

Aromatic Polyamides. XII. Effect of the Polymeric Unit Linkage Position on the Thermal decomposition and Flammability of the Unsubstituted and Halogen-Substituted Aromatic Polyamides

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Synopsis

The synthesis, thermal characterization, and oxygen index of aromatic polyamides varying with polymeric unit linkage positions (*meta* and/or *para* units) and halogen substitution have been reported. It has been found that polyamides containing *para* units are more thermal stable than those containing *meta* units. There is no significant effect of the main chain structure studied here on either the pyrolysis pathways or flammability of similarly halogen substituted polyamides.

INTRODUCTION

The previous studies¹ on the *para-para* linked aromatic polyamides (PPT) derived from terephthaloyl chloride and various halogen substituted 1,4-phenylenediamines showed that halogen substitution significantly affected the thermal and flame resistant behavior of these polyamides. As these characteristics can be also dependent upon the polymeric backbone rigidity,^{2,3} in this work we extended these studies to the similarly halogen substituted aromatic polyamides containing *meta-meta*, *meta-para*, and *para-meta* polymeric unit linkages (Table I).

Based on our results, general correlations between the polyamide chemical and main chain structure, and their thermal or flame resistance have been described.

EXPERIMENTAL

Materials*

The commercially available 1,3-phenylenediamine, 1,4-phenylenediamine and 2-chloro-1,3-phenylenediamine were purified by multiple crystallization from toluene or benzene. The starting materials used for the preparation of the various halogenated *meta*-phenylenediamines are listed in Table II.

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TABLE I
 Aromatic Polyamides Studied

Polyamide Formula ^a	Main Chain Structure	Code
	<i>Meta—Meta</i> (<i>M—M</i>)	PMI
	<i>Meta—Para</i> (<i>M—P</i>)	PMPT
	<i>Para—Meta</i> (<i>P—M</i>)	PPI
	<i>Para—Para</i> (<i>P—P</i>)	PPT

^a $X_1 = \text{H}$; $X_2 = \text{H, F, Cl, Br}$; $X_1 = \text{F}$; $X_2 = \text{F}$; $X_1 = \text{Cl}$; $X_2 = \text{Cl}$; $X_1 = \text{Br}$; $X_2 = \text{Br}$.

The isophthaloyl chloride and *N,N*-dimethylacetamide were each purified by vacuum distillation. Other chemicals were used without purification.

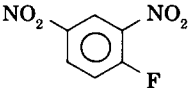
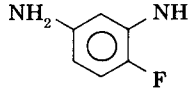
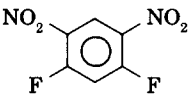
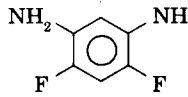
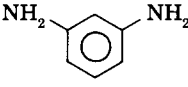
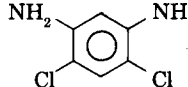
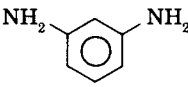
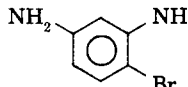
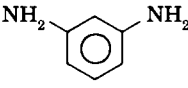
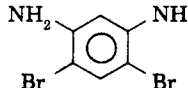
Preparations

Monomers and polymers

The preparation of the mono- and di-halogen substituted 1,4-phenylenediamines has been described previously.¹ The starting materials and a brief description of the synthesis procedures for the various halogenated 1,3-phenylenediamines, which were prepared in this laboratory by described in literature procedures⁴⁻⁸ are summarized in Table II. The structures of these diamines were proved by microanalysis (C, H, N, halogen) and the melting point (mp) or boiling point (bp) temperatures.

The polyamides were prepared by polycondensation reaction of the various *meta*- or *para*-phenylenediamines with the equimolar amounts of the iso- or tere-phthaloyl chlorides in *N,N*-dimethylacetamide (concentration of diamine was 1 mol/L) at low temperature.⁹ These were purified and dried similarly to the previously described method used for the preparation of the *para-para* linked polyamides.¹

TABLE II
 1,3-Phenylene-diamines: Synthesis Data

Starting material	Procedure	Final Product		Reference
		Structure	MP ^a (°C)	
	Reduction over Pd/C		bp ^b 152–153 22 mmHg	4
	Reduction over SnCl ₂ /HCl		112–113	4–6
	Acetylation: AcOH/Ac ₂ O Chlorination: NaOCl Treatment with AcOH Hydrolysis: NaOH Crystallization: benzene		138–139	7
	Formylation: HCOOH Bromination: Br ₂ /AcOH Hydrolysis: HCl Crystallization: benzene		110–111	8
	Acetylation: AcOH/AcOH Bromination: Br ₂ /AcOH Hydrolysis: HCl Crystallization: AcOH		134–135	7

^a Melting point temperature (°C).^b Boiling point temperature (°C).

Measurements

The following previously described¹ measurements have been used in this study:

- analytical methods (microanalysis, IR, mp temperature) to prove the amine's or polyamide's structures;
- inherent viscosity (η_{inh}) determinations to evaluate the molecular weight of polyamides;
- thermogravimetric analysis (TGA) to describe the thermal decomposition process; and
- oxygen index measurements to estimate resistance to flame.

RESULTS AND DISCUSSION

In the Tables III and IV, the detailed structures of the polyamides studied and in Table V their molecular weights as characterized by inherent viscosities are presented. As can be seen from the Figures 1 and 2, the unsubstituted polyamides gave thermogravimetric (TG) curves with one onset of weight loss, whereas those containing halogen gave TG curves of

TABLE III
Polyamides Derived from Isophthaloyl Chloride and Various Halogenated 1,3- and 1,4-Phenylene-diamines

Substitution	Polymer Structure	
	<i>Meta—Meta</i> (PMI)	<i>Para—Meta</i> (PPI)
H		
Mono-F		
Mono-Cl		
Mono-Br		
Di-F		
Di-Cl		
Di-Br		

different shapes. These showed two on-sets associated with two temperature ranges of increased rate of weight loss and the plateau initiated at temperature around 500°C. This plateau was longer and more distinctly marked for di-halogenated than for mono-halogenated polymers.

The derivative TG curves (DTG) were unimodal for unsubstituted (Fig. 3) and multimodal for the halogen containing polyamides (Figs. 4 and 5) regardless of their main chain structure. In considering polyamides having the same polymeric unit linkage positions, the general effect of halogen substitution of the thermal decomposition course as determined by TGA was similar to that described previously for *para-para* polyamides.¹

It can be seen from the Figures 4 and 5 or Tables VI and VII, that the temperature of the first maximum on the DTG curve and that of the temperature of the maximum rate of weight loss (T_{\max} I) are higher for unsubstituted, fluorine or chlorine substituents than for bromine substituents. The temperature range of the second maximum on the DTG curve and consequently the second T_{\max} (T_{\max} II) seem not to be affected by changing the type of substitution. They are dependent on the number of substituents and are higher for di-halogenated than for mono-halogenated polyamides.

The shape of this second maximum on the DTG curve of halogenated polyamides appears to be affected by both the halogen substitution and the

TABLE IV
Polyamides Derived from Terephthaloyl Chloride and Halogenated 1,3- and 1,4-Phenylene-diamines

Substitution	Polymer Structure	
	<i>Meta-Para</i> (PMPT)	<i>Para-Para</i> (PPT)
H		
Mono-F		
Mono-Cl		
Mono-Br		
Di-F		
Di-Cl		
Di-Br		

polymeric unit linkage position. These effects are illustrated in Figure 6, where the DTG curves for the fluorinated and brominated polyamides are shown. It can be seen from these figures, that the second maximum is sharper for fluorinated PPT and PMPT (containing *para-para* or *meta-para* units), than for the remaining mono- and di-substituted polyamides. In addition to those observations, some differences can be observed in the shape of the first maximums on the DTG curves, which are bimodal for the bro-

TABLE V
Inherent Viscosities^a (η_{inh}) of Polyamides Studied

Substitution	<i>Meta-meta</i> (PMI)	<i>Para-meta</i> (PPI)	<i>Meta-para</i> (PMPT)	<i>Para-para</i> (PPT)
H	0.46	0.57	1.11	0.88
Mono-F	0.31	0.25	0.29	0.62
Mono-Cl	0.41	0.20	0.28	0.84
Mono-Br	0.26	0.34	0.74	0.99
Di-F	0.32	0.74	0.49	1.52
Di-Cl	0.26	0.48	0.46	0.65
Di-Br	0.30	0.29	0.28	0.20

^a Inherent viscosity: 0.5 g/100 mL in conc. H₂SO₄; temperature 25°C.

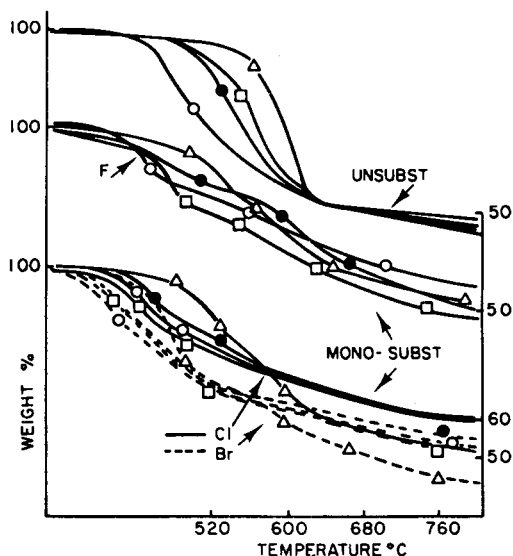


Fig. 1. TG curves for unsubstituted and mono-halogenated polyamides: (○) PMI, (●) PMPT, (□) PPI, (△) PPT.

minated and unimodal for the fluorinated or chlorinated polymers (Fig. 4, 5, and 6).

The effect of the polymeric unit linkage positions on the thermal decomposition (in a nitrogen atmosphere) of the aromatic polyamides is well presented in Figure 7 by comparison of the DTG curves for mono-halogenated *meta-meta* (PMI) to those for similarly substituted *para-para* (PPT) polyamides. Although the bimodal character of these curves for both structures is observed, the PPT's curves showed the significantly higher temperatures

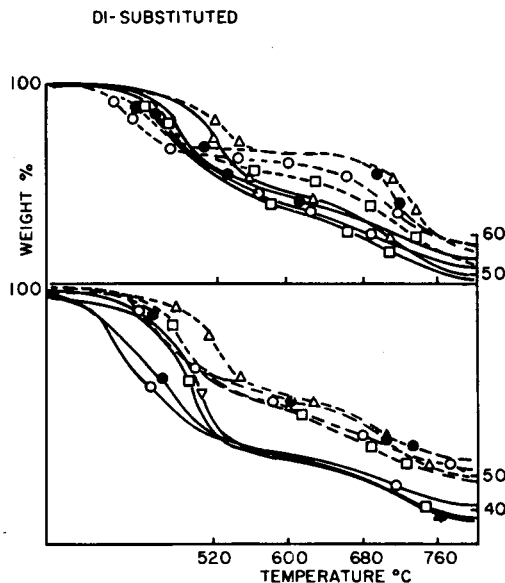


Fig. 2. TG curves for di-halogenated polyamides: (○) PMI, (●) PMPT, (□) PPI, (△) PPT.

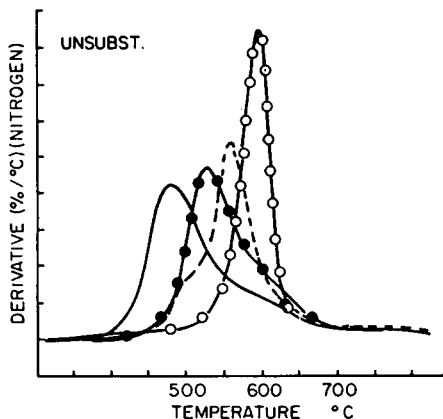


Fig. 3. DTG curves for unsubstituted polyamides: (—) PMI, (●) PMPT, (---) PPI, (○) PPT.

for the first maximum and more distinctly marked and sharper second maximums.

As is illustrated by the diagram in Figure 8, the thermal stability as described by the initial decomposition temperature (IDT) decreased with halogen substitution and the main chain structure in the following orders: $H > F \geq Cl > Br$ and PPT (*para-para*) > PPI (*para-meta*) \geq PMPT (*meta-para*) > PMI (*meta-meta*).

The diagram in Figure 9 illustrates the variation of the char yield versus oxygen index. It can be seen from this diagram, that in general, for the polyamides studied (exceptions are the brominated PA), substitution of halogen into the aromatic ring of amine moiety involved increasing both the oxygen index and char yield. From the results on the unsubstituted, fluoro-

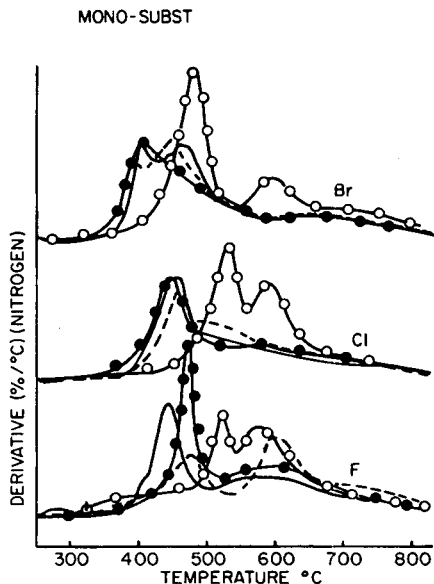


Fig. 4. DTG Curves for mono-halogen substituted polyamides: (—) PMI, (●) PMPT, (---) PPI, (○) PPT.

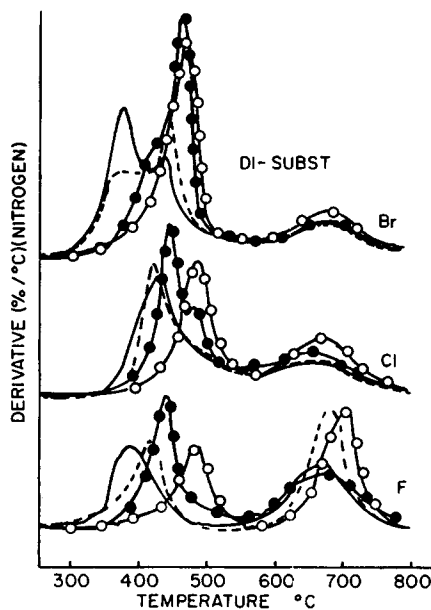


Fig. 5. DTG curves for di-halogen substituted Polyamides: (—) PMI, (●) PMPT, (---) PPI, (○) PPT.

and chloro-substituted PAs the higher values of oxygen index were related to the higher char yield polymers. The lower char yields for the brominated polyamides, particularly for the di-substituted polyamides, can be explained by relatively higher weight contribution of bromine which was released during pyrolysis. The major effect on the oxygen index was associated with the type of halogen. Thus, for the unsubstituted polyamides the values of OI were around 40%, whereas for fluorinated or chlorinated and brominated polyamides were around 50 and 60%, respectively.

Results obtained in this work are consistent with the data reported in the previous papers^{1,2,10-12} from this laboratory and describe the general

TABLE VI
Temperatures (°C) of Maximum Rate of Weight Loss (T_{\max}) of *Meta-Meta* (PMI) and *Para-Meta* (PPI) Polyamides

Substitution	<i>Meta-meta</i> (PMI)		<i>Para-meta</i> (PPI)	
	T_{\max} I	T_{\max} II	T_{\max} I	T_{\max} II
H	475	—	530	—
Mono-F	450	590	470	600
Mono-Cl	450	—	450	570
Mono-Br	400	650	410	630
	460		480	
Di-F	425	700	500	720
Di-Cl	460	700	490	700
Di-Br	400	700	500	700
	460			

TABLE VII
Temperatures (°C) of Maximum Rate of Weight Loss (T_{\max}) of *Meta-Para* (PMPT) and *Para-Para* (PPT) Polyamides

Substitution	<i>Meta-para</i> (PMPT)		<i>Para-para</i> (PPT)	
	T_{\max} I	T_{\max} II	T_{\max} I	T_{\max} II
H	560	—	600	—
Mono-F	465	600	550	600
Mono-Cl	460	—	530	600
Mono-Br	400	630	480	620
	460			
Di-F	460	730	520	730
Di-Cl	460	700	520	710
Di-Br	400	700	500	710
	460			

correlation between halogen substituents and structural effects on thermal and flammability properties of aromatic polyamides.

These results indicate that the thermal decomposition of aromatic polyamides studied here depends upon both the type of substituted halogen and the position of the polymeric unit linkages. The thermal stability of these polyamides increased in the following order: Br < Cl < F < H and *meta-meta* < *meta-para* ≤ *para-meta* < *para-para*. This indicates the importance of the halogen releasing process and the chain rigidity on the polyamide's pyrolysis in the absence of an oxygen.

The TGA data showed that substitution of halogen changed the thermal decomposition course of polyamides from one-stage to two-stage process. The temperature range of the first maximums on the DTG curves were dependent upon both the type of halogen and polymeric unit linkage positions. However, the temperature range of the second maximum was as-

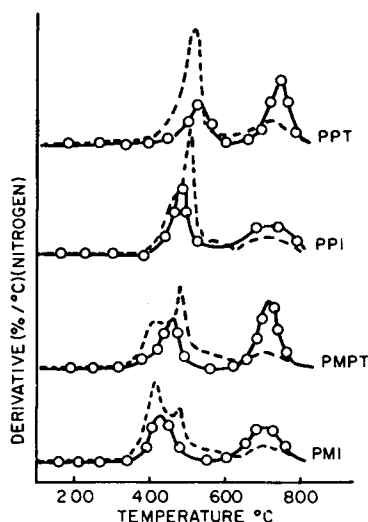


Fig. 6. DTG curves for (○) di-fluoro and (---) di-bromo substituted polyamides.

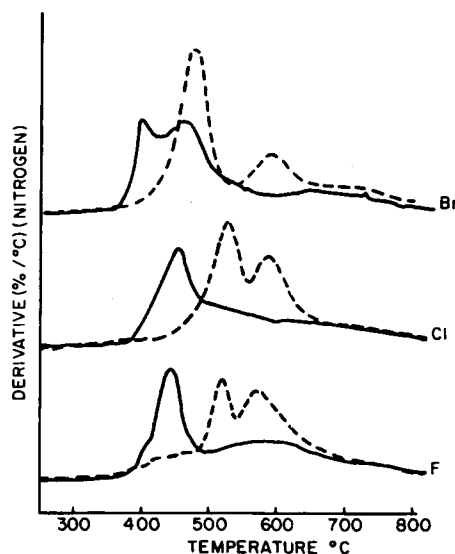


Fig. 7. DTG curves for mono-halogen substituted (—) PMI (*meta-meta*) and (---) PPT (*para-para*).

sociated with a number of substituted halogens only and was higher for di-substituted polyamides. This observation supports previously suggested¹⁰⁻¹³ pathways for the pyrolysis of the poly(1,3-phenylene-phthalamide)s containing halogen bonded onto the aromatic ring of the diamine moiety in the ortho position to the NH group. Among these pathways, ring forming processes have been suggested. These processes with elimination of hydrogen halide lead to formation of the new thermal stable materials containing benzoxazole for mono-halogenated or di-benzoxazole units for di-halogenated polyamides.¹ These reactions, in addition to the possible crosslinking as a result of homolytic halogen release were responsible for the enhanced char yield of the halogenated polyamides studied here. This enhanced char yield seems to be one of the important parameters determining the flame resistance of these polyamides.

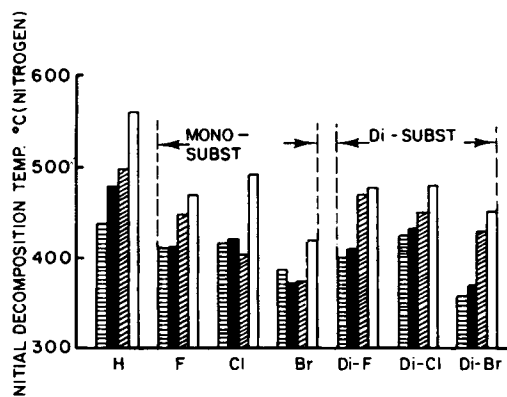


Fig. 8. Effect of halogen substitution and the polymeric unit linkage position on the initial decomposition temperature (IDT) of polyamides: ▨, PMI (*meta-meta*); ▩, PMPT (*meta-para*); ▤, PPI (*para-meta*); □, PPT (*para-para*).

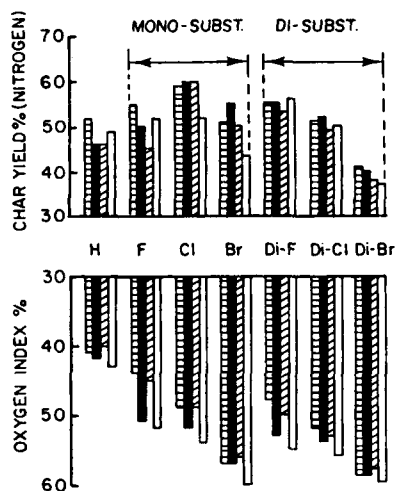


Fig. 9. Effect of halogen substitution and the polymeric unit linkage position on the char yield (800°C) and oxygen index (0.1) of polyamides: \square , PMI (meta-meta); \blacksquare , PMPT (meta-para); \boxtimes , PPI (para-meta); \square , PPT (para-para).

The oxygen index, which was higher for the halogenated polyamides than for those non-containing halogen, increased with the halogen substitution in the following order: Br > Cl \geq F. This follows the effectiveness of halogens in polymer fire retardancy as a result of vapor phase reactions.¹⁴ These data and enhanced char yield indicate, that halogens imparted flame retardancy to these polyamides by vapor phase and condensed phase mechanisms.

The additional studies on the mechanism of pyrolysis and flame retardancy of these polyamides are recently in progress in this laboratory and will be discussed in the subsequent publications.

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References

1. M. Kapuscinka and E. M. Pearce, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 3989 (1984) (accompanied paper: Part XI).
2. Y. P. Khanna and E. M. Pearce, *J. Appl. Polym. Sci.*, **27**, 2053 (1982).
3. C. Arnold, Jr., *J. Polym. Sci. Macrom. Rev.*, **14**, 317 (1982).
4. S. Sugawara and N. Ishikawa, *Nippon Kagaku Kaishi*, **1**, 161 (1972).
5. S. Sugawara and N. Ishikawa, *Kogyo Kagaku Zasshi*, **72**, 11, 2425 (1969).
6. B. H. Nicolet and W. I. Ray, *J. Am. Chem. Soc.*, **49**, 1801 (1927).
7. G. T. Morgan, *J. Am. Chem. Soc.*, **77**, 1202 (1900).
8. R. D. Haworth and W. O. Sykes, *J. Chem. Soc.*, **311** (1944).
9. P. W. Morgan, *Macromolecules*, **10**, 1381 (1977).
10. Y. P. Khanna, E. M. Pearce, J. S. Smith, D. T. Burkitt, H. Njuguma, D. M. Hindenland and B. D. Forman, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 2817 (1981).
11. A. C. Karydas, M. Kapuscinka and E. M. Pearce, *Eur. Polym. J.*, **19**, 935 (1983).
12. Y. P. Khanna and E. M. Pearce, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 2835 (1981).
13. A. C. Karydas, W. T. Whang and E. M. Pearce, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 847 (1984).
14. R. R. Hindersinn and S. Witschard in *Flame Retardancy of Polymeric Materials*, Vol. 4, W. C. Kuryla and A. J. Pappa, Eds., Dekker, N. Y. 1978, chapter 1.

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