

INVESTIGATION OF PHENYLENE SULFIDE POLYMERS

by

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Abstract

The investigation of phenylene sulfide polymers has been divided into four areas of endeavor. These are a kinetic study of a model reaction, monomer synthesis, polymerization, and determination of polymer properties. From the results of the kinetic study and monomer synthesis coupled with the early results in the other two fields cuprous *p*-bromothiophenoxide has been chosen as the monomer of choice for the preparation of linear phenylene sulfide polymers. Later work on this monomer has shown that a number average degree of polymerization greater than 400 can be obtained either by solid state or solution polymerization. This polymer which has useful polymeric properties is stable in air or nitrogen to 450°C and forms a polymeric residue stable to 900°C under nitrogen.

Introduction

The investigation of phenylene sulfide polymers is being conducted under Air Force Contract Number AF 33(616)-7251; Project Number 7340, "Non-metallic and Composite Materials"; Task Number 73404, "New Chemicals and Methods". It is administered under the direction of Materials Central, Directorate of Materials and Processes, Aeronautical Systems Division with Mr. G. A. Loughran as the Project Engineer. This work is being performed in the Plastics Department Research Laboratories of The Dow Chemical Company, Midland, Michigan. The purpose of this work is to obtain a useful plastic material which is thermally stable.

The initial work on phenylene sulfide polymers was done by Dr. A. D. Macallum of London, Ontario. He discovered that this polymer could be prepared by the sequence of reactions shown in Figure 1.

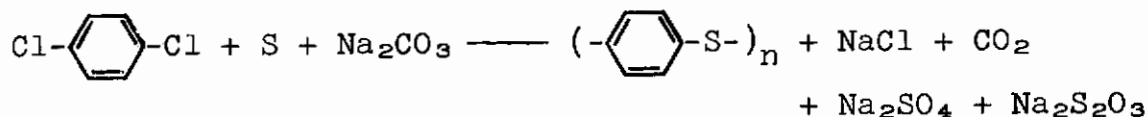


Figure 1. Macallum Polymerization

Since Dow makes p-dichlorobenzene and the other two starting materials are inexpensive, the patents for this work were purchased from Dr. Macallum by The Dow Chemical Company in 1954. Subsequent studies were carried on in the Plastics Department Research Laboratories.

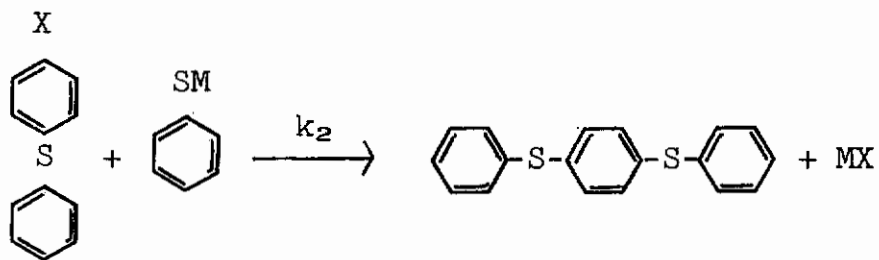
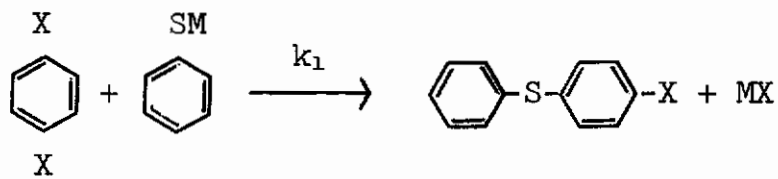
It soon became apparent that the Macallum polymerization would be a difficult reaction to control since the yields and the polymer properties were very unpredictable. In addition the polymeric material obtained was somewhat branched and or lightly crosslinked, and also there was always found an insoluble, infusible highly crosslinked material. Consequently, it was decided to prepare a more readily characterizable polymer namely a linear polymer from the condensation polymerization of such species as p-halothiophenoxides. In the course of the investigation on linear phenylene sulfide polymers four different aspects of the problem were studied. These were (1) a kinetic study of the polymerization on model compounds, (2) monomer synthesis, (3) polymerization studies, and (4) determination of the polymer properties.

Kinetic Studies

The first phase of our work was to study the basic polymerization reactions. Since isolation of individual products from a polymerization reaction would be at best difficult, it was decided to investigate a model reaction. From this it was hoped to determine the relative reactivities of the various halogens and cations used as well as the side reactions involved in the use of each halogen and cation. Having this information then, a monomer system could be chosen which would have the greatest possibility of producing a high molecular weight polymer by condensation polymerization.

The system studied is depicted in Figure 2. As can be seen, the reaction takes place in two steps. In the first step p-dihalo-benzene and thiophenoxide react to give p-halophenyl phenyl sulfide. This then reacts with more thiophenoxide in the second step to give 1,4-bis(phenylthio)benzene.

For the kinetic consideration of the reaction, it was treated as a competitive, consecutive second order reaction. Due to the nature of this type of kinetic treatment the individual rate constants are extremely difficult to determine accurately. However, thanks to Dr. Turner Alfrey, Jr. who worked out the mathematical treatment we were able to obtain quite easily the ratio of the rate constants. This ratio then makes it possible to determine whether a halogen opposite a sulfide linkage (k_2) is more reactive than one opposite the same halogen (k_1). It should be mentioned that when the two halogens have the same reactivity, the ratio of k_2/k_1 equals 0.5.



X = F, Cl, Br, I
M = Na, Li, K, Cu

Figure 2. MODEL REACTION FOR KINETIC STUDIES

Conclusions

The starting materials for this study needed to be very pure since by-products were going to be studied also. Consequently the commercial *p*-dihalobenzenes were recrystallized and then checked for purity by gas-liquid chromatography prior to use. The thiophenoxide after purification was checked for purity by potentiometric titration with silver nitrate. Both reagents had a purity of greater than 99%.

All the reaction and workup procedures were standardized to avoid introducing errors from this source. The reactions were run in sealed glass ampoules under an argon atmosphere. The ampoules were placed in steel jackets and preheated in a molten salt bath at 500°C for one minute and forty seconds. Then they were placed in the preheated bomb rocker and allowed to react for the desired time. Zero time for reactions carried out at 250°C was taken as four minutes after the introduction of the bomb into the molten salt bath since calibration runs had indicated that this was the time required for the bomb to reach the reaction temperature. For reaction times of greater than six hours preheat treatment was felt to be unnecessary.

After the reaction was completed, the ampoules were frozen in liquid nitrogen and opened. The contents were extracted with carbon disulfide and then with water. The water extract was titrated with silver nitrate to determine the amount of halide ion liberated. The carbon disulfide extract was analyzed on a model 300 F&M high temperature, linear programmed gas-liquid chromatograph. A sample chromatogram is shown in Figure 3. This figure shows the separation of the products obtained in a typical reaction mixture and their order of elution. Durene, peak 4, is an internal standard. Peaks 8 and 9 are the products of the first and second reactions, respectively (Figure 2). An example of the results from a typical analysis is shown in Table I. As can be seen the results are quite good giving essentially a complete material balance. On the average, however, the results fall in a range of $\pm 5\%$ of the values given in Table I.

Two of the products listed in Table I, diphenyl sulfide and diphenyl disulfide, occur in rather small amounts. These are the major by-products in the reaction and amount to 0.2-0.4% of the total products in a solution reaction and 0.2-0.7% in a reaction without solvent. The diphenyl disulfide undoubtedly arises from thiophenoxide being oxidized during the workup. The diphenyl sulfide may arise from disproportionation of the thiophenoxide during the reaction. Other by-products found in only trace quantities are benzene, halobenzene, and free halogen. From the by-product studies it became apparent that in the reaction of sodium thiophenoxide with *p*-dihalobenzene the order of by-product production for the respective halogens was $I > F > Br \sim Cl$.

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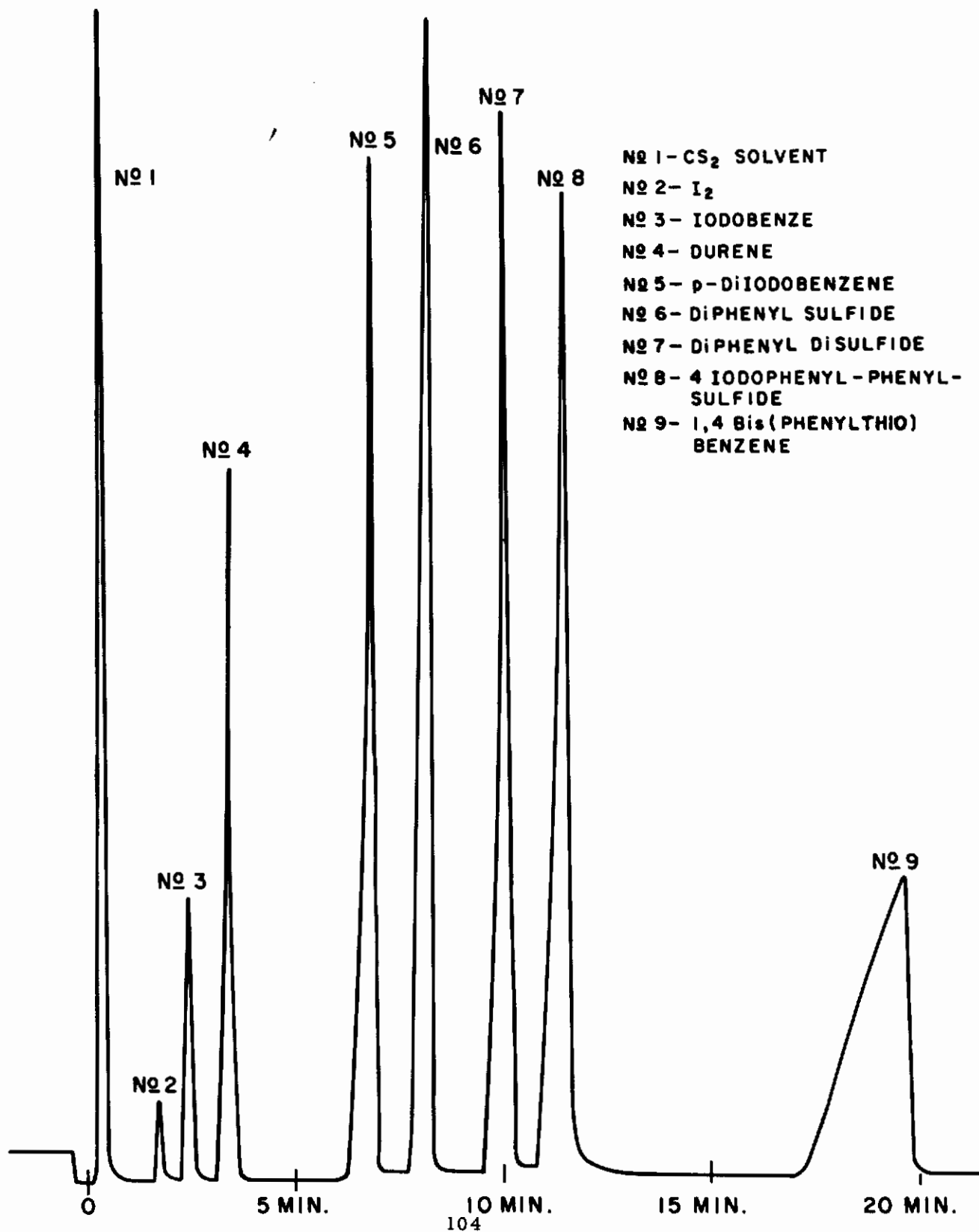


FIGURE 3. MODEL GAS-LIQUID CHROMATOGRAM OF REACTION PRODUCTS

TABLE I

Complete Material Balance of the Reaction of Sodium Thiophenoxide with p-Diodobenzene

Reactants:	<u>Moles</u>
sodium thiophenoxide	0.0200
<u>p</u> -diodobenzene	0.0100
Products:	
sodium iodide	0.01635
sodium thiophenoxide	0.00342
<u>p</u> -diodobenzene	0.00033
<u>p</u> -iodophenyl sulfide	0.00297
<u>p</u> -bis (phenylthio) benzene	0.00660
phenyl sulfide	0.00011
phenyl disulfide	0.00035
Material Balance:	
	<u>%</u>
iodine accounted for	99.9
sulfur accounted for	102.0
benzene accounted for	101.4

Contrails

The order of ease of halogen displacement, however, does not parallel exactly that for by-product production. Some of the kinetic data from the model reactions is shown in Table II. The relative reactivities of the various halogens can be ascertained from the percent dihalobenzene reacted in a given length of time. Seventy-seven percent of the *p*-difluorobenzene reacted in twelve hours while in the case of the chloro, bromo, and iodo compounds the same extent of reaction is achieved in about five hours, fifteen minutes, and ten minutes respectively as shown by Table II. Therefore the order of reactivity of the dihalobenzenes must be $I > Br > Cl > F$ for the overall reaction.

In order to determine the relative reactivities of the respective halogens under the same circumstances in each case and without complications by consecutive, competing reactions, the reaction of *p*-halophenyl phenyl sulfide with thiophenoxide was studied. The results are given in Table III. It can immediately be seen that the order of replaceability of a halogen opposite a sulfide linkage is $I > Br > F \sim Cl$ or essentially the same order exhibited in Table II.

Table II also contains some interesting data in the form of k_2/k_1 ratios. These ratios show that an iodine opposite an iodine has about the same reactivity as one opposite a sulfide. (The ratio is about 0.5.) In the case of bromine, however, the bromine opposite a sulfide is 1.5 times more reactive than one opposite a bromine. With chlorine this factor goes to about three times and with fluorine to seventy times. This suggests that in a monomer system containing an aryl fluoride a preferential formation of polymer might be observed. If this happens, it would be possible to obtain high molecular weights at relatively low conversions. Some results in the polymerization studies shed some light on this subject, and it will be discussed further.

It might be mentioned that the k_2 's given in Table III should represent the k_2 's in the model reaction. Therefore these in conjunction with the k_2/k_1 ratio should allow the k_1 's for the model reaction to be calculated.

In addition to the effect on reactivity that the halogen substituent had, it might be expected that the cation associated with the thiophenoxide might show some effect. The results of this study are given in Table IV. From the percent dihalobenzene reacted in a given time it can be seen that the lithium and cuprous salts are both more reactive than the sodium. In addition, since the cuprous salt is reacting with a less reactive halogen and still gives about the same percent reaction as the lithium salt, the cuprous salt must be the more reactive of the two. This gives an order of reactivity of $Cu > Li > Na$.

TABLE II

Rates of Solution Reactions of
Various p-Dihalobenzenes


<u>p-Dihalobenzene</u>	<u>Time (hrs.)</u>	<u>% X--X Reacted</u>	<u>k₂/k₁</u>	<u>Average</u>
ØF ₂	4.25	50.2	37.9	34.2
	12.0	76.9	30.4	
ØCl ₂	0.25	17.1	1.77	1.84
	0.25	13.4	1.64	
	5.00	70.3	1.98	
	5.00	70.3	1.95	
ØBr ₂	0.25	79.0	0.900	0.860
	0.25	69.9	0.870	
	0.50	83.7	0.804	
ØI ₂	0.18	75.3	0.548	0.543
	0.18	80.0	0.537	

TABLE IIISolution Reactions of
4-Halophenylphenyl Sulfide

<u>Compound</u>	<u>Second Order Rate Constant</u> <u>k_2 (l/mole min.)</u>
F ϕ S ϕ	0.10 \pm 0.02
Cl ϕ S ϕ	0.094
Br ϕ S ϕ	0.15 \pm 0.03
I ϕ S ϕ	0.65 \pm 0.17

TABLE IV

Reactivity of Thiophenoxide Salts
with p-Dihalobenzene

<u>Salt</u>	<u>Dihalo- benzene</u>	<u>Time (hrs)</u>	<u>Temp. °C</u>	<u>% X--X Reacted</u>	<u>k₂/k₁</u>	<u>Average</u>
LiSØ	ØI ₂	0.25	250	87.5	0.584	0.579
		0.25	250	90.0	0.573	
NaSØ	ØI ₂	0.25	250	75.3	0.548	0.543
		0.25	250	80.0	0.537	
NaSØ	ØBr ₂	0.25	250	79.0	0.900	0.860
		0.25	250	80.9	0.870	
		0.50	250	83.7	0.804	
CuSØ	ØBr ₂	0.17	250	83.9	-	
		1.00	200	80.1	-	
		2.00	200	87.5	-	

The above results coupled with the ease of preparation of the various species, should enable a choice of a monomer to be made. It has been found that the ease of preparation of the thiophenoxides was $\text{Cu} > \text{Na} \sim \text{K} > \text{Li}$ while that for the aryl halide was $\text{Br} > \text{Cl} > \text{F} > \text{I}$. This along with the orders of reactivity and of by-product production indicates that the best choice for monomer would be cuprous p-bromothiophenoxide. In addition, due to the possibilities of preferential formation of polymer, p-fluorothiophenoxide should be considered.

Monomer Synthesis

At the same time that the kinetic studies were being carried out, attempts were being made to synthesize all the possible monomer variations. There were three general methods used for the synthesis of the substituted thiophenols desired for the monomers. These are shown in Figure 4. The first involves preparation of the diazonium salt from the appropriate p-haloaniline. This is converted to the xanthate.¹ The xanthate is then pyrolyzed to the desired p-halothiophenol.¹ This technique, however, is long and tedious resulting in a low overall yield of approximately 35-40%. Consequently simpler methods which could give higher yields were desired for the three p-halothiophenols, fluoro, bromo and iodo, which could not be obtained commercially.

It was described in the literature² (reaction 2, Figure 4) that treatment of thiophenol with bromine gave the bis-(4-bromophenyl) disulfide in essentially a quantitative yield. This material can be reduced to p-bromothiophenol by zinc-acid reduction (80% yield),³ by sodium borohydride-aluminum chloride reduction (95-99% yield),⁴ or by a sodium hydroxide-dextrose reduction (70% yield).⁵

When an attempt was made to prepare p-iodothiophenol by the same procedure as used for the preparation of bis-(4-bromophenyl) disulfide it was discovered that very little iodo disulfide was formed from iodine and thiophenol. The major product is thi-anthrene. Consequently a different process was needed, and this is shown in the third reaction and its alternate in Figure 4. Treatment of iodobenzene with sulfur trioxide results in an 81% of p-iodobenzenesulfonic acid anhydride monohydrate after seven hours at -60°C .⁶ Treatment of the anhydride so formed with hydrobromic acid in acetic acid converts it to the disulfide in a 70% yield.⁷ Overall yield to p-iodothiophenol is about 57%. The alternate route, treatment of iodobenzene with chlorosulfonic acid, suffers from a serious side reaction namely the formation of sulfone. Consequently the maximum yield of sulfonyl chloride obtained was 48%. The reduction of the sulfonyl chloride to the disulfide, however, was almost quantitative using hydrobromic acid in acetic acid.⁷ This gives an overall yield to p-iodothiophenol of 45%.

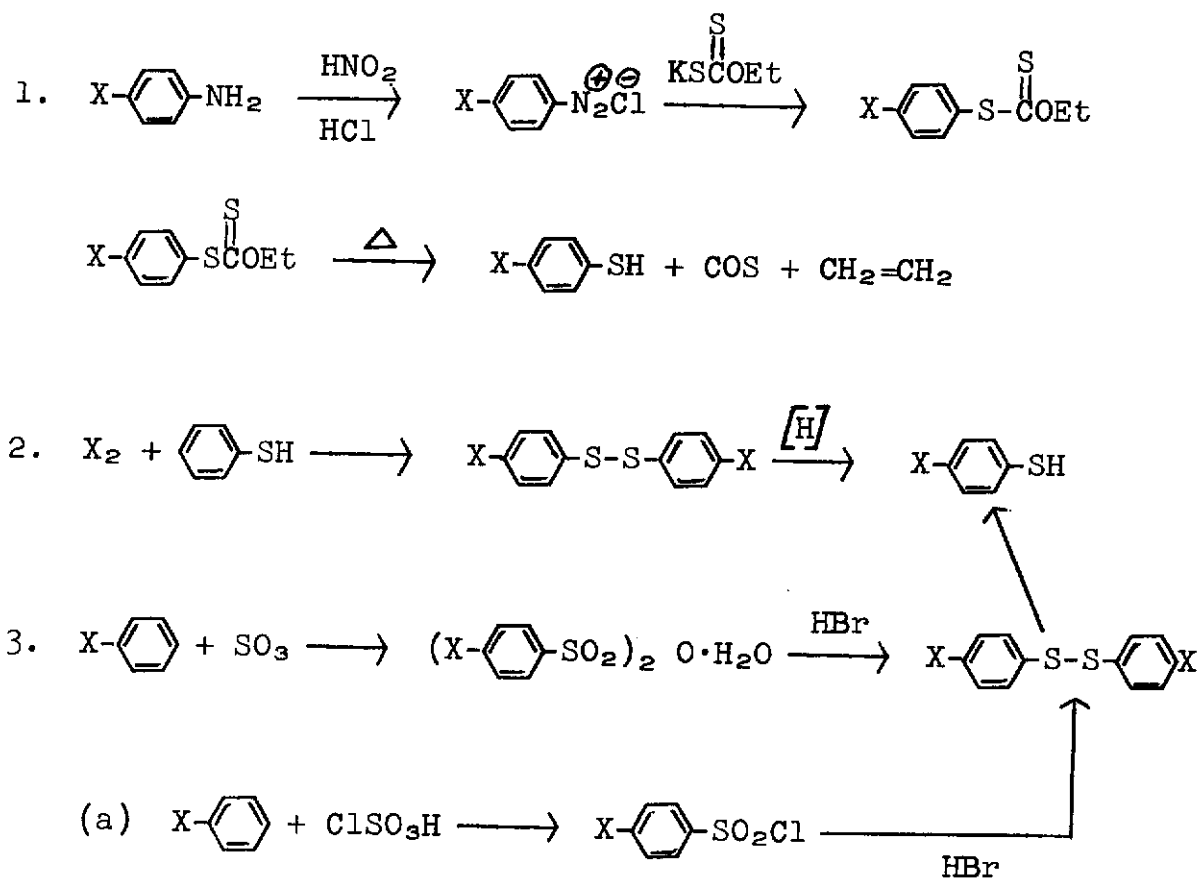


Figure 4. THIOPHENOL SYNTHESIS

Conclusions

A point in the favor of the *p*-iodobenzenesulfonyl chloride route is that the sulfonyl chloride is not converted to an unusable product if it becomes warm as the corresponding sulfonic acid anhydride monohydrate is.

From the substituted thiophenols the salts could be obtained in greater than 95% yield as shown in Figure 5. Reaction (1), the first one tried in an effort to prepare the sodium salts, was successful. Purity and yield, however, frequently suffer due to the environmental instability of the sodium hydride. Consequently a better method of preparing sodium salts in addition to techniques for preparing the other salts was desired.

Lithium salts are conveniently prepared by reaction (2) while reaction (3) provides an easy route to the cuprous salts. The cuprous salts provide one distinct advantage over the other monomers. This is their much greater stability to air and moisture which allow them to be handled outside of a drybox during workup.

The reaction shown in method (4) provides a very good synthesis of sodium and potassium salts. This involves treatment of the thiophenol with a sodium-naphthalene complex for sodium salts and a potassium-anthracene complex for potassium salts. The complexes are very readily prepared and react instantly with the thiophenol. Further work showed that reduction of the appropriate disulfide to the substituted thiophenol was unnecessary when using the complexes since the complex was capable of a selective reduction of the disulfide bond yielding the desired salt.

Reaction (5a) illustrates an alternate means of obtaining the cuprous salt. This procedure suffers only from contamination of the monomer by unreacted copper metal while that in reaction (3) suffers from impurities in the cuprous oxide. As yet neither technique has been chosen as the preferred one.

Listed in Table V are the various monomers synthesized along with the monomer purities and the overall yields from the starting materials. In the four cases showing yields of less than 90% the cause is in the substituted thiophenol synthesis with the exception of lithium *p*-bromothiophenoxide. In this case the low yield is due to the lithiation reaction.

Some explanation concerning the entries for the copper salt purities is needed. Since the insolubility of the copper monomers eliminated most analytical methods for purity determinations and since elemental analysis was not accurate enough to give precise values, the purity of these materials were not known more exactly than indicated in Table V.

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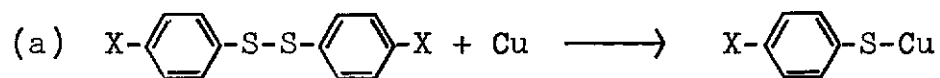
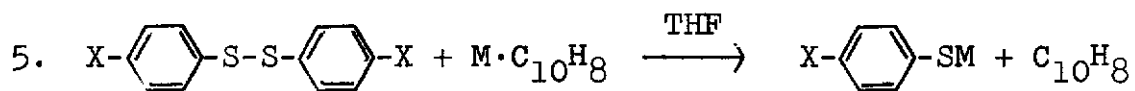
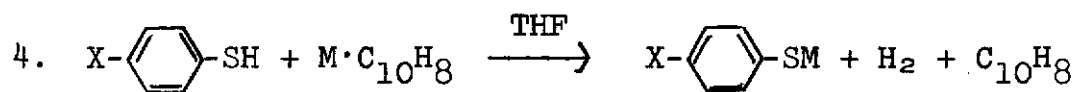
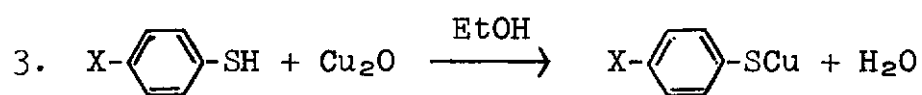
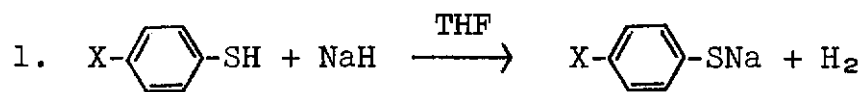

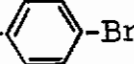
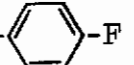
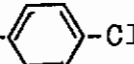

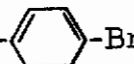
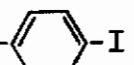
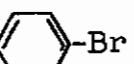
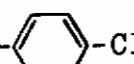
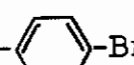

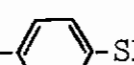
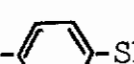


Figure 5. SALT PREPARATION

TABLE V

<u>Monomer</u>	<u>Overall Yield</u> <u>%</u>	<u>Purity</u> <u>%</u>
LiS-  -Cl	95.0	96.3
LiS-  -Br	37.0	90.0
NaS-  -F	50.5	98.8
NaS-  -Cl	95.0	97.2
NaS-  -Cl	95.0	98.0
NaS-  -Br	91.0	96.5
NaS-  -I	30.0	100
KS-  -Br	92.5	100
CuS-  -Cl	97.9	> 95.0
CuS-  -Br	91.9	> 95.0
CuS-  -Br	36.2	> 95.0
LiS-  -SLi	68.0	96.0
NaS-  -SNa	93.0	100

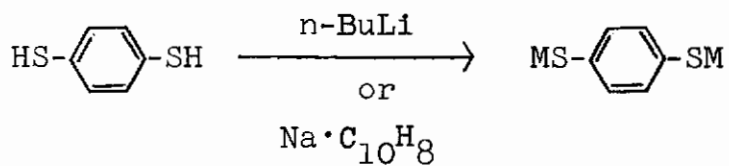
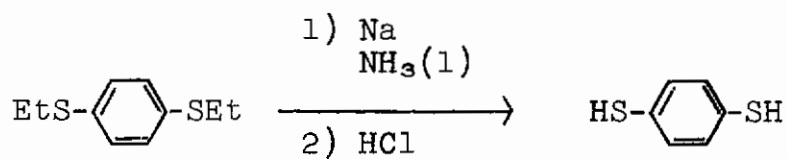
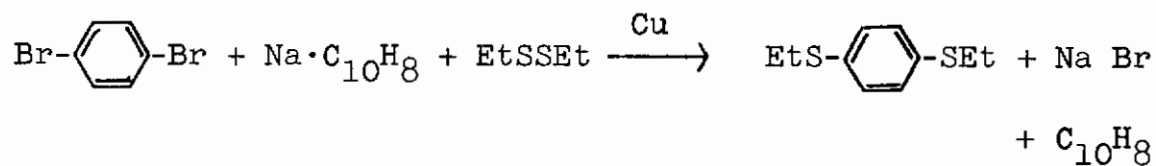


Figure 6. DISALT SYNTHESIS

The last two entries in Table V are examples of monomers, which would be used in an A-A, B-B condensation system where the B-B monomer would be a p-dihalobenzene. These disalts were prepared in the manner shown in Figure 6. The p-dibromobenzene is treated with the product from the reaction of sodium-naphthalene complex with diethyl disulfide in the presence of copper dust, namely sodium ethylmercaptide. This results in the formation of 1,4-bis(ethylthio)benzene. The bis sulfide so formed is cleaved by sodium in liquid ammonia to give, on acidification, 1,4-benzenedithiol. Treatment of the 1,4-benzenedithiol with n-butyllithium results in the dilithium salt. Alternatively the 1,4-benzenedithiol can be treated with sodium-naphthalene complex to give the disodium salt in the yields and purities shown in Table V.

Polymerization

Once the monomers had been synthesized, their polymerization reactions were studied. The ampoules were prepared by the same general technique used in the kinetic studies. The workup, however, was somewhat different. After the ampoule was cooled and opened, the contents were extracted twice with boiling water, and the water extract was titrated potentiometrically for halide ion with silver nitrate to determine the monomer conversion. The residue was heated to reflux in diphenyl ether. Then the resulting solution was filtered, and the filtrate poured into cold methanol to precipitate the polymer. The precipitate was filtered off, washed with acetone and dried under vacuum at 80-120°C for several hours. Yields were based on the vacuum dried polymer obtained.

Polymerizations were carried out in the solid state or in solution. It was found earlier that if the monomer was polymerized above its melting point in the absence of solvent an uncontrollable reaction ensued leading to a black charred mass. The maximum temperature that could be used was 10-15° below the monomer melting point. The usual temperatures employed were 200° and 250°C. The solid state polymerization appears to be just that. In no instance was the presence of liquid observed and the particle size of the material in the ampoule appeared to be unchanged. The only visual change appeared to be a very slight change in color.

The solution reactions were run in quinoline, diphenyl ether and pyridine at about 1 M concentration. Pyridine seemed to give the best results and showed a fifty fold enhancement in rate over the solid state reactions at the same temperatures.

Two types of monomer systems were investigated, the A-A, B-B and the A-B. In the first system there is one inherent disadvantage; the two monomers must be present in exactly stoichiometric quantities to achieve a high molecular weight polymer. With the A-B monomers this is automatically taken care of due to the nature of

the monomer.

In the A-A, B-B system, two different monomer sets have been briefly considered. The results are given in Table VI. In the case of the dilithium salt a low yield of low melting polymer was obtained. With the disodium salt very little, if any, polymeric material was obtained.

Some results from the kinetic studies could shed some light on the above results. When sodium thiophenoxide was heated in pyridine for twelve hours at 250°C no apparent reaction occurred. When p-dibromobenzene was treated under the same conditions a black insoluble, infusible mass was obtained. Therefore what may be occurring is that, due to the low reactivity of the disodium salt, the pyridine is degrading the p-dibromobenzene before any appreciable amounts of polymer can be formed. However, the more reactive dilithium salt reacts with the p-dibromobenzene to give some polymer before the pyridine degradation reaction becomes dominate.

Since the A-B system has a built in stoichiometric balance, since it is easier to prepare, and since the results have been much better with this system than with the A-A, B-B system the A-B monomers have been studied more extensively.

One of the monomers studied was sodium p-fluorothiophenoxide. The results are given in Table VII. Although the first two runs are at somewhat higher temperatures than is usually employed, their results are quite interesting. As has been mentioned previously fluoroderivatives have a potentiality for preferential polymer formation. In the first two runs we have some evidence which bears on this question. Condensation polymerization theory predicts that for conversions of 58% and 79% the number average degree of polymerization, \bar{x}_n , obtained for the polymers would be 2 and 3 respectively. However, the \bar{x}_n 's observed were 9 and 7 respectively. This may be an indication that preferential polymer formation is taking place.

Tables VIII and IX show the results for two more monomers, the sodium and potassium salts of p-bromothiophenol. The results in Table VIII exhibit several interesting features. One is the effect of pyridine that was mentioned before, a fifty fold enhancement in rate over the solid state reaction. Another is the rate enhancement of pyridine over quinoline. In addition it might be noted that the percent of bromine continues to decrease, indicating continued polymerization, even after titration of liberated bromide ion indicates a complete reaction. One feature of distinct importance is the fact that \bar{x}_n reaches a maximum, at 24 hours, and then decreases. This apparent decrease in molecular weight after an optimum reaction time appears in all of the polymerizations studied and is signalled by a drop in melt viscosity, melting point and

TABLE VI

A-A and B-B Polymerizations

250° Pyridine Solvent


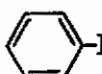

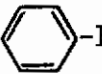

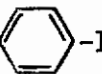

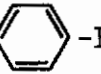


<u>A-A</u>	<u>B-B</u>	<u>Time (hrs)</u>	<u>Polymer Yield %</u>	<u>M. P. °C</u>
LiS-  -SLi	Br-  -Br	6	39	220-230
NaS-  -SNa	Br-  -Br	1	7	<100
NaS-  -SNa	Br-  -Br	6	6	<100
NaS-  -SNa	Br-  -Br	12	8	<100

TABLE VII

Polymerization of NaS--F

<u>Time (Hrs)</u>	<u>Temp. °C</u>	<u>% Conversion</u>	<u>M. P. °C</u>	<u>\overline{DP}_{Br}</u>	<u>System</u>
2	320	58.0	~265	9	Pyridine
72	320	79.0	>300	7	Solid State
6	250	91.0	272-280	-	Pyridine


TABLE VIII

Polymerization of NaS--Br at 250°C

<u>Solvent</u>	<u>Time (hrs)</u>	<u>% Conversion</u>	<u>Polymer</u>			
			<u>% Br</u>	<u>% S</u>	<u>M. P. °C</u>	<u>\overline{DP}_{Br}</u>
None	36	79.2	-	-	-	-
None	140	93.0	-	-	-	-
Quinoline*	24	91.3	-	-	-	-
Pyridine	1	72.0	13.2	31.3	160-200	5
Pyridine	2	97.8	6.00	28.9	240	12
Pyridine	3	97.6	3.75	27.1	240-250	19
Pyridine	6	100.0	1.50	29.1	260	48
Pyridine	12	100.0	0.67	29.4	265	122
Pyridine	24	100.0	0.58	29.0	-	156
Pyridine	36	100.0	0.69	29.2	265	107

* Reaction Temperature 280°C.

TABLE IX


Solution Polymerization of KS--Br

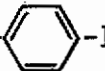
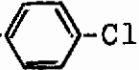
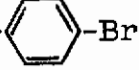
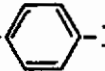
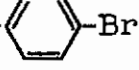
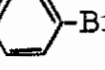
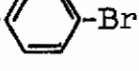
<u>Temp.</u> <u>°C</u>	<u>Time</u> <u>(hrs)</u>	<u>%</u> <u>Conversion</u>	<u>%</u> <u>Polymer</u>	<u>M. P.</u> <u>°C</u>	<u>DP*</u>
250	1	80.7	-	~260	-
250	2	90.6	-	~264	20
250	3	100.0	-	~265	36
250	8	100.0	55	262-269	33
250	24	100.0	77	257-263	78
250	36	100.0	60	238-245	202
250	3**	100.0	54	263-268	38
250	8**	100.0	47	260-265	32
200	38	92.3	64	262-266	17
200	53	92.5	59	263-268	18

*DP from Br end group analysis

** CuBr added

TABLE X

Polymerization of (p)X--SM
at 250°C in Pyridine

<u>Monomer</u>	<u>Polymer % Yield</u>	<u>M. P. °C</u>	<u>k₂</u>
NaS-  -F	63	272-280	0.026
NaS-  -Cl	62	245-260	0.011
NaS-  -Br	75-80	260-265	0.13
NaS-  -I	42	225-240	1.01
LiS-  -Br	20	243-248	2.57
KS-  -Br	80	265-269	0.096
CuS-  -Br	97	283-287	> 3.0

Contrails

yield. Table IX shows both the drop in melting point and yield occurring after 24 hours reaction time.

Table IX also shows two other features of interest. One is the lack of catalytic effect of cuprous bromide as shown by runs 7 and 8 versus 3 and 4. The other is a temperature effect on the rate as shown by the last two runs. This latter effect amounts to a sixteen fold decrease in rate for the 50° drop in temperature.

Table X summarizes the results of the preliminary studies on all the A-B type monomers investigated. The yields given are the maximum polymer yields obtained with the particular monomer. The melting points are also maxima and give an indication of relative molecular weights attained in each case. The last statement is true since we have found that the higher the melting point the higher average molecular weight up to the crystalline melting point of the polymer, 287°C. The rate constants are overall constants based on second order kinetics.

From the first four entries it can be seen that the ease of halogen displacement is essentially the same as that found in the model reactions namely $I > Br > F > Cl$. In addition it can be seen that the best polymer, as indicated by melting point, resulted from the p-fluoro and p-bromothiophenoxides with the p-bromo giving the best yield.

From the third, fifth, sixth and seventh entries it can be seen that the effect of the cation on the rate is also the same as that found in the model reactions being $Cu > Li > Na > K$. In this set of entries, however, cuprous p-bromothiophenoxide has by far the best yield and melting point. In fact these values are the best of all those obtained. Consequently the monomer chosen for further study was cuprous p-bromothiophenoxide. This is the same monomer that the kinetic studies indicated to be the preferable one.

Cuprous p-bromothiophenoxide, therefore was extensively studied under four different reaction conditions. These were 200° and 250°C in the solid state and in pyridine. The results are given in Figures 7-10. The solid line represents the yields observed while the dashed line refers to the melting points. In each case a maximum is reached after a given reaction time beyond which the yield and the melting point decrease. These maxima in melting point and yield are 280°C and 90% yield for five days at 200°C in the solid state; 278°C and 78% yield for two and one-half days at 250°C in the solid state; 278°C and 95% yield for 32 hours at 200°C in pyridine; and 287°C and 90% yield for 16-32 hours at 250°C in pyridine. From these results the best polymerization conditions would appear to be 16-32 hours at 250°C in pyridine or five days at 200°C in the solid state.

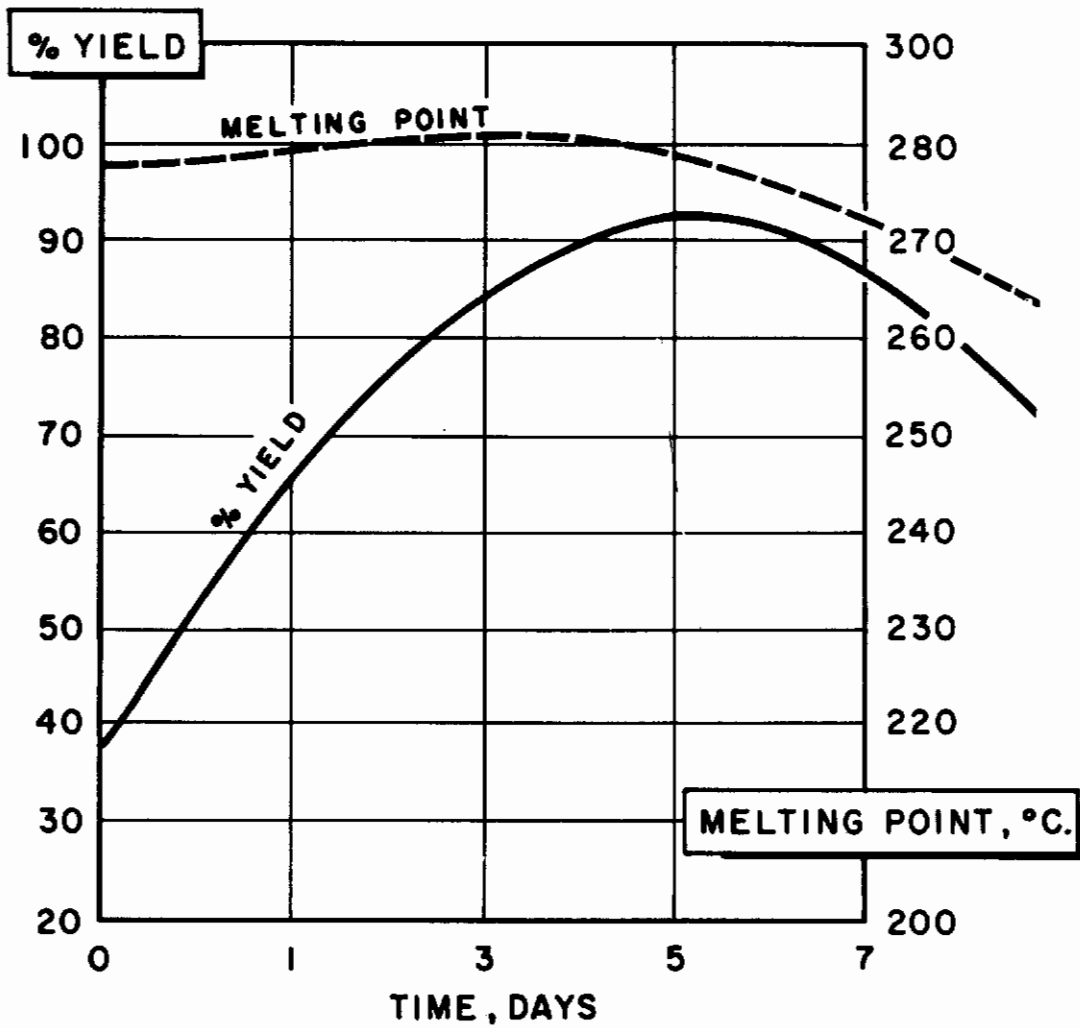


FIGURE 7. $Br \phi SCu$, SOLID STATE, $200^{\circ}C$.

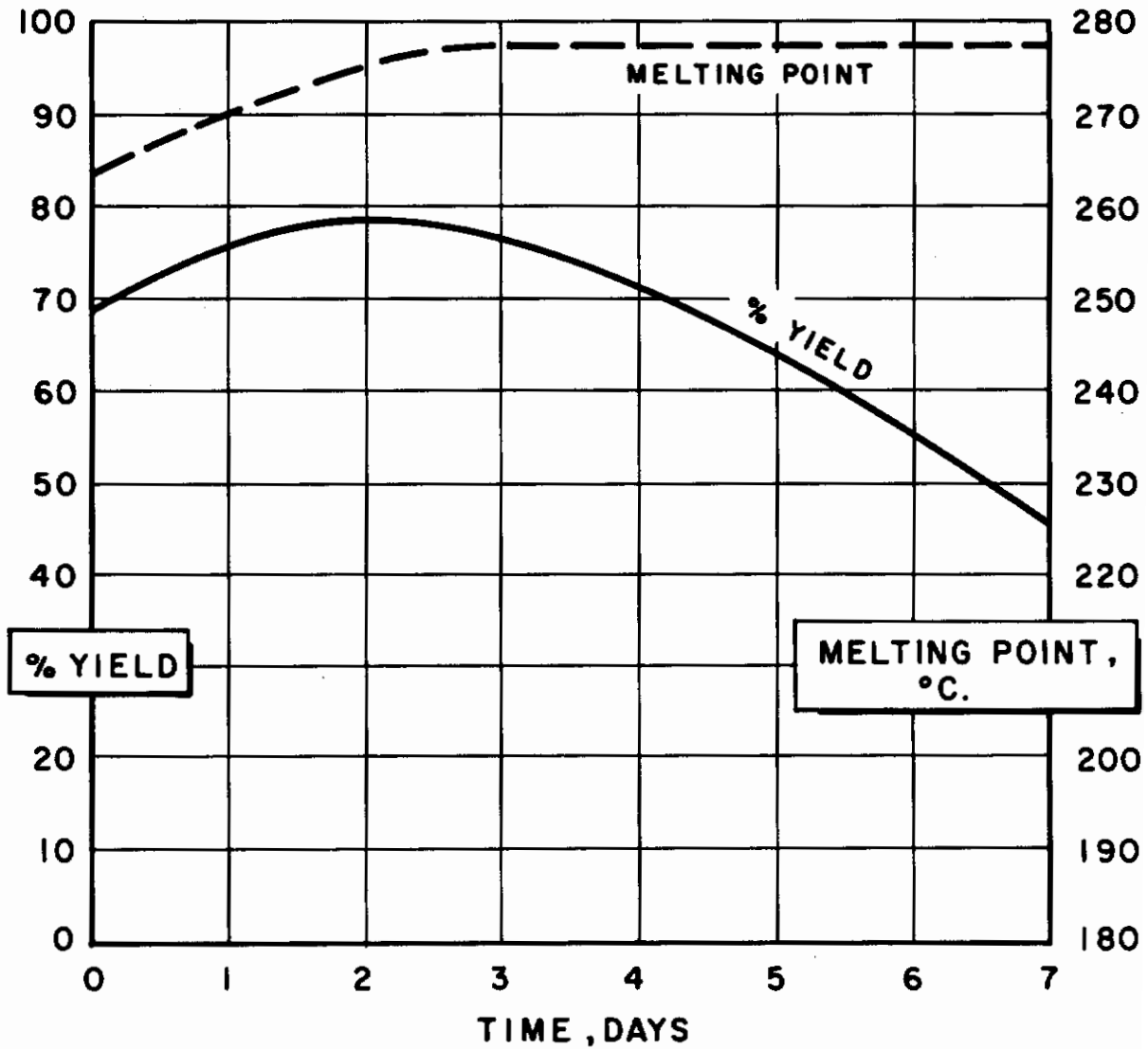


FIGURE 8. $\text{CuS} \phi \text{Br}$, SOLID STATE, 250°C .

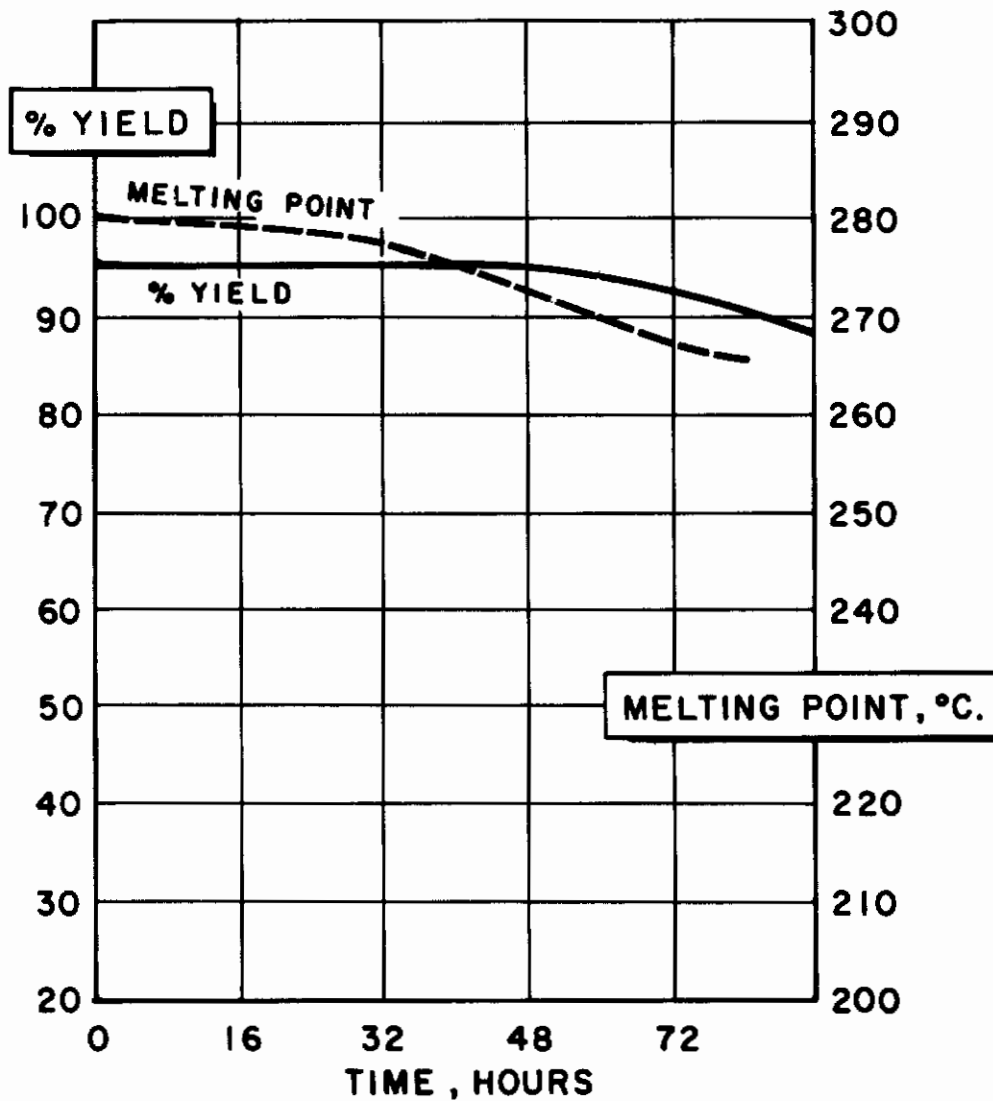


FIGURE 9. $\text{Br}\phi\text{SCu}$, PYRIDINE, 200°C .

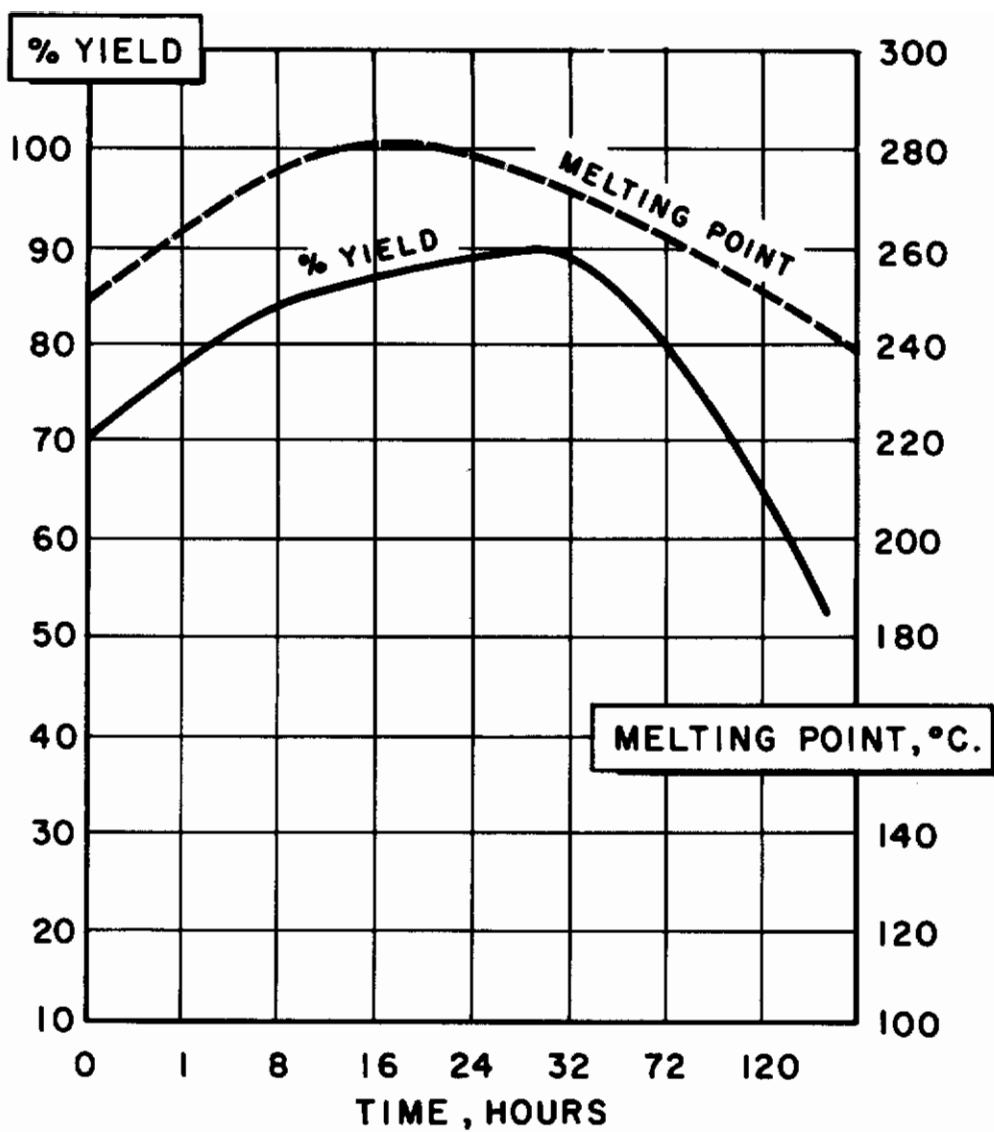


FIGURE 10. $Br \phi SCu$, PYRIDINE, $250^{\circ}C$.

Therefore when a scale up in the polymerization reaction was desired, 16 hours at 250°C in pyridine was selected for the reaction conditions. The first attempts were carried out in glass lined high pressure reactors. In each case, however, the liner broke and low yields resulted. In addition to the low yield, the bomb temperature could not be measured any closer than 50-60°C in the second experiment since the thermowell had to be removed. Consequently the polymer in this case was very poor, as indicated by the melting point, undoubtedly due to too low a reaction temperature.

In order to avoid the difficulties, at least temporarily, of the solution polymerizations, it was decided to polymerize at 212°C in the solid state. The last three runs in Table XI show the results of this work. The runs were made for five, six and one-half, and nine days. The fact that reaction times greater than five days were needed to obtain a polymer with good properties, run 5, is probably due to the lack of agitation in the ampoules. This would probably cause a temperature gradient in the reactants from 212°C on the outside of the ampoule to much less than 200°C in the center. After prolonged reaction times this gradient would disappear, but the overall reaction would be slowed down.

In addition to the polymerization studies a preliminary investigation of repolymerization of low molecular weight material was made. From the elemental analyses of the polymers it was discovered that the amounts of copper and bromine in the polymer were about equal. This suggested that the polymer end groups remained intact during workup. Consequently it should be possible to polymerize the polymers further by subjecting them again to polymerization conditions. The results of these attempts are given in Table XII. It can immediately be seen from the melting points that essentially no change has taken place under any of the conditions used. However, some increase in molecular weight is indicated by an increase in solution viscosity (Figure 15).

Polymer Properties

During the course of the polymerization studies the properties of the polymers produced were investigated. Much of this investigation was concerned with molecular weight determinations on the polymer. From the scatter observed in the percent sulfur in the polymer, Table VIII, it can be seen that sulfur analysis is of no use for molecular weight determinations. The percent bromine is useful for determinations at lower molecular weight, Table VIII, but as would be expected it fails at higher molecular weight. Therefore it was decided to investigate the melt viscosity of the polymers.

TABLE XILarge Bomb Polymerizations

<u>Time (Hrs)</u>	<u>Temp. °C</u>	<u>Solvent</u>	<u>% Yield</u>	<u>M. P. °C</u>
15-1/2	250	Pyridine	52.7	278-285
16	250	Pyridine	78.7	255-265
120	212	None	71.8	259-260
156	212	None	61.7	264-274
216	212	None	> 95.0	279-290

TABLE XIIRepolymerization

<u>Temp.</u> <u>°C</u>	<u>Time</u> <u>(hrs)</u>	<u>Solvent</u>	<u>%</u> <u>Yield</u>	<u>M. P.</u> <u>°C</u>
250	0	Pyridine	-	265-278
250	12-1/2	Pyridine	62.4	265-275
250	12	Pyridine	69.3	275-282
200	0	None	-	265-272
200	24	None	94.0	255-270
200	72	None	89.7	265-273

Contrails

The apparatus used is shown in Figure 11. The polymer is packed into the capillary in the viscometer so as to give a bubble free column. The side arm on the tube is for introduction of a vacuum or an inert gas. The calibration lines on both tube and plunger serve as a means of timing the plunger drop. The plunger has a narrow tip which slides into the capillary as well as a cap on which weights can be placed.

The heating apparatus for the viscometer is shown in Figure 12. The central well is used for the viscometer and the two thermowells for determining the temperature at both ends of the capillary tube in the viscometer. The temperature in the center well was calibrated against thermometers in both thermowells in order to provide two independent measures of the center well temperature.

Since viscosity determinations are capable of giving only relative molecular weights, it was necessary to calibrate the technique. This was done by determining the viscosities of polymers whose bromine analyses were believed to be reliable.

The results of the melt viscosity determinations at 303°C are given in Figures 13 and 14 for solution polymerizations at 200° and 250°C and for solid state polymerizations at 200° and 250°C respectively. In each case the viscosity rapidly increases to a maximum and then falls off about as rapidly. The maxima occur at 8000 poises for 32 hours at 200°C in pyridine, 230,000 poises for 16 hours at 200°C in pyridine, 26,000 poises for 5 days at 200°C in the solid state, and 6000 poises for 3 days at 250°C in the solid state. The highest two maxima 230,000 poises and 26,000 poises correspond roughly to \bar{x}_n 's of 400 and 200 respectively. These maxima occur at about the same regions in reaction time that polymer melting points and percent yields show maxima. Apparently some degradation process is taking place which becomes dominate after the polymerization reaction has slowed down. In addition infusible, insoluble materials are found at prolonged reaction times indicating a crosslinking reaction also. The fact that the appearance of maxima occurs in both solution and solid state polymerizations would indicate that pyridine is not responsible for the degradation. The actual culprit may be the salt produced during polymerization. This is suggested by the data in Figure 15. These are the results of solution viscosity determinations on repolymerization reactions. As can be seen no maxima occur. Instead the viscosity rises steadily with increasing reaction time. Since on workup of the polymer prior to repolymerization the halide salt was removed, this would seem to indicate that this material is indeed the culprit.

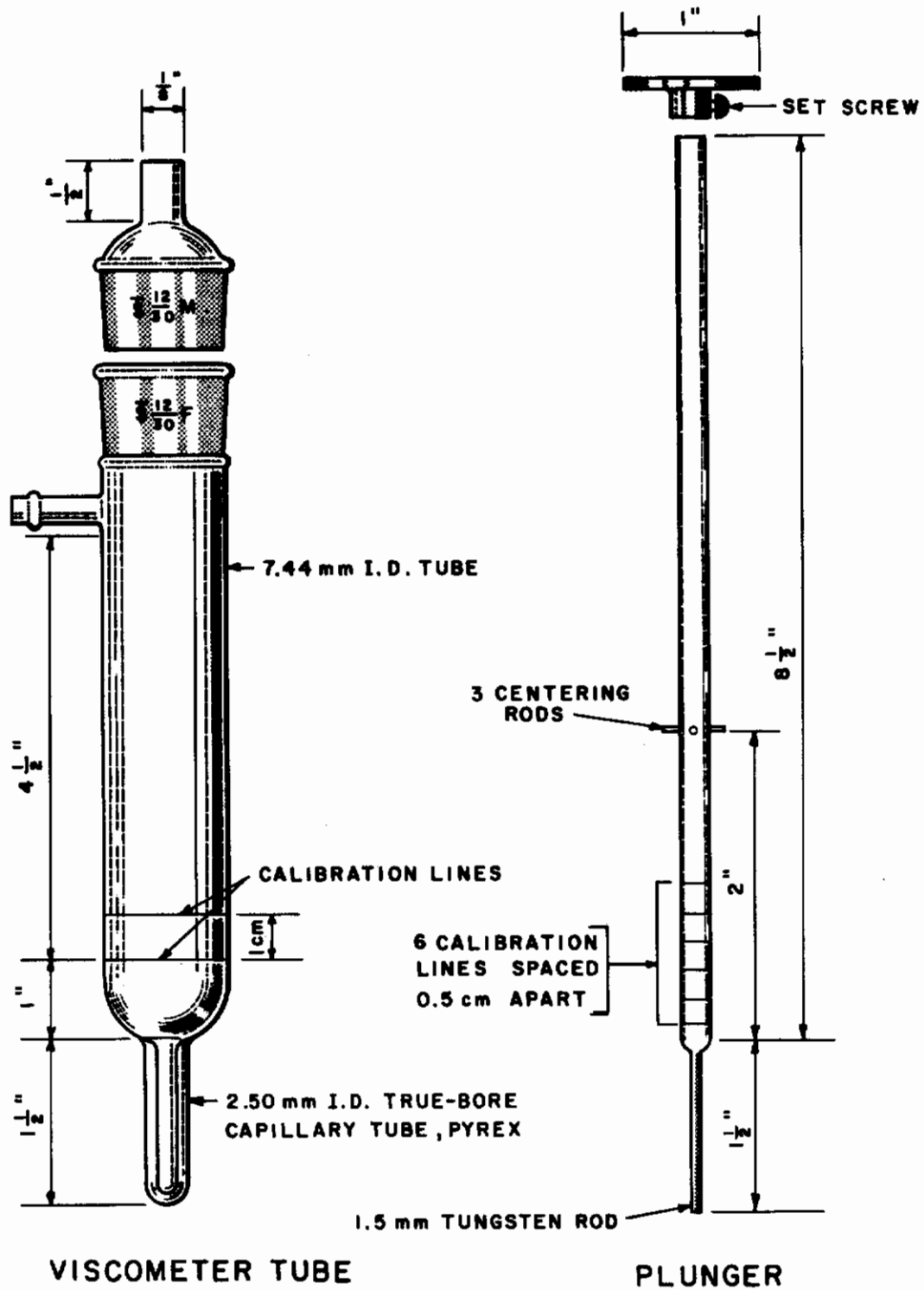


FIGURE 11. MELT VISCOMETER

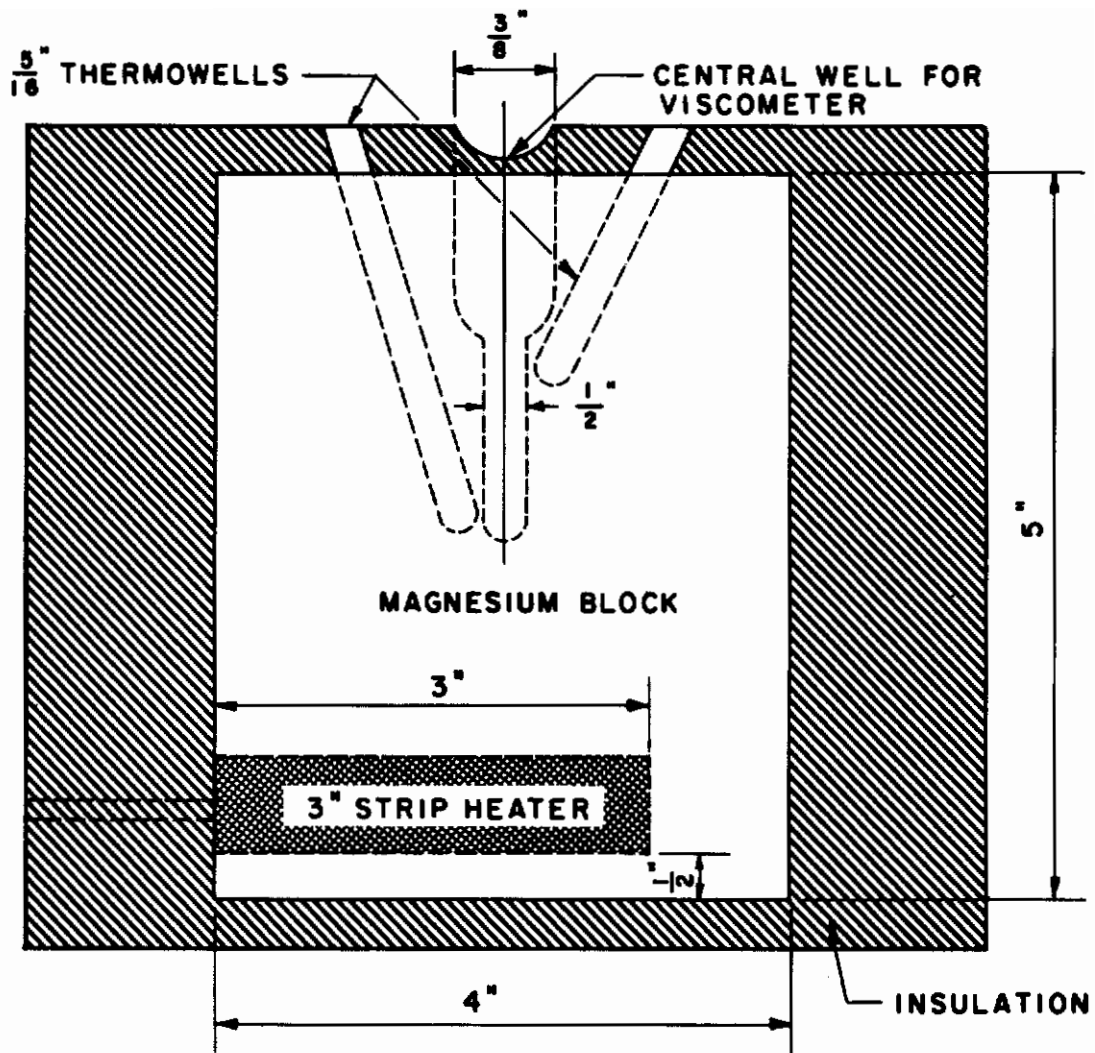


FIGURE 12. HEATING BLOCK FOR VISCOMETER

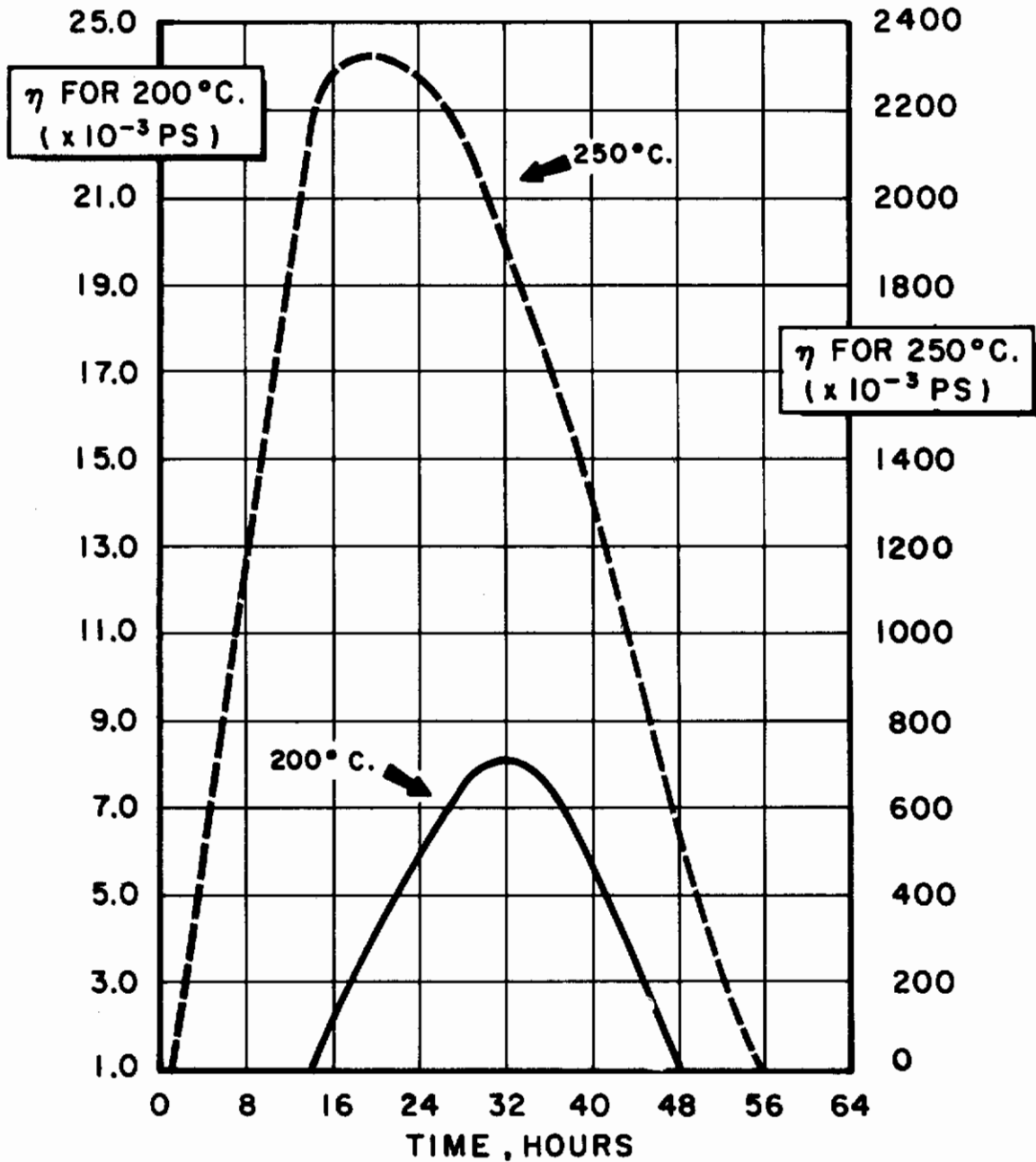


FIGURE 13. MELT VISCOSITY-POLYMERIZED IN SOLUTION

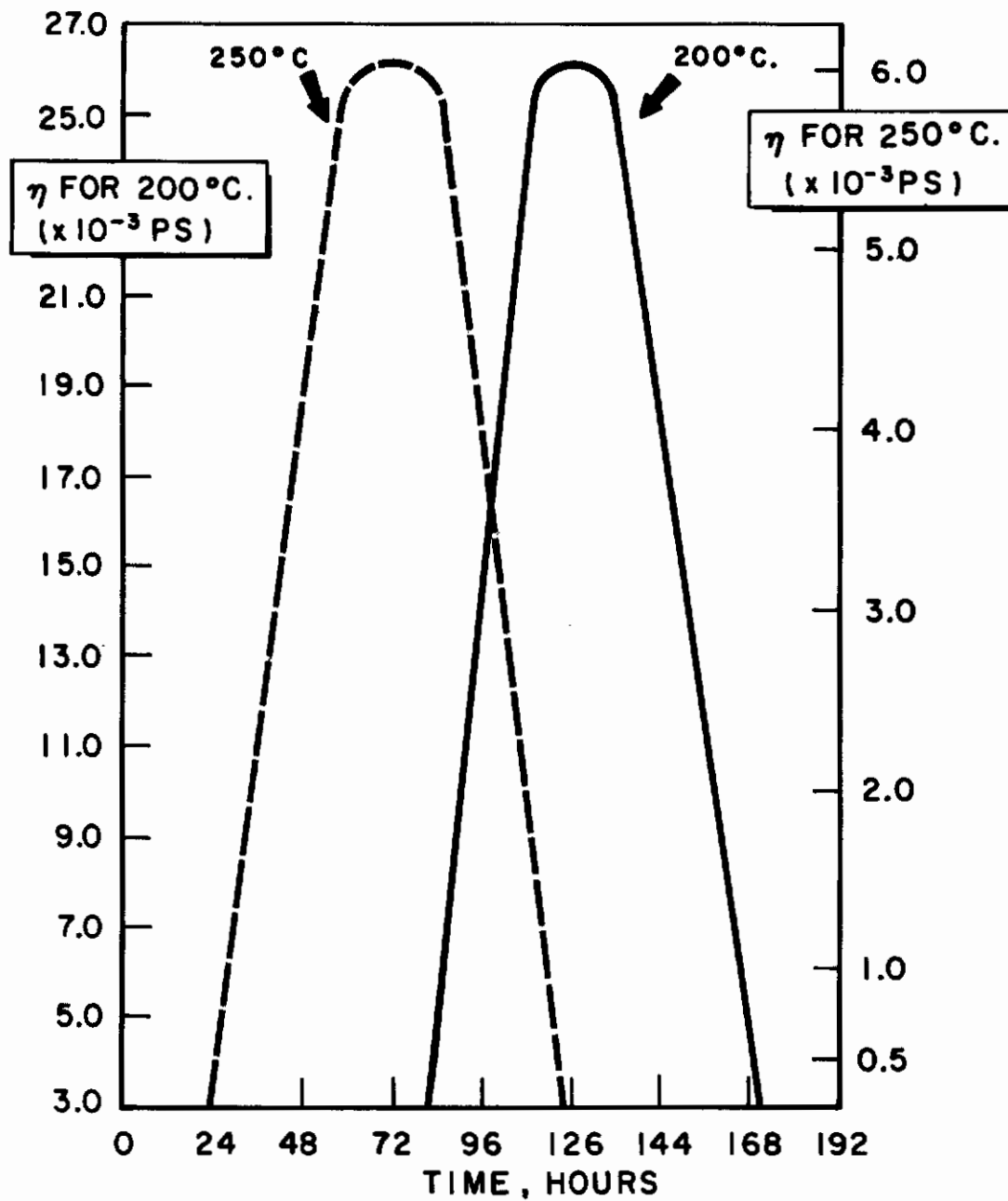


FIGURE 14. MELT VISCOSITY-POLYMERIZED IN SOLID STATE

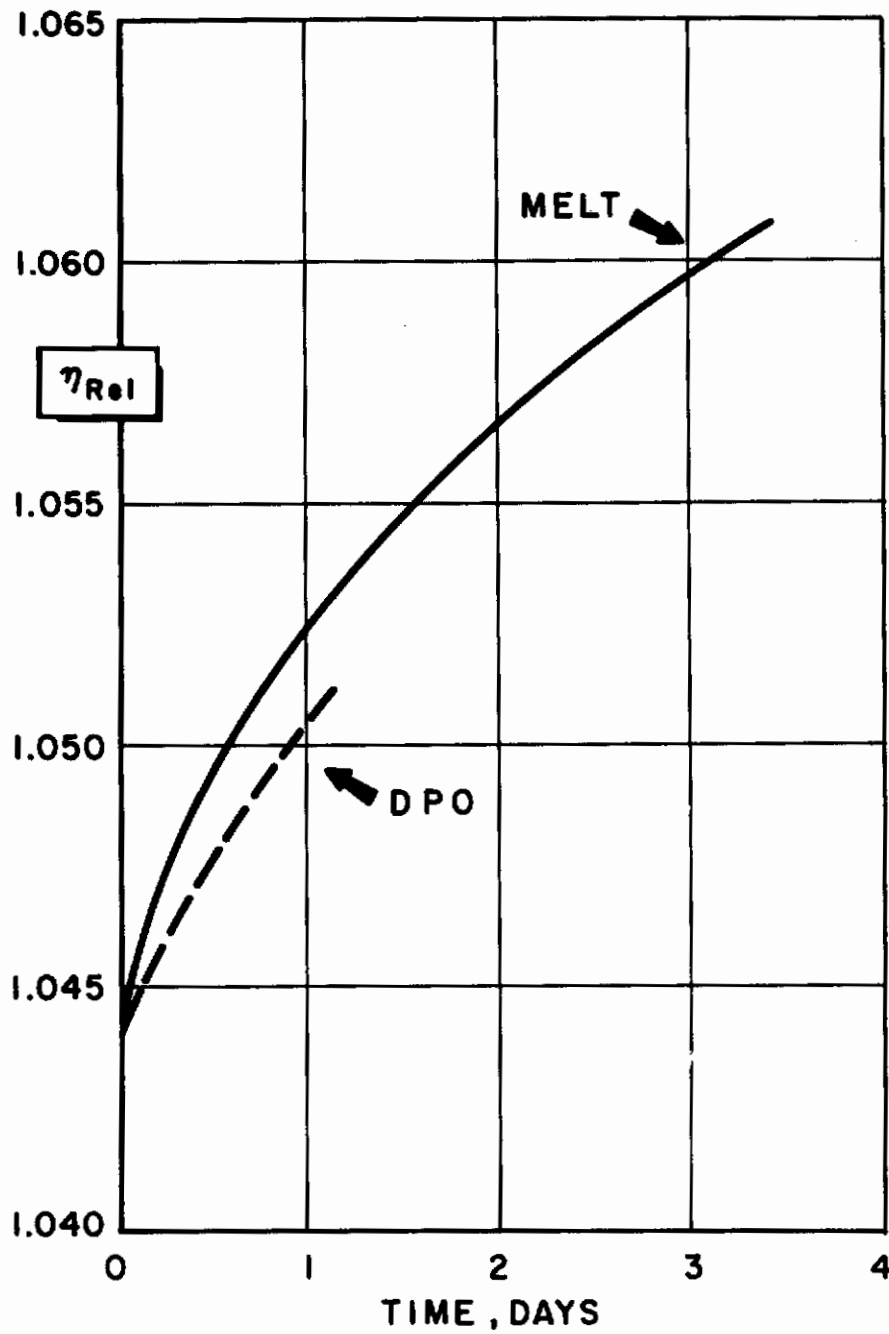


FIGURE 15. SOLUTION VISCOSITY-REPOLYMERIZATION

Contrails

In addition to the melt viscosity work, solution viscosities have also been determined. These were carried out on a 1% polymer solution in diphenyl ether at 250°C. The results correlate quite well with the melt viscosity results. However, this technique has one advantage in that it can be used to classify polymers as to molecular weight whose melt viscosity is too low to measure.

Another property investigated was the solubility of the polymer. Since phenylene sulfide polymer is a highly crystalline material, a high boiling solvent is required. The results of solubility tests with such solvents is given in Table XIII. The polymer is insoluble in the first four solvents listed, and it reacts with sulfuric acid. In diphenyl ether and diphenyl sulfide, however, at least a 1% solution can be attained at reflux. The polymer, due to its crystalline nature, then precipitates on cooling at about 200°C in diphenyl ether and somewhat lower, 170°C, in diphenyl sulfide. It is the solubility of the polymer in diphenyl ether which made solution viscosity determinations possible as well as providing a means of separating the polymer from the other products of polymerization.

A preliminary investigation of the fabrication properties of the polymer was also made. It was found that a fiber could be pulled from the melt of a polymer of high enough molecular weight. This fiber was fairly strong and flexible.

Somewhat more time was spent on the compression molding properties. The higher molecular weight materials could be molded into a fairly tough, flexible film that was at least partially transparent. The film could be folded and creased without cracking. An additional property was noted during the molding operations. This was the great tenacity with which the polymer adhered to the metal molding plates or to glass. In one case the polymer stripped the metal coating from the plate instead of breaking free from it. The polymer did not adhere to Teflon, but the color and transparency of the film were much worse when Teflon was used as a molding plate.

One of the most important properties investigated was the thermal stability of the polymer. Figure 16 shows the results of the thermal gravimetric analysis of some polymer samples sent to Wright-Patterson Air Force Base for testing. Under either air or nitrogen polyphenylene sulfide is stable to about 450°C. At this point degradation sets in slowly until, in air, the polymer is essentially gone at 700°C. In nitrogen, however, degradation appears to cease at 600°C, and a thermally stable residue is formed which resists further degradation up to 900°C.

Since it would be very desirable to know if this thermally stable residue has useful properties, several samples were treated

TABLE XIIISolubility of Phenylene Sulfide Polymers

<u>Solvent</u>	<u>Solubility at Reflux</u>	<u>Precipitation Temperature</u>
Pyridine	0.0%	-
2,4-Lutidine	0.0%	-
Toluene	0.0%	-
Polyether	0.0%	-
Diphenyl Oxide	$\cong 1.0\%$	200°C
Diphenyl Sulfide	$\cong 1.0\%$	170°C
H ₂ SO ₄	Reacts	-

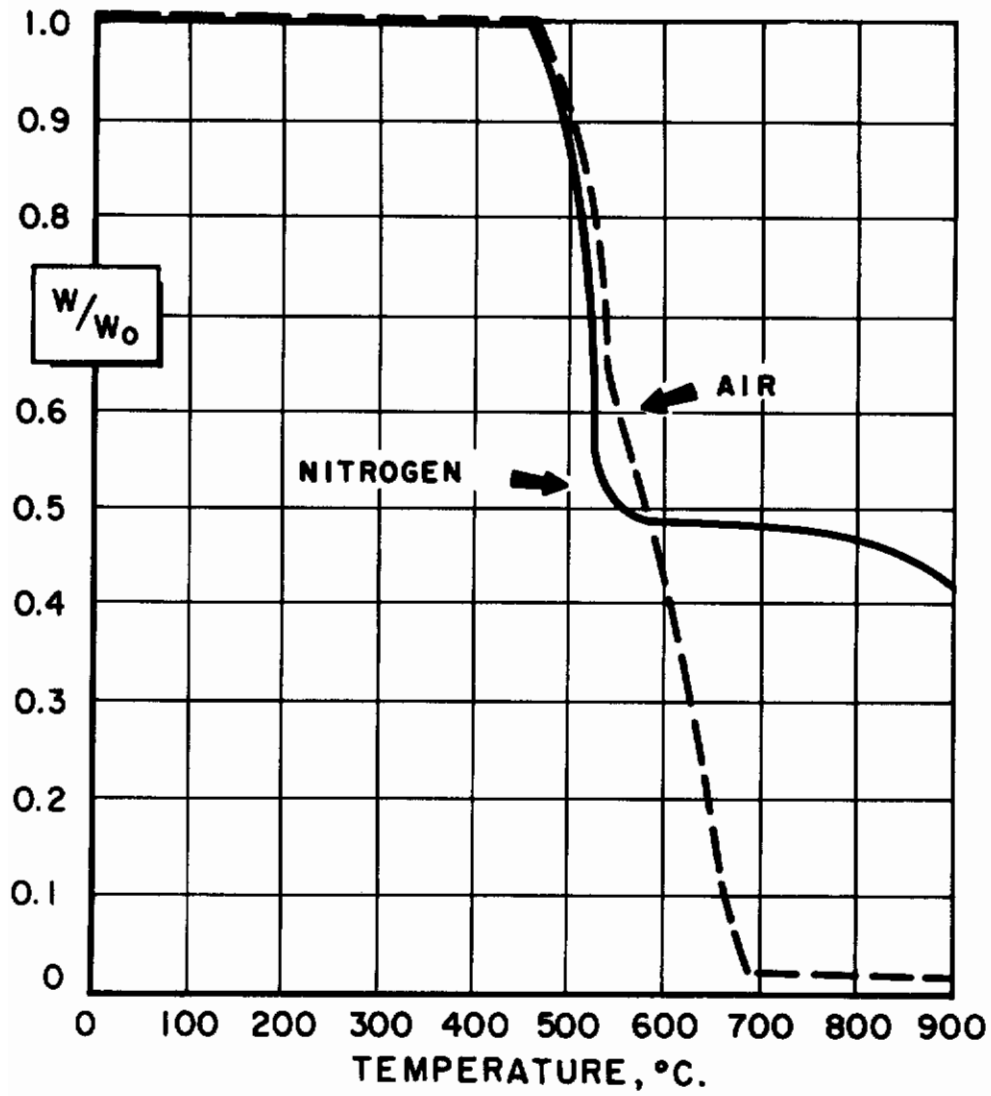


FIGURE 16. THERMAL GRAVIMETRIC ANALYSIS

Contrails

at 400°C and 500°C under nitrogen to determine what properties the residue did have. The results are given in Table XIV. In each case a black glassy material was obtained which probably was cross-linked. The best material resulted from treatment at 400°C for 65-70 hours which gave a material with better properties than the original material even though some degradation had occurred. Treatment at 500°C for prolonged periods of time seems to be too drastic resulting in a material with poor molding properties. After only three hours at 500°C, though, the material still has good molding properties.

One interesting feature of the heat treatment was that material having good molding properties appeared only after solubility in diphenyl ether had disappeared. Thus the two runs that produced material that was still soluble in diphenyl ether gave only poor to fair films while the insoluble materials with the exception of that from 24 hours at 500°C gave good to excellent films.

Another interesting feature was the effect of molecular weight on weight loss and film properties. The molecular weights are roughly in the order polymer (3) > polymer (1) > polymer (2). The weight losses for a given treatment time, however, are in the reverse order, polymer (2) > polymer (1) > polymer (3). The film properties also appear to correlate with the molecular weight of the starting materials. In other words the material produced from the highest molecular weight starting material gave the best film and vice versa.

From the results obtained with the larger polymerizations along with the properties of the polymer and the heat treated material the phenylene sulfide polymer appears to be potentially a very useful material.

Acknowledgments

We wish to express our appreciation for the able direction of the contract work provided by the former director of the contract, Dr. R. W. Lenz, from the inception of the contract in April, 1960 to August, 1961 when he left the Midland Division to join the Eastern Research Laboratory of The Dow Chemical Company.

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TABLE XIV
Heat Treatment of Low Molecular Weight Polymer

Starting Polymer	Time (hrs)	Temp. °C	M. P. °C	Weight Loss %	Diphenyl Ether Solubility %	Film Properties	
						Toughness	Adherence Appearance
Polymer 1	0	-	265-270	-	100	Very poor	Very poor Opaque
	3	500	> 600	30	0	Good	Very good Transparent
	24	500	> 600	56	0	Too high	melting and brittle
	20	400	283-287	16	99	Very poor	Very poor Opaque
	40	400	285-290	22	99	Fair	Good Transparent
	68.5	400	> 600	27	0	Very good	Very good Transparent
Polymer 2	0	-	262-265	-	100	Poor	Poor Opaque
	3	500	> 600	38	0	Good	Good Transparent
Polymer 3	0	-	264-274	-	100	Very poor	Very poor Opaque
	70	400	> 600	18	0	Excellent	Excellent Transparent