Aromatic Polyamides. XI. Effect of the Halogen Substitution on the Thermal and Flammability Behavior of Poly(1,4-Phenylene Terephthalamide)

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Synopsis

This article concerns the synthesis and characterization of poly(1,4-phenylene terephthalamide) and halogenated derivatives thereof. It was found that the halogen substitution affected significantly the thermal characteristic and flame resistance of that polyamide. In a nonoxygen atmosphere two-step decomposition process for the halogenated, while only one-step for unsubstituted polyamides were observed. The results supported the previous suggestion, that in the case of the halogenated polyamides the char yield enhancement and the flame resistance improvement are associated with halogen release and ring-forming reactions during their pyrolysis.

INTRODUCTION

As was reported,[1-4] chlorine or fluorine, when bonded onto the phenylenediamine polymeric units, affected the thermal behavior of aromatic polyamides. It has been found, that polyamides derived from ortho- chloro-substituted aromatic diamines gave enhanced char yields and higher resistance to flame in comparison to those prepared from unsubstituted or containing other types of substituent amines. In attempts to explain this observation, Pearce and co-workers[5,6] have investigated the mechanism of thermal decomposition of chlorinated polyamides, and suggested, that the high char yield for these polymers is partly due to the iminolization of the amide group followed by intramolecular cyclization to form a benzoxazole structure while HCl is eliminated.

The objective of this research effort was to examine systematically the variation the thermal and flammability properties of poly(1,4-phenylene terephthalamide)s (PPT) derived from 2-mono- or di-2,5-halogenated 1,4-phenylenediamines (Table I). The amines containing fluorine, chlorine or bromine have been used for polymer preparations (Table II). This study allowed us to establish a correlations between halogen substitution and the course of thermal decomposition, and that between char yield and flammability for aromatic polyamides containing *para–para* polymeric unit linkages.

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TABLE I
Poly(1,4-Phenylene Terephthalamide)s Studied

Polymer structure	Substitution	Code	η_{inh} [a]
−[NH−C₆H₄−NH−CO−C₆H₄−CO]−ₙ	H	PPT	0.88
−[NH−C₆H₃(F)−NH−CO−C₆H₄−CO]−ₙ	Mono-F	2-F-PPT	0.62
−[NH−C₆H₃(Cl)−NH−CO−C₆H₄−CO]−ₙ	Mono-Cl	2-Cl-PPT	0.84
−[NH−C₆H₃(Br)−NH−CO−C₆H₄−CO]−ₙ	Mono-Br	2-Br-PPT	0.99
−[NH−C₆H₂(F)(F)−NH−CO−C₆H₄−CO]−ₙ	Di-F	2,5-F-PPT	1.52
−[NH−C₆H₂(Cl)(Cl)−NH−CO−C₆H₄−CO]−ₙ	Di-Cl	2,5-Cl-PPT	0.65
−[NH−C₆H₂(Br)(Br)−NH−CO−C₆H₄−CO]−ₙ	Di-Br	2,5-Br-PPT	0.20

[a] Inherent viscosity (conc. H_2SO_4, 0.5 g/100 ml, 25°C).

EXPERIMENTAL
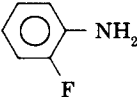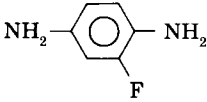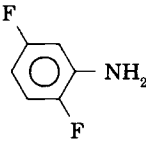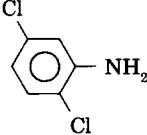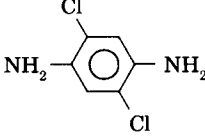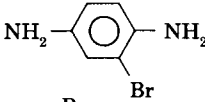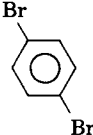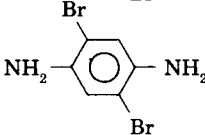
Materials*

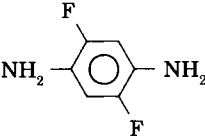The commercially available 1,4-phenylenediamine and other amines used as the starting materials for the various halogenated amine monomers (Table II) were purified by multiple crystallization from toluene or benzene. 2-chloro-1,4-phenylenediamine was used without purification.

The terephthaloyl chloride and hexamethylphosphoramide (HMPA) were each purified by vacuum distillation. Other chemicals such as tin chloride, acids, and solvents were used without additional purification.

* All materials were purchased from Aldrich Chemical Company, Metchuchen, .J.

TABLE II
1,4-Phenylene Diamines: Synthesis Data

Starting material	Procedure	Final product		Reference
		Structure	mp (°C)	
2-fluoroaniline (NH$_2$, F ortho)	Acetylation: AcOH/AC$_2$O Nitration: fuming HNO$_3$ Hydrolysis: H$_2$SO$_4$ Reduction: SnCl$_2$/HCl	NH$_2$—C$_6$H$_3$(F)—NH$_2$	78	7–9
2,6-difluoroaniline (NH$_2$, two F)	Acetylation: as above Nitration: fuming HNO$_3$/H$_2$SO$_4$/AcOH Hydrolysis: SnCl$_2$/HCl Crystallization: ethanol	NH$_2$—C$_6$H$_2$(F)(F)—NH$_2$	129	9
2,4-dichloroaniline (Cl, NH$_2$, Cl)	Acetylation and nitration: as above Extraction of product with benzene Hydrolysis, reduction and crystalization: as above	NH$_2$—C$_6$H$_2$(Cl)(Cl)—NH$_2$	164	10–14
NO$_2$—C$_6$H$_4$—NO$_2$	Bromination: Br/HCl Reduction: SnCl$_2$/HCl Crystalization: CCl$_4$	NH$_2$—C$_6$H$_3$(Br)—NH$_2$	75	7–15
Br—C$_6$H$_4$—Br	Nitration: HNO$_3$/H$_2$SO$_4$ Multiply crystallization from dioxane Reduction: SnCl$_4$/HCl Crystallization: benzene	NH$_2$—C$_6$H$_2$(Br)(Br)—NH$_2$	184	15–16

Preparations

Monomers and Polymers

The various mono- and di-substituted 1,4-phenylenediamines were prepared by described in literature procedures[7-16] with several modifications. These procedures, starting materials and diamines prepared are summarized in Table II. The diamine chemical structures were characterized by microanalyses (C, H, N, halogen), and the melting point temperatures (mp).

The aromatic polyamides were syntesized by reactions of various 1,4-phenylenediamines studied with equimolar quantities of terephthaloyl chloride in hexamethylphosphoramide at 1 mol/L concentration of diamine using low temperature.[17] Triethylamine (TEA) was added as a HCl acceptor, in the case of the 2-chloro-1,4-phenylenediamine hydrochloride was used as the diamine monomer.

After precipitation with water and multiple washing with water and acetone, polymers were vacuum dried for 48 h at 160°C.

The halogen amounts in those polyamides were examined by the elemental analysis (C, H, N, halogen). The polyamide's molecular weights were evaluated by the inherent viscosity measurements (Table I).

Measurments

Microanalyses (C, H, N, halogen) were carried out at Schwarzkopf Laboratory, Woodside, NY.

Infrared spectra were recorded on a Perkin Elmer Model 567 spectrophotometer.

Melting point temperatures were determined on the melting point apparatus (Electrothermal, Ltd.)

Inherent Viscosities $(\eta)_{inh}$ of polymers were determined in concentrated H_2SO_4 at 25°C with a Cannon–Ubbelohde viscometer. The solution concentrations were 0.5 g/100 ml.

Thermal properties of polyamides were studied by thermogravimetric analyses (TGA) using a DuPont 1090 Thermal Analyzer with a 951 TGA module, with a heating rate of 20°C/min under a nitrogen atmosphere.

Flammability of polymers was measured by the oxygen index (OI) using the General Electric Oxygen Index Equipment. Oxygen index is defined as the minimum concentration of oxygen in an oxygen–nitrogen atmosphere, that is necessary to initiate and support a flame:

$$OI = \frac{\text{volume of } O_2}{\text{volume of } O_2 + \text{volume of } N_2} \ (\%)$$

OI measurements were carried out with the samples of polymer in the form of pressed thin tablets.

RESULTS AND DISCUSSION

In Table III various characteristic thermal decomposition temperatures for the polyamides studied are summarized. It can be seen, that the polyamides containing halogen began to decompose at lower temperature compared to the unsubstituted polyamides. The bromine substituted PPT showed the lowest initial decomposition temperatures. All the halogen substituted PPT's gave two temperatures of maximum rate of weight loss (T_{max}). The first T_{max} $(T_{max} \text{ I})$ depended on the type of halogen and decreased with the halogen molecular weight. The second T_{max} $(T_{max} \text{ II})$ seems not to be affected by that parameter, but is associated with a number of substituents. It was about 100°C higher for the di-halogenated polyamides than for the mono-halogenated polyamides.

As can be seen in Figures 1 and 2, the unsubstituted PPT gave the thermal gravimetric (TG) curve characterized by one on-set, whereas the TG curves of the halogenated PPTs exhibited the plateau initiated at temperature around 500°C (Table III) and two on-sets associated with the two-stage decomposition process. It was reflected on the shape of the derivative thermal

TABLE III
Effect of the Halogen Substitution on the Thermal Behavior of Poly(1,4-Phenylene Terephthalamide)s

| Polymer code | IDT[a] | T_{max}[b] | | T_p[c] |
		T_{max} I	T_{max} II	
PPT (H)	560	600	—	—
2-F-PPT (Mono-F)	469	550	600	530
2-Cl-PPT (Mono-Cl)	494	530	600	550
2-Br-PPT (Mono-Br)	420	480	620	510
2,5-F-PPT (Di-F)	478	520	730	550
2,5-Cl-PPT (Di-Cl)	481	521	710	550
2,5-Br-PPT (Di-Br)	460	510	710	530

[a] Initial decomposition temperature.
[b] Temperature of maximum rate of weight loss (T_{max} I, first maximum; T_{max} II, second maximum).
[c] Initial plateau temperature.

gravimetric curves (DTG), which were bimodal for all halogenated polyamides studied.

Although the overall decomposition process for the halogenated PPT's, as determined by TGA, occurred in the similar way, the detailed situation
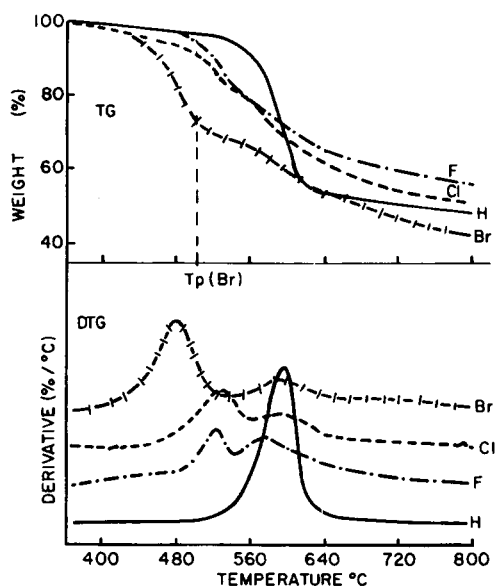

Fig. 1. TG and DTG curves for unsubstituted and mono-halogen substituted PPT. Atmosphere, nitrogen; heating rate, 20°C/min. (—) unsubstituted, (— · —) mono-F, (– – –) mono-Cl, (–|–) mono-Br. T_p, example of the initial plateau temperature for the mono–bromo substituted PPT.
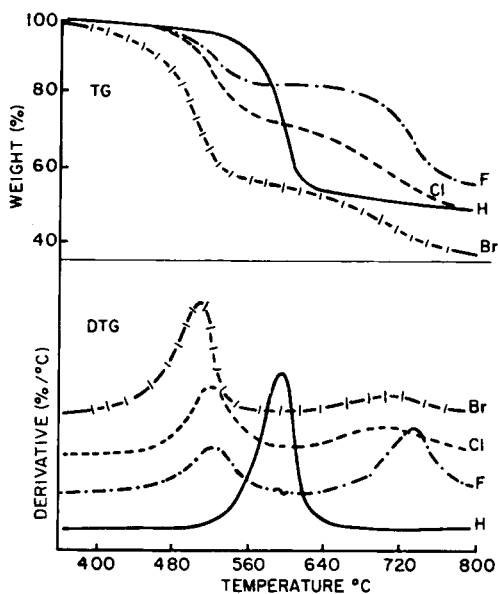
Fig. 2.   TG and DTG Curves for unsubstituted and di-halogen substituted PPT. Atmosphere, nitrogen; heating rate, 20°C/min. (—) unsubstituted, (— · —) mono-F, (- - -) mono-Cl, (-|-) mono-Br.

differed substantially due to the type and number of halogens. As can be seen from Figure 3, the plateau extended between the two on-sets of the TG curves was longer and more distinctly marked for di-fluorinated PPT, than for that containing one fluorine. The same phenomena can be observed for chlorinated and brominated PPT's. Other interesting differences can be seen from Figure 4, where the DTG curves for all the polyamides studied here are depicted. Although all DTG curves for the halogen containing polyamides were bimodal the positions of the first and the second maximums are associated with the type and/or number of halogens. With an increase of the molecular weight of the substituted halogen, the first maximum shifted into a lower temperature and there was no significant effect of the number of substituents on the position of that maximum. The position of the second maximum was rather independent of the type of halogen, but was associated with the number of them. This maximum corresponded to a temperature around 600°C for mono-halogenated and around 700°C for
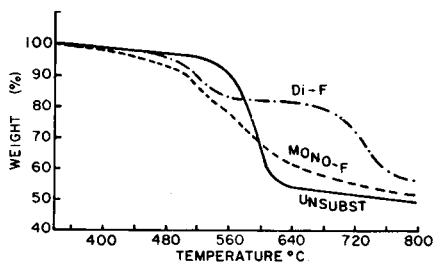

Fig. 3.   TG Curves for unsubstituted, mono-fluoro, and di-fluoro substituted PPT. Atmosphere, nitrogen; heating rate, 20°C min.
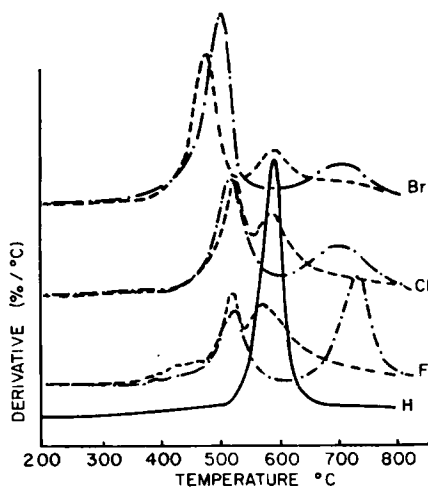
Fig. 4.   DTG Curves for (—) unsubstituted, (- - -) Mono- and (- · -) di-halogen substituted PPT.

di-halogenated PPT. The height of both maximums on the DTG curves of the halogenated PPT depended mainly upon the type of substituent. The first maximum is higher for the type of halogen in the following order: Br > Cl > F, whereas the second maximum's height was changing in the opposite direction.

The effect of the halogen substitution on the char yield (pyrolysis residue) of PPTs, as determined by TGA, and on the flammability, as measured by oxygen index, is illustrated by data summarized in Table IV and Figure 5. As can be seen, the char yield depended on both the type and a number of substituted halogens and increased in the following order: di-F > F ≈ Cl

TABLE IV
Effect of the Halogen Substitution on the Char Yield and Oxygen Index of Poly(1,4-Phenylene Terephthalamide)s

| Polymer Code | Char yield | | | Recalculated char yield[b] 800°C (%) | Oxygen index (%) |
	T_p[a] (%)	700°C (%)	800°C (%)		
PPT	—	52	49	49	43
2-F-PPT (Mono-F)	82	56	52	56	52
2-Cl-PPT (Mono-Cl)	80	56	52	63	54
2-Br-PPT (Mono-Br)	70	49	43	57	60
2,5-F-PPT (Di-F)	82	76	56	65	55
2,5-Cl-PPT (Di-Cl)	75	60	50	65	56
2,5-Br-PPT (Di-Br)	58	46	37	62	60

[a] Char yield at the initial plateau temperature (T_p).

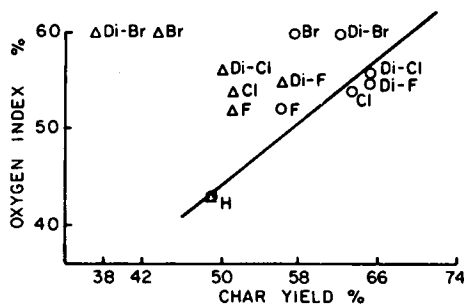[b] Char yield based on the nonhalogen part of polyamide (taken as the TG initial weight).

Fig. 5. Oxygen index versus char yield. (△) experimental char yield (from TG curve), (○) "recalculated" char yield — based on the nonhalogen part of the polymer.

> di-Cl ≈ H > Br > di-Br. More remarkable was the increase in the "recalculated" char yield, based on the nonhalogen part of polymer taken as the TG initial weight. In this case the "recalculated" char yield increased as follows: di-halogenated > mono-halogenated > unsubstituted. For the fluorinated and chlorinated polyamides that char yield followed the oxygen indices, and approximately corresponded to the well known linear relationship between oxygen index and char yield for polymers containing C, H, O elements[18] (Fig. 5). These results showed, that the halogen substitution, particularly bromine, significantly improved the flame resistance of the polyamide studied, as the oxygen index increased from around 40% for the unsubstituted to around 60% for the brominated PPT.

Results obtained in this work indicate, that halogen incorporation in the aromatic ring of the diamine moiety affects the thermal decomposition course (in a nitrogen atmosphere) of poly(1,4-phenyleneterephthalamide) (PPT).

The thermal stability of polyamides studied decreased with the halogen substitution in the following order: Br < Cl ≤ F < H. This approximately follows the C-halogen bond dissociation energies. This effect and the linear character of the relationship between the weight loss measured at the initial plateau temperature on the TG curve (T_p) and the halogen content (Fig. 6) indicate the importance of halogen release in the thermal decomposition pathways of the halogenated polyamides.

As was shown by TGA data for samples heated in a nitrogen atmosphere, the two-stage decomposition process was typical for halogen containing
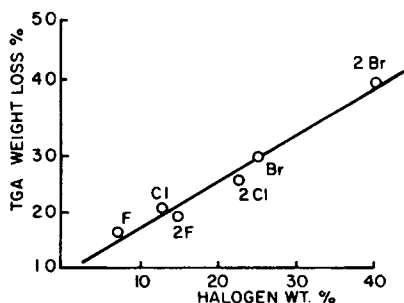

Fig. 6. Char yield at the initial plateau temperature (T_p) versus the halogen wt % of polymer.

polyamides, whereas a one-stage process is observed for the unhalogenated analog. The obtained results provide additional evidence to the previously suggested[2,5,6,19] ring forming reactions to be occurred during the nonoxygen pyrolysis of halogenated poly(1,3-phenylene isophthalamide)s and extend this mechanism to the fluorinated, chlorinated or brominated poly(1,4-phenylene-terephthalamide)s. Thus, there were some characteristic features on the TGA curves of those polyamides, which were associated with the presence of the halogens such as fluorine, chlorine, or bromine attached to the aromatic ring of the diamine moiety in *ortho* position to the NH. These were the extended plateau on the TG curve initiated at temperature around 400°C, the multimodal DTG curves and the effect of halogen number on the T_{max} II. Only explanation of those phenomenas are reactions leading to the more stable heterocyclic structures formation.

This occurred by imminolization followed by the intramolecular elimination of the hydrogen halide as is shown in Figure 7. As a result, new thermally stable materials were produced. The thermal stability of these materials was affected by the number of halogens incorporated into the starting polyamide. This appears to indicate, that structures containing benzoxazole units for mono-halogenated (reaction 1) and those containing bi-benzoxazole units for di-halogenated polyamides (reaction 2) were formed. The temperatures for the maximum rate of decomposition (T_{max} II) of these new materials were consistent with those reported in the literature for polybenzoxazole (around 600°C)[20] and polybi-benzoxazole (around 700°C).[21] The general similarity of the DTG curves for all halogenated polyamides studied here indicates, that during heating of these polyamides in absence of oxygen the benzoxazole or bibenzoxazole units were produced regardless of the type of halogen attached onto polyamide. As is shown in Figure 8, the preheated to 600°C di-fluorinated PPT became thermal stable at 600°C, when heated isothermally in a nitrogen atmosphere (about 1% of weight loss).

These ring forming reactions and the possibility for increased crosslinking by the combination of free radicals formed as a result of halogen release lead to increases in char yield, and accounted in part for the higher oxygen
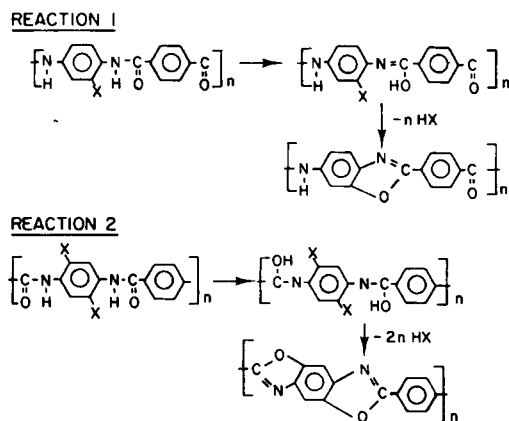

Fig. 7.   Possible ring-forming reactions during nonoxygen pyrolysis of the halogenated polyamides studied.
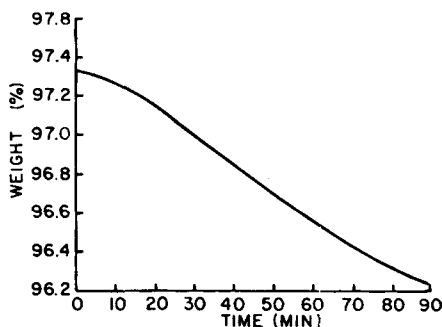
Fig. 8. Isothermal TG Curve at 600°C for the di-fluoro substituted PPT (sample was preliminary heated to 600°C; atmosphere, nitrogen).

indices of halogenated polyamides. The oxygen index of these polyamides increased with halogen substitution in the following order: Br > Cl ≥ F and followed the vapor phase effectiveness for polymer fire retardancy.[22] These results indicate, that halogen imparts flame retardancy to these polyamides by both vapor phase and condensed phase mechanism, as was previously suggested by Pearce and co-workers.[2]

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