

## THE PREPARATION AND EVALUATION OF POLY(PHENYLENE)TRIAZOLES

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### ABSTRACT

This research was carried out for the purpose of evaluating poly(phenylene)triazoles for use in fiber and film applications at high temperatures. Initial work emphasized the preparation, purification and characterization of the necessary intermediate compounds for the preparation of poly(phenylene)triazoles from reactions of phenylene-bis-tetrazoles.

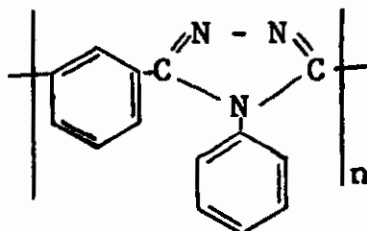
1,4- and 1,3-Bis[3,4-diphenyl-1,2,4-triazolyl-5] benzenes were prepared as model compounds containing the desired triazole structure in combination with the para- and meta-phenylene groups. Thermal evaluation of these compounds by differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) showed them to be stable to their melting points with no weight-loss up to 500°C.

Efforts to prepare high molecular weight poly(phenylene)-triazoles by the reactions of phenylene-bis-tetrazoles with diimino-chlorides under a variety of conditions have thus far been unsuccessful. Improved solvent systems are being sought, and butyrolactone-pyridine mixtures appear to be the most promising of those tried.

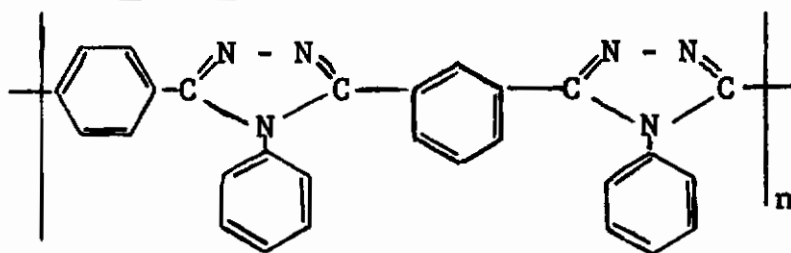
An alternate synthesis approach to prepare polytriazoles by condensing diacid hydrazides with diamides in the presence of hydrazine at elevated temperatures and pressures has resulted in products of uncertain compositions.

## I. INTRODUCTION

Among the polyaromatic systems investigated by Abshire and Marvel,<sup>1</sup> two examples of poly(phenylene)triazoles, poly(3,5-bis-m-phenylene-4-phenyl)-1,2,4-triazole,



and poly(3-m-,5-p-phenylene-4-phenyl)-1,2,4-triazole,



were reported. These polymers showed reasonably good thermal stability and were considered to be potential candidates for high temperature fiber and film applications. However, in order to obtain fibers and films of the poly(phenylene)-triazoles for evaluations in high temperature applications, it is necessary to find means for preparing higher molecular weight polymers; this is the principal objective of the work reported in this paper. Approaches taken to attain this goal include:

- (1) The preparation of high-purity polymerization intermediates.
- (2) The preparation and characterization of model phenylene-triazole compounds for reference purposes.
- (3) The screening and evaluation of polymerization solvents and techniques.



## 1. Preparation of High-Purity Polymerization Intermediates

In most condensation polymerizations high-purity reactants are necessary to obtain high molecular weight polymers of known composition and properties. Therefore, a program of synthesis, purification and characterization was undertaken to provide supplies of high-purity *m*- and *p*-phenylene-bis-tetrazoles and N,N'-diphenyl-iso- and tere-phthalimino-chlorides for use in subsequent condensation polymerization studies. The synthesis routes used for preparing these compounds were those followed by Abshire and Marvel<sup>1</sup> with some modifications to individual reactions. The purifications of these compounds were greatly facilitated by the use of high-purity intermediates in their preparations. Consequently, the iso- and tere-phthalonitriles used in the preparations of the bis-tetrazoles, and the N,N'-diphenyl-iso- and tere-phthalamides used in the preparations of the imino-chlorides were rigorously purified.

High-purity iso- and tere-phthalonitriles were obtained from the corresponding acids in 50-60% yields by a single-step synthesis. A mixture of the acid, urea and dehydrating catalyst was stirred and heated in adiponitrile until all of the dinitrile had distilled from the mixture with the aid of an ammonia sweep gas. The isophthalonitrile, thus obtained, was purified by recrystallization from methanol; and the tere-phthalonitrile was recrystallized from dimethylformamide (DMF) and/or n-butyl alcohol.

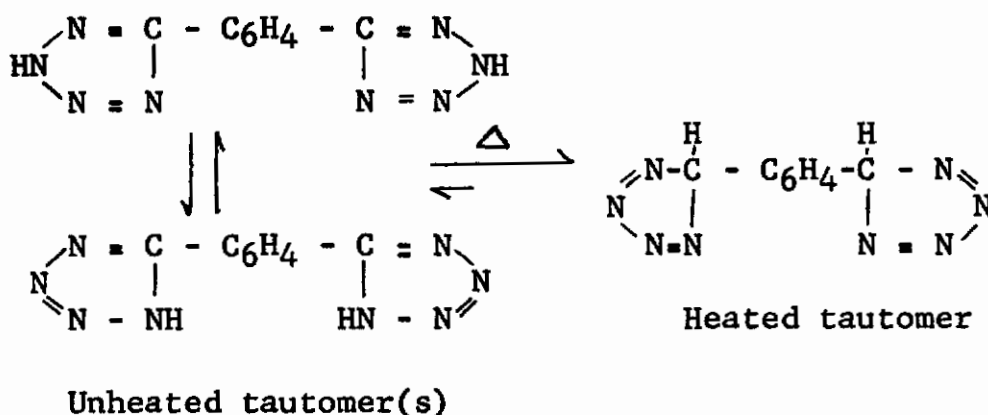
N,N'-Diphenyl-iso- and tere-phthalamides were prepared in 90-95% yields by use of the Schotten-Baumann technique. Aniline was added to a mixture of a benzene solution of the diacid chloride slurried with an aqueous sodium bicarbonate solution. Analytically pure N,N'-diphenylisophthalamide (m.p. 282-283.5°C; reported<sup>3</sup> m.p., 245-250°C) was obtained by recrystallizations from cyclohexanone and butyrolactone. Analytically pure N,N'-diphenylterephthalamide (m.p. 336.0-336.2°C) was obtained by recrystallizations from DMF and butyrolactone.

Several improved synthesis procedures for 5-aryltetrazoles have been reported in the recent literature<sup>4,5,6</sup>. Herbst and Wilson<sup>4</sup> pointed out that higher boiling solvents facilitated the reaction of hydrazoic acid with aryl nitriles to

give 5-aryltetrazoles. They developed a procedure wherein n-butyl alcohol was used as the reaction solvent, and hydrazoic acid was generated in situ from sodium azide and glacial acetic acid. The reaction was complete after heating under reflux for six days. Huisgen, Sauer, Sturm and Markgraf<sup>5</sup> prepared 5-aryltetrazoles in ethylene glycol monomethyl ether as the solvent. They used lithium azide in place of hydrazoic acid. By this procedure the reaction was complete after heating under reflux for five days. Finnegan, Henry and Lofquist<sup>6</sup> prepared 5-phenyltetrazole in quantitative yield by heating benzonitrile and ammonium azide in DMF at 125°C for seven hours. These authors also pointed out that the reaction was subject to acid catalysis.

A quantitative yield of *p*-phenylene-bis-tetrazole was obtained after only three hours by heating under reflux a mixture of terephthalonitrile and hydrazoic acid (generated in situ) in diethylene glycol monoethyl ether. A 95% yield of *m*-phenylene-bis-tetrazole was similarly obtained after 24 hours of heating under reflux in ethylene glycol monomethyl ether. Analytically pure *p*-phenylene-bis-tetrazole (decomposition point 302°C) was obtained by recrystallization from DMF. *m*-Phenylene-bis-tetrazole (decomposition point 275°C) was purified by recrystallizations from methanol and pyridine.

Interesting phenomena observed in the determinations of some of the physical properties of *m*- and *p*-phenylene-bis-tetrazoles led us to propose the occurrence of the following heat sensitive tautomeric shift:





The tautomerization of the unheated tetrazole in solution was discussed by Herbst<sup>7</sup>. Occurrence of a thermal tautomerization is supported by the following observations:

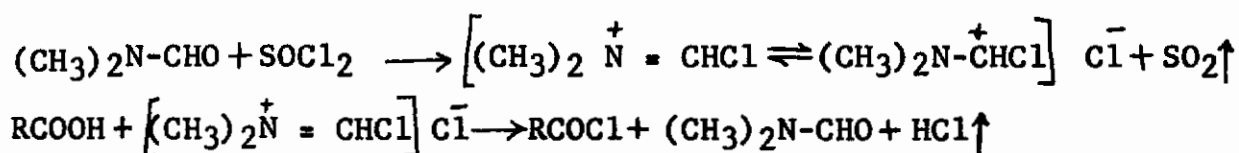
The DTA thermograms of p-phenylene-bis-tetrazole (Figure 1) and m-phenylene-bis-tetrazole (Figure 2) exhibited very strong endothermic peaks in the temperature range of 90-180°C. A TGA weight-loss plot of m-phenylene-bis-tetrazole showed negligible weight-loss below its decomposition point. DTA thermograms of samples of p-phenylene-bis-tetrazole and m-phenylene-bis-tetrazole which had been heated at 125°C overnight and then cooled to room temperature showed no endothermic peaks (Figures 3 and 4, respectively). Also, the infrared spectra of the heated samples showed no characteristic peaks for  $>\text{N-H}$  ( $3350\text{ cm}^{-1}$ ) or  $>\text{C} = \text{N-}$  ( $1600\text{ cm}^{-1}$ ) which were present in the spectra of the unheated samples. X-ray diffraction patterns of the heated and unheated m-phenylene-bis-tetrazole showed distinctly different crystalline lattices. Microscopic examination of the unheated m-phenylene-bis-tetrazole on a hot stage, under polarized light, revealed the formation of minute, weakly birefringent crystals around the original sample at about 130°C. Similar examination of a preheated sample of m-phenylene-bis-tetrazole showed no such crystal formation in this temperature range.

Samples of the two tetrazoles which were heated at 130°C overnight, dissolved in sodium carbonate solution and reprecipitated by the addition of acid, showed identical characteristics to those of the unheated samples. Also, a sample of the m-phenylene-bis-tetrazole which had been heated and then recrystallized from methanol showed identical characteristics to those of the unheated tetrazole. A sample of heated m-phenylene-bis-tetrazole, after standing at room temperature for one week, exhibited an identical infrared spectrum to that of the freshly heated sample. However, after standing for three weeks in a desiccator, the infrared spectrum of the sample showed the presence of a small, but significant  $>\text{N-H}$  peak at  $3350\text{ cm}^{-1}$ .

In light of the facile reversion in solution of the heated tetrazole forms to those of the unheated forms, the identical ultraviolet spectra of the heated and unheated p-phenylene-bis-tetrazole in methanol was not surprising. Both samples of p-phenylene-bis-tetrazole showed strong absorption peaks at  $265\text{ m}\mu$ .

Abshire and Marvel<sup>1</sup> reported the preparation of N,N'-diphenylisophthalimino-chloride by heating a mixture of N,N'-diphenylisophthalamide and excess thionyl chloride under reflux for twelve hours. This was an application of the general procedure developed by von Braun and Pinkernelle<sup>8</sup> for the preparation of imino-chlorides from amides derived from aromatic acids. We obtained N,N'-diphenylisophthalimino-chloride in 92% yield by heating a mixture of the amide and a large excess of thionyl chloride under reflux overnight. Similarly, we obtained a 40% yield of crude N,N'-diphenylterephthalimino-chloride, although Marvel<sup>3</sup> had noted that they had been unsuccessful in preparing the para-isomer by this general procedure.

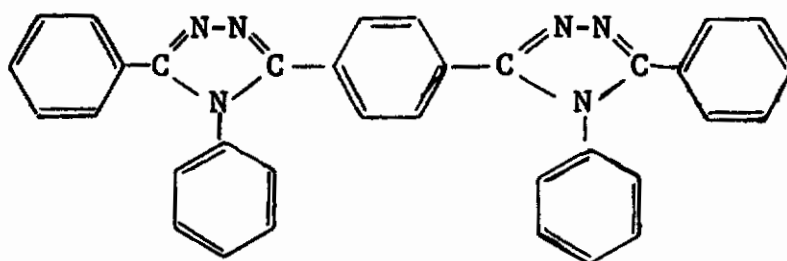
Bosshard et al.<sup>9</sup> reported the excellent catalytic effect of DMF on the preparations of acid chlorides from free acids which did not react with thionyl chloride in the absence of a catalyst. These authors attributed the catalytic activity of the DMF to the formation of a more reactive intermediate.



Similarly, we found DMF to be a catalyst in the preparations of imino-chlorides by the method of von Braun and Pinkernelle<sup>8</sup>. By adding a catalytic amount of DMF to the reaction mixture, N,N'-diphenylisophthalimino-chloride (m.p. 149-150.4°C; reported m.p., 155-156°C) was obtained in 98.5% yield after heating under reflux for only three hours. The imino-chloride, which is extremely sensitive to moisture, was purified by recrystallization from isooctane under anhydrous conditions. N,N'-Diphenylterephthalimino-chloride (m.p. 194-195°C) was similarly obtained in 84% yield after heating the reaction mixture under reflux for a day. This imino-chloride, also extremely moisture sensitive, was recrystallized from tetrahydrofuran under anhydrous conditions.

## 2. Preparation and Characterization of Model Phenylene-triazole Compounds

Huisgen, Sauer and Seidel<sup>2</sup> reported the preparation of 1,4-bis [3,4-diphenyl-1,2,4-triazolyl-(5)] benzene,



from the reaction of p-phenylene-bis-tetrazole and N-phenylbenzimidino-chloride. This compound contains the p-phenylenetriazole repeating unit, which we hope to obtain in the polymer from the reaction of p-phenylene-bis-tetrazole with N,N'-diphenylterephthalimino-chloride. This p-phenylenetriazole (m.p. 425.5°C) was prepared according to the procedure described by Huisgen et al.<sup>2</sup> to serve as a model compound. The infrared spectrum of this compound should serve as a useful reference for detecting or substantiating the presence of the p-phenylenetriazole system in polymerization products. A study of the thermal stability of this model compound should give some insight into the general thermal stability of the p-phenylenetriazole polymer system. A DTA thermogram (Figure 5) showed it to be stable up to its melting point at 430°C, but an exothermic reaction commenced immediately after, or simultaneously with, the melting. However, a TGA weight-loss plot (Figure 6) showed no significant weight-loss up to 500°C, at which temperature general degradation occurred. Inherent viscosity data were obtained on the model compound (M.W. 517) in formic acid to be used as a guide in estimating the molecular weights of low molecular weight p-phenylenetriazole polymer samples.

The corresponding m-phenylenetriazole model compound, 1,3-bis[3,4-diphenyl-1,2,4-triazolyl-(5)]benzene, a previously unreported compound, was prepared by the reaction of m-phenylene-bis-tetrazole and N-phenylbenzimidino-chloride. The melting point of this meta-phenylenetriazole model compound, 243.5°-244.0°C, was surprisingly low compared to that of the para-isomer, 425.5°C. However, the TGA weight-loss plot of the model meta-compound (Figure 7), like that of the para-compound, showed no significant weight-loss below its decomposition point at 500°C. Again, the DTA thermogram of this model compound (Figure 8) showed it to be stable up to its melting point with a slowly

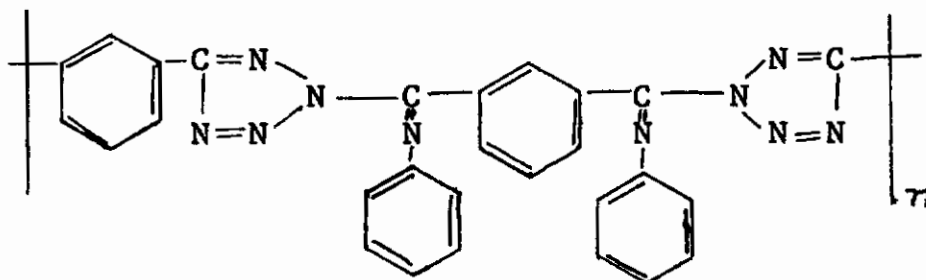


increasing exothermic reaction beginning immediately after melting had occurred. The infrared spectrum of the meta-compound was quite similar to that of the para-isomer, having similar principal peaks at  $1500\text{ cm}^{-1}$ ,  $1470\text{ cm}^{-1}$ , and  $1425\text{ cm}^{-1}$ . Substantiation of the identity of the meta-model compound was fairly well completed by a satisfactory elemental analyses report.

### 3. Screening and Evaluation of Polymerization Solvents and Techniques

Huisgen et al.<sup>2</sup> and Marvel<sup>3</sup> prepared triazole compounds by heating 5-substituted tetrazoles and imino-chlorides in pyridine. We followed this general procedure using the phenylene-bis-tetrazoles and phthalimino-chlorides at reflux temperature ( $115^{\circ}\text{C}$ ) and at  $90^{\circ}\text{C}$  for 96 and 120 hours, respectively. Precipitation of the polymers from the hot reaction mixtures resulted in products of low molecular weights. At  $90^{\circ}\text{C}$ , the reaction appeared to produce a mixture of polymers containing both triazole and tetrazole rings. Evidence for this was the evolution of gas on heating the polymer and an exothermic reaction at  $275\text{--}285^{\circ}\text{C}$  as shown by a DTA thermogram. This led us to prepare and isolate the intermediate tetrazole polymer and study its thermal conversion to the polytriazole structure.

Polymerization of m-phenylene-bis-tetrazole and  $N,N'$ -diphenylisophthalimino-chloride in refluxing tetrahydrofuran (THF), containing sufficient potassium carbonate to neutralize the hydrogen chloride released, produced a product believed to be largely the intermediate tetrazole polymer:

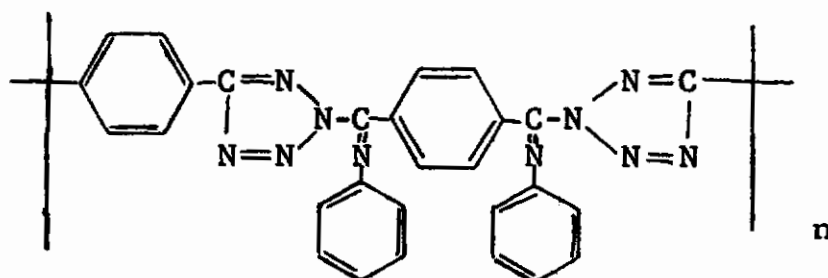


The DTA thermogram of this material (Figure 9) showed a very strong exotherm at  $290\text{--}310^{\circ}\text{C}$ . This type of exotherm was also observed for the tetrazole monomer (Figure 2) at a slightly

higher temperature and was interpreted as decomposition of the tetrazole ring. A TGA weight-loss plot (Figure 10) for this sample showed little weight-loss below 290°C. At 290°C a sudden weight-loss of 12.7% occurred. This temperature corresponded to the DTA exotherm and the weight-loss compared favorably with the calculated weight-loss of 12.95% in going from a polytetrazole to a polytriazole structure. There was little additional weight-loss from 290°C to 450°C, indicating good thermal stability for the assumed triazole structure in that range. From 450°C to 600°C, considerable weight was lost leaving a completely carbonized residue. The weight-percent of this residue agreed with the theoretical carbon content (68%) of the starting polytetrazole sample. The tetrazole polymer was soluble in formic acid; however, low viscosity values indicated a very low molecular weight for the polymer.

A sample of the tetrazole polymer in adiponitrile was slowly heated to 270°C. The evolution of gas during heating and the almost complete elimination of the exotherm at 300°C from the DTA thermogram of the resulting material were strong indications of conversion to the polytriazole structure. Infrared absorption spectra of the heated and unheated polymer, while different, could not be conclusively interpreted. On heating the dry, powdered tetrazole polymer to 300°C, vigorous evolution of gas occurred resulting in a brittle, amber-colored foam. Carbonization occurred more readily with the dry polymer than with an adiponitrile solution of the material.

The polymerization procedure using refluxing THF as solvent was repeated with *p*-phenylene-bis-tetrazole and *N,N'*-diphenyl-terephthalimino-chloride to give the isomeric *p*-phenylene tetrazole polymer:



The DTA thermogram of this material (Figure 11) showed the characteristic tetrazole decomposition exotherm at 305-325°C. The TGA weight-loss plot (Figure 12) was similar to that of

the poly(m-phenylene)tetrazole except in the upper temperature range. A 3.8% loss of weight occurred up to 300°C. The sharp loss of 13.3% of sample weight observed at 300°C compared well with the calculated theoretical loss of nitrogen in going from the polytetrazole to the polytriazole structure. Above 300°C this material was less stable than the poly(m-phenylene)triazole product. A weight-loss of 6.2% occurred between 300°C and 400°C and rapid carbonization was indicated above 400°C.

Sauer, Huisgen and Sturm<sup>10</sup> reported the tetrazole anion to be more thermally stable than the substituted or free tetrazoles. Previous poly(phenylene)triazoles obtained by the reactions of the phenylene-bis-tetrazoles and the diimino-chlorides have contained some residual tetrazole rings. It seemed possible that the triazole rings would be formed progressively at the ends of the growing polymer chains if the diimino-chloride were added to the disodium salt of the phenylene-bis-tetrazole at a temperature such that the less thermally stable substituted tetrazole rings would decompose as they were formed. To investigate this possibility, the disodium salt of m-phenylene-bis-tetrazole was prepared in DMF and heated to 140-145°C which effected complete solution of the tetrazole salt. A hot solution of N,N'-diphenylisophthalimino-chloride in DMF was added dropwise to the hot salt solution causing simultaneous gas evolution and the precipitation of an orange-colored solid. Work-up of this reaction mixture by a rather tedious procedure resulted in the isolation of an 82.6% yield of polymer. However, this polymer was shown by a DTA thermogram to contain some unchanged tetrazole rings. Viscosity data indicated a molecular weight of probably not much more than 1000.

The difficulties encountered in the preparations of poly-(phenylene)triazoles of sufficiently high molecular weight to have fiber forming characteristics seemed to center around the insolubility of the initially formed polymers in the solvent media used. Hot DMF containing 5% dissolved lithium chloride was found to dissolve about 15% of its weight of the low molecular weight polymer. However, only decomposition products were obtained from the addition of N,N'-diphenylisophthalimino-chloride to disodium m-phenylene-bis-tetrazolate in this salt solution at 140-150°C.

The possibility existed that the imino-chloride may have been reacting with the hot DMF. Therefore, hot pyridine containing



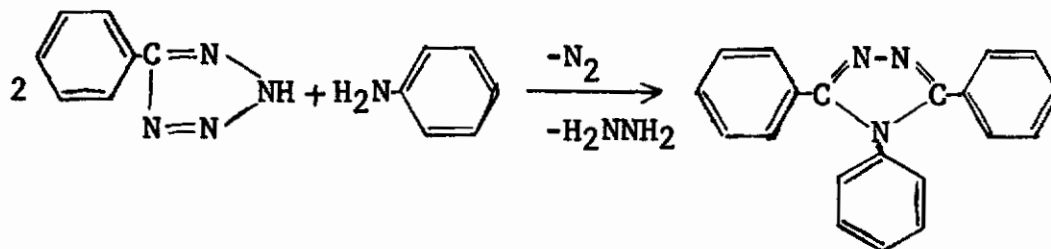
5% dissolved lithium chloride was substituted for the DMF-lithium chloride solvent, and a warm solution of the free tetrazole was added to a hot solution of the imino-chloride. The only product isolated was a light brown powder which decomposed to tar with gas evolution above 270°C.

Low molecular weight *m*-phenylenetriazole polymer was observed to be soluble in boiling nitrobenzene forming a viscous dope. However, *m*-phenylene-bis-tetrazole was not readily soluble in this solvent and appeared to react with the nitrobenzene under reflux. In hopes that nitrobenzene would prove to be a satisfactory polymerization medium, N,N'-diphenylisophthalimino-chloride and *m*-phenylene-bis-tetrazole were mixed in nitrobenzene at room temperature. No noticeable reaction occurred, although the imino-chloride dissolved. On heating, gas evolution occurred at about 100°C. The only product isolated from the mixture decomposed to a viscous black tar at 360°C.

Attempts were also made to prepare the polytriazoles from the tetrazoles and imino-chlorides in the presence of quinoline, tri-*n*-butylamine and dimethylacetamide. Again product precipitated from the hot reaction mixtures and only low molecular weight polymers were obtained.

Further efforts to find satisfactory solvents in which to prepare high molecular weight poly(phenylene)triazoles by solution techniques have indicated that N-methyl-2-pyrrolidone and mixtures of butyrolactone and pyridine may have promise for this purpose.

Huisgen<sup>11</sup> reported that the thermolysis of 5-phenyltetrazole in aniline gave a 63% yield of 3,4,5-triphenyl-1,2,4-triazole.



This reaction offers a potentially much easier route to the poly(phenylene)triazole systems which avoids the use of the difficultly obtainable imino-chlorides. To investigate this



route, a study of the thermolysis of m-phenylene-bis-tetrazole in aniline was initiated. After stirring a sample of m-phenylene-bis-tetrazole in a large excess of refluxing aniline for three days, the solution was quite dark and there appeared to be no increase in the viscosity of the solution. Only a small amount of resinous material was isolated. This product decomposed at about 230°C with distillation of a clear, colorless liquid. The infrared spectrum of this resinous product showed the presence of the triazole ring, but more closely resembled that of a p-phenylene compound than that of a m-phenylene compound. This indicated the occurrence of a thermally induced rearrangement on the phenylene ring. Another thermolysis reaction between m-phenylene-bis-tetrazole and aniline with dimethylsulfoxide as a solvent and anhydrous zinc chloride as a catalyst resulted in a vigorous decomposition of the reaction mixture.

High molecular weight polymers are usually obtained from polymerizations in which interfacial techniques are employed. However, the extreme susceptibility of the imino-chlorides to hydrolysis makes the use of these compounds impractical in interfacial polymerizations. Addition of a basic aqueous solution of m-phenylene-bis-tetrazole to a solution of N,N'-diphenylisophthalimino-chloride in chloroform resulted in the complete hydrolysis of the imino-chloride and the recovery of the corresponding amide.

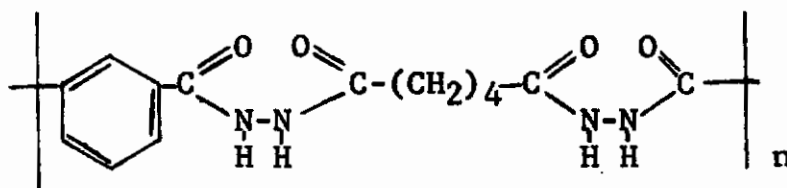
Exploratory attempts to prepare poly(phenylene)triazoles by heating finely ground mixtures of the phenylene-bis-tetrazoles and phthalimino-chlorides in the solid state resulted in products which were soluble in concentrated sulfuric acid. These materials appeared to contain tetrazole units as was evidenced by DTA exotherms in the range of 260-280°C.

## B. Polytriazoles from Diacid Hydrazides

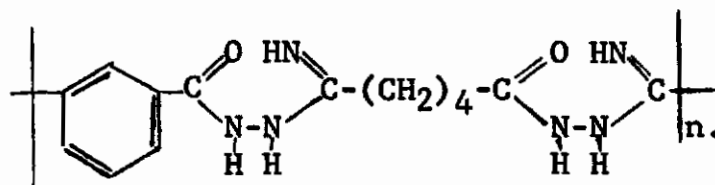
In view of the lack of success of efforts to produce high molecular weight poly(phenylene)triazole by the bis-tetrazole route, the study of a dihydrazide approach to polytriazoles was initiated. Bates, Fisher and Wheatly<sup>12</sup> described the polymerization of various aliphatic diacid hydrazides in the presence of hydrazine to give 4-amino-1,2,4-polytriazoles. When a diamide was reacted with the diacid hydrazide, a 1,2,4-polytriazole was formed.

We chose to study the reaction, first using an aliphatic diamide (adipamide) and an aromatic dihydrazide (isophthalic or terephthalic dihydrazide) in order to form a product which might be fusible and thus more easily handled. The intermediate dihydrazides, isophthalic dihydrazide and terephthalic dihydrazide, were easily synthesized by reacting the dimethyl esters with hydrazine according to the general procedure of Davidis<sup>13</sup>. Ethanol was found to be a satisfactory reaction solvent for the preparation of isophthalic dihydrazide, but was less suitable for the terephthalic analog. However, reasonably high yields (65%) of the terephthalic dihydrazide were obtained in dimethylacetamide. Recrystallizations of the crude reaction products from hot water provided convenient means of purification. The dihydrazides were characterized by melting points, infrared spectra and elemental analyses.

Initial polymerization reactions were carried out at atmospheric pressure in the absence of hydrazine. The reaction of equimolar quantities of isophthalic dihydrazide and adipamide at 200°C and atmospheric pressure produced a clear melt from which ammonia was evolved as the viscosity gradually increased. The viscosity of the reaction melt increased rapidly when the pressure was lowered to 0.5 mm. Hg. Long fibers were easily drawn from this viscous melt; however, they became brittle on cooling, probably because of low polymer molecular weight. Elemental analyses indicated a probable polyhydrazide structure for the material:



However, the fact that the nitrogen content was somewhat high (20.24% vs. 18.42% calculated) and the oxygen content low (20.55% vs. 21.05%) showed contamination by a material of higher nitrogen content, perhaps a structure of the type:



Heating the polymer for several hours at 250°C resulted in some discoloration and loss of water. The viscosity of the resulting polymer, though somewhat higher, did not indicate crosslinking to any significant degree. Solubility in warm formic acid also helped to rule out crosslinking. Elemental analyses indicated a polyoxadiazole structure to be the main product; possibly with some polytriazole as a contaminant. These structures would result from the dehydration of the structures proposed above for the initial polymer.

The above polymerization reaction was repeated in the presence of hydrazine in a small, stirred autoclave. The temperature was maintained at 200°C and the pressure was held at 250 psig for a period of four hours. After a vacuum finishing cycle, a fusible polymer was obtained (m.p. 220°-225° with gas evolution at 240°C). This material was soluble in formic acid, had an inherent viscosity of 0.349 (0.5% in formic acid) and was found to contain 32.77% nitrogen and 6.81% oxygen. Since these values fit none of the anticipated structures, it was concluded that the polymer probably contained several structures. On heating the polymeric reaction product to 280°C over a period of two hours, the material became infusible, though soluble in hot formic acid; and the inherent viscosity increased to 1.174.

It seemed of interest to explore the possibilities of spinning the original polymer into fiber and then, through a heat treatment of the fiber, convert it into the more stable material. However, fibers formed from the molten polymer were too brittle for evaluation. Efforts made to obtain a less brittle fiber by wet-spinning a 30% solids, formic acid dope were unsuccessful. Extremely poor coagulation of the fiber in the spin bath occurred as a probable result of the low molecular weight of the polymer. It had been hoped that sufficient orientation of the polymer could have been attained in the swelled state to impart strength to the fiber. Studies are planned to determine the proper set of reaction variables for increasing the molecular weight of the polymer and to extend the polymerization reaction to include aromatic intermediates.

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Figure 1

DTA Thermogram of *p*-Phenylene-bis-tetrazole

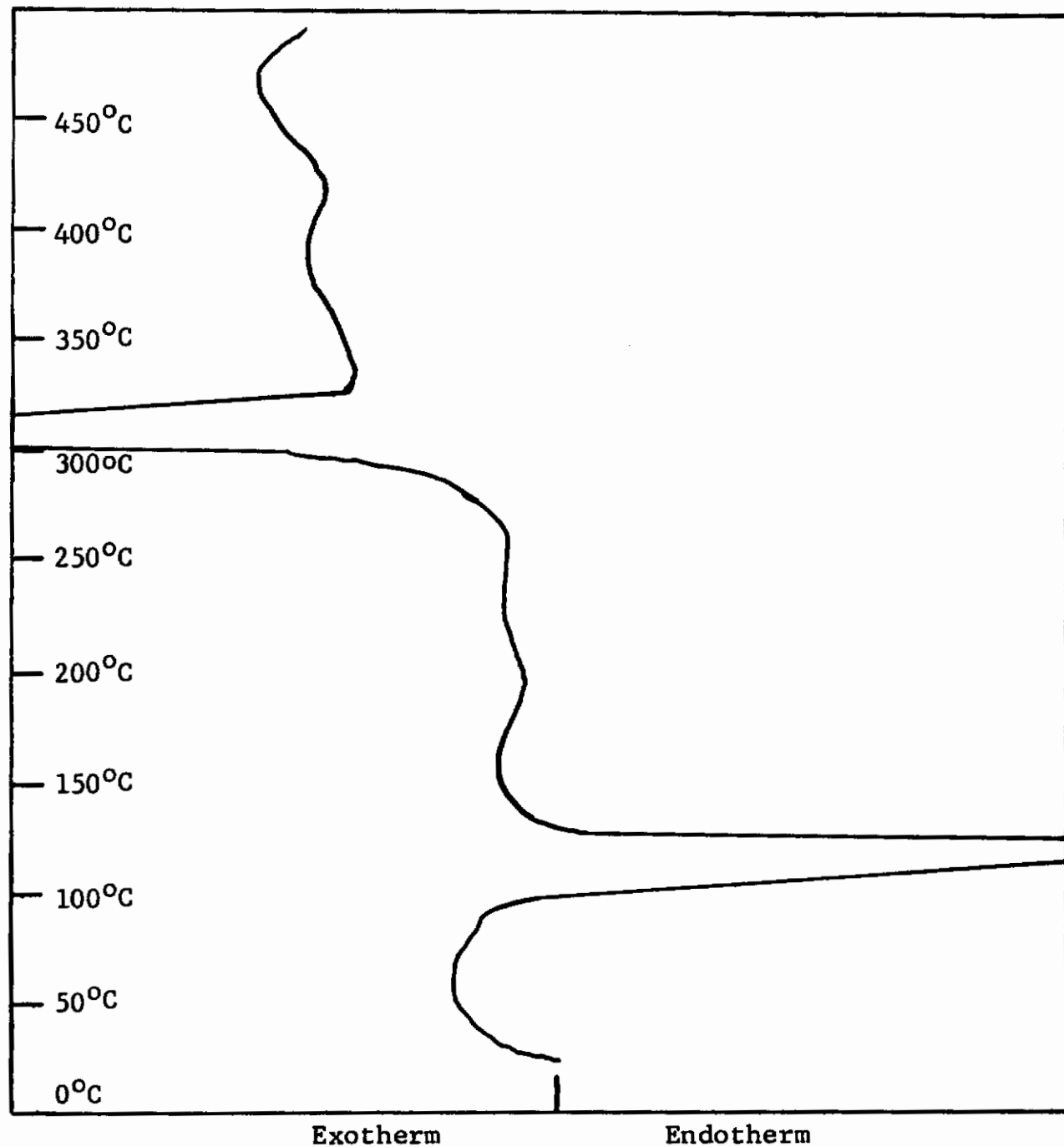


Figure 2

DTA Thermogram of m-Phenylene-bis-tetrazole

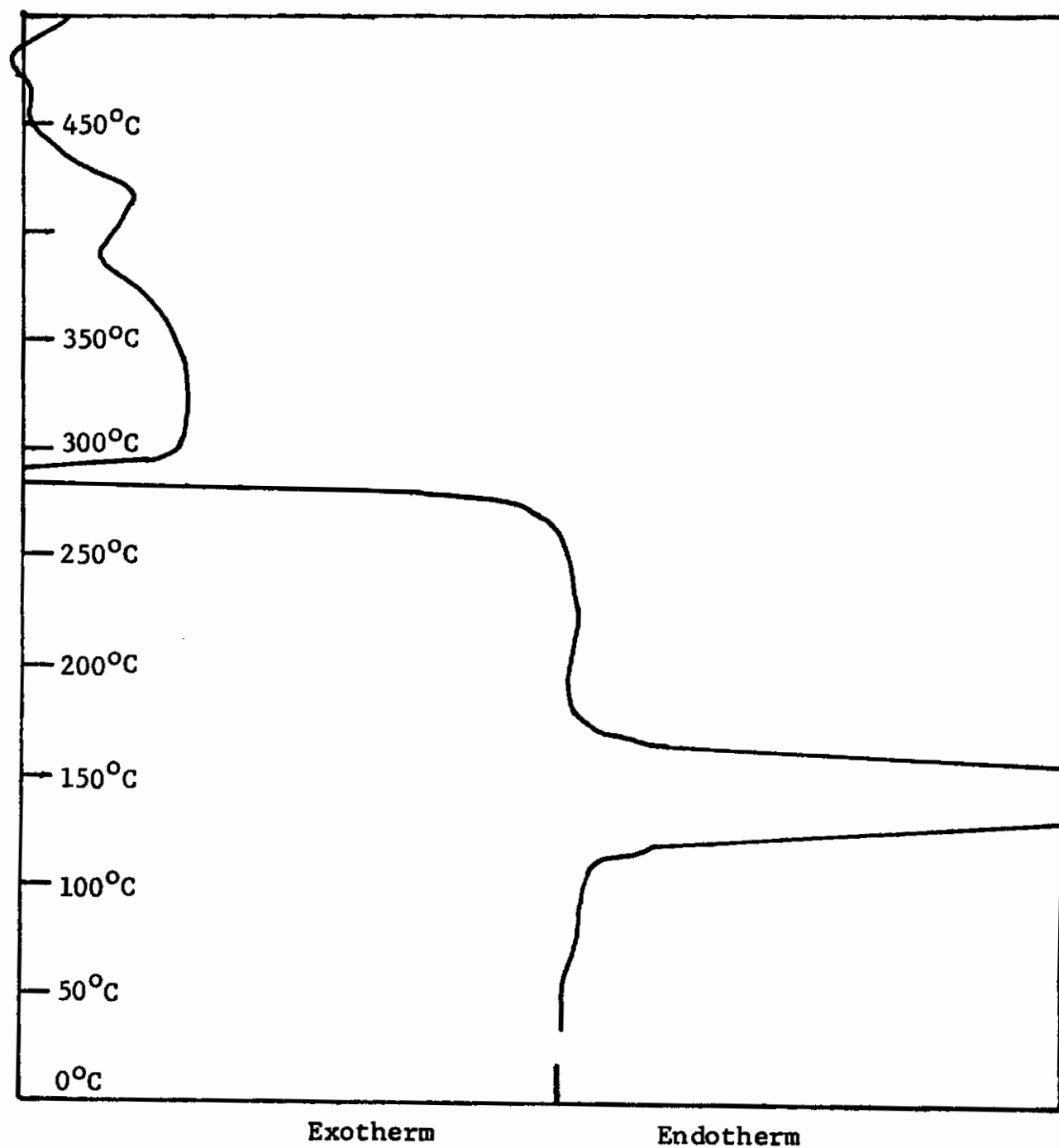


Figure 3

DTA Thermogram of Heated p-Phenylene-bis-tetrazole

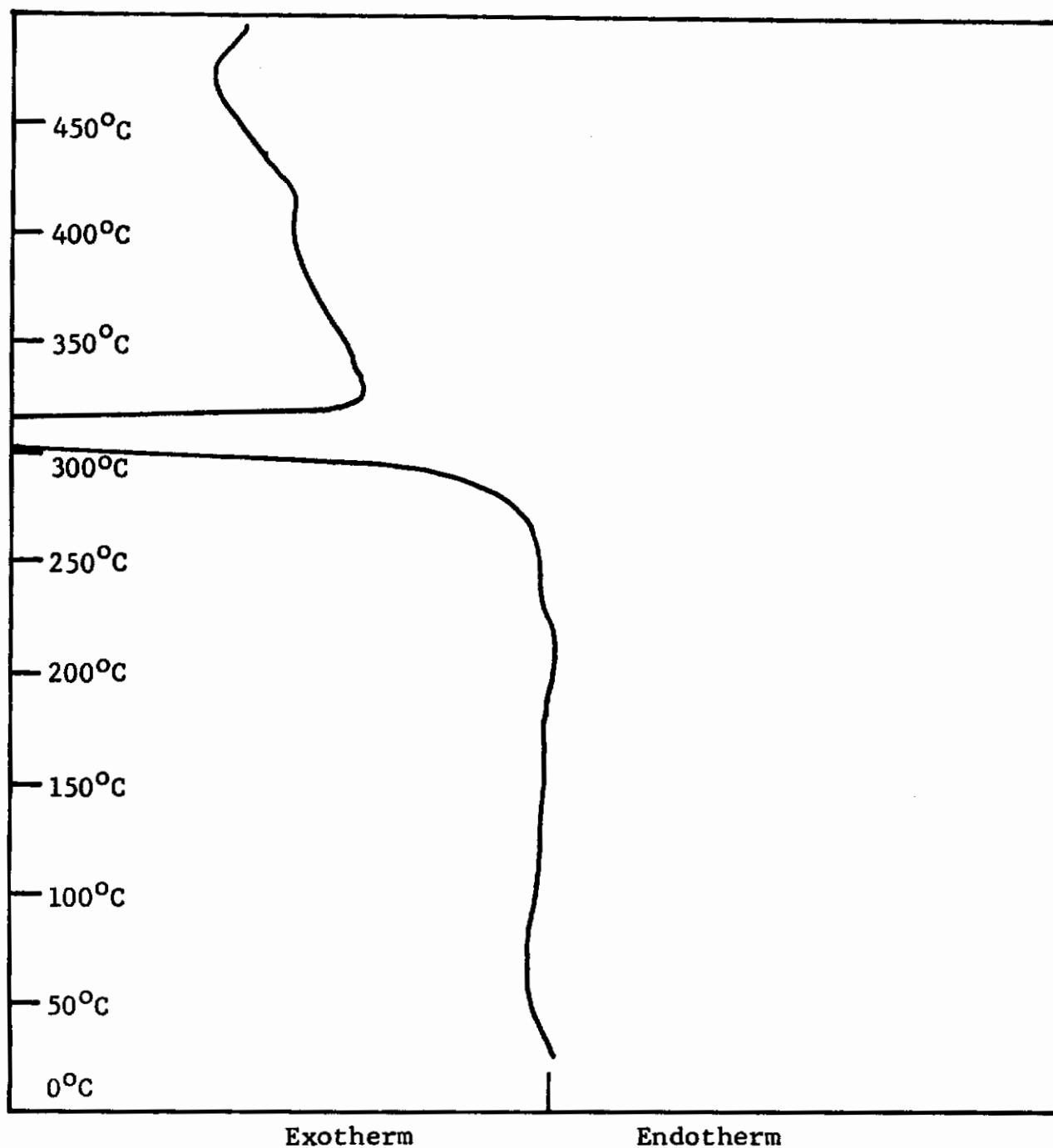


Figure 4

DTA Thermogram of Heated m-Phenylene-bis-tetrazole

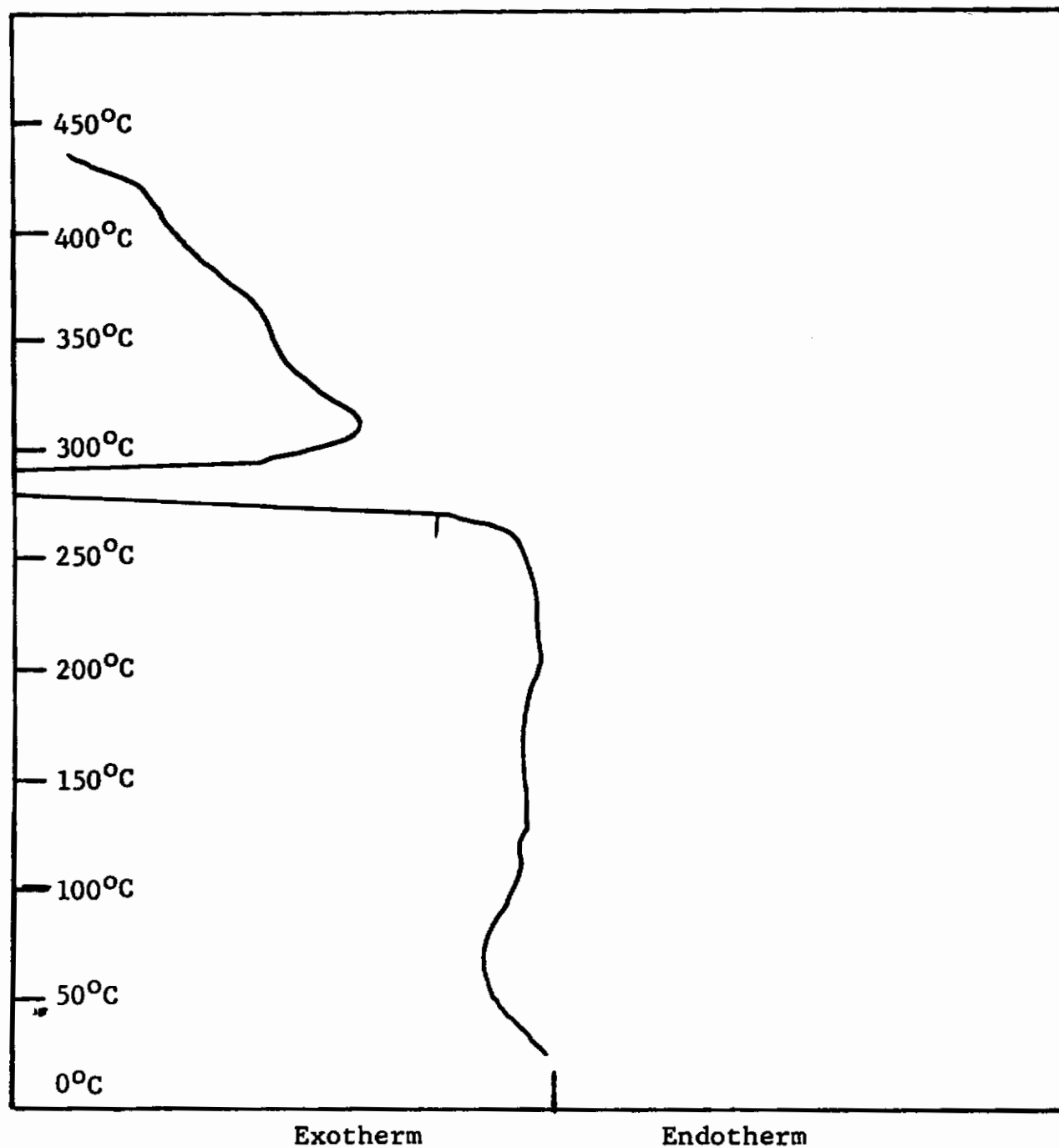




Figure 5

DTA Thermogram of 1,4-Bis[3,4-diphenyl-1,2,4-triazoyl-(5)]benzene

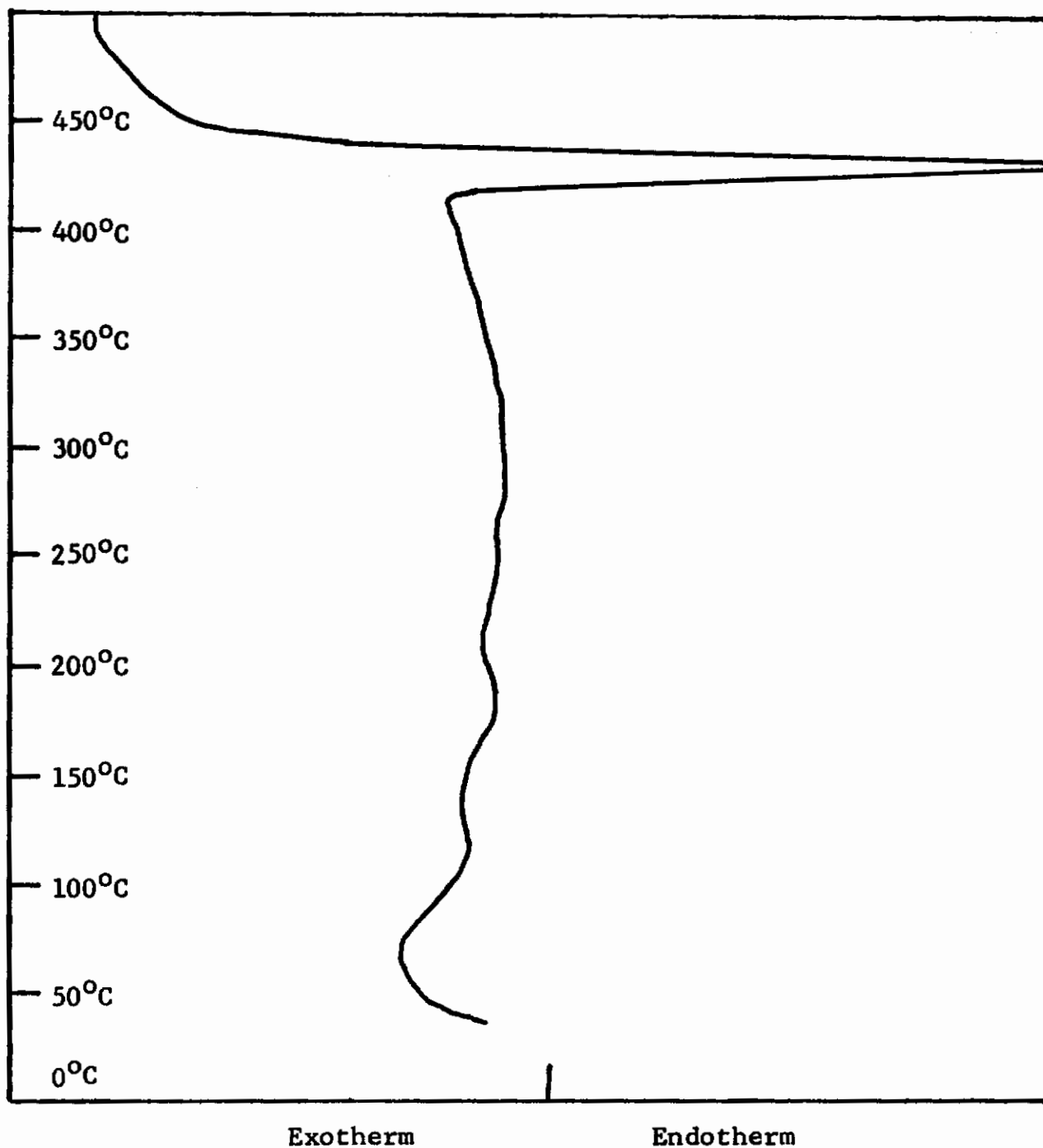


Figure 6

TGA Weight-loss Plot of  
1,4-Bis[3,4-diphenyl-1,2,4-triazoyl-(5)]benzene

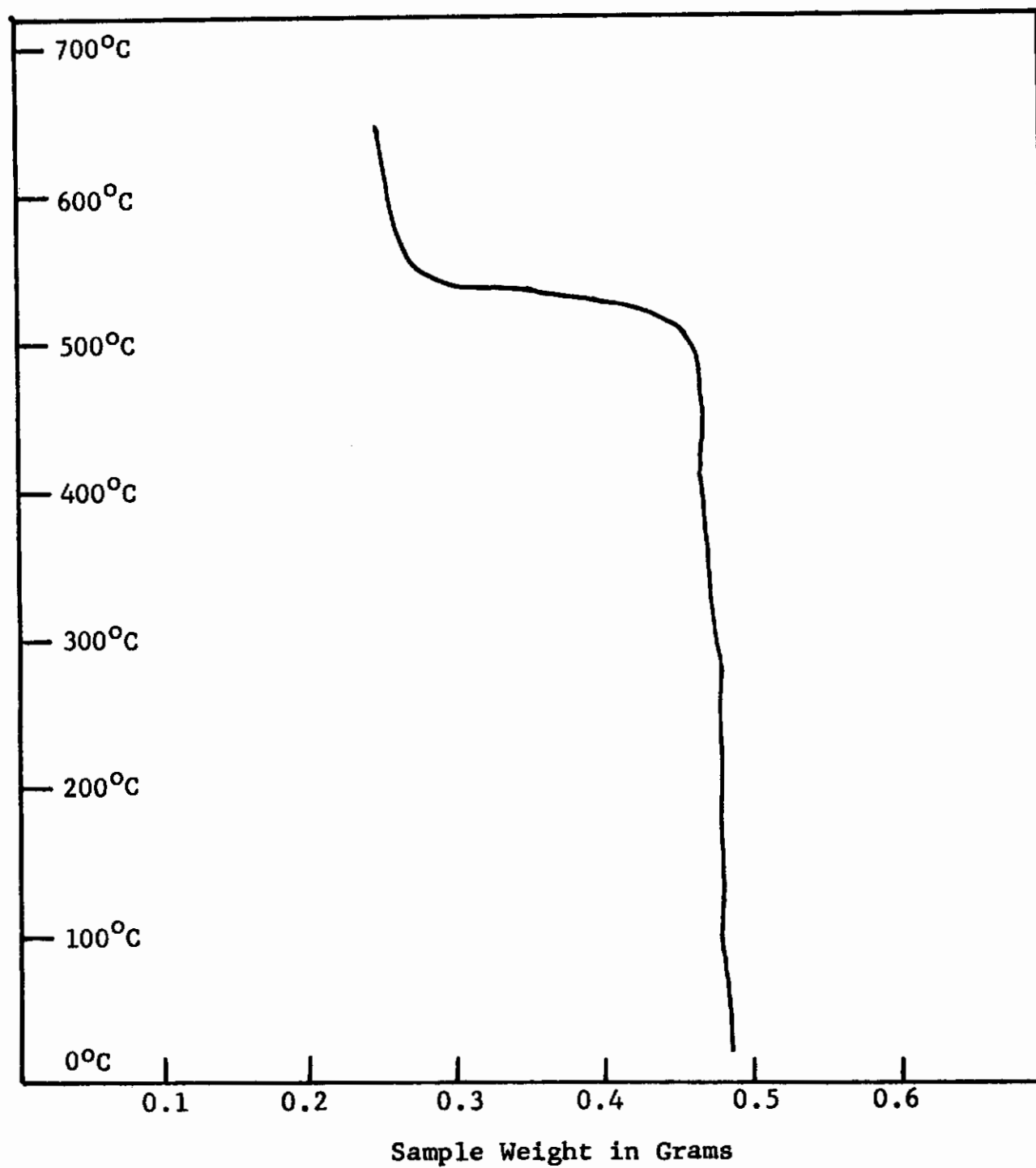


Figure 7

TGA Weight-loss Plot of  
1,3-Bis[3,4-diphenyl-1,2,4-triazoyl-(5)]benzene

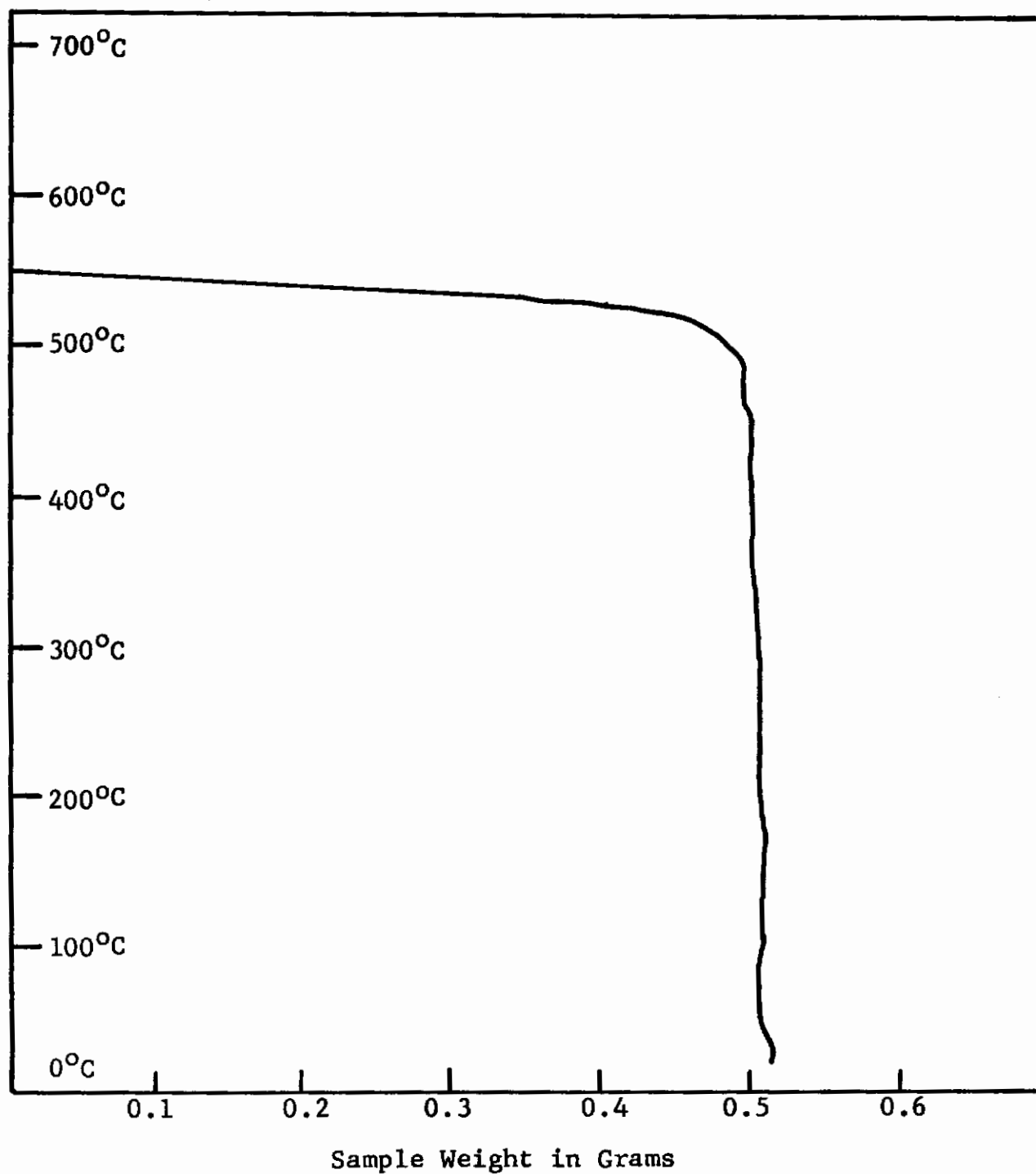


Figure 8

DTA Thermogram of 1,3-Bis [3,4-diphenyl-1,2,4-triazoyl-(5)]benzene

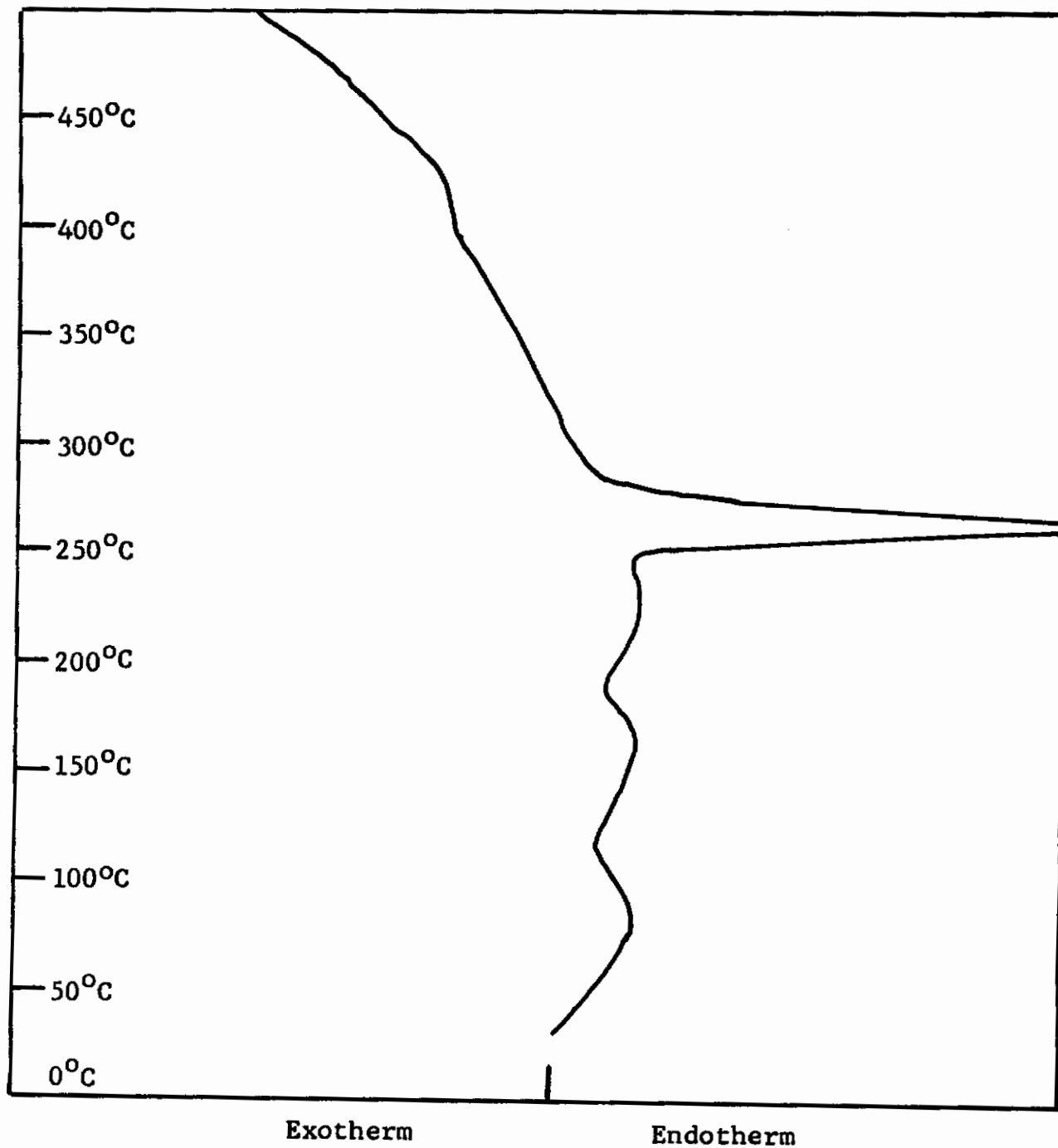




Figure 9

DTA Thermogram of Poly(m-phenylene)tetrazole

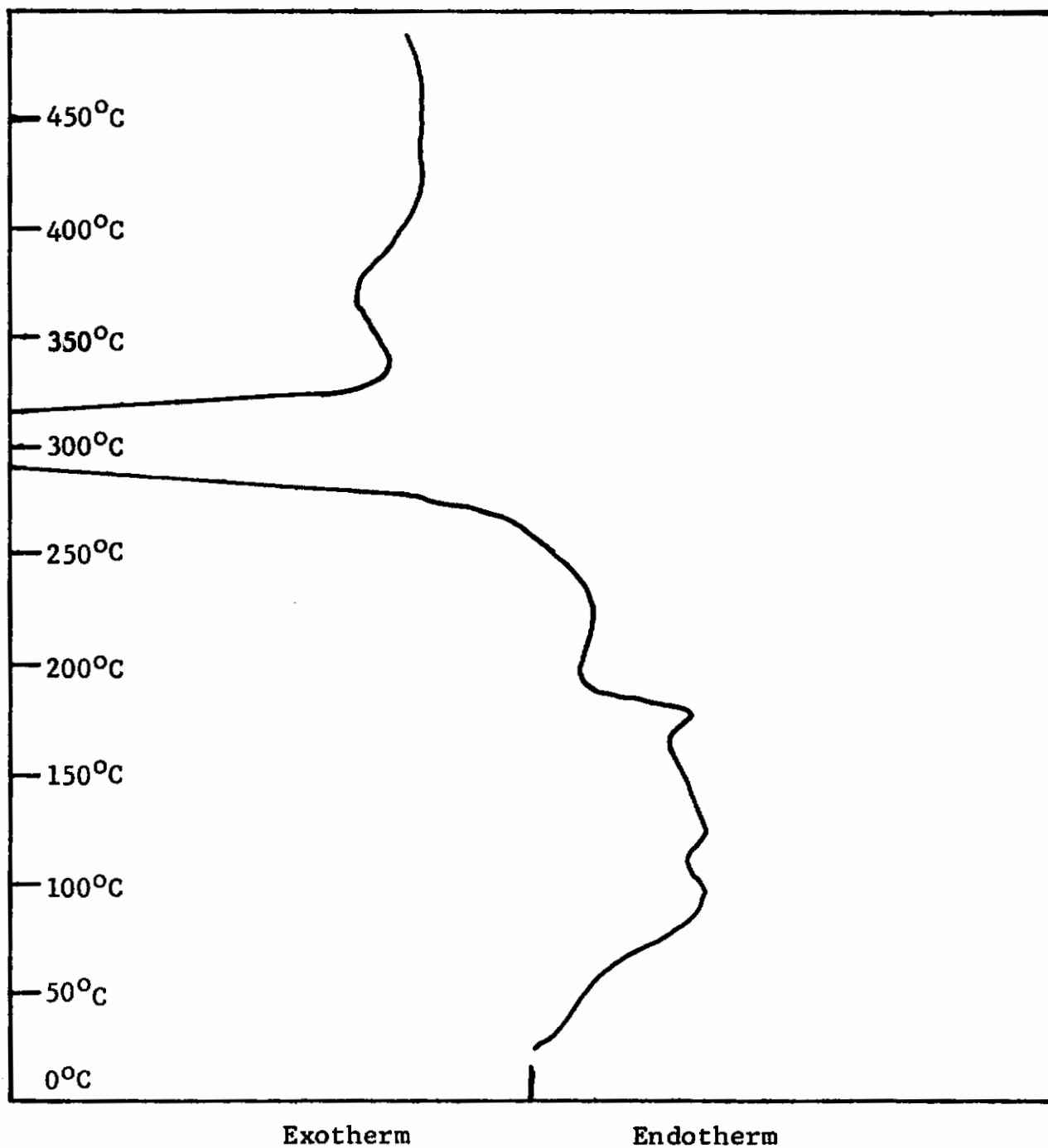


Figure 10

TGA Weight-loss Plot of Poly(m-phenylene)tetrazole

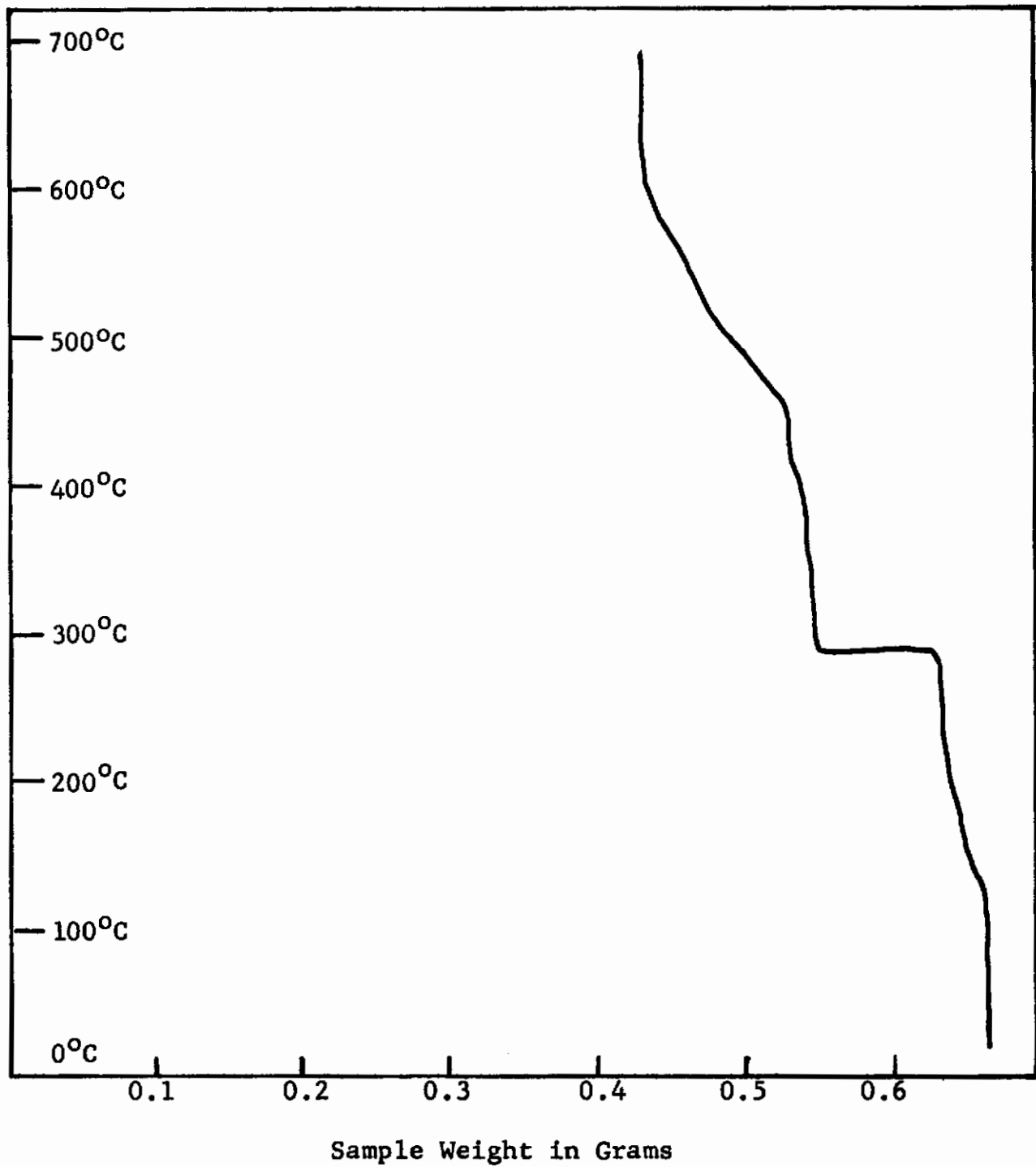


Figure 11

DTA Thermogram of Poly(p-phenylene)tetrazole

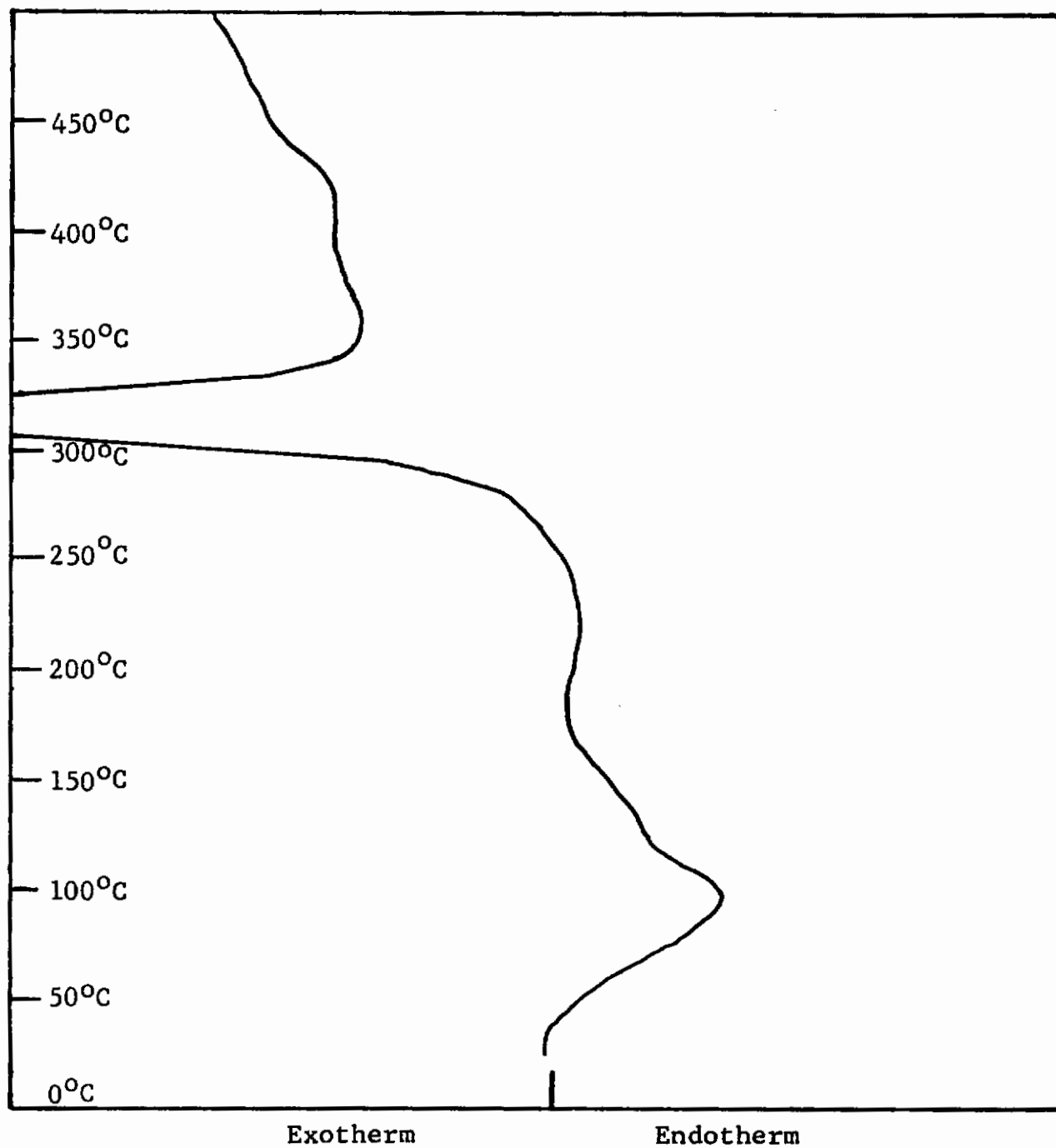


Figure 12

TGA Weight-loss Plot of Poly(p-phenylene)tetrazole

