United States Rubber

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DEVELOPMENT DEPARTMENT

QUARTERLY PROGRESS REPORT #7

February 1, 1963 - April 30, 1963

Synthesis of Regulated Structure Polyphenylether-Siloxane Block Copolymers

Contract # DA-19-020-ORD-5507

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ABSTRACT

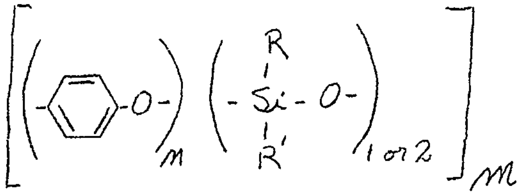
Condensation of 4,4'-dihydroxydiphenylether with dichlorosilanes has resulted in polymers of relatively high molecular weight. A crosslinking reaction occurred simultaneously precluding measurement of the exact degree of polymerization, but monomer purity has been shown to be of critical importance.

An quarter-replicate factorial experiment to assess the effects of changes in temperature, reaction time, and reactant concentrations has been completed. Alkaline hydrolysis of 4,4'-dibromodiphenylether results in a mixture of as many as eleven different, organic compounds. The experimental results point the way toward elimination of some of these compounds as by-products in the synthesis of 4,4'-dihydroxydiphenylether.

A few trials has shown that it is possible to form 4,4'-dihydroxydiphenylether through intermolecular dehydration of hydroquinone. Hydroxy substituted polyphenylethers might also result from similar reactions.

I. Introduction

This contract is directed toward the synthesis of high temperature elastomers consisting of regulated structure, polyphenylether siloxane block copolymers of the type:



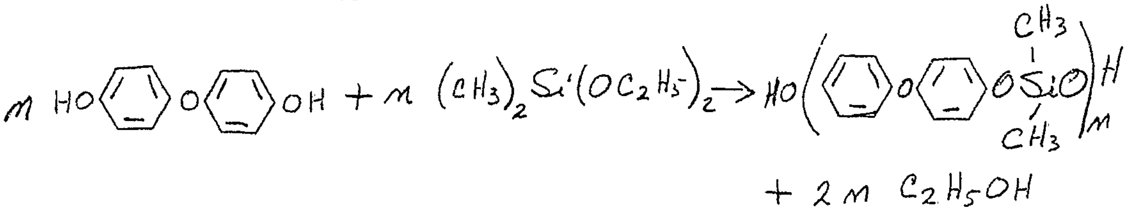
where:

n = 2, 3, ...10...

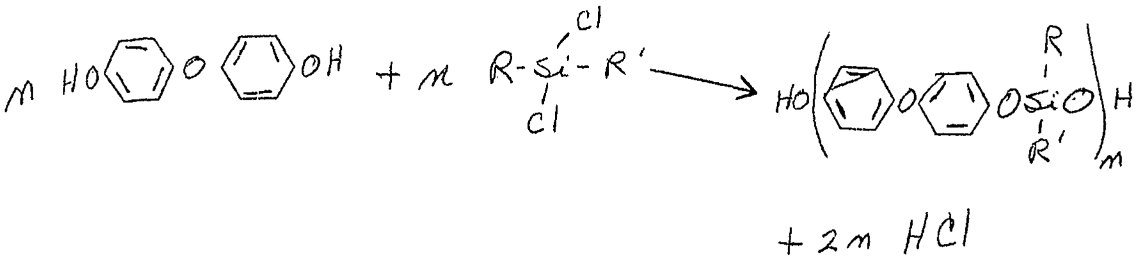
m = 100, ...300...

R & R' are alkyl, aryl, or vinyl groups

The principle effort thus far has been directed toward the synthesis of the monomer units. This having been done, a number of polymerizations have been carried out. Two polymerizations were carried out by an alcoholysis condensation reaction of the type:



The other polymerizations were carried out as direct condensations between the chlorosilanes and dihydroxydiphenylethers, for example:



Polymerizations reported previously have resulted in polymers of low molecular weight, and a painstaking effort was made to identify and remove any impurities in the monomers which might act to limit the molecular weight, either as diluents or "chain stoppers". As a result, polymers of high molecular weight have been produced for the first time.

An experimental design was set up earlier to determine which reaction conditions would result in the cleanest yield of 4,4'-dihydroxydiphenylether, one of the monomers. The work on this series of experiments is nearing completion and some indications of desirable reaction conditions are available. Thin layer chromatography has proved invaluable in this work, resulting in the separation of 11 compounds in these reaction mixtures.

The work of monomer synthesis is now directed to the preparation of dihydroxy derivatives of polyphenylethers. Dehydration of hydroquinone or resorcinol is being considered as a possible route as is the condensation of aryl halides with the same compounds.

The polymers mentioned above are of relatively high molecular weight, but are insoluble in common organic solvents. It is believed that these polymers were crosslinked during reaction. The immediate problem here is to avoid such premature crosslinking.

II. Discussion & Results

A. Polymerization

Five attempts were made to condense DHDPE with silanes. Two of these resulted in polymers of relatively high molecular weight, and two resulted in unexplained mishaps.

Polymerization 734-51A was designed to use equimolar quantities of the reactants and to result in a 28% solution of polymer in xylene. The reaction proceeded steadily, and the relative flow time reached 190 in 193 hours. Shortly thereafter, the polymer began to precipitate from solution and the relative flow time of the remaining solution dropped to 22. This drop may be only a concentration effect. FIGURE I presents graphically the data for this reaction. 95.5% of the theoretical amount of HCl was recovered.

The xylene was removed from the reaction vessel and replaced by tetrahydrofuran, a solvent used successfully with previous samples. The polymer broke up into swollen chunks, but would not dissolve. None of the common organic solvents dissolved the polymer. Boiling o-dichlorobenzene dissolved a portion, but not all, of the polymer. The molecular weight of this soluble portion is not yet available, and it is not possible to determine the molecular weight of the whole polymer, but a sample taken when the relative flow time was 1.8 has a molecular weight of 1350.

This polymer was subjected to TGA measurements in nitrogen at a heating rate of approximately 5°C./min. until a temperature of 360°C. was reached. The polymer was then held at this temperature for four hours. The weight loss was 10% up to 360°C. An additional 20% was lost during the four hours at 360°C. These measurements are shown graphically in FIGURES II and III.

A bulk polymerization was run primarily as a check on materials when a solution polymerization, 734-42A, appeared to be atypical. This bulk polymerization, 734-45A, employed equimolar quantities of DHDPE and DPDCS*. The mixture was heated for three hours at 205°C., then placed in a vacuum oven at 140°C. After 96 hours in the oven, this polymer was an amber solid even at 140°C. This polymer, too, is insoluble in common organic solvents.

These two polymerizations should be compared. In each case, solid polymers are obtained which are thought to have a relatively high molecular weight. In the case of 51A, insolubility could be easily explained as being due to cross-linking through the pendant vinyl groups present. In the bulk polymerization, 45A, the MVDCS was omitted as a matter of convenience, and there are no vinyl groups present. In view of the narrow boiling point ranges observed during the distillation of the silanes, it seems unlikely that any tri- or tetra-functional silanes are present. However, this is more probable as an explanation than an attempt to explain the insolubility as being due to extremely high molecular weight. Although the latter explanation is not impossible, it is more likely that a polymer would precipitate at low degrees of polymerization than at high degrees of polymerization, except possibly for molecules which can be approximated as rigid rods. Molecular entanglement is not a tenable explanation for the original precipitation because the polymer cannot be redissolved. Polyfunctional silanes as contaminants are the most likely reason for the polymer precipitation at this point.

A solution polymerization, 734-42A, was run in a manner similar to the previously discussed solution polymerization. This, however, was designed to produce a 10% polymer solution in xylene. The silane was added as long as the relative flow time increased after each addition, and eventually 150% of the equimolar quantity of silane was added. The relative flow time reached 1.25 (see FIGURE IV), and 97.6% of the theoretical amount of HCl was trapped. Of course, the mistake made in this polymerization was in the timing. It was thought that the relative flow time would increase rather rapidly, and excess silane was added before the polymer chains had had time to grow appreciably.

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* DPDCS is diphenyldichlorosilane, MVDCS is methylvinyl dichlorosilane.

This polymerization, the first of the series, was atypical in several respects. An unexplained green cast appeared in the acid trap. This disappeared when the xylene was distilled from the reaction vessel at the end of the reaction. The polymer's appearance was unusual: it was tan in color rather than amber, liquid at room temperature rather than solid, and its appearance suggested a dispersion. Tetrahydrofuran was used to dissolve the syrupy polymer, and a white, granular material (2.5%) was left behind. The syrupy polymer, when freed of tetrahydrofuran was an amber fluid which slowly changed to a brittle glass when stored in the vacuum oven at 140°C. Elemental analysis of the syrup is consistent with that of a copolymer of diphenylether with siloxanes.

The granular powder was found to have an initial melting point range of 304-310°C. A portion, however, melted only at 400-440°C. The material is definitely organic in character, and is an amber, viscous fluid when melted. Infrared and elemental analyses are not yet available for this material.

Two further attempts at solution polymerization, 734-59A and 60B, are worth mentioning only because of the completely unexpected results. No polymers were obtained because of loss of the monomer solutions.

In the first case, a 10% solution of DHDPE in boiling xylene was prepared. The source of heat was removed temporarily to allow inspection of the flask, and the DHDPE began to precipitate. The heat of crystallization was apparently great enough to cause furious boiling and the solution foamed into all parts of the apparatus, depositing DHDPE as it went.

In the second case, this mishap was avoided and the silanes were added. The reaction mixture suddenly boiled up and generated enough pressure to blow a weight buret from its joint. The reaction mixture then followed the buret. Although all the silane was added initially, it is not felt that this was responsible for the mishap. The condensation proceeds sufficiently slowly that its heat of reaction should not be responsible for the increased boiling rate. No satisfactory explanation has been devised.

B. Synthesis of 4,4'-Dihydroxydiphenylether

1. Alkaline Hydrolysis of 4,4'-Dibromodiphenylether

An experimental design to determine the effects of temperature, reaction time, and concentrations of reactants upon the hydrolysis of 4,4'-dibromodiphenylether (DBDPE) to 4,4'-dihydroxydiphenylether (DHDPE) was mentioned briefly in the previous Quarterly Report. TABLE II shows the experimental conditions for eight experiments which form a quarter replicate of a complete factorial design. TABLE III presents the results determined by the techniques of thin layer chromatography and TABLE IV contains the results of statistical analysis of the results.

Eleven distinct components were discovered in the reaction mixtures as shown in the tables and in FIGURE V. These include DHDPE and DBDPE, of course, as well as alkoxy substituted compounds, but it is difficult to imagine eleven compounds which could result from this reaction. Fraction 5 is DHDPE, fraction 11 is DBDPE; the other fractions are not identified as yet. It is possible, however, to discuss the results even before the compounds are known. Those fractions which are closest to DHDPE in solubility characteristics should be minimized at the same time as the yield of DHDPE is increased in order to simplify purification of the desired product. TABLE IV shows how this may be done.

TABLE IV contains the changes to be expected in the various fractions for a unit change in the variables under consideration. It is evident that increasing the time of reaction, the alcohol to water ratio, or the temperature will increase the percent of DHDPE in the organic materials. Increasing the temperature, however, will also increase the percentage of contaminants. The first indications are, then, that the water to alcohol ratio should be high and the reaction time should be as long as practical (within limits). The temperature should be kept low, again within limits. It would be highly speculative to say more on the basis of these eight experiments. All the variables listed, including the interactions, are confounded by other effects. It would require eight more experiments plus a few replicates to clearly establish the effects. Interactions which would be of interest, for example, might include DBDPE concentration with time and temperature as well as catalyst-temperature interactions.

The coefficients for the effect of changing reaction time are of interest. Some of the compounds appear to disappear if the time is increased while other appear. It would be of scientific interest to see if there is any correlation between these results and the much earlier speculations concerning consecutive or sequential reactions. However, as a reliable means of preparing DHDPE is now available, no further work is planned for this series of experiments beyond the analytical work now in progress.

It can be noted further that an increase in the alkalinity of the reaction mixture increases the yield of DHDPE (compare experiments Y60 and Y61 with Y62 and Y63). Also, the very real effect of reaction vessel conditioning shows in experiments Y59 and Y70.

2. Condensation of Hydroquinone

In Quarterly Progress Report #6, several instances were cited in which heating of DHDPE under vacuum resulted in the formation of hydroquinone. In the hope that this reaction could be reversed, several experiments have been run to try to remove water from hydroquinone. The expected product would be DHDPE and, perhaps, the dihydroxy derivatives of the polyphenylethers.

Dehydration has been attempted using sulfuric acid, orthophosphoric acid, and pyrophosphoric acid as dehydrating agents. A 2.5% yield of DHDPE was obtained with orthophosphoric acid demonstrating that the reaction is possible. A decision as to whether or not this might be a fruitful synthesis for polyphenylether derivatives awaits analytical results.

III. Experimental

A. Polymerization

1. Monomer Preparations

The condensation polymerizations discussed all involve DHDPE and DPDCS. Some contain MVDCS as well. The preparation and purification of the DHDPE has been treated in detail in earlier reports. It is sufficient to say here that both samples used are essentially pure by thin layer chromatography. The material coded 141-7A has a hydroxyl number of 549.7, 141-28A has a hydroxyl number of 555.3. The theoretical value would be 554.9.

The silanes were purified by distillation. MVDCS (Union Carbide A-157) was distilled at atmospheric pressure under nitrogen. A Vigreaux column was used. A forerun amounting to 20% boiled over the range 75 - 83°C., largely in two fractions. The main fraction distilled at 92.0 - 92.4°C. and amounted to 50% of the raw stock. The product is a colorless liquid.

Vacuum distillation through a Widmer column was used to purify DPDCS. A nitrogen purge eliminated oxygen from the system. The raw stock appeared to be relatively pure. After a very small forerun, DPDCS distilled in the temperature range 143.0 - 143.5°C. at 6 mm. Hg. This too was a colorless liquid.

2. Polymerizations

Bulk polymerization is accomplished quite simply if MVDCS is not included. DHDPE and DPDCS are added in equimolar quantities to an open flask which is then heated to a relatively high temperature on a hot plate. Hydrogen chloride evolution results in bubbling which can be used to assess the rate of reaction. When the reaction begins to slow, the flask is then moved to a vacuum oven where it can be conveniently stored at 140°C. for extended periods of time.

Solution polymerization requires a more elaborate apparatus. A 500 ml. R.B. flask was used as the reaction vessel in all the solution polymerizations discussed in this report. This flask was equipped with a reflux condenser, a dropping funnel (for silanes), and a viscometer. Nitrogen is continuously introduced into the system to maintain a slight positive pressure. Exit gases pass through a glass frit in a vessel filled with sodium hydroxide solution to trap evolved hydrogen chloride.

In general, the DHDPE and xylene are introduced into the apparatus and heated to reflux (140°C.) to bring about solution. The silanes are then added. Flow time of the reaction mixture through the viscometer is measured relative to the flow time at the start, and is used as a measure of reaction. Disappearance of hydroxide from the trap is also used to determine the extent of reaction.

Specific quantities of the reactants used are given in TABLE I below. Results of these polymerizations are given graphically in FIGURES II and III, and in the discussion.

TABLE I

Condensation Polymerization

Polymer no.	DHDPE no.	DHDPE moles	DPDCS moles	MVDCS moles	Xylene mls.
734-42A	141-7A	0.1236	0.1721	0.0133	500
734-45A	141-7A	0.02954	0.02952	-	0
734-51A	141-28A	0.1236	0.1072	0.0164	125
734-59A	141-28A	0.0992	-	-	180
734-60B	141-28A	0.1013	0.1013	-	180

3. Thermal Gravimetric Analysis

An analytical balance has been modified to allow simple determination of changes in weight of a sample as a function of time at elevated temperatures. One pan of the balance has been replaced by a palladium wire which passes through the floor of the balance case to a pyrex chamber. A platinum crucible hangs from the wire inside this chamber, and a thermocouple can be inserted into the crucible. Provision is made to displace the air present with nitrogen or any other gas by purging. The pyrex chamber is wound with a nichrome heating element so that the temperature of the sample can be raised to 500°C. Lower temperatures are obtained through the use of a variable voltage supply for the heater. Weight changes are determined by manual use of the balance. Weight changes at constant temperature as a function of time are easily determined through manual operation of the balance. Weight changes at a fixed rate of temperature change can be obtained by manipulation of the voltage supply to the heater.

B. Syntheses

1. Thin Layer Chromatography-Alkaline Hydrolysis

The various reaction mixtures were neutralized with concentrated HCl and extracted with ether. The aqueous portions were then boiled to drive off any remaining 2-propanol. The lack of precipitates forming on cooling indicated that all organic material had been successfully extracted.

The solids content of the ether extracts was measured and are included in TABLE III under "Total Organics Weight". A small amount of each ether extract was evaporated and the solids redissolved in dioxane in preparation for thin layer chromatography.

Of a wide range of solvents tested by developing test plates, the solvent system affording the best and most complete separation was the mixture benzene, methanol, dioxane in the ratios 85:10:5. The separation achieved by this solvent system for the various reaction mixtures is illustrated in FIGURE V.

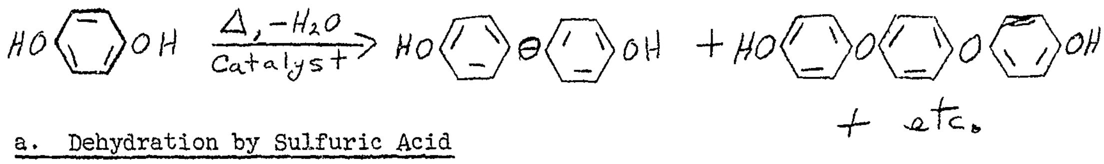
The RF values given in FIGURE V are approximate values since the values were not constant throughout a given chromatogram due to evaporation effects at the edge of the plate, local variations in solvent vapor composition, etc. In fact, it was earlier anticipated that the process could be speeded up by developing 5 plates in a tank at a time which resulted in spacing between plates of about 1-1.5 inches. It was soon found that this caused a baffling effect, seriously affecting the uniformity of the solvent vapor composition over the plate surfaces, and resulting in wide variations of the RF values in any given chromatogram. Reducing the number of plates per tank to two alleviated this problem but did not entirely eliminate it.

For the preparative work, five 20 x 20 cm. plates were developed for each of the factorial reactions. The general location of the zones was determined by spraying one of the five plates with chromic acid solution after which the plate was baked in an oven to char the organic material. This indicator technique gave guidelines by which the zones on the untreated plates could be recognized under an ultra-violet light source. The various zones were removed from the plates by scraping off the substrate in each zone area. The divided substrate areas were eluted with tetrahydrofuran to isolate the organic materials. The various solutions were then evaporated in tared containers. It should be noted that on a few occasions where developed plates stood overnight before removing the material, the zones of material became slightly discolored.

TABLE III lists the results of the thin layer chromatography work up of the factorial experiment. Eleven components in all were isolated. The amount in which they occurred in each reaction is indicated in the table as a weight percent of the total organic material present in the reaction mixture. The percent theoretical yield of the desired product, fraction 5, and the percent unreacted portion of the starting material, fraction 11, are also included in the table.

The various materials were collected into the eleven common fractions. Difficulty is being experienced in crystallizing these materials and, therefore, melting point and infrared data are not yet available.

2. Synthesis of 4,4'-Dihydroxydiphenylether via the Intermolecular Dehydration of Hydroquinone



a. Dehydration by Sulfuric Acid

1. 25 gm. of hydroquinone was readily dissolved in 150 cc. of concentrated H_2SO_4 and allowed to stand overnight. The solution was then added to a large volume of water and neutralized with 50% NaOH. No desired product was isolated.

2. A similar solution was heated at 60°C. overnight. A white precipitate in the amount of ca. 1 gm. formed slowly. After suction filtering the diluted reaction mixture, the white precipitate slowly became gray brown and took on an oily appearance and odor. The melting point range covers about 50° beginning at 110°C. This is believed to be a sulfonated hydroquinone and not the desired product.

3. Again a similar solution was heated at ca. 150°C. overnight. A black oily mixture resulted and no attempt was made to work up the reaction mixture.

b. Dehydration by Orthophosphoric Acid

1. 25 gm. of hydroquinone was added to 150 cc. of 85% orthophosphoric acid and heated at 150°C. overnight. The resulting dark reaction mixture was neutralized with 50% NaOH precipitating 0.56 gm. of a product having an infrared spectrum identical with that of 4,4'-dihydroxydiphenylether. This product, which amounts to a 2.5% yield, will be purified for melt point and molecular weight determinations.

2. 5.5 gm. of hydroquinone and 30 cc. of 85% orthophosphoric acid were placed in a thick walled pyrex tube which was then sealed so that the reaction mixture filled 3/4 of the tube. The reaction, carried out at 155°C. for four days, resulted in a black reaction mixture. Materials isolated were:

a.	black crystalline residue	- 1.1 gm.
b.	black viscous tar	- 0.5 gm.
c.	black amorphous residue	- 0.3 gm.
d.	brown crystalline ppt.	- 1.5 gm.
e.	oil residue	- 0.8 gm.

Infrared spectra will be obtained.

3. 22 gm. of hydroquinone was placed in a round bottom flask with 125 cc. of 85% orthophosphoric acid. The flask was fitted with an air condenser led to the house vacuum. The reaction was run at 160°C. under vacuum for four days and resulted in a black tarry reaction mixture. Two materials isolated were:

a.	brown precipitate	- 0.5 gm.
b.	dark brown viscous tar	- 1.5 gm.

Infrared spectra will be obtained.

c. Dehydration by Pyrophosphoric Acid

$$P_2O_5 + 2\,H_3PO_4 \cdot H_2O \longrightarrow 2H_4P_2O_7$$

$$H_4P_2O_7 + H_2O \longrightarrow H_3PO_4$$

1. 22 gm. of hydroquinone was dissolved in 50 cc. dioxane, the solution then being added to a mixture of 7.1 gm. of phosphorous pentoxide and 21.4 gm. of 85% orthophosphoric acid in a round bottom flask fitted with an air condenser. The reaction was refluxed gently overnight. No desired product was isolated from the reaction mixture although no carbonization occurred either.

2. 22 gm. of hydroquinone was added to a mixture of 15 gm. of phosphorous pentoxide and 125 cc. of 85% orthophosphoric acid in a round bottom flask fitted with an air condenser the top of which was led to the house vacuum. The reaction mixture was heated at 150°C. under vacuum overnight and resulted in 9 gm. of a black tar having a phenol or formaldehyde odor. The tar is slowly crystallizing and further analysis will await infrared results.

d. Dehydration by Oxalic Acid

1. 5 gm. of hydroquinone, dissolved in 50 cc. of dioxane, was added to 5 gm. of oxalic acid in a florence flask fitted with an air condenser. The reaction was gently refluxed overnight. No desired product was obtained.

IV. Projected Work

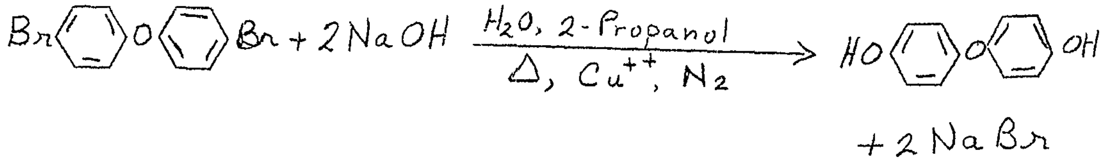
1. Determine cause of crosslinking during polymerization.
2. Continue polymerization study to determine optimum reaction conditions.
3. Start synthesis of meta-oriented, hydroxy substituted phenylether as monomer for copolymerization.
4. Complete study of hydroquinone dehydration as a source of monomers.

Manhours expended, April, 1963

R. MacFarlane, Jr.	96 hours
E. S. Yankura	168 hours

TABLE II

Factorial Experiment



Exp. #	m NaOH / m DBPE	Temp. °C.	cc. Alcohol / cc. H_2O	m DBDPE / l. Sol.	Time Hrs.	m Catalyst (in Cu^{++}) / m DBDPE
Y59	4.38	185	1	1/3	6	0
Y60	8.76	210	1/3	1/6	3	0.0188
Y61	8.76	210	1	1/3	6	0.0188
*Y62	4.38	210	1/3	1/3	3	0.0188
*Y63	4.38	210	1	2/3	6	0.0188
*Y64	4.38	185	1/3	2/3	3	0.0944
*Y65	4.38	185	1	1/3	6	0.0944
*Y66	4.38	185	1	1/3	3	0.0188
*Y67	4.38	185	1/3	2/3	6	0.0188
*Y68	4.38	210	1	2/3	3	0.0944
Y69	4.38	210	1/3	1/3	6	0.0188
Y70	4.38	185	1	1/3	6	0
*Y71	4.38	210	1/3	1/3	6	0.0944

* Belongs to eight reactions representing quarter replicate of the factorial series. Note that experiment Y69 was erroneously reported as part of the quarter replicate in QPR #6.

TABLE III

Results of Preparative Thin Layer Chromatography

Exp. #	Total Organics Wt. (gms.)	Weight % of Total Organic Material in Fraction											Yield of DHDPE % of Theory	Unreacted DBDPE %
		1	2	3	4	5	6	7	8	9	10	11		
Y59	49.7	14.7		16.1								69.1	0.0	62.3
Y60	20.1	6.3		15.2		17.5	10.6	10.0		17.7		22.5	20.8	41.0
*Y61	37.9	11.2			12.8	19.0		16.6	18.6	5.6	5.8	10.3	21.3	7.1
*Y62	35.3	16.6	Trace		30.5	10.4		4.9	8.9	10.5	6.9	11.2	10.9	7.2
*Y63	99.2	12.3	4.6		7.8	16.3		5.5		10.8	4.9	37.8	23.9	34.1
*Y64	102.1	Trace		7.8		3.7	2.4			0.8		85.3	5.6	79.1
*Y65	42.6	17.0				23.9		11.2		15.0	13.5	19.4	30.1	15.0
*Y66	44.9	1.4		16.4		17.5	13.6			17.1		33.9	23.2	27.6
*Y67	99.1	9.2			12.7	12.3	9.9			23.4		32.4	18.0	29.2
*Y68	72.4	11.7				18.5	13.3	21.2	8.0	9.3	2.8	15.2	19.8	10.0
Y69	33.7	11.8			11.2	10.9		7.3	16.9	21.4	8.7	11.7	10.8	7.2
Y70	53.8	12.9				16.4				16.2		54.5	26.1	53.3
*Y71	31.3	12.9			20.7	19.6		14.3	11.6	8.7	12.1		18.1	0

TABLE IV

Change in Weight Percent of Fractions
for Unit Changes in Reaction Conditions

Variable	Fraction Number 1	2+3+4	5	6+7+8	9	10	11
Average	10.14	12.56	15.28	15.60	11.95	5.02	29.40
Time	0.82	-2.48	5.50	-4.95	5.05	5.20	-14.15
Catalyst/DBDPE	0.52	-10.88	2.30	9.80	-7.00	4.15	1.15
[DBDPE]	-3.68	-8.68	-5.15	-1.05	-1.75	-6.20	26.55
Alcohol/Water	0.92	-10.72	7.55	-0.40	2.20	0.55	-5.65
Temperature	6.48	-6.68	1.85	12.65	-4.25	3.30	-26.70
Interactions							
Time x $\frac{\text{Alcohol}}{\text{Water}}$	2.68	-0.22	-3.40	-14.75	-5.35	2.60	18.05
$\frac{\text{Catalyst}}{\text{DBDPE}}$ x $\frac{\text{Alcohol}}{\text{Water}}$	6.98	-3.52	2.00	7.50	-5.20	1.55	-19.70

"Unit Changes" for the reaction conditions are:

Time — 1.5 hours [DBDPE] — 1/6 mole/liter

Catalyst/DBDPE — 0.0378 Alcohol/Water — 1/3

Temperature - 12.5°C.

As an example, a 1.5 hour change in reaction time should result in a 5.50% change in the weight percent of fraction number 5.

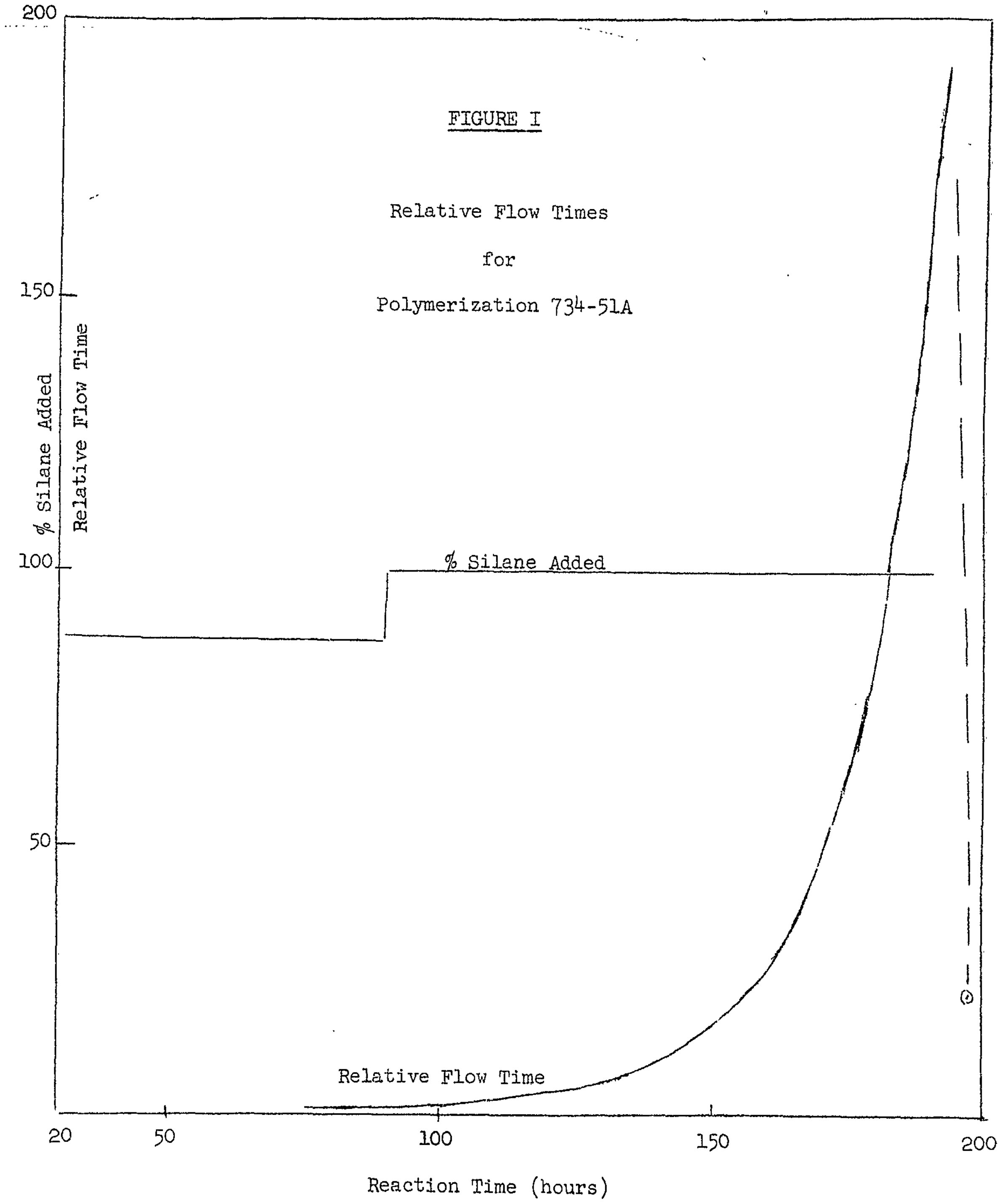


FIGURE I

Relative Flow Times

for

Polymerization 734-51A

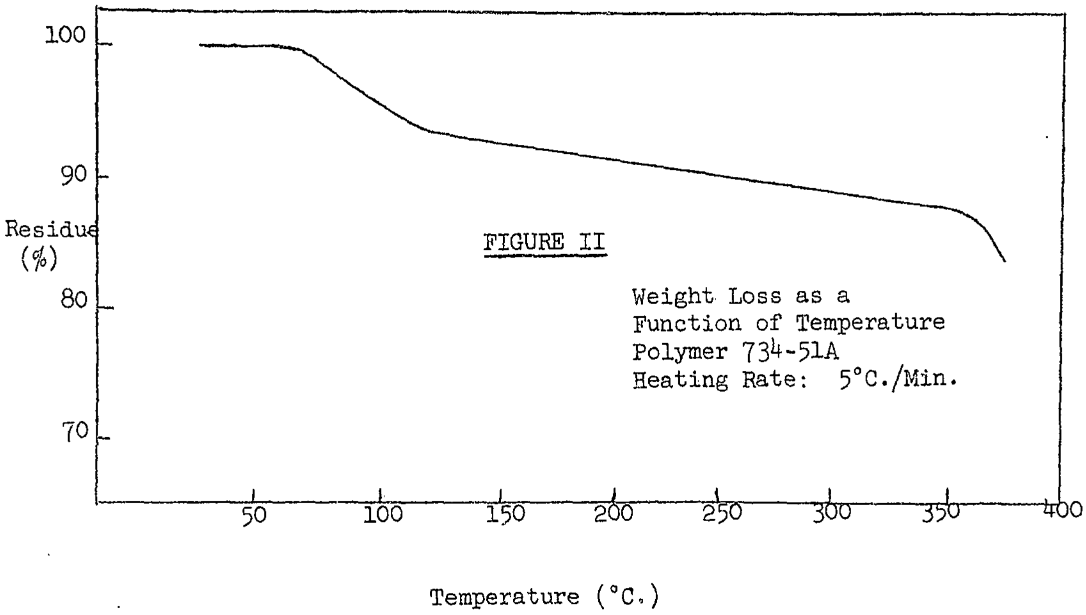


FIGURE II

Weight Loss as a Function of Temperature Polymer 734-51A Heating Rate: 5°C./Min.

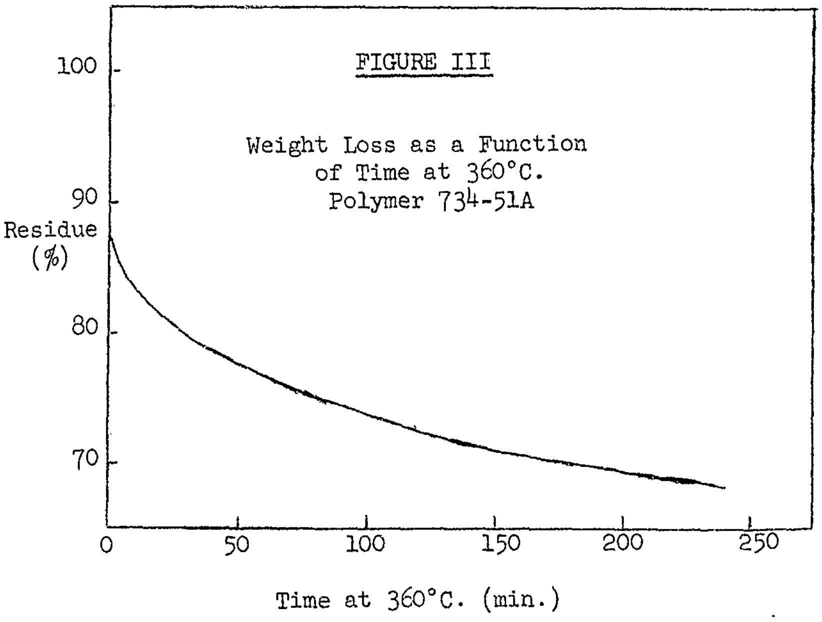


FIGURE III

Weight Loss as a Function of Time at 360°C. Polymer 734-51A

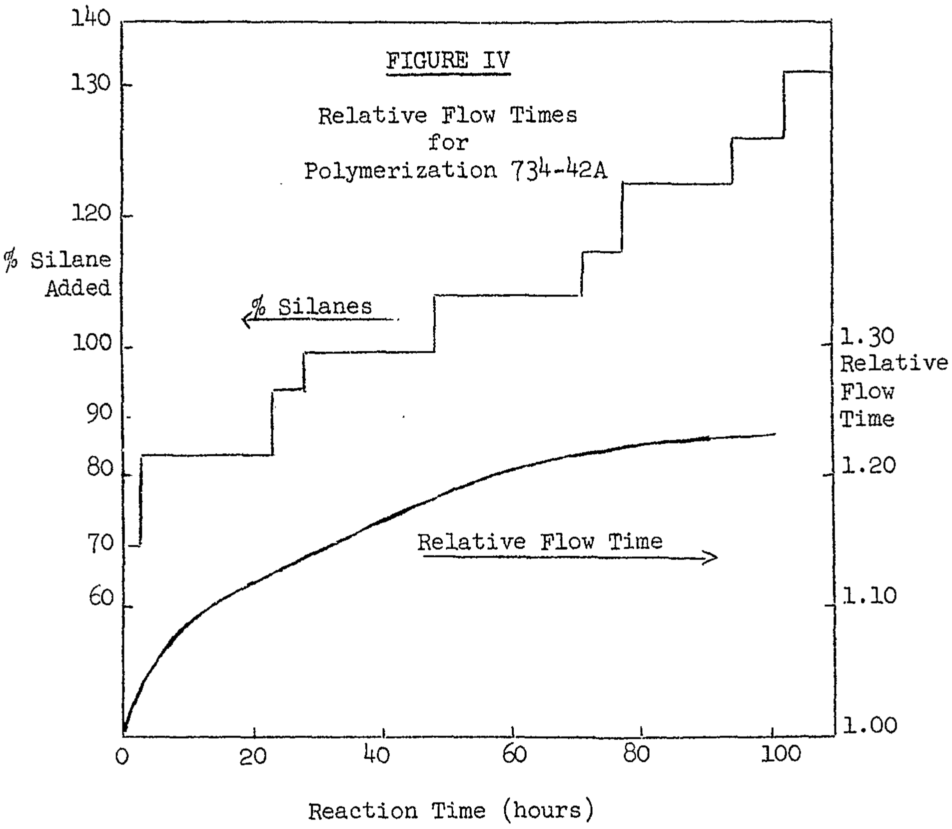
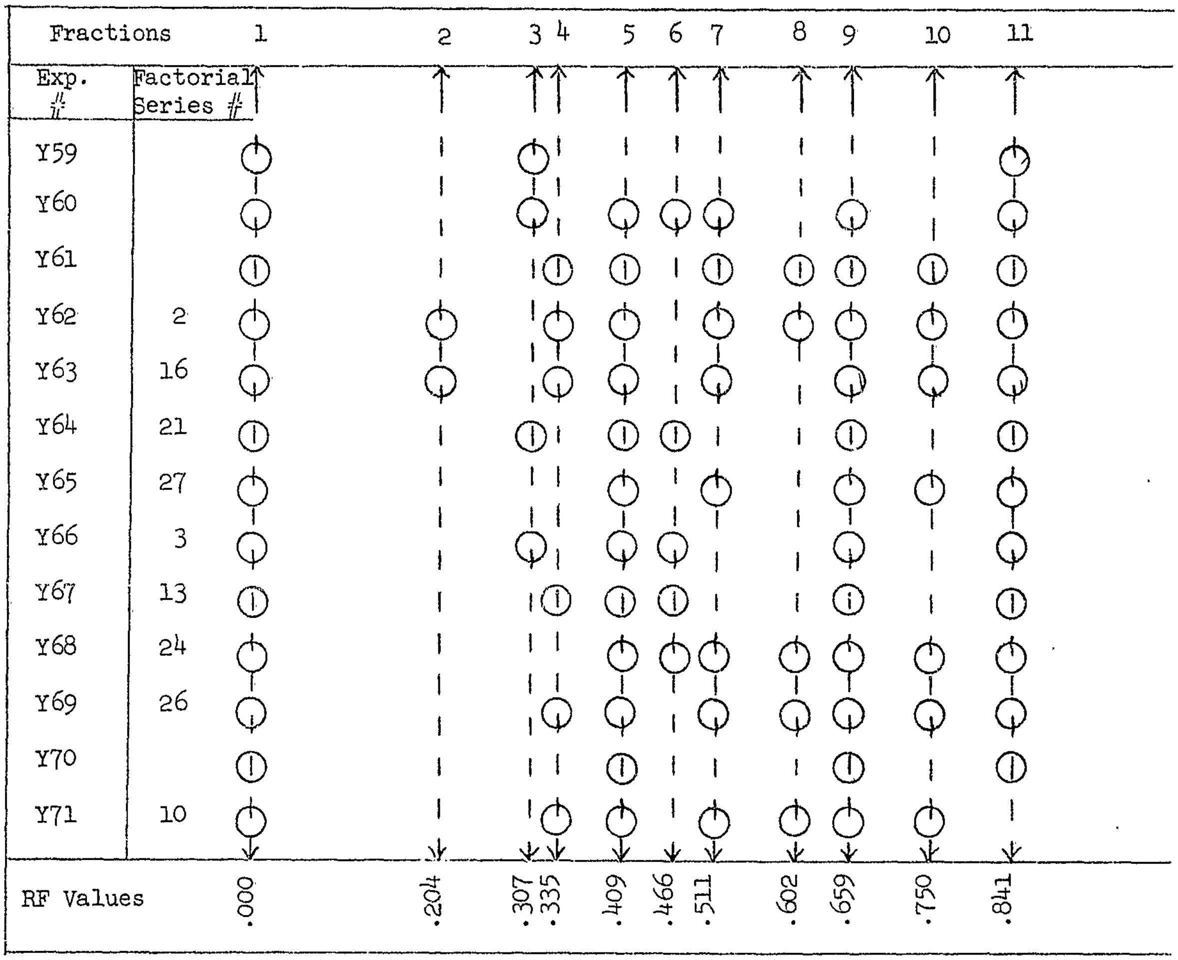


FIGURE IV
Relative Flow Times
for
Polymerization 734-42A
140
130
120
% Silane Added
100
90
80
70
60
% Silanes
Relative Flow Time
1.30
Relative Flow Time
1.20
1.10
1.00
0
20
40
60
80
100
Reaction Time (hours)

FIGURE V

Representative Thin Layer Chromatogram
Factorial Experiment Work Up
Developer - Benzene, Methanol, Dioxane, 85:10:5



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