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Studies on Some Newer Thermally Stable Polyamides

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ABSTRACT

Some newer polyamides were synthesized and characterized by their elemental, IR spectral, and thermal analysis. The thermal decomposition of such polymers was investigated by using programmed and isothermal thermogravimetric analysis. Reaction rates and overall activation energies were calculated from isothermal weight loss studies. Differential thermal analysis was used to determine the melting points of polyamides. These results indicate that the polymers decompose above 185°C the steep weight loss occurred mainly between 250 and 310°C. Most of the polyamides were soluble in organic solvents and exhibited inherent viscosity in the range of 0.12 to 0.42.

INTRODUCTION

The intrinsic and oxidative stability of aromatic structures have long been recognized, and various polymers have been prepared in which aromatic rings are linked together in chains. In most of the cases the connected groups are less stable than the rings [1], and the stability of polymers depends on the nature of connecting groups. Among more stable linking groups which have been used are amides and imides [2, 3]. Recently, copolyamides with good thermal stability

have been reported by many workers [4-6]. Previously we have also synthesized and studied the properties of different types of polyhydrazides and polyamides. They were shown to have better thermal stability and good solubility in organic solvents [7-9].

In continuation of our earlier work, we have made an effort to synthesize some diamines (with and without preformed carbonamide linkage) and studied their copolymerization with different aliphatic and aromatic dicarboxylic acid chlorides with the object of obtaining polyamides with high thermal stability and better solubility. A comparative study of their infrared spectra, thermal properties, inherent viscosities, and solubility has also been made and better results were obtained.

EXPERIMENTAL

Preparation of Monomers

Synthesis of Diacid Chlorides

Diacid chlorides were prepared from their corresponding dicarboxylic acids by conventional methods.

Synthesis of Diamines

Synthesis of 4-Amino-4'-(p-aminobenzamido)-diphenylamine.

4-Nitro-4'-acetamidodiphenylamine. The amine was prepared according to the known method [10]. Yield, 64%. IR (KBr): 3200(-NH-), 1670(-CO-N-), 1580 cm^{-1} (-NO₂). Mass: m/z -271 (M⁺).

Analysis: Calculated for C₁₄H₁₃N₃O₃: C, 61.99; H, 4.43; N, 15.49%. Found: C, 61.79; H, 4.20; N, 15.12%.

4-Nitro-4'-(p-nitrobenzamido)diphenylamine. A solution of p-nitrobenzoylchloride (1.85 g, 0.01 mol) in dry benzene (10 mL) was added dropwise to a stirred solution of 4-nitro-4'-aminodiphenylamine (2.29 g, 0.01 mol) (obtained from the hydrolysis of 4-nitro-4'-acetamidodiphenylamine) in dry benzene (10 mL). The mixture was refluxed for 4 h. The excess of benzene was removed in vacuo. The solid mass thus obtained was filtered and crystallized from ethanol.

Yield, 2.26 g (60%), mp 270°C. IR (KBr): 3100(-NH-), 1650(-CO-N-), 1560 cm^{-1} (-NO₂), Mass: m/z -378 (M⁺).

Analysis: Calculated for C₁₉H₁₄N₄O₅: C, 60.32; H, 3.70; N, 14.82%. Found: C, 60.00; H, 3.52; N, 14.48%.

4-Amino-4'-(p-aminobenzamido)diphenylamine. A solution of 4-nitro-4'-(p-nitrobenzamido)diphenylamine (3.78 g, 0.01 mol) in THF (100 mL) was shaken with Raney nickel (1.5 g) and hydrogen under 2.5

kg/cm² in a Paar hydrogenator for 14 h. The catalyst was filtered off and the solvent removed in vacuo. The solid mass was crystallized from ethanol. Yield, 1.5 g (50%), mp 280°C. IR (KBr): 3400 (–NH₂), 3100 (–NH–), 1650 cm⁻¹ (–CO–N–), Mass: m/z-318 (M⁺).

Analysis: Calculated for C₁₉H₁₈N₄O: C, 71.69; H, 5.66; N, 17.61%.

Found: C, 71.50; H, 5.43; N, 17.33%.

Other diamines, viz., 4,4'-diaminodiphenylamine, N-(4-aminobenzoyl)-p-phenylenediamine and N-(4-aminobenzoyl)-m-phenylenediamine, were prepared according to the procedures reported earlier [11-13].

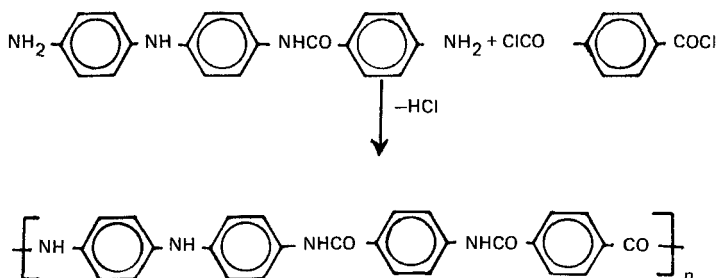
Polymerization

Better results were obtained by low temperature solution polymerization than by any other type of polymerization. A typical example of the polymerization of 4-amino-4'-(p-aminobenzamido)diphenylamine with terephthaloyl chloride is given below.

4-Amino-4'-(p-aminobenzamido)diphenylamine (15.9 g) was dissolved in N-methylpyrrolidone (160 mL) and cooled below -20°C. A solution of terephthaloyl chloride (8.37 g) was slowly added to it with constant stirring over 2 h. It was then neutralized by the addition of lithium hydroxide (95% of the needed amount to neutralize HCl formed during the reaction). The polymer solution was stirred at room temperature for 8 h and then poured into a 10% methanol solution in water. Crystalline polymer precipitated, was filtered, washed with acetone, and dried. Yield, 90% (20.16 g), mp 250°C.

Analysis: Calculated for C₂₇H₂₀N₄O₃: C, 72.32; H, 4.46; N, 12.50%.

Found: C, 72.30; H, 4.40; N, 12.43%.



MEASUREMENTS

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was carried out in air at a heating rate of 5°C/min. The sample size was about 100 mg.

Differential scanning calorimetry (DSC) was performed. The energy of activation E_a of thermal decomposition was obtained from an analysis of data from DSC at four different heating rates (5, 10, 15 and 20°C/min) according to the equation

$$\log (\phi/T^2) = -E_a/2.303RT + \text{constant}$$

where ϕ is the heating rate, R is the gas constant, and T is the decomposition temperature. In this study T is that of the vertex of the exothermic peak in the DSC curve.

Infrared spectra were obtained on a Perkin-Elmer Infrared 157 and 177 spectrophotometer.

RESULTS AND DISCUSSION

All the polyamides were soluble in strong acids such as concentrated sulfuric acid and trifluoroacetic acid, and the solubility of polyamides in polar solvents increased in the order $V > IV > III > II > I$. In general, the solubility of polymers is inversely related to its crystallinity. Polyamides formed from aromatic acid chlorides were less soluble than aliphatic acid chlorides. Polyamides containing *m*-phenylene units exhibited better solubility in comparison to *p*-phenylene units containing polymers.

Inherent viscosity values of polyamides were observed in the range of 0.12 to 0.42 (Table 1). Results showed that an elongation of carbon chains of aliphatic diacid chlorides and a change in the ring from meta to para isomers increases the inherent viscosity remarkably.

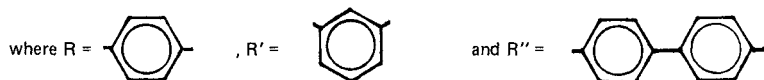
The polymers thus obtained were identified by means of infrared spectroscopy and elemental analysis. IR spectra of the polymers show a characteristic absorption in the 3200-3400 cm^{-1} range with higher intensity due to $-\text{NH}-$ stretching vibration. The polymers also show an absorption band between 1650 and 1680 cm^{-1} for $-\text{CO}-\text{N}-$ linkage. These spectra closely resemble the model compounds. IR spectra showed that the peaks of *p*-phenylene units containing polymer were more pronounced in comparison to *m*-phenylene units containing polymers. It may be interpreted that the polymerization of *p*-substituted monomers results in more ordered structures which is in accordance with the observations of Preston and co-workers [14, 15].

Somewhat lower values of C, H, and N% were observed than the calculated values from the repeating units of polymers. The same observations have also been recorded with polymers by other workers [16, 17].

The TGA and DTA profiles of polyamides I, II, III, IV and IX are shown in Figs. 1 and 2, respectively. The crystalline polyamide IX

TABLE 1. Inherent Viscosity of Copolymers

Code	Structure of repeating unit	η_{inh} at 30°C
I	$-\text{HN}-\text{R}-\text{CONH}-\text{R}-\text{NHCOCH}_2\text{O}-\text{R}-\text{OCH}_2\text{CO}-$	0.28
II	$-\text{HN}-\text{R}-\text{CONH}-\text{R}-\text{NHCOCH}_2\text{O}-\text{R}'-\text{OCH}_2\text{CO}-$	0.25
III	$-\text{HN}-\text{R}'-\text{CONH}-\text{R}-\text{NHCOCH}_2\text{O}-\text{R}-\text{OCH}_2\text{CO}-$	0.24
IV	$-\text{HN}-\text{R}'-\text{CONH}-\text{R}-\text{NHCOOH}_2\text{O}-\text{R}'-\text{OCH}_2\text{CO}-$	0.21
V	$-\text{HN}-\text{R}'-\text{CONH}-\text{R}'-\text{HNC OCH}_2\text{O}-\text{R}-\text{OCH}_2\text{CO}-$	0.15
VI	$-\text{HN}-\text{R}'-\text{CONH}-\text{R}'-\text{NHCOCH}_2\text{O}-\text{R}'-\text{OCH}_2\text{CO}-$	0.12
VII	$-\text{HN}-\text{R}''-\text{NHCOCH}_2\text{O}-\text{R}-\text{OCH}_2\text{CO}-$	0.19
VIII	$-\text{HN}-\text{R}''-\text{NHCOCH}_2\text{O}-\text{R}'-\text{OCH}_2\text{CO}-$	0.17
IX	$-\text{HN}-\text{R}-\text{NH}-\text{R}-\text{NHCOCH}_2\text{O}-\text{R}-\text{OCH}_2\text{CO}-$	0.22
X	$-\text{HN}-\text{R}-\text{NH}-\text{R}-\text{NHCOCH}_2\text{O}-\text{R}'-\text{OCH}_2\text{CO}-$	0.20
XI	$-\text{HN}-\text{R}-\text{NH}-\text{R}-\text{CONH}-\text{R}-\text{NHCOCH}_2\text{O}-\text{R}-\text{OCH}_2\text{CO}-$	0.42
XII	$-\text{HN}-\text{R}-\text{NH}-\text{R}-\text{CONH}-\text{R}-\text{NHCOCH}_2\text{O}-\text{R}'-\text{OCH}_2\text{CO}-$	0.39
XIII	$-\text{HN}-\text{R}-\text{NH}-\text{R}-\text{CONH}-\text{R}-\text{NHCO}-\text{R}-\text{CO}-$	0.35
XIV	$-\text{HN}-\text{R}-\text{NH}-\text{R}-\text{CONH}-\text{R}-\text{NHCO}-\text{R}'-\text{CO}-$	0.32
XV	$-\text{HN}-\text{R}-\text{NH}-\text{R}-\text{CONH}-\text{R}-\text{NHCO}-(\text{CH}_2)_4\text{CO}-$	0.26
XVI	$-\text{HN}-\text{R}-\text{NH}-\text{R}-\text{CONH}-\text{R}-\text{NHCO}-(\text{CH}_2)_8\text{CO}-$	0.29



exhibited a monotonous curve of DTA having an endotherm above 360°C. All the polyamides started to decompose above 185°C, and a steep weight loss occurred mainly in the range of 250 to 310°C.

The thermal properties of some polyamides are summarized in Table 2. Polymers XI and XIII melted at higher temperatures than XII and XIV, respectively. These results suggest that thermal stability of the polyamides is greatly influenced by variation in the isomeric forms of diamines. It may be interpreted that on going from meta to para isomeric polymers, there is an enhancement in thermal stability. Replacement of amino linkage by an amide linkage in monomers also increases the thermal stability to some extent.

Table 3 shows that the thermodynamic parameters of the pyrolysis

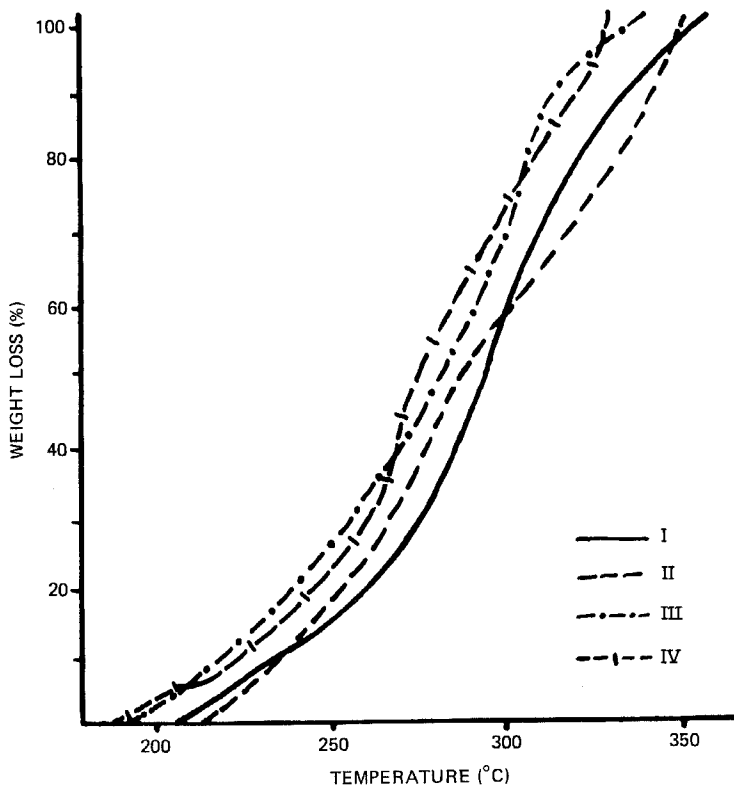


FIG. 1. TGA curves of Polymers I, II, III, and IV in air.

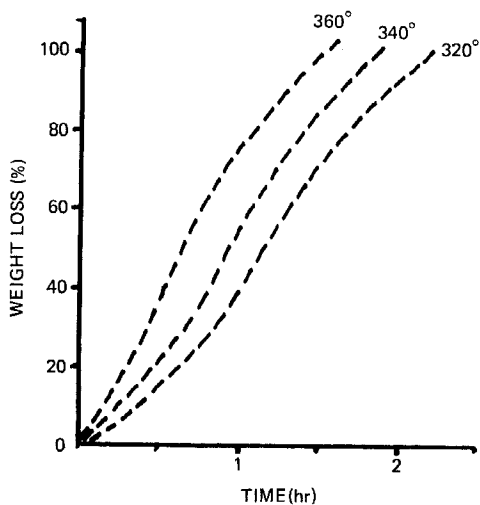


FIG. 2. Thermal degradation of Polymer IX.

TABLE 2. Thermal Properties of Polyamides

Polymer code	TDT ^a (°C)	DT at difference weight losses					D _{max} ^b
		20%	40%	60%	80%	100%	
XI	216	260	288	314	344	390	355
XII	220	256	282	320	346	380	340
XIII	198	232	266	318	342	372	325
XIV	212	244	270	300	336	366	310

^aInitial decomposition temperature.

^bDecomposition maximum.

TABLE 3. Thermodynamic Parameters of the Pyrolysis of Polyamides at 400°C Determined from DSC Data

Code	Decomposition temperatures at various heating rates (°C)				E _a (kcal/mol)
	5°C/min	10°C/min	15°C/min	20°C/min	
VII	302	312	317	321	49.74
VIII	290	311	316	322	40.53
XV	323	330	336	340	57.58
XVI	329	337	342	348	70.93

in the vicinity of 400°C determined from DSC value of E_a explains the thermal stability. Polyamides XV and XVI exhibited higher values of activation energy for thermal decomposition. It is probable that the production of an amorphous region in the closely packed structure participates essentially in the thermal decomposition of high melting polymers and consequently requires higher values of E_a. Marshal and Todd [18] reported the value of E_a for viscous flow in the case of thermal degradation of poly(ethylene-terephthalate), and it is about 40 kcal/mol. On the other hand, Patterson and Sheldon [19] observed high values (77 and 88 kcal/mol) for dyeing with disperse dyes. So, if production of the amorphous region participates in the rate-determining step, the apparent value of E_a should be more than 40 kcal/mol. Higher values of E_a for polymers XVII and XV exhibit the effect of change in length of carbon chain of aliphatic acid chlorides.

These results suggest that by selecting the proper structural combinations, it is possible to obtain polyamides with better solubility and higher thermal stability.

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