Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Isomeric and Substituent Effects in Some Dibenzoylbenzene-Diamine Polymers

A. A. Volpe[a]; L. G. Kaufman[a]; R. G. Dondero[ab]
[a] Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey [b] Interchemical Corporation, Clifton, New Jersey

To cite this Article Volpe, A. A. , Kaufman, L. G. and Dondero, R. G.(1969) 'Isomeric and Substituent Effects in Some Dibenzoylbenzene-Diamine Polymers', Journal of Macromolecular Science, Part A, 3: 6, 1087 — 1103

To link to this Article: DOI: 10.1080/10601326908051939

URL: http://dx.doi.org/10.1080/10601326908051939

J. MACROMOL. SCI.–CHEM., A3(6), pp. 1087-1103, October, 1969

Isomeric and Substituent Effects in Some Dibenzoylbenzene-Diamine Polymers

A. A. VOLPE, L. G. KAUFMAN, and R. G. DONDERO*
Department of Chemistry and Chemical Engineering
Stevens Institute of Technology
Hoboken, New Jersey

SUMMARY

This investigation was undertaken to determine the properties of a series of polymers based upon various aromatic diamines and several isomeric diketones. Consequently, six isomeric polymers were synthesized by the acid-catalyzed polycondensation of p- and m-dibenzoylbenzene with o-, p-, and m-phenylenediamine. Two fluorine-containing, isomeric polymers were also synthesized by condensing m-dibenzoylbenzene with tetrafluoro-m-phenylenediamine and tetrafluoro-p-phenylenediamine. Comparative thermal stabilities of the products both in air and under a nitrogen atmosphere were investigated by thermogravimetric analysis. Several of the polymers exhibited a high degree of thermal stability and all of the polymers exhibited essentially the same resistance to initial thermal decomposition in the oxidative as well as the nonoxidative atmosphere. A correlation of molecular structure and geometry with thermal stability and solubility is discussed and a mechanism for initial thermal decomposition of some of the polymers is proposed.

INTRODUCTION

The thermal stability of polymeric Schiff bases synthesized from

---

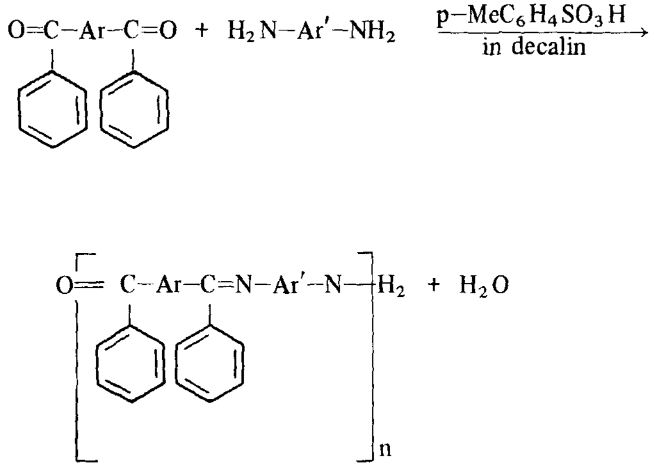
*Interchemical Corporation, Clifton, New Jersey.

dicarbonyls (usually terephthalaldehyde) and aromatic diamines has been reported by several investigators [1-4]. There are, however, relatively few reports in which a diketone is used as the starting dicarbonyl [5, 6]. Consequently, this investigation was undertaken to synthesize and determine the properties of a series of polymers based upon various aromatic diamines and the several isomeric dibenzoylbenzenes.

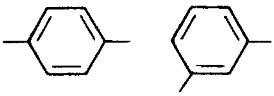
Six isomeric polymers have been obtained from the acid-catalyzed polycondensation of p-dibenzoylbenzene with o-, m-, and p-phenylenediamine and from the acid-catalyzed polycondensation of m-dibenzoylbenzene with the same three isomeric diamines. The synthesis of the dicarbonyl monomers was accomplished by the Friedel-Crafts reaction of terephthaloyl chloride and isophthaloyl chloride with benzene to yield the respective dibenzoylbenzenes. Our attempts to synthesize polymers using commercially available o-dibenzoylbenzene were unsuccessful.

It was possible to determine the general effect of the pendent phenyl groups coming off the polymer backbone upon thermal stability and polymer solubility. It was also possible to determine the effects of molecular geometry, due to the o-, m-, and p-linkages of the isomeric aromatic diamines and dibenzoylbenzenes used, upon solubility and thermal stability.

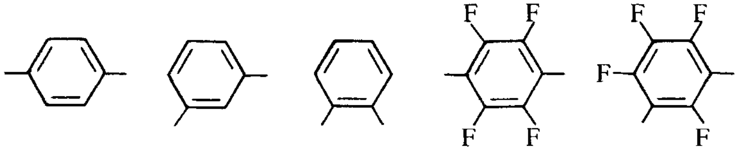
The effect upon thermal stability of the substitution of C–F bonds for some C–H bonds was also investigated by means of the polycondensation of m-dibenzoylbenzene with tetrafluoro-m-phenylenediamine and tetrafluoro-p-phenylenediamine. The general polymerization reaction and the specific isomeric monomers used were as follows:



Ar =



Ar′ =



EXPERIMENTAL

Reagents

Commercial grades of o-, m-, and p-phenylenediamine, purified by recrystallization from hot water, melted, respectively, at 102, 62-63, and 139-140°C.

Commercial p-toluenesulfonic acid monohydrate melted at 104-105°C.

Commercial terephthaloyl chloride, mp 82-84°C, and isophthaloyl chloride, mp 43-44°C, were used as obtained.

Commercial grades of tetrafluoro-m-phenylenediamine and tetrafluoro-p-phenylenediamine melted, respectively, at 130-131 and 147-148°C and were also used as obtained.

All solvents were dried over calcium hydride.

Analytical Methods

Infrared Spectra. The spectra of Nujol suspensions of the products were obtained with a Perkin-Elmer infracord.

Mass Spectroscopy. The mass spectrum of m-dibenzoylbenzene was obtained on a Type 21-103C Consolidated Electrodynamics Corp. spectrometer.

Thermogravimetric Analysis (TGA). Comparative thermal stabilities of the polymer products were investigated in air and under a nitrogen atmosphere with a du Pont 950 instrument programmed for a heating rate of 6°C/min and with a gas flow rate of 40 ml/min.

Preparation of p-Dibenzoylbenzene

Approximately 200 ml of dry, freshly distilled benzene were added to a 500-ml, three-necked flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and reflux condenser. To the benzene were added 20.3 g (0.10 mole) of terephthaloyl chloride and 28.4 g (0.213 mole) of $AlCl_3$. The mixture was stirred and heated slowly to reflux in order to control the rate of escaping HCl. The resulting yellow solution was heated overnight at reflux temperature, after which it was cooled to room temperature and 100 ml of 10% aqueous HCl were added slowly with stirring. The resulting clear solution was then washed with 500 ml of water in three portions and then dried over anhydrous magnesium sulfate.

Upon evaporation of the solvent, 15.7 g (55% yield) of crude product were obtained. Recrystallization from a 1:1 mixture of acetone-hexane yielded a white crystalline material which melted at 158-160°C (reported [7] mp 159-160°C). Its infrared spectrum was identical wiith that of an authentic sample of p-dibenzoylbenzene (Sadtler spectrum no. 20927). Analysis: Calculated for $C_{20}H_{14}O_2$: C, 83.90%; H, 4.89%. Found: C, 83.95%; H, 4.77%.

Preparation of m-Dibenzoylbenzene

A typical Friedel-Crafts acylation was also used for the synthesis of this dicarbonyl. In a 500-ml, two-necked flask fitted with a reflux condenser and drying tube were placed 81.2 g (0.40 mole) of isophthaloyl chloride in 350 ml of benzene. Over a 20-min period, 113 g (0.85 mole) of anhydrous $AlCl_3$ were added with stirring. The mixture was then refluxed for 4 hr in a water bath. While still hot, the mixture was poured into a beaker containing 500 g of crushed ice and 200 ml of concentrated HCl in order to dissolve the aluminum salts. This mixture was then put into a separatory funnel, and the upper brown benzene layer was washed first with 100 ml of 40% NaOH and then with 200 ml of water. The benzene layer was then dried over anhydrous magnesium sulfate.

After the excess benzene was distilled off with a rotary evaporator on a steam bath, the remaining liquid was cooled in an ice bath whereupon it solidified. The crude product was recrystallized from 95% ethanol to give 47 g (41% yield) of a white, crystalline material. The infrared spectrum showed a carbonyl peak at 6.0μ, and the mass spectrum showed a parent peak at m/e = 286 along with the expected molecular fragment peaks. The melting point of the material was 109-110°V (reported [8, 9] mp 100°C). However, the spectroscopic and analytical evidence, as well as the results of subsequent reactions, confirmed that the product obtained was, indeed, m-dibenzoylbenzene. Analysis: Calculated for $C_{20}H_{14}O_2$: C, 83.90%; H, 4.89%. Found: C, 83.81%; H, 4.51%.

Preparation of a Poly(Dibenzoylbenzene-Phenylenediamine)

For a typical polymerization a mixture of 0.715 g (0.0025 mole) of m-dibenzoylbenzene, 0.27 g (0.0025 mole) of p-phenylenediamine, and 0.05 g of p-toluenesulfonic acid monohydrate were refluxed in 70 ml of dry "decalin" (decahydronapthalene) with stirring for 24 hr. The reaction was conducted in a nitrogen atmosphere and the condenser was fitted with a Dean-Stark trap. The mixture was cooled and the yellow solid which precipitated was collected by filtration. This powdery solid was purified by extraction with equal amounts of water and 95% ethanol for 24 hr in a Soxhlet apparatus. The compound was then dried in an oven at 100°C for 1 hr to give 0.56 g (62% yield) of the final product, which did not melt below 300°C. The infrared spectrum of a Nujol mull of the polymer indicated an absorption band at 6.1-6.2μ, which indicated the presence of C=N bonds [10]. Properties of the polymer and other analyses are given in Table 1.

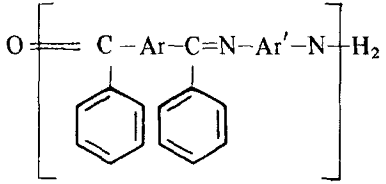
DISCUSSION OF RESULTS

Dibenzoylbenzenes were condensed with various unsubstituted and fluorine-substituted phenylenediamines in a high-boiling solvent (decalin, bp 189°C) in order to obtain maximum molecular weights (Table 1). The yields of products, all of which were colored, varied from 50 to 82% for the nonfluorinated polymers and were not affected by increasing the reaction times. The yields of the two fluorinated polymers were 18 and 54%. Work is currently in progress to determine the effect of increased reaction times upon yield for these systems.

In the para series of polymers (those synthesized using p-dibenzoylbenzene), the isomer prepared from p-dibenzoylbenzene and p-phenylenediamine, and henceforth designated as the para-para isomer in keeping with nomenclature first introduced by D'Alelio et al. [11], had the highest melting point, was insoluble in common solvents, and was obtained in highest yield. The para-meta and para-ortho isomers melted at least 150°C lower than the para-para and were soluble in benzene, chloroform, and acetone. As a result of their solubility, molecular weight determinations were carried out by vapor pressure osmometry and the results indicated that the para-ortho system was a trimer while the para-meta was a dimer.

Although repeated efforts were made to purify the para series polymers, elemental analyses consistently showed low values for nitrogen. This has been a common occurrence with polymeric Schiff bases, as evidenced by

Table 1. Products from Polymerization of Dibenzoylbenzenes with Phenylenediamines



$O{=}[C(C_6H_5)-Ar-C(C_6H_5){=}N-Ar'-N]{=}H_2$

Polymer No.	Ar-Ar′	Yield %	Color	mp, °C^a	Solvents	Molecular weight^b	Analysis, %, (calculated)^c and found C	H	N
I	para-para	82	Yellow	> 300			(87.10) 86.95	(5.03) 5.01	(7.83) 7.85
II	para-meta	75	Yellow-orange	165	Benzene, acetone chloroform	720	(85.00) 86.60	(5.18) 5.49	(7.64) 6.32
III	para-ortho	72	Yellow	160	Benzene, acetone chloroform	1030	(85.70) 85.78	(5.13) 5.66	(7.69) 6.08
IV	meta-para	62	Dark yellow	>300			(87.10) 87.28	(5.03) 4.96	(7.83) 7.67

V	meta-meta	50	Orange	188		(86.40)	(5.10)	(7.73)
						86.54	5.26	7.31
VI	meta-ortho	65	Yellow	265		(87.10)	(5.03)	(7.83)
						87.22	5.19	7.63
VII	meta-tetrafluoro-para	54	Yellow	> 300		(72.56)	(3.26)	(6.51)
						72.66	3.26	6.34
VIII	meta-tetrafluoro-meta	18	White	> 300		(72.56)	(3.26)	(6.51)
						72.46	3.52	6.34

[a] Uncorrected.

[b] Vapor pressure osmometry using benzene as solvent.

[c] Calculated values for high polymers, ignoring the end groups except for II (calculated for a dimer), III (calculated for a trimer), and V (calculated for a pentamer).

the fact that Popov et al. [12] prepared nine polyazines which were low in nitrogen by at least 0.9%. In addition, the para-meta isomer gave a poor analysis for carbon as compared with that calculated for a dimer. This may have been due to the presence of higher-molecular-weight polymer which contains a higher percentage of carbon. Elemental analysis of the para-ortho isomer, however, was in fair agreement with the calculated values for a trimer, and that of the para-para isomer was in very good agreement with the calculated values for a high polymer in which the number of end groups was considered to be negligible.

The meta series of polymers (those synthesized from m-dibenzoylbenzene and phenylenediamines) also exhibited an expected correlation between their melting points and their elemental analyses. The analytical values for the lowest melting isomer (meta-meta, mp 188°C) were, except for a slightly low nitrogen value, in very good agreement with the calculated values for a pentamer, whereas the higher melting isomers (meta-para, mp 300°C and meta-ortho, mp 265°C) were in excellent agreement with the calculated values for a high polymer. It was also found that none of these polymers exhibited sufficient solubility for molecular weight determinations by vapor pressure osmometry.

The fluorine-containing polymers, as expected, had high melting points and preliminary tests indicated that they were insoluble in common solvents. Elemental analyses and other data are given in Table 1.

THERMAL STABILITY

All of the nonfluorinated polymers, when heated in nitrogen and in air at a rate of 6°C/min, exhibited thermal stability up to at least 450°C. Predictably, the para-para polymer exhibited the highest resistance to thermal decomposition. Thermogravimetric analysis indicated that it underwent less than 5% weight loss at 500°C in nitrogen and less than 10% weight loss at 500°C in air (Fig. 1). In nitrogen at 800°C, polymer weight loss was approximately 46%. Since the pendent phenyl groups constitute 43.5% of each polymer repeat unit, it is possible that thermal decomposition is essentially due to C—C single bond cleavage between a carbon atom in the polymer backbone and the pendent phenyl carbon atom to which it is bonded. In air all of the polymer sample was oxidized and volatilized at approximately 700°C.

The para-meta dimer and the para-ortho trimer exhibited thermal stabilities which were similar to each other but which were markedly less

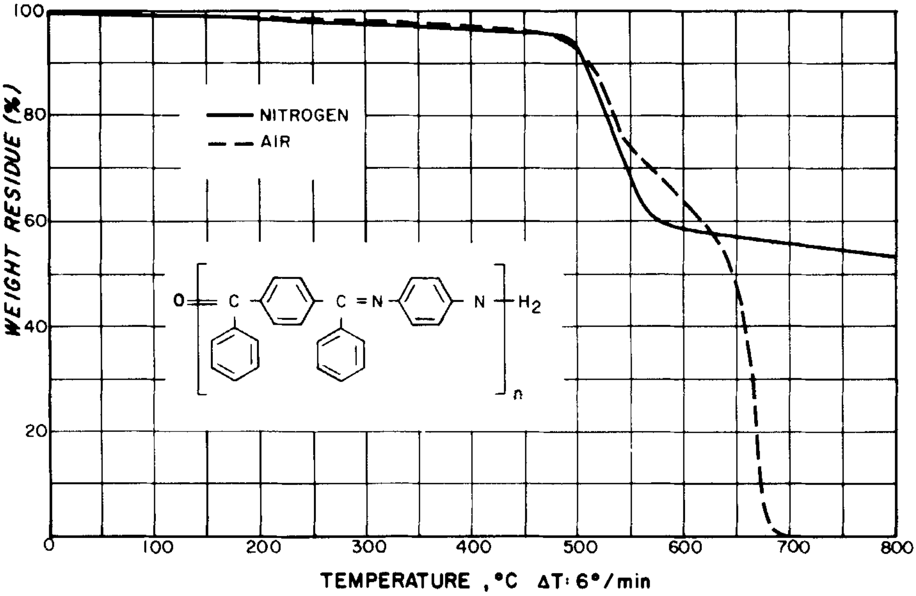


Fig. 1. TGA of the p-dibenzoylbenzene-p-phenylenediamine system.

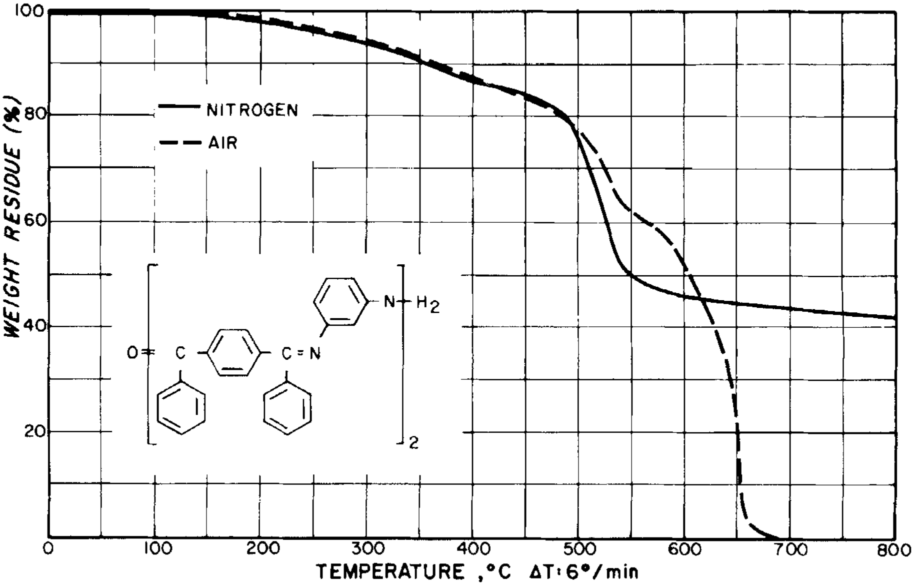


Fig. 2. TGA of the p-dibenzoylbenzene-m-phenylenediamine system.

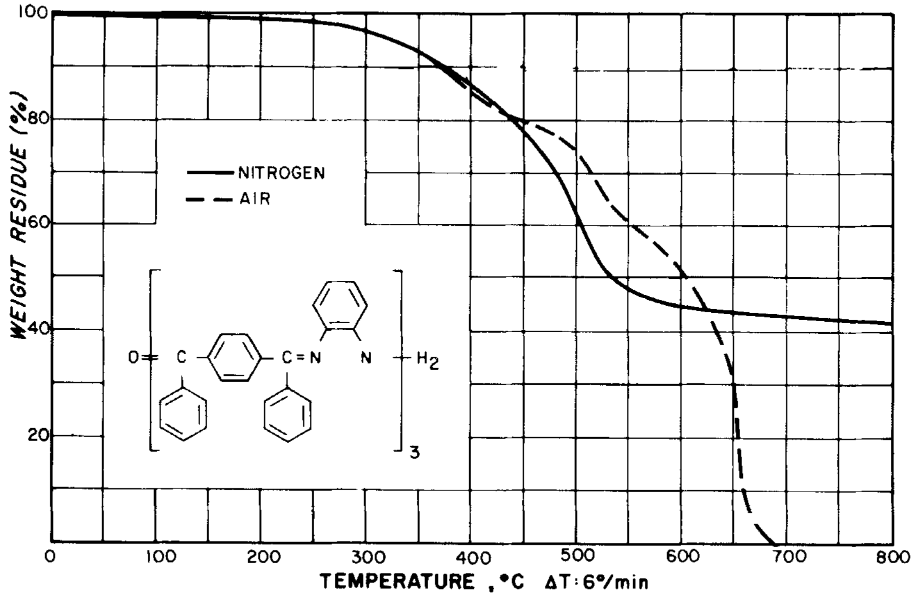


Fig. 3. TGA of the p-dibenzoylbenzene-o-phenylenediamine system.

than that of the para-para isomer. They underwent approximately 14% weight loss both in nitrogen and in air at 400°C (Figs. 2, 3). However, the weight loss in nitrogen at 800°C was only about 58% for both systems. Complete loss of sample in air took place just below 700°C for both systems.

In the meta series, each polymer exhibited the same high degree of stability both in air and in a nitrogen atmosphere. Less than 5% weight loss was observed at 400°C in nitrogen for all three systems and less than 10% weight loss was observed in air (Figs. 4, 5, and 6). As in the para series, decomposition seemed to be predominantly due to thermal cleavage of the pendent phenyl groups since the weight losses in nitrogen at 800°C were 51% for the meta-para, 49% for the meta-meta, and 56% for the meta-ortho isomer. In air, all of the samples underwent complete oxidation and volatilization at 650-700°C.

Introduction of fluorine substituents onto the polymer backbone did not increase thermal stability but, in fact, decreased it somewhat. The polymer prepared from m-dibenzoylbenzene and tetrafluoro-p-phenylenediamine underwent catastrophic degradation in nitrogen just above 400°C with more than 90% weight loss taking place at 800°C (Fig. 7). The meta-tetrafluoro-meta polymer also exhibited a weight loss at about 400°C in nitrogen

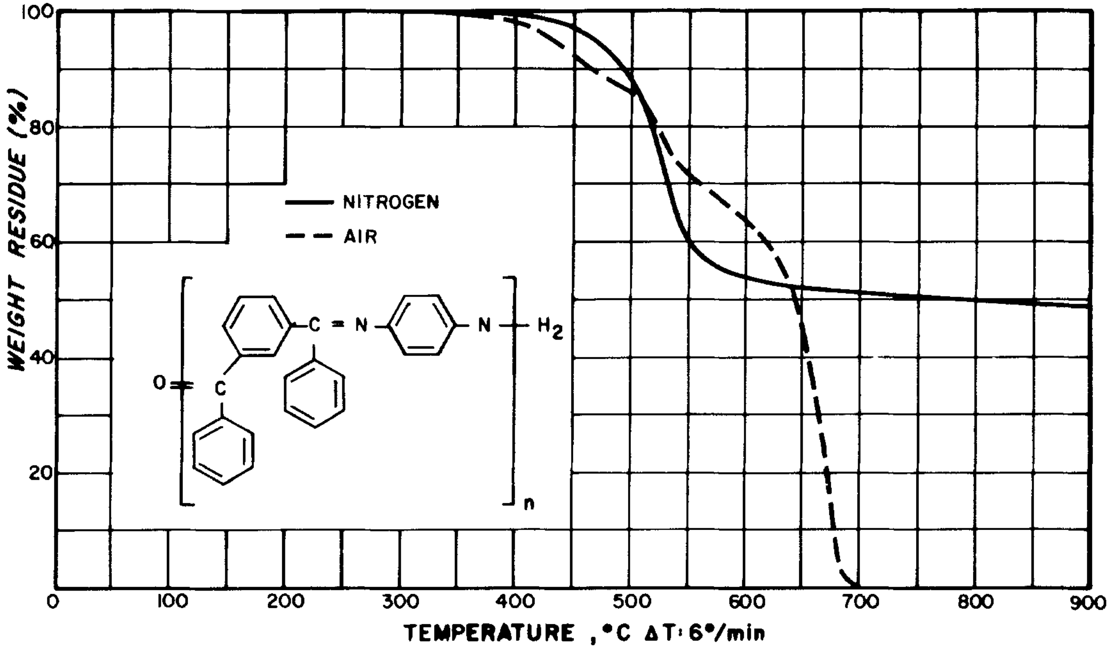


Fig. 4. TGA of the m-dibenzoylbenzene-p-phenylenediamine system.

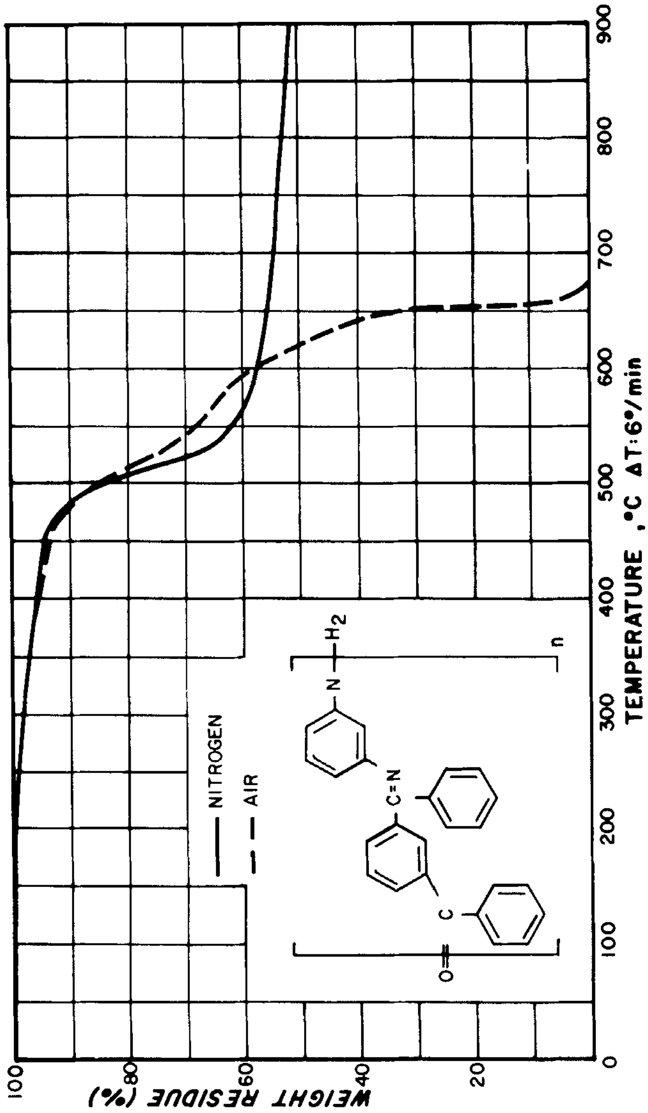


Fig. 5. TGA of the m-dibenzoylbenzene-m-phenylenediamine system.

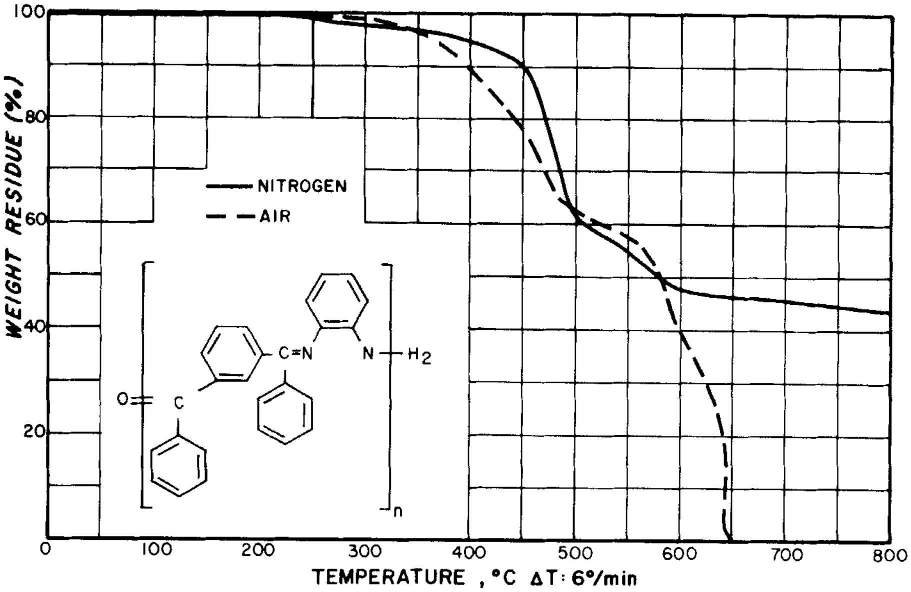


Fig. 6. TGA of the m-dibenzoylbenzene-o-phenylenediamine system.

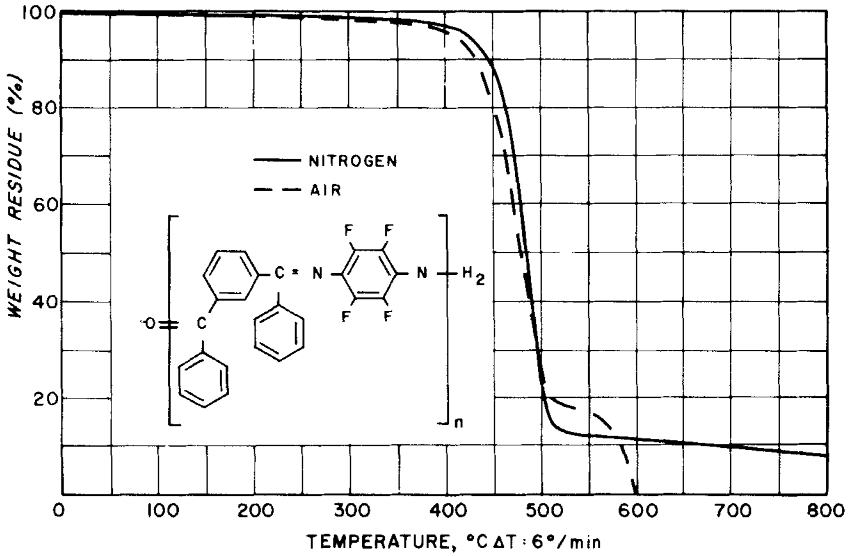


Fig. 7. TGA of the m-dibenzoylbenzene-tetrafluoro-p-phenylenediamine system.

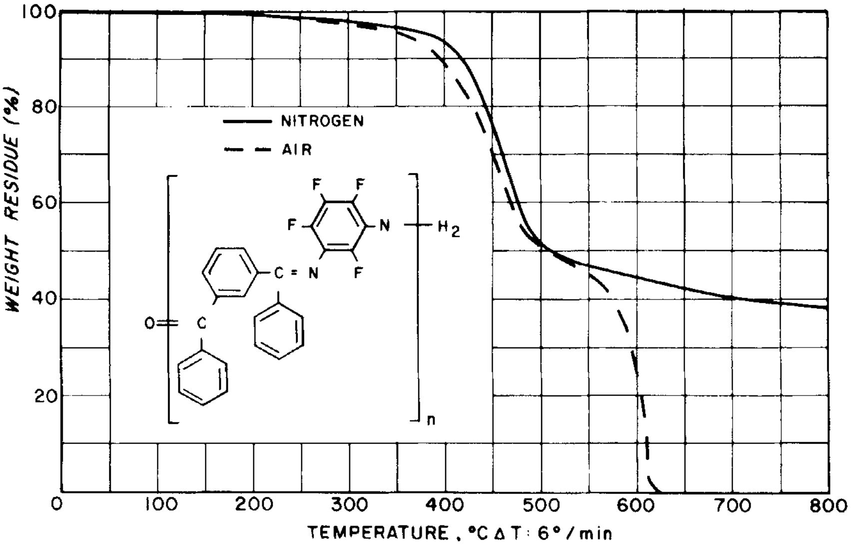


Fig. 8. TGA of the m-dibenzoylbenzene-tetrafluoro-m-phenylenediamine system.

although its degradation was less catastrophic. About 62% weight loss was observed at 800°C (Fig. 8). Both polymers were stable to 400°C in air, and complete volatilization and oxidation took place at 600-625°C.

Although the introduction of a small number of C—F bonds did not increase thermal stability, it would still be of interest to observe what the effect of a larger number of C—F bonds in the polymer would be.

The overall objective of this investigation has been to correlate the changes in molecular structure and geometry of the polymers studied to some of their physical properties. The information obtained thus far has been useful in indicating the most fruitful approaches to the synthesis of polymeric systems with the desirable characteristics of good thermal resistance and ease of processability.

ACKNOWLEDGMENT

We are indebted to the Office of Naval Research for their financial assistance, which supported this investigation in part. We are also grateful to the National Aeronautics and Space Administration for their support in the form of a fellowship for one of the authors.

REFERENCES

[1] A. D. Delman, A. A. Stein, and B. B. Simms, *J. Macromol. Sci.*, **A1**, 147 (1967).

[2] E. Dyer and C. C. Anderson, *J. Polymer Sci.*, 5, 1659 (1967).

[3] B. E. Davydov, B. A. Krentsel, Y. A. Popov, and L. V. Prokofyeva, *Vysokomolekul. Soedin.*, 5, 321 (1963).

[4] S. S. Stivala, G. R. Sacco, and L. Reich, *J. Polymer Sci.*, **B2**, 943 (1964).

[5] Y. A. Popov, B. E. Davydov, N. A. Kubasova, B. A. Krentsel, and I. I. Konstantinov, *Polymer Sci., USSR*, 7, 921 (1965).

[6] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**, 1251 (1967).

[7] *Beilstein Org. Chem.*, 7, 829.

[8] E. Ador, *Ber.*, **13**, 320 (1880).

[9] P. A. Cantor, *J. Chem. Eng. Data*, 8, 459 (1963).

[10] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 2nd ed., Wiley, New York, 1958, chapter 15.

[11] G. F. D'Alelio, R. K. Schoenig, and J. V. Crivello, *J. Macromol. Sci.*, **A1**, 1299 (1967).

[12] Y. A. Popov, B. E. Davydov, N. A. Kubasova, B. A. Krentsel, and I. I. Konstantinov, *Vysokomolekul. Soedin.*, 7, 835 (1965).

Accepted by editor May 22, 1969
Received for publication July 3, 1969

Discussion of Paper by A. A. Volpe, L. G. Kaufman, and R. G. Dondero

Isomeric and Substituent Effects in Some Dibenzoylbenzene-Diamine Polymers

G. C. Berry: 1) Are the polymers you described soluble in strong acids? 2) Are any of the polymers crystalline as recovered? 3) Are the fluorinated derivatives soluble? 4) Do you have any information concerning the nature of the residue from pyrolysis in nitrogen?

A. A. Volpe: 1) We have not determined the solubility of these polymers in other than the most common solvents.

We intend to do so, however. 2) We are also planning to investigate crystallinity and semiconductivity properties of these polymers. I would expect the more symmetrical molecules to be crystalline. 3) Not in any of the common solvents tried. 4) The residue has the appearance of pyrolytic graphite, although it has structural integrity.

H. Levine: Is it possible that the trimer or dimer are large ring systems? What does the infrared show for the $C=O$ absorption?

A. A. Volpe: The infrared spectra indicate that the dimer and trimer are simply low-molecular-weight linear species. The $C=O$ absorption is still present in these systems, whereas the $C=O$ band is essentially removed during the reactions which yield high polymers.

G. F. D'Alelio: Related work on the isomeric and substituent effects versus properties of the polyketanils has been carried out at Notre Dame, and two papers are now in press *(J. Macromol. Sci.-Chem).* The AB polymers, isomeric to Professor Volpe's AA-BB type polymers have been synthesized, and our AB polymer from p-aminobenzophenone is comparable to his AA-BB product. However, our polymers were made in melt systems to achieve tractability.

A. A. Volpe: Would increasing the number of $C-F$ bonds increase the thermal stability of these polymers?

G. F. D'Alelio: Our experience indicates that the answer is no. In fact, the perfluoropolymers are more unstable than unsubstituted polymers.

P. Throckmorton: Would introduction of F into pendent phenyl groups perhaps actually decrease thermal stability because the $C-C$ bond of the pendent group to backbone would be weaker?

A. A. Volpe: Yes. It probably would not enhance the thermal stability at all. Our plan is to introduce more C—F bonds on the polymer backbone and not on the pendent phenyl groups.