

Aromatic Polyamides. V. Substituent Effect on Thermal Properties

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Synopsis

Some wholly aromatic polyamides derived from unsubstituted and chloro- and nitro-substituted diamines have been studied from the viewpoint of their thermal stability, thermo-oxidative stability, and thermal transitions. General relationships between thermal stability of a polymer and its chemical structure are described. Decrease in thermal stability of poly(1,3-phenyleneisophthalamide) and poly(1,4-phenyleneterephthalamide) due to substituents has been explained and supported in part by infrared spectral data. The effect of electron-withdrawing substituents such as chloro and nitro in increasing the thermo-oxidative resistance of the polyamides is pointed out. The thermal transitions (T_g and T_m) of these polymers are also reported. All the polyamides exhibit a broad exothermic peak in the 630–700°C temperature range, which probably corresponds to reactions (crosslinking and cyclization) responsible for the high char yield of these systems.

INTRODUCTION

Poly(1,3-phenyleneisophthalamide) and poly(1,4-phenyleneterephthalamide), commercially known as Nomex and Kevlar, respectively, belong to the class of high-temperature polymers. Properties such as high thermal stability of these aromatic polyamides depend primarily on their chain stiffness.¹⁻³ Chain rigidity in these materials, however, also causes insolubility in common organic solvents. Attempts have been made to increase the solubility of aromatic polyamides through the use of substituted diamines or diacids.⁴ This type of modification generally reduces the thermal stability. Takatsuka et al.⁴ have attributed the higher solubility and lower thermal stability of substituted aromatic polyamides to their looser packing.

The present study describes and explains the effect of substituents on the thermal and thermo-oxidative stabilities and the transition temperatures of poly(1,3-phenyleneisophthalamide) and poly(1,4-phenyleneterephthalamide).

EXPERIMENTAL

Polymer synthesis. Synthesis of the polymeric materials studied here has been reported elsewhere.⁵

Thermogravimetric analysis (TGA). Thermal stability of the polyamides was studied by thermogravimetric analysis using a du Pont 990 thermal analyzer with a 951-TGA module. The experiments were carried out in an argon atmosphere with about 25 mg sample in a platinum pan and at a heating rate of 10°C/min. Thermo-oxidative stability of the polymers was determined under

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identical conditions except that air and oxygen atmospheres were used instead of argon.

Differential scanning calorimetry (DSC). Thermal transitions of the materials were determined by DSC using a du Pont 990 thermal analyzer. The studies were made with about 10 mg sample in a crimped aluminum pan, at a heating rate of 10°C/min and in argon atmosphere.

Differential thermal analysis (DTA). Thermal degradation of the polyamides was also investigated by DTA experiments carried out on a du Pont 990 system equipped with a 1200°C DTA furnace.

RESULTS AND DISCUSSION

Before discussing the thermal stabilities of various polyamides, it is worthwhile to outline the relationship of the thermal stability of a polymer to its chemical structure.

Relationship of Thermal Stability to Chemical Structure

Maximum thermal stability in polymers is usually obtained⁶ when (a) thermally unreactive ring structures constitute a major portion of the polymer composition; (b) maximum use is made of resonance stabilization; (c) high bond energy exists between the atoms in the chain; (d) cohesive energy density is high from chain length, crystallinity, and van der Waals forces.

An aromatic ring in the backbone of the chain is not only relatively thermally unreactive but also increases the rigidity.⁷ Stiffer chains resist thermally induced vibrations, and therefore a higher temperature is required for their degradation. Chain stiffness, and hence thermal stability, is further increased by stronger intermolecular bonding arising, for example, from van der Waals forces and hydrogen and/or polar bonding. Backbone rigidity can also be increased by substituting flexible bridging groups such as —O—, —CH₂—, etc., by a chain-stiffening group such as a phenyl group. Increased resonance effects which are enhanced by coplanarity also stiffen the backbone.⁸ For instance, a para isomer is stiffer than its meta counterpart, which in turn is stronger than the ortho isomer. Moreover, the rigidity of the 1,4-phenylene group is enhanced if it is flanked by carbonyl (>C=O) groups rather than secondary amine (—NH—) or methylene (—CH₂—) functionalities, this being attributed to the fact that the two carbonyls and the *p*-phenylene groups resonate as a unit in a planar structure.⁷ Finally, an increase in steric hindrance can cause increased chain stiffening. It is well documented that, in general, increased backbone rigidity leads to an increase in thermal stability.⁸

Thermal Stability of Polyamides

Keeping in view the structure–stability relationships described above, we can explain the thermal degradation characteristics of our polyamides. The thermal stability data as determined by dynamic TGA technique are summarized in Table I.

The weight loss characteristics of our poly(1,3-phenyleneisophthalamide), PMI, are similar to those of the commercial product (Nomex) as reported by

TABLE I
Thermal Degradation of Aromatic Polyamides

Polyamide		Structure	η_{inh}	Thermogravimetric Analysis ²						
Code	Name			3- IDT, C	% Weight Loss at, C				4 T _{max} , C	
PMI	Poly(1,3-phenylene isophthalamide)		0.98	440	400	450	500	600	700	480
PCI	Poly(chloro-2,4-phenylene isophthalamide)		0.79	425	0.8	8.5	19.0	29.5	37.0	460
PPT	Poly(1,4-phenylene terephthalamide)		1.74	555	0.3	1.0	1.6	27.5	39.0	585
PCT	Poly(chloro-2,5-phenylene terephthalamide)		0.83	475	2.0	4.0	8.5	31.0	38.5	530
PDT	Poly(2,6-Dichloro-1,4-phenylene terephthalamide)		0.60	475	1.0	2.5	10.0	32.5	46.0	515
PNT	Poly(nitro-2,5-phenylene terephthalamide)		0.75	400	6.0	31.0	31.5	36.0	44.5	415

- (1) Determined on a 0.5 g/dL solution in concentrated H₂SO₄ at 25°C.
- (2) du Pont TGA-951, 10°C/min heating rate, ~23 mg sample in platinum pan, argon atmosphere.
- (3) Initial decomposition temperature; obtained by extrapolation of the initial degradation portion of the TGA curve.
- (4) Temperature at which the maximum rate of weight loss occurs.

Brown and Ennis.⁹ Upon the introduction of a chloro substituent ortho to one of the amide groups, a decrease in thermal stability is observed (Fig. 1); e.g., the initial decomposition temperature (IDT) and the temperature of the maximum rate of weight loss (T_{\max}) of PMI are lowered by 15 and 20°C, respectively. A lower stability of poly(chloro,2-4-phenyleneisophthalamide), PCI, compared to PMI may be attributed to its lower chain rigidity which is caused by one or more of the following factors:

(a) Poly(chloro-2,4-phenyleneisophthalamide) appears to have relatively weaker intermolecular bonding forces than poly(1,3-phenyleneisophthalamide). The latter, according to our IR data,⁵ showed a medium absorption band at 3270 cm^{-1} attributed to hydrogen-bonded N—H group. The chloro polyamide, however, exhibited two N—H stretching peaks; one, at 3370 cm^{-1} , was assigned to a N—H group less strongly H bonded than that in the unsubstituted material; and the other, at 3420 cm^{-1} , to N—H vibration free of H bonding. Moreover, the carbonyl (C=O) stretching band of PCI occurs at a 10 cm^{-1} higher frequency than that of PMI (1670 vs. 1660 cm^{-1}), which again implies reduced hydrogen bond strength in poly(chloro-2,4-phenyleneisophthalamide).

(b) Intermolecular forces in PCI would further be reduced due to its amorphous nature. Poly(1,3-phenyleneisophthalamide), on the other hand, exhibits partial crystalline behavior (the sample used for comparison had about 5% crystallinity).

(c) The chloro substituent can disturb the structural symmetry of the polymer segments leading to decreased resonance effects and hence lower backbone rigidity.

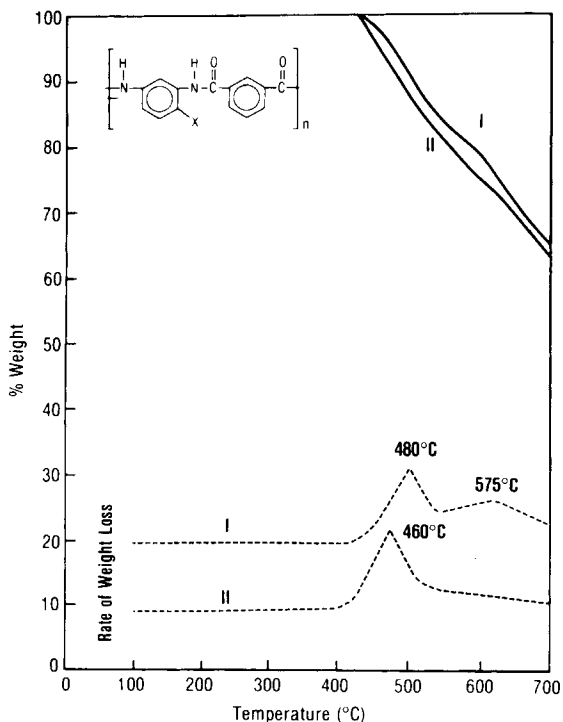


Fig. 1. Substituent effect on thermal stability of poly(1,3-phenyleneisophthalamide). I: X = H, $\eta_{\text{inh}} = 0.98$; II: X = H, $\eta_{\text{inh}} = 0.78$.

The decrease in chain stiffness probably offsets any increase caused by the steric hindrance of the chlorine to the free rotation around the N—C_{arm} bond. It is important to note that molecular weight does not affect the thermal stability of PCI and PMI in the molecular weight range we are dealing with.¹⁰ Thus, the differences in thermal stabilities of the two polyamides described above are due to structural variations and not to the molecular weight effects.

The thermal degradation curve of our poly(1,4-phenyleneterephthalamide), PPT, is very much identical to that of the commercial polymer⁹ (Kevlar). Presence of a chlorine in the diamine ring at the ortho position lowers the stability of PPT drastically; the IDT and T_{max} are lowered by 80 and 55°C, respectively (Fig. 2). Thus, the effect of a chlorine on the thermal stability is much more detrimental in the case of PPT as compared to PMI. One of the possible explanations could be that *p*-phenylene linkages in poly(1,4-phenyleneterephthalamide) give rise to an extremely rigid rod-like structure and that the introduction of a substituent disturbs the structural symmetry significantly which then leads to decreased resonance stabilization. This, combined with reduced intermolecular bonding strength (lower H bonding strength supported by IR data, lower crystallinity, looser crystalline packing, etc.), can result in a lower thermal stability of poly(chloro-2,5-phenyleneterephthalamide), PCT, as compared to PPT. Poly(1,3-phenyleneisophthalamide), on the other hand, is comparatively flexible due to the presence of less stiff *m*-phenylene linkages, and therefore the presence of a substituent does not cause a dramatic decrease in the thermal stability.

As indicated by the data in Table 1, the addition of another chloro substituent causes little or no further decrease in thermal stability. Substitution of a nitro group in PPT lowers its stability tremendously; the polymer undergoes a cata-

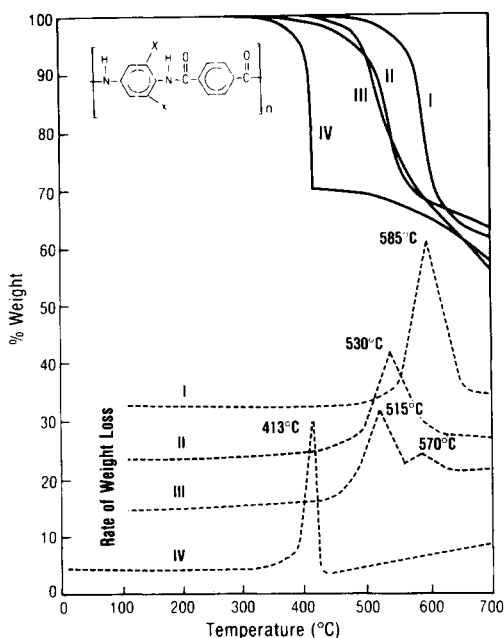


Fig. 2. Substituent effect on thermal stability of poly(1,4-phenyleneterephthalamide). I: X = H, X' = H; II: X = Cl, X' = H; III: X = Cl, X' = Cl; IV: X = NO₂, X' = H.

strophic degradation at $\sim 410^\circ\text{C}$ accompanied by $\sim 32\%$ weight loss and a large amount of heat liberation. In the case of poly(1,4-phenyleneterephthalamide), these substituents may be ranked in the following manner of their decreasing influence on the thermal stability: $\text{NO}_2 > 2\text{Cl} \geq \text{Cl}$. The effect of substitution on thermal stability of poly(1,3-phenyleneisophthalamide) and poly(1,4-phenyleneterephthalamide) is illustrated in Figures 1 and 2.

Thermo-oxidative Stability of Polyamides

Figures 1 and 2 demonstrate that polyamides of the PMI and PPT series undergo extensive carbonization upon nonoxidative degradation leaving 54–64% char at 700°C . In these polymers, the thermal degradation is initiated by chain scission¹⁰ at the amide functional groups which then leads to a carbonaceous product; the latter continues to carbonize with a small accompanying weight loss as it is heated to higher temperatures. Thermo-oxidative degradation of these polyamides, on the other hand, takes place in two major steps with no residue by 700°C (Fig. 3). The first step represents the thermal degradation leading to char residue, while the second step involves thermal as well as oxidative degradation.

The effect of chlorine on the thermo-oxidative stability of PMI is illustrated in Figure 3. As discussed before, the result of chlorine substitution is to reduce the thermal stability of PMI. Interestingly, Figure 3 points out that chlorine tends to enhance the thermo-oxidative stability of the char. The influence of chlorine on the oxidative stability of poly(1,3-phenyleneisophthalamide) can be clearly observed when we compare the effect of the atmosphere (argon, air, and oxygen) on PMI and PCI. The comparisons are shown in Figures 4 and 5,

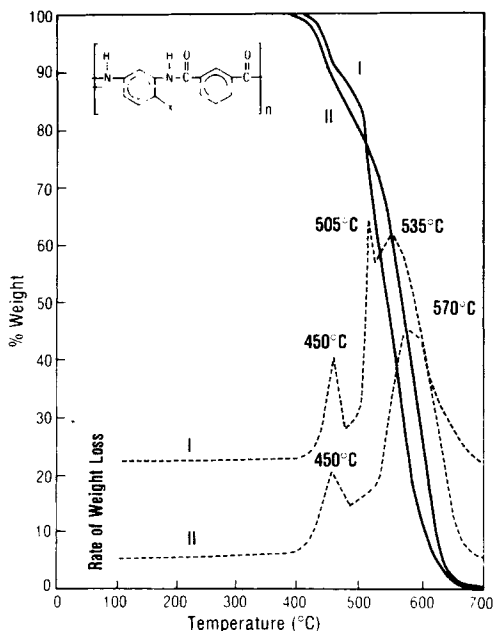


Fig. 3. Substituent effect on thermo-oxidative stability of poly(1,3-phenyleneisophthalamide). I: X = H; II: X = Cl.

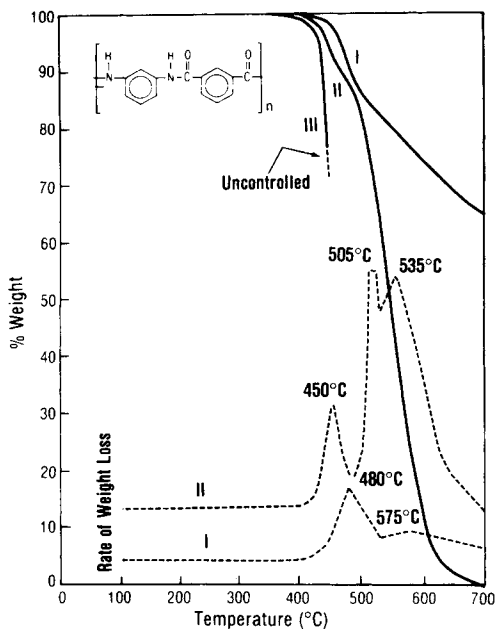


Fig. 4. Effect of medium on stability of poly(1,3-phenyleneisophthalamide). I: Argon; II: air; III: oxygen.

and the data summarized in Table II. The data show that when the atmosphere is changed from argon to air, the IDT and T_{\max} of PMI, for the first step, are lowered by 15 and 30°C, respectively. In the case of PCI, on the other hand, the

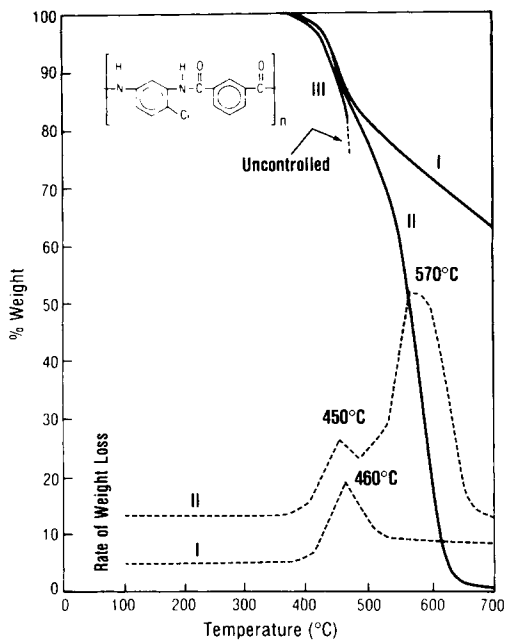
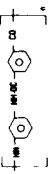
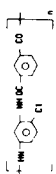


Fig. 5. Effect of medium on stability of poly(chloro-2,4-phenyleneisophthalamide). I: Argon; II: air; III: oxygen.

TABLE II
Substituent Effect on the Thermal and Thermo-oxidative Stability of Isophthalamides

Polyamides		Structure	$\eta_{inh}^{(1)}$	Medium	IOT, °C ⁽³⁾	Thermogravimetric Analysis ⁽²⁾						T _{max} , °C ⁽⁴⁾			
Code	Name					400	450	500	600	700	Step I	Step II	Step I	Step II	
PMI	Poly(1,3-phenylene isophthalamide)		0.98	Argon	440	0.3	3.0	15.3	27.5	35.5	480	575			
				Air	425	0.2	7.5	18.0	91.0	100	450	505+	535		
				Oxygen	425	0.7	Material burns at about 445°C								
PCI	Poly(chloro-2,4-phenylene isophthalamide)		0.79	Argon	425	0.8	8.5	19.0	29.5	37.0	460				
				Air	415	0.8	9.5	21.0	81.0	100	460	570			
				Oxygen	415	1.0	11.5	Material burns at about 475°C						440	

(1) Determined on a 0.5 g/dL solution of concentrated H₂SO₄ at 25°C.

(2) du Pont TGA-951, 10°C/min heating rate, ~23 mg sample in platinum pan.

(3) Initial decomposition temperature; obtained by extrapolation of the initial degradation portion of the TGA curve.

(4) Temperature at which maximum rate of weight loss occurs.

corresponding lowering is only 10°C, in both IDT and T_{\max} . Moreover, the T_{\max} for the second, step representing thermal and oxidative degradations, is at least 35°C higher for PCI. Additionally, in an oxygen atmosphere PCI burns at about 30°C higher than PMI. All the foregoing observations suggest that the thermo-oxidative resistance of poly(1,3-phenyleneisophthalamide) is greatly enhanced upon the substitution of chlorine.

Substituents such as Cl and NO₂ on poly(1,4-phenyleneterephthalamide) also lead to a similar effect (Table III). For example, changing the medium from argon to air lowers the IDT of PPT by 40°C (step I), whereas in substituted polymers the corresponding lowering is not more than 5°C. Similarly, the T_{\max} of the unsubstituted polyamide is lowered by 50°C in air compared to a decrease of only 0–15°C for the substituted PPT polymers.

Increase in the thermo-oxidative stability of PMI and PPT in the presence of Cl and NO₂ substituents can be readily understood. The groups like Cl, NO₂, CO₂R, SO₃H, etc., by virtue of having at least one strongly electron-attracting atom and a double bond conjugated to the benzene ring through resonance, cause an electron displacement away from the nucleus and toward the group.¹¹ Consequently, these groups deactivate the benzene ring from an electrophilic attack. Thus, the introduction of electron-acceptor groups into the macromolecule leads to deactivation of the free radicals formed and therefore lowers the rate of oxidation of the polymer.¹²

Additional information regarding the degradation mechanism can be obtained by considering the effect of the atmosphere on the weight loss characteristics of PMI and PCI (Figs. 4 and 5). The similarity of the initial portions (up to about 10–15%) of the degradation of PMI in argon and air suggests that the polymer's initial decomposition involves oxidation only to a minor extent. Interestingly, the 15% initial weight loss portion of the degradation curve of PCI remains essentially unchanged regardless of the atmosphere (argon, air, oxygen). This strongly suggests that poly(chloro-2,4-phenyleneisophthalamide) begins to degrade by thermal bond scission even in an oxygen atmosphere.

Thermal Transitions of Polyamides

Table IV summarizes the thermal transitions of these polyamides as determined by DSC. The glass transition temperatures (T_g) for poly(1,3-phenyleneisophthalamide) and poly(chloro-2,4-phenyleneisophthalamide) are found to be 270 and 265°C, respectively. The relationship of T_g versus molecular weight has been studied for both the polymers, and it appears that the T_g values of 270 and 265°C for PMI and PCI, respectively, represent the limiting values. Moreover, since these temperatures were determined upon reheat (i.e., initial heat up to just above the T_g , followed by cooling to RT and subsequent reheating), the influence of thermal history on T_g has been eliminated. The lower T_g of the chloropolyamide can be attributed to its relatively lower chain stiffness.

The DSC thermogram of poly(1,3-phenyleneisophthalamide) shows a small endotherm at 417°C which represents the polymer melting (T_m) in spite of a small accompanying weight loss (<1%) due to degradation. Poly(chloro-2,4-phenyleneisophthalamide), on the other hand, seems to be predominantly amorphous.

TABLE III
Substituent Effect on the Thermal and Thermo-oxidative Stability of Terephthalamides

Polyamide		Thermogravimetric Analysis ⁽²⁾										
Code	Name	Structure	$\eta_{inh}^{(1)}$	Me- dium	Int. °C ⁽³⁾	% Weight Loss at, °C				T max. °C ⁽⁴⁾		
						400	450	500	600	700	Step I	Step II
PPT	Poly(1,4-phenylene terephthalamide)		1.74	Argon	555	0.3	1.0	1.6	27.5	39.0	585	585
PCT	Poly(chloro-2,5-phenylene terephthalamide)		0.83	Argon	475	2.0	4.0	8.5	31.0	38.5	530	530
PDT	Poly(2,6-Dichloro-1,4-phenylene terephthalamide)		0.60	Argon	475	1.0	2.5	10.0	32.5	46.0	515	515
PNT	Poly(nitro-2,5-phenylene terephthalamide)		0.75	Argon	400	6.0	31.0	31.5	36.0	44.5	415	415
				Air	400	6.5	31.4	38.0	91.0	100	415	515

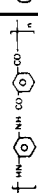
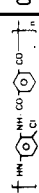

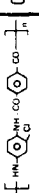
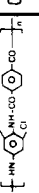
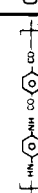
(1) Determined on a 0.5 g/dL solution in concentrated H₂SO₄ at 25°C.

(2) du Pont TGA-951, 10°C/min heating rate, ~23 mg sample in platinum pan.

(3) Initial decomposition temperature; obtained by extrapolation of the initial degradation portion of the TGA curve.

(4) Temperature at which maximum rate of weight loss occurs.

TABLE IV
Thermal Transitions in Aromatic Polyamides

Code	Polyamide		η_{inh}	(1)		Glass and Melting Transitions		(4)		Remarks
	Name	Structure		T_g , °C	ΔT_m , °C	Melting Behavior	Charring Process (Exothermic)	Peak Temperature, °C		
									(3) T_m , °C	
PMI	Poly(1,3-phenylene isophthalamide)		0.98	270	417	0.6	~ 700 (Broad)	Partially-Crystalline Melting accompanied by decomposition.		
PCI	Poly(chloro-2,4-phenylene isophthalamide)		0.79	265	—	—	~ 630 (Broad)	Amorphous		
PPT	Poly(1,4-phenylene terephthalamide)		1.74	—	555	5.5	~ 650 (Broad)	Highly-crystalline. Melting accompanied by decomposition		
PCT	Poly(chloro-2,5-phenylene terephthalamide)		0.83	—	462 + 519	5.0	~ 630 (Broad)	Highly-crystalline. Melting accompanied by decomposition		
PDT	Poly(2,6-Dichloro-1,4-phenylene terephthalamide)		0.60	—	504	11.0	~ 690 (Broad)	Highly-crystalline. No transition occurs prior to sharp exothermic decomposition at ~405 °C.		
PNT	Poly(nitro-2,5-phenylene terephthalamide)		0.75	—	—	—	405 (Very Sharp). ~660 (Broad)	Highly-crystalline. No transition occurs prior to sharp exothermic decomposition at ~405 °C.		

(1) Determined in a 0.5 g/dL solution in concentration H_2SO_4 at 25°C.

(2) du Pont 990, DSC in argon, 10°C/min heating rate, 11.5 ± 0.3 mg in crimped aluminum pan.

(3) du Pont 951, TGA in argon, 10°C/min heating rate, 23 mg sample in platinum pan.

(4) du Pont 990, DTA in argon, 10°C/min heating rate, 10.5 ± 0.5 sample in alumina cup.

Poly(1,4-phenyleneterephthalamide) and its substituted polyamides appear to be highly crystalline, and therefore the T_g could not be determined. The T_m of PPT is close to its literature value of 560°C.⁹ Addition of one or two chlorine substituents to PPT lowers its melting point drastically (462 + 519°C and 504°C, respectively, compared to 555°C). Owing to their high melting points, all these polyamides melt with accompanying degradation. A lower melting point in the presence of a substituent may be expected in this case as a result of factors such as increased chain flexibility, possibly lower crystallinity, and lower intermolecular forces accompanying loose crystalline packing. The nitro-substituted polymer shows no sign of T_g or T_m and undergoes a catastrophic degradation of ~410°C with extensive heat liberation.

High-temperature DTA of all these polyamides exhibits a broad exotherm with a peak temperature at 630–700°C. This exotherm covers the temperature region where the cyclization and crosslinking reactions leading to char formation take place.

CONCLUSIONS

The decrease in thermal stability of poly(1,3-phenyleneisophthalamide) and poly(1,4-phenyleneterephthalamide) as a result of substitution can be attributed to loss in chain stiffness. The latter could originate from factors such as reduced intermolecular forces (lower H-bond strength, lower crystallinity) and decreased resonance effects. A similar explanation appears to be valid for the lower T_g and T_m values of the substituted polyamides. Electron-withdrawing substituents such as Cl and NO₂ increase the thermo-oxidative resistance of these polyamides.

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Received August 7, 1981

Accepted November 24, 1981