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Synthesis of Some Novel Polyamides

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NOTE

SYNTHESIS OF SOME NOVEL POLYAMIDES

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INTRODUCTION

Among various high-temperature organic polymers, the aromatic polyamides have shown excellent thermal stability due to the stiffness of the polymer chain and hydrogen bonding of the amide groups, but had limited solubility in most organic solvents [1-3].

With this in mind, an attempt has been made to synthesize aromatic polyamides with good thermal stability and better solubility in organic solvents [4]. Their comparative thermal stability, inherent viscosity, solubility, etc. have been determined.

EXPERIMENTAL

Preparation of Monomers

The diamines, 4,4′-diaminodiphenylamine, *N*-(4-aminobenzoyl)-*p*-phenylenediamine, *N*-(4-aminobenzoyl)-*m*-phenylenediamine, *N*-(3-aminobenzoyl)-*m*-phenylenediamine, 4-amino-4′-(*p*-aminobenzamido)-diphenylamine, and acid chlorides of 1,1′-binaphthyl-4,4′-dioxyacetic acid and 1,1′-binaphthyl-2,2′-dioxyacetic acid, were prepared according to the procedure reported earlier [4-6].

Low-Temperature Solution Polymerization

A 10% solution of amine was cooled below -20°C, and the solution of diacid chloride was slowly added to it with constant stirring over 2 h. It was neutralized by the addition of 95% of the theoretical amount of LiOH needed to neutralize HCl formed.The highly viscous solution was stirred at room temperature for 8 h and then poured into 10% methanol. A crystalline polymer was obtained. The polyamides prepared by this method are recorded in Table 1. Inherent viscosities were determined at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C.

RESULTS AND DISCUSSION

The inherent viscosities of the polyamides were in the range of 0.19 to 0.66 (Table 1). They varied in regular fashion according to the monomer units. It appears that a change from *meta* to *para* isomer increased the inherent viscosity remarkably.

The IR spectra of the polymers show a characteristic absorption band in the 3250-3400 cm^{-1} region (–NH stretching) and between 1640-1680 cm^{-1} ($>$C=O). The IR peaks of the *para* isomers were more pronounced than the corresponding *meta* isomer. It may be concluded that the polymerization of *p*-substituted monomers results in more ordered structures [7].

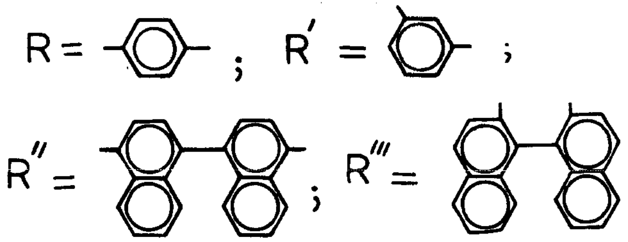
THERMAL PROPERTIES

The TGA results (Fig. 1) indicate that the thermal stability of these polyamides, although not outstanding, increased in the order VIII < VI < V < IV < III. In general, decomposition started above 180°C. The small weight loss below 180°C is due to loss of moisture and solvents. The main region for weight loss was normally found at 265-365°C. The order of thermal stability may be explained by assuming that change from the 2,2′-dihydroxy-1,1′-binaphthyl ring to the 4,4′-dihydroxy-1,1′-binaphthyl ring as well as from *meta* to *para* increases the thermal stability.

The crystalline Polyamide I exhibited a monotonous DTA curve having an endotherm about 430°C. One hundred percent volatilization of Polymer I took place at 390, 410, and 430°C in 3.0, 2.6, and 2.1 h, respectively. The relatively modest thermal and oxidative stability of these polyamides is evidently due to the $-\mathrm{OCH_2}$ and –NH units in the backbone.

TABLE 1. Inherent Viscosity of Copolymers

Code	Structure of repeating unit	η_{inh}, dL/g
I	$-HN-R-NH-R-NHCOCH_2O-R''-OCH_2CO-$	0.66
II	$-HN-R-NH-R-NHCOCH_2O-R'''-OCH_2CO-$	0.60
III	$-HN-R-CONH-R-NHCOCH_2O-R''-OCH_2CO-$	0.43
IV	$-HN-R-CONH-R-NHCOCH_2O-R'''-OCH_2CO-$	0.30
V	$-HN-R-CONH-R'-NHCOCH_2O-R''-OCH_2CO-$	0.39
VI	$-HN-R-CONH-R'-NHCOCH_2O-R'''-OCH_2CO-$	0.25
VII	$-HN-R'-CONH-R'-NHCOCH_2O-R''-OCH_2CO-$	0.33
VIII	$-HN-R'-CONH-R'-NHCOCH_2O-R'''-OCH_2CO-$	0.19
IX	$-HN-R-CONH-R-NH-R-NHCOCH_2O-R''-OCH_2CO-$	0.53
X	$-HN-R-CONH-R-NH-R-NHCOCH_2O-R'''-OCH_2CO-$	0.49



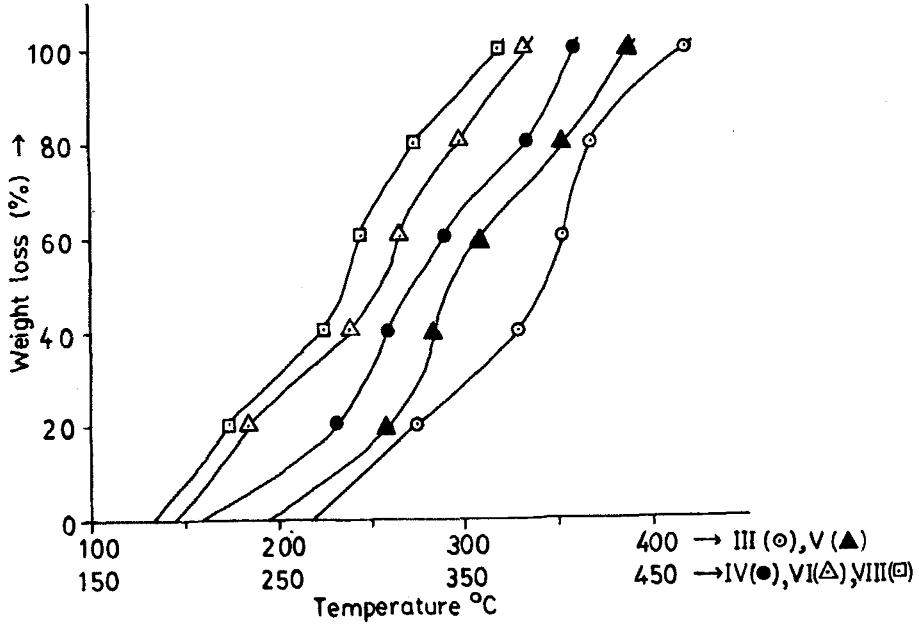


FIG. 1. TGA curves of polymers in air.

SOLUBILITY

All the polyamides were soluble in strong acids, e.g., sulfuric acid and trifluoroacetic acid, as well as in polar solvents such as dimethylformamide and dimethylacetamide (Table 2). The solubility increases in the order: III < IV < VI < VII < VIII. As expected, the solubility decreased with increasing crystallinity.

TABLE 2. Solubility of Polyamides

Solvent	Solubility[a] Polymer III	Polymer IV	Polymer VI	Polymer VII	Polymer VIII
H_2SO_4 (concentrated)	++	++	++	++	++
CF_3COOH	++	++	++	++	++
Pyridine	-	+	+	+	++
DMF	+	++	++	++	++
DMAc	++	++	++	++	++
DMSO	-	±	±	+	++
Ethanol	-	-	±	+	+
Acetone	-	-	-	-	-
Benzene	-	-	-	-	±

[a] Solubility: (++) soluble at room temperature
(+) soluble on heating
(±) partially soluble or swollen
(-) insoluble

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