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SYNTHESIS AND CHARACTERIZATION OF POLY BENZOYLPROPIONAMIDES

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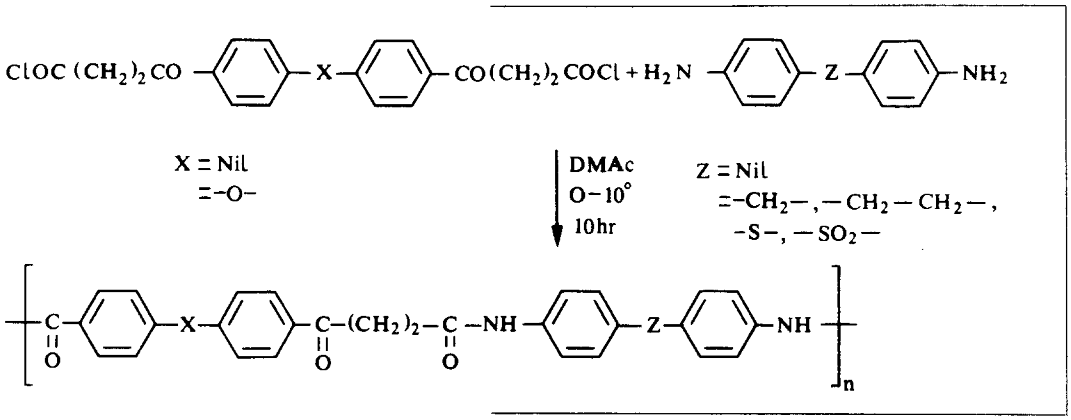
Abstract—Linear polyamides having viscosities in the range of 0.12–0.41 dl/g have been prepared from bisbenzoyl propionic acids and aromatic diamines by low temperature solution polycondensation in 80–85% yield. Their solubility characteristics were studied in various solvents e.g. DMF, DMAC, HMPT, H_2SO_4. These polyamides are amorphous in nature; their densities range from 1.2 to 1.8 g/cm^3. Their thermal properties were examined by TGA and DTA. The two stage decomposition phenomenon observed in TGA is in agreement with the DTA results. The integral procedural decomposition temperatures were calculated and found to exceed 250 in almost all cases.

INTRODUCTION

Aromatic polyamides having reasonable thermal stability and good solubility are of current interest. An understanding of the relationship between structure and physicochemical properties of these polyamides would be helpful in making thermally resistant, tractable polymers[1, 2]. For this reason, polyamides have been prepared by condensing bisbenzoyl propionylchloride and oxybisbenzoyl propionyl chloride with five different diamines and their properties studied. The general method of preparation can be represented thus:



Since the mode of preparation is well documented[3], the present study mainly deals with the effect of structural changes on the properties of these polyamides.

EXPERIMENTAL

Materials

The starting diamines were prepared, according to the method of Akin *et al.*[4]. Bisbenzoyl propionic acid (BBPA) and oxybisbenzoyl propionic acid (OBPA) were prepared by published methods[5].

Measurements

i.r. Spectra were obtained on P.E. 257 spectrometer using KBr pellets. X-ray diffractograms were taken with Philips P.W. 1140 instruments using CuK$_\alpha$ radiation. Thermogravimetric analysis were performed in a Stanton thermoblance with a heating rate of 6 /min in air. Differential thermal analyses were done on Fisher model 260 F under air with a heating rate of 25 /min.

Polymerisation

The diacidchloride (0.01 mol) was added to the diamine (0.01 mol) in DMAc at 0–10 and stirred for 10 hr. The polyamide obtained by pouring the reaction mixture into water was filtered off, washed with methanol and dried under vacuum. Yield 85%.

i.r. = (NH—) 3350 cm^{-1}, (C=O) 1760 cm^{-1}, 1670 cm^{-1}.

RESULTS AND DISCUSSION

These benzoyl propionamides have characteristic i.r. absorption at 3350 cm^{-1} (—NH—), 1760 cm^{-1} (keto carbonyl) and 1670 cm^{-1} (amide carbonyl) Fig. 1. The value 1760 cm^{-1} for a keto carbonyl is slightly high, but it has been confirmed to be that of the keto group by chemical means. The keto acid was reduced with hydrazine hydrate and KOH and the bisphenyl butyric acid so obtained was condensed with a dihydrazide to give a polyhydrazide. This newly obtained polyhydrazide does not have a 1760 cm^{-1} band showing that the 1760 cm^{-1} band was mainly due to the keto group.

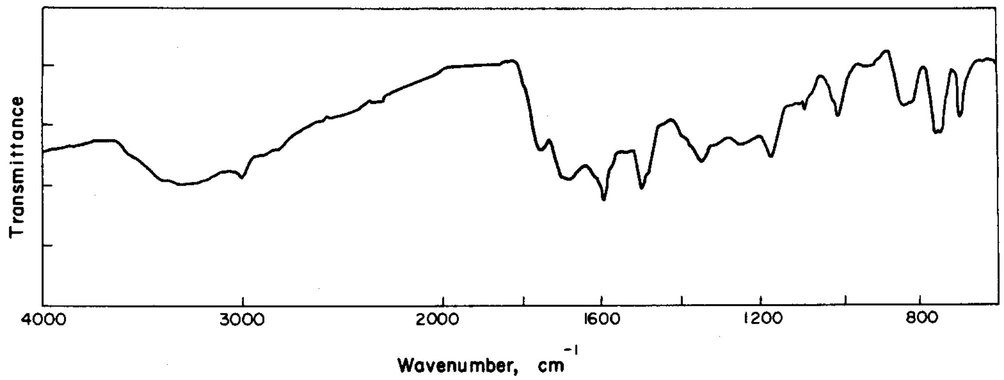


Fig. 1. i.r. Spectrum of a polybenzoyl propionamide.

Table 1. Physical properties of the polyamides

	Monomers		Solubilities in						Density	Viscosity
Polymers	Acid	Diamines	DMF	DMSO	DMAc	HMPT	m-cresol	H_2SO_4	(g/cm^3)	(dl/g)
I	BBPA	Bis(4-aminophenyl)methane	+ +	+ +	+ +	+ +	+ +	+ +	1.54	0.21
II	BBPA	Bis(4-aminophenyl)ethane	+ +	+ +	+ +	+ +	+ +	+ +	1.26	0.13
III	BBPA	Benzidine	+ +	+ +	+ +	+ +	+ +	+ +	1.39	0.23
IV	BBPA	Bis(4-aminophenyl)sulfide	+ +	+ +	+ +	+ +	+ +	+ +	1.58	0.24
V	BBPA	Bis(4-aminophenyl)sulfone	+ +	+ +	+ +	+ +	+ +	+ +	1.46	0.41
VI	OBPA	Bis(4-aminophenyl)methane	+ +	+ +	+ +	+ +	+ +	+ +	1.48	0.16
VII	OBPA	Bis(4-aminophenyl)ethane	+	+	+	+	+	+	1.54	—
VIII	OBPA	Benzidine	+	+	+	+	+	+	1.40	—
IX	OBPA	Bis(4-aminophenyl)sulfide	+	+	+	+	+	+	1.70	—
X	OBPA	Bis(4-aminophenyl)sulfone	+	+	+	+	+	+	1.73	—

+ +—Soluble; +—Sparingly soluble.

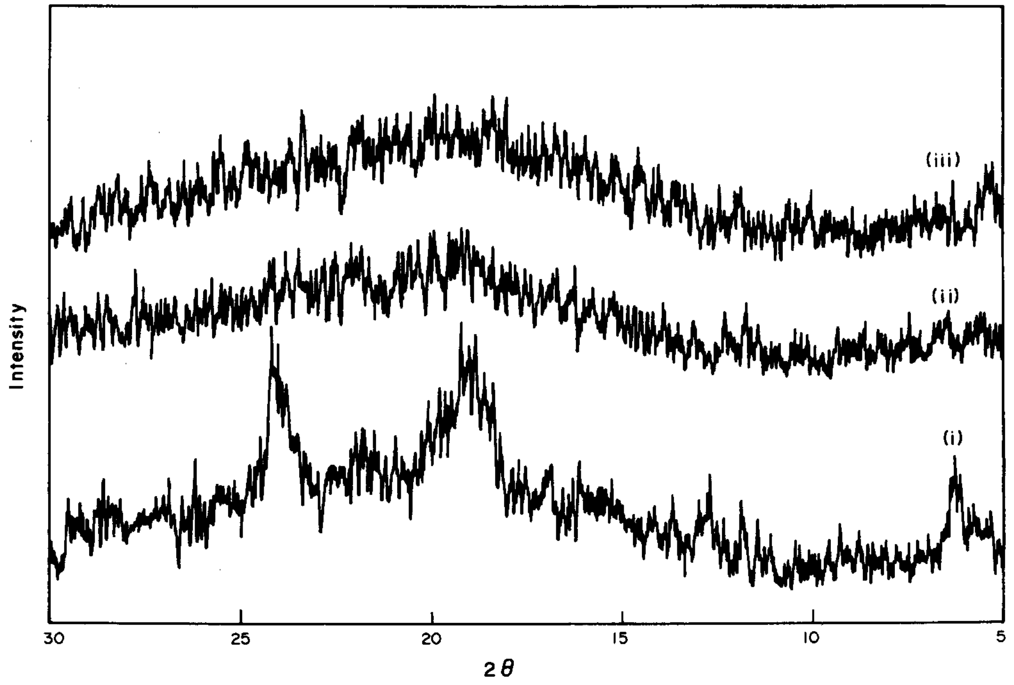


Fig. 2. X-ray diffractograms of polymers. (i) BBPA-benzidine; (ii) OBPA-benzidine; (iii) BBPA-bis(4-amino phenyl)ethane.

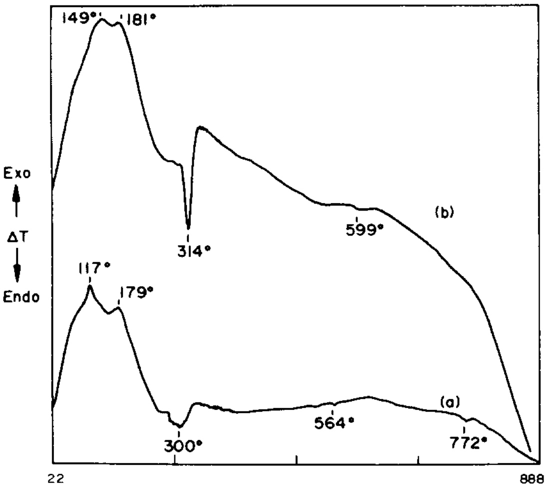


Fig. 3. Differential thermograms of the polymers. (a) OBPA–benzidine; (b) BBPA–benzidine.

Solubilities of these polyamides depend mainly on the monomeric acids from which they were prepared. Polymers derived from BBPA are freely soluble in solvents like DMF, DMAc, HMPT etc. (Table 1) whereas some of the polyamides obtained from OBPA are not freely soluble in these amide solvents. Viscosoties of the soluble polymers were determined in DMF containing 4% $LiNO_3$ (see Table 1).

Densities were determined using hexane as non-solvent; they range from 1.2 to 1.8 g/cm^3 (Table 1). X-ray diffractograms of all these polyamides indicate amorphous nature except for that derived from BBPA and benzidine. The partially crystalline nature of the latter polymer can be attributed to the realatively rigid structural arrangement of the polymer chain. Presence of any other group in the acid moiety or in the diamine part reduces the crystallinity considerably. For example the presence of increased number of CH_2 group or ether linkages induces flexibility and thereby decreases crystallinity (see Fig. 2).

Table 2. Thermal properties of the polyamides

Sample No.	Polymer	Temperature in °C at weight loss of 10%	20%	30%	40%	50%	100%	IPdt (°C)
1	**I**	220	330	430	470	505	700	322.5
2	**II**	185	275	480	535	555	660	331.4
3	**III**	220	300	400	455	500	640	314.7
4	**IV**	235	310	470	510	530	650	345.3
5	**V**	100	130	280	420	500	685	217.0
6	**VI**	190	250	300	380	435	600	262.8
7	**VII**	190	250	335	435	480	640	273.0
8	**VIII**	150	225	365	420	465	600	275.0
9	**IX**	175	270	340	430	470	625	284.0
10	**X**	190	325	415	485	535	660	295.5

Thermal properties were studied using TGA and DTA. The differential thermograms were taken in air. All cases show a well defined exotherm in the region 130–200° followed by two endotherms (Fig. 3). The exotherm is due to polymer crystallization. This type of crystallization is known to occur on heating due to the rearrangement of the polymer chains in the amorphous region. Such a structural change is difficult to find by X-ray measurements. Hatakeyama and Kanetsuna[6] also observed such a structural change in the vicinity of T_g without change in X-ray pattern.

The first endotherm which follows the exotherm is due to the first stage decomposition (in the 200–350° region). These are well defined whereas the second endotherm in the 500° region is not pronounced, in agreement with the TGA results. In TGA also a two stage decomposition is observed, but the second stage decomposition is not very clear for some of the polymers.

The general pattern is a rapid weight loss in the initial stage followed by a gradual decomposition up to 500°. Afterwards again the degradation is fast and the total weight decomposes before 700° (Fig. 4). The temperature at which there is a weight loss of 10% of the original weight of the polymers was selected as measure of the thermal stability. The thermal properties are summarized in Table 2. It is evident from the

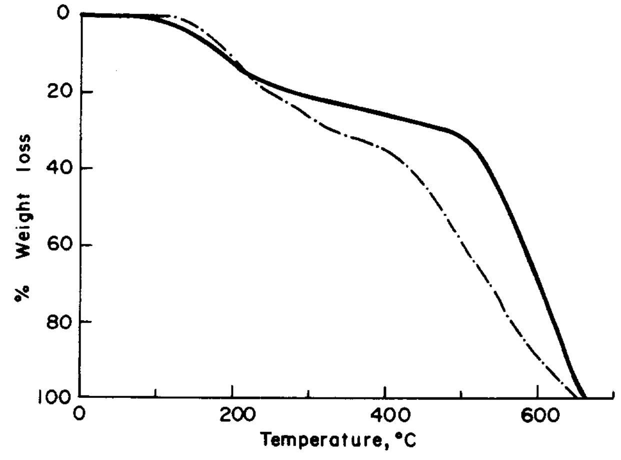


Fig. 4. Thermograms of BBPA and OBPA polymers. —— BBPA–bis(4-aminophenyl ethane); --- OBPA–bis(4-aminophenyl ethane).

initial weight weight loss, total degradation and also from the percentage of decomposition that the OBPA polymers are comparatively less stable than the BBPA polymers. This difference is due to the flexibility induced in the polymer chain by the ether linkage. The relative stabilities of these polymers can be clearly understood from their integral procedural decomposition temperature values (Table 2).

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