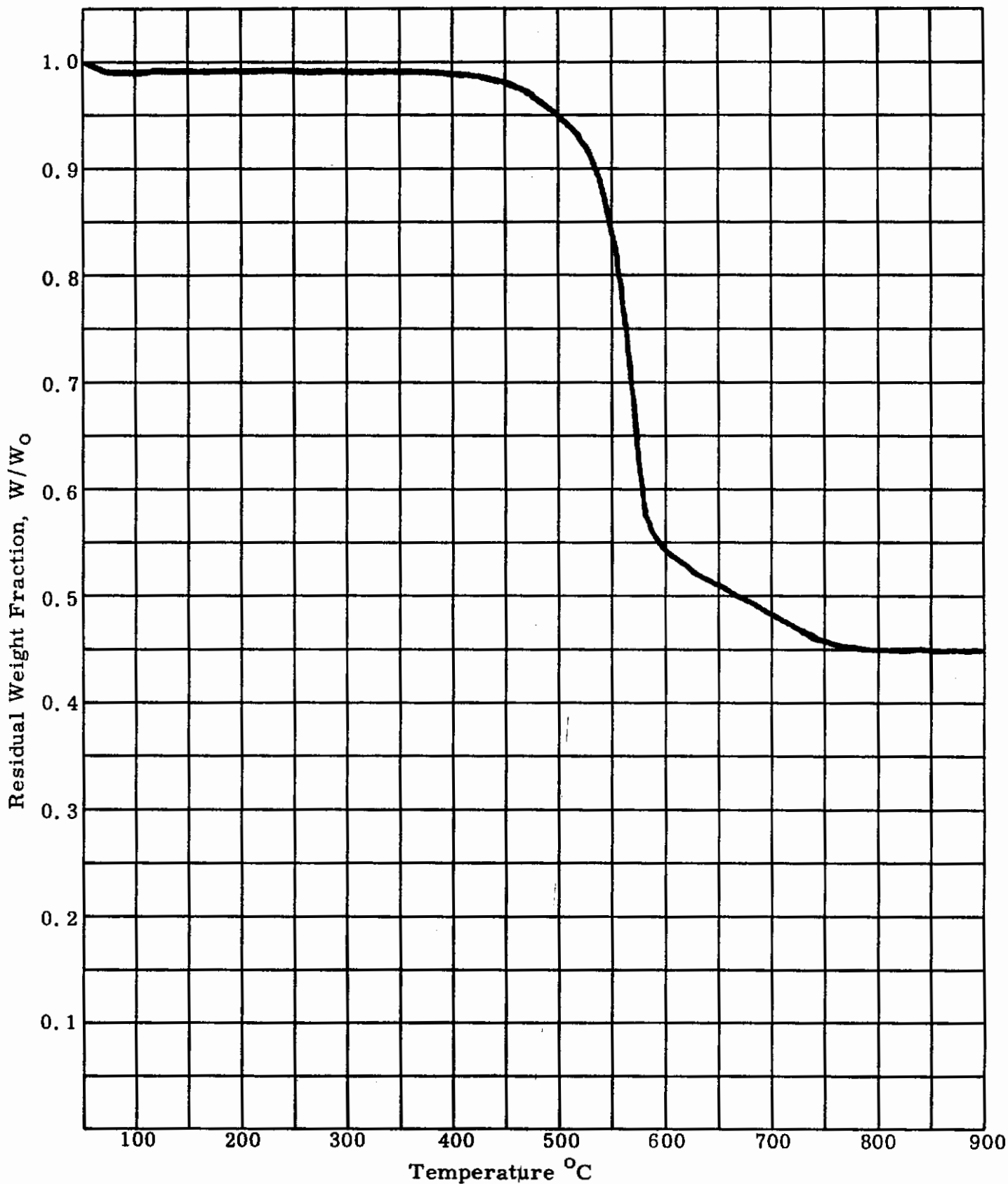


Figure 1. TGA In Dry Nitrogen At 180°C Per Hour For Poly-m-phenoxyene ( $M_{VPO} = 3900$ )

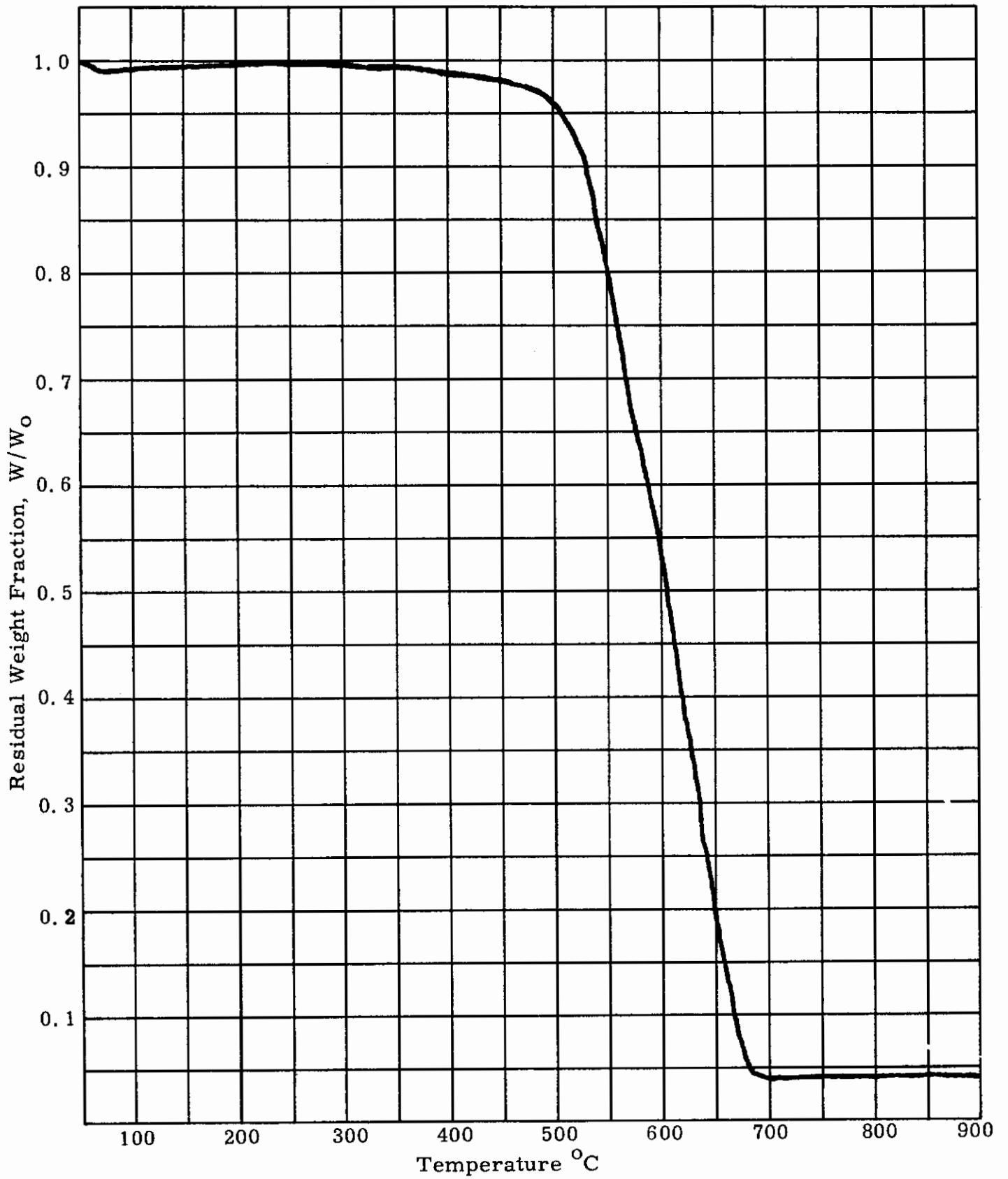


Figure 2. TGA In Air At 180°C Per Hour For Poly-m-phenoxyene ( $\bar{M}_{VPO} = 3900$ )