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AROMATIC POLYAMIDES—IX

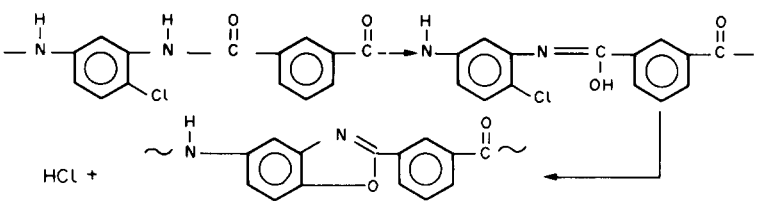
SYNTHESIS AND THERMAL PROPERTIES OF SOME *N*-METHYLATED AROMATIC POLYAMIDES

A. C. KARYDAS, M. KAPUŚCIŃSKA and E. M. PEARCE
Polymer Research Institute, Polytechnic Institute of New York, Brooklyn, NY 11201, U.S.A.

Abstract—The synthesis and thermal properties of a series of *N*-methylated aromatic polyamides based on chlorinated and unsubstituted diamines are reported. Thermal degradation of these polyamides provides further support for the iminolization–cyclization mechanism proposed by Khanna *et al.* [1,2] [*J. Polym. Sci., Polym. Chem. Ed.* **19**, 2817, 2835 (1981)] to explain the unusually high char yield of chlorinated aromatic polyamides.

INTRODUCTION

Wholly aromatic polyamides are well known for their superior resistance to heat. Chaudhuri *et al.* [3] have reported a correlation between char yield and substituents incorporated onto the polymer backbone. It was found that the chlorine substituted polymer (based on chloro-2,4-phenylene diamine and isophthaloyl chloride) exhibited an unusually high char yield. In their attempt to explain this observation, Khanna *et al.* [1] reported a detailed investigation of the mechanism of stabilization by chlorine. They concluded that high char yield is partly due to the iminolization of the amide group. The iminol then cyclizes to form a benzoxazole structure while HCl is eliminated:



In this study, we report the synthesis and thermal stability of several *N*-methylated, non-iminolizable, unsubstituted and chloro-substituted aromatic polyamides.

EXPERIMENTAL

Purification of materials

Commercially available [4] samples of 1,3-phenylene diamine and 2,4 diamino-chlorobenzene were recrystallized to constant melting point yielding white solids. Isophthaloyl and terephthaloyl chloride were purified by vacuum distillation. Dimethyl acetamide and dimethyl sulphoxide were each vacuum distilled over calcium hydride to yield colourless liquids. Methyl iodide was distilled before use. Dry sodium hydride was used without further purification.

SYNTHESIS OF POLYAMIDES

Non-methylated polyamides, namely poly(1,3-phenylene-isophthalamide) (PMI), poly(4-chloro-1,3-phenylene-isophthalamide) (4Cl-PMI), poly(1,3-phenylene-terephthalamide) (PMPT), and poly(4-chloro-1,3phenylene-terephthalamide) (4Cl-PMPT) were prepared by previously described procedures [5, 6].

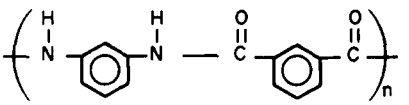
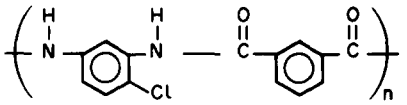
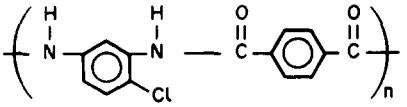
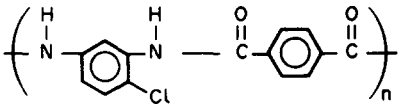
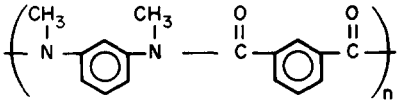
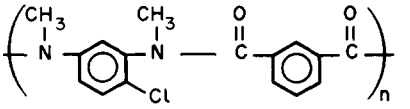
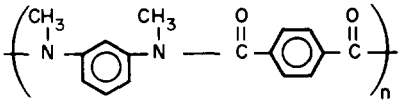
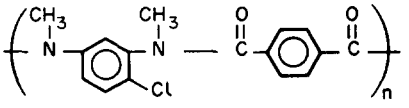
The *N*-methylated analogues of PMI, 4Cl-PMI, PMPT and 4Cl-PMPT were prepared by the following method [7]: dimethyl sulphoxide (150 ml) and dry sodium hydride (0.025 mol) were placed in a round-bottom flask equipped with a N_2 inlet, a mechanical stirrer, a dropping funnel and a gas outlet, and the flask was purged with N_2. The heterogeneous mixture was vigorously stirred at room temperature for about 1 hr when the temperature rose to 75°. After all the sodium hydride was consumed, the polyamide (0.025 mol amide-units) was added. The mixture was stirred for 5 hr, then methyl iodide 0.027 mol) was added dropwise, and the solution was stirred overnight at room temperature. The polymer was precipitated by pouring the solution into a large excess of hot, magnetically stirred water; it was filtered, washed several times with water and finally dried under vacuum at *ca.* 106° for 40 hr.

Structures and codes of all investigated polyamides and their inherent viscosities are summarized in Table 1.

CHARACTERIZATION OF MATERIALS

The structures and composition of all *N*-methylated polyamides were confirmed by elemental analysis (Schwartzkopf microanalytical Laboratories) and by i.r. and NMR spectroscopy.

Table 1. Structures, codes and inherent viscosities of polyamides

Structure	Code	η_{inh}*
	PMI	0.43
	4 Cl-PMI	0.41
	PMPT	1.11
	4 Cl-PMPT	0.28
	PMI-N-M	0.22
	4 Cl-PMI-N-M	0.27
	PMPT-N-M	0.51
	4 Cl-PMPT-N-M	0.19

*Measured in conc. H_2SO_4 (C = 5 g/l).

I.R. spectra were obtained in the form of KBr pellets, using a Perkin–Elmer 567 i.r. spectrophotometer. NMR spectra were recorded on a Varian HA60 spectrometer (60 MHz) at room temperature, using tetramethyl silane as internal standard. Deuterated dimethyl sulphoxide was used as solvent.

Inherent viscosities were measured in concentrated H_2SO_4 at 25°, using a Cannon–Ubbelohde viscometer. The solution concentration was 5 g/l.

The thermal stabilities of the polyamides were determined by thermogravimetric analysis employing a DuPont 1090 thermal analyser equipped with a 951 TGA module. The experiments were conducted under N_2 with a heating rate of 20°/min.

RESULTS AND DISCUSSION

The synthesis and characterization of the non-methylated polymers have been previously reported. The spectral data of all the *N*-methylated polymers are consistent with the proposed structures. The carbon-to-nitrogen ratio obtained by elemental analysis indicated quantitative *N*-alkylation for all polymers.

In the i.r. specta, we observe that an absorption at 3300 cm^{-1}, corresponding to the N–H stretch, is absent. The amide II band (1550 cm^{-1}) attributable to C–N–H bending is also absent. All polymers exhibit a strong carbonyl absorption at 1650 cm^{-1}. The presence of the methyl group is verified by the

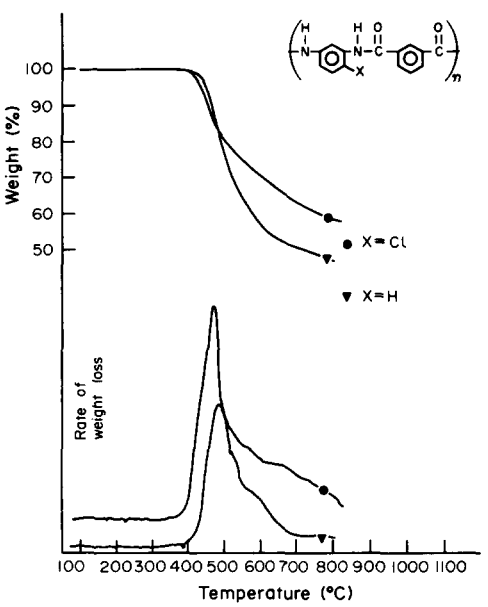


Fig. 1. Effect of chlorine on the thermal stability of PMI.

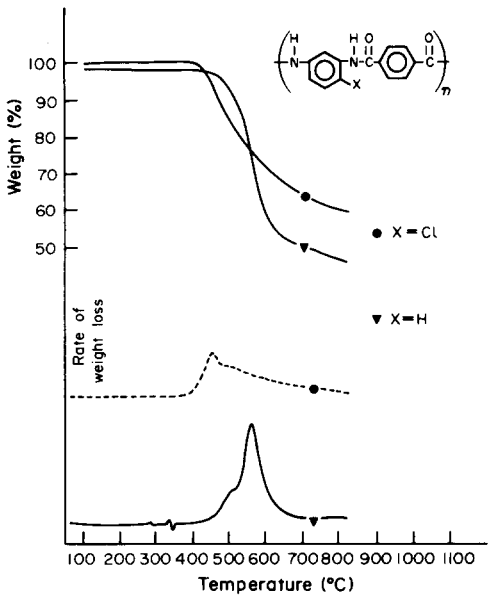


Fig. 2. Effect of chlorine on the thermal stability of PMPT.

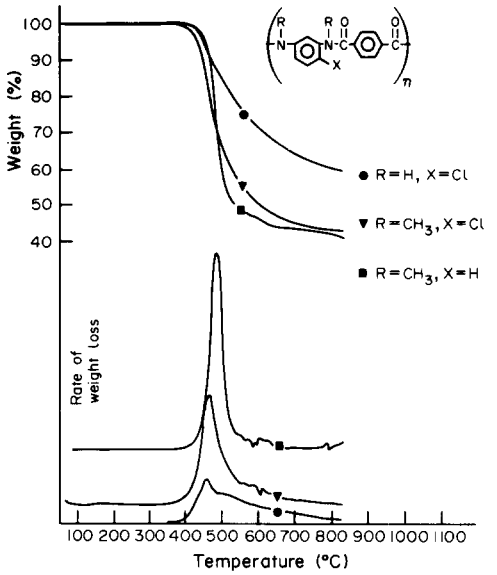


Fig. 4. Substituent effect on the thermal stability of PMPT.

absorptions at *ca.* 2900 cm^{-1} ($-CH_3$ stretching), 1370 cm^{-1} ($-CH_3$ bending) and 730 cm^{-1} (N-CH_3).

All NMR spectra consist of complex absorptions in the aromatic region (δ = 6.8–8 ppm) and a methyl singlet (δ = 3.2 ppm) corresponding to the nitrogen bonded methyl group. The degree of alkylation was calculated from the relative area of aromatic to aliphatic protons and found to be 100% in all cases. Absence of the proton resonance of the amide groups (δ = 10.5–11.5 ppm) provided further support to the calculated high degree of alkylation.

A comparison of the TGA curves of PMI, 4 Cl-PMI, PMPT and 4 Cl-PMPT (Figs 1 and 2) reveals that the chlorinated polymers exhibit a 10–15% higher char yield. The major contributing factor is believed to be the fused (benzoxazole) ring formation [1, 2]. The broad shoulder peaks on the derivative curves are believed to correspond to the degradation of the benzoxazole containing polymers. A detailed investigation of leaving group effects [8] provides adequate support for this proposal.

Upon methylation of the amide nitrogen, the shoulder peaks disappear indicating that benzoxazole units are not being formed (Figs 3 and 4). Both *N*-methylated PMI and *N*-methylated PMPT seem to degrade by mechanisms similar to the degradation mechanisms of their chlorinated analogues. This is in accord with the expected results since *N*-methylation inhibits iminolization and therefore benzoxazole formation. The lower thermal stability and significantly lower char yield of the *N*-methylated polymers is concordant with previously reported results [7].

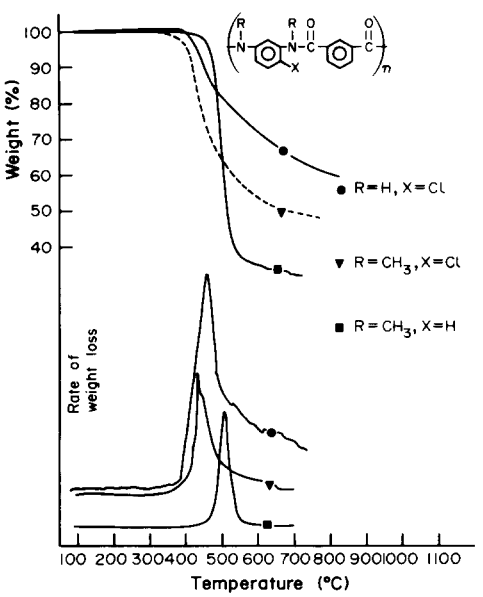


Fig. 3. Substituent effect on the thermal stability of PMI.

CONCLUSIONS

The present study provides additional support for the iminolization–cyclization mechanism proposed [1, 2] to explain the high char yield of chlorinated aromatic polyamides. Pyrolysis studies are being presently conducted on both the *N*-methylated polymers and their model diamides to establish the absence of benzoxazole units in the pyrolysis products. The results of these studies will be reported in a later publication.

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Dedication—This paper is respectfully dedicated to Professor Oto Wichterle on the occasion of his 70th birthday.

REFERENCES

1. Y. P. Khanna, E. M. Pearce, J. S. Smith, D. T. Burkitt, H. Njuguna, D. M. Hindenland and B. D. Forman, *J. Polym. Sci., Polym. Chem. Ed.* **19**, 2817 (1981).
2. Y. P. Khanna and E. M. Pearce, *J. Polym. Sci., Polym. Chem. Ed.* **19**, 2835 (1981).

3. A. K. Chaudhuri, B. Y. Min and E. M. Pearce, *J. Polym. Sci., Polym. Chem. Ed.* **18,** 2949 (1980).
4. All materials were purchased from Aldrich Chemical Co., Metuchen, New Jersey.
5. S. L. Kwolek, P. W. Morgan and W. R. Sorenson, U.S. Patent 3,063,966 (1962).
6. Y. P. Khanna, E. M. Pearce, B. D. Forman and D. A. Bini, *J. Polym. Sci., Polym. Chem. Ed.* **19,** 2799 (1981).
7. M. Takayanagi and T. Katayose, *J. Polym. Sci., Polym. Chem. Ed.* **19,** 1333 (1981).
8. M. Kapuścinska and E. M. Pearce, *Eur. Polym. J.*, submitted for publication.