Eur. Polym. J. Vol. 28, No. 4, pp. 363–366, 1992
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0014-3057/92 $5.00 + 0.00

POLYAMIDES CONTAINING ARYLENE, ETHER AND KETONE LINKAGES

V. L. Rao* and P. V. Prabhakaran
Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre,
Thiruvananthapuram 695022, India

(Received 5 May 1991; in revised form 2 September 1991)

Abstract—Several aromatic polyamides were prepared from aromatic dicarboxylic acids with two diamines containing carbonyl and ether connecting groups between the aromatic rings; the phosphorylation route was used. The synthesis of these diamines involves a nucleophilic displacement reaction in dipolar aprotic solvent with the alkali metal salt of *p*-aminophenol/*m*-aminophenol and an activated aromatic difluoro compound. The polymers were characterized by solution viscosity, elemental analysis, thermogravimetric analysis, differential scanning calorimetry and X-ray diffraction. The polymers, obtained in 85–95% yield, possessed inherent viscosities in the range 0.32–0.68 dl/g and glass transition temperatures between 114 and 170°C. The effects of the structure on properties such as solubility, molecular weight, T_g, crystallinity and thermal behaviour were also studied.

INTRODUCTION

Wholly aromatic polyamides possess excellent mechanical properties and thermal stability; however, they are difficult to process because of limited solubility and high glass transition (T_g) or melt temperatures because of chain stiffness and intermolecular hydrogen-bonding between amide groups [1–3]. The processing of these polymers by thermoplastic methods has been greatly hindered because they tend to degrade before or at the softening or melting temperatures [4]. Various attempts have been made to reduce T_g or melting temperature of aromatic polyamides to make them processable, either by introducing flexible groups between phenyl rings [5, 9–11] or by methyl substituted phenylene linkage [6, 14, 15] or by *N*-alkyl substitution [7, 8]. These polymers have better solubility in organic solvents and some of them have been proposed as candidates for thermotropic liquid crystalline polymers [12].

Polymers containing ether and ketone groups connected by aromatic rings will have enhanced chain flexibility and lower T_g. One such polymer is poly(ether ether ketone) (PEEK, Imperial Chemical Industries), which is melt processable.

It appears that polymers containing ether, carbonyl and amide groups connected by aromatic rings within the polymeric backbone have not been studied in detail. These polymers are expected to have the advantages of both PEEK and polyaramid in properties such as ease of processability, with better thermo-mechanical properties and good hydrolytic and thermo-oxidative stability. With this objective, synthesis, characterization and thermal behaviour of various polyaramides, derived from aromatic dicarboxylic acids with ether ketone diamines, were examined.

EXPERIMENTAL PROCEDURES

Materials

High purity 4,4′-difluorobenzophenone (DFBP) (Aldrich) was used as received. 4-Aminophenol (Aldrich) was crystallized from ethanol and then sublimed in vacuum (0.3 mm) at a temperature ranging from 105 to 110°C. 3-Aminophenol (Aldrich) was crystallized from toluene (m.p. 122–123°C). Anhydrous potassium carbonate (BDH, India) was dried in vacuum at 100°C. *N*-*N*′-dimethylacetamide (DMAc) was distilled in vacuum over calcium hydride and stored over 4 Å molecular sieves. Terephthalic acid (TPA) (Fluka), isophthalic acid (IPA) (Koch-Light) and 2,5-pyridine dicarboxylic acid (PDA) (U.S. Materials Company) were of high purity and used without further purification. Triphenyl phosphite (TPP) (Fluka) was fractionally distilled under reduced pressure. High purity anhydrous LiCl and $CaCl_2$ were dried at 180 to 200°C for 12 hr. *N*-methylpyrrolidone (NMP) was distilled in vacuum over phosphorous pentoxide and stored over 4 Å molecular sieves. Pyridine was refluxed over NaOH pellets, distilled and stored over 4 Å molecular sieves.

Monomer synthesis

4,4-Bis (4-aminophenoxy) benzophenone (B_4ABP) and 4,4-bis (3-aminophenoxy)benzophenone (B_3ABP) monomers were synthesized by nucleophilic displacement reaction of DFBP with 4-aminophenol or 3-aminophenol in the presence of K_2CO_3 using DMAc as solvent by the procedure described earlier [13]. B_4ABP m.p.: 150–152°C; B_3ABP m.p.: 138–140°C. Elemental analyses (CHN) for both B_4ABP and B_3ABP monomers are in close agreement with calculated values.

Polymer synthesis

In a typical experiment, 2.5 mmol of the acid (TPA, IPA and PDA) and 2.5 mmol (0.9915 g) of the amine were added to a solution of 40 ml NMP with 20 ml pyridine already containing 2.0 and 0.75 g of dissolved $CaCl_2$ and LiCl respectively. To this system was added 5 mmol (1.55 g) of triphenylphosphite. The reaction mixture was stirred at 100° for 2 hr under N_2. The polymer formed was precipitated in water, stirred well and washed with acetone, and then vacuum dried at 80°C for 8–10 hr. The yields, elemental analyses and inherent viscosities are given in Table 1.

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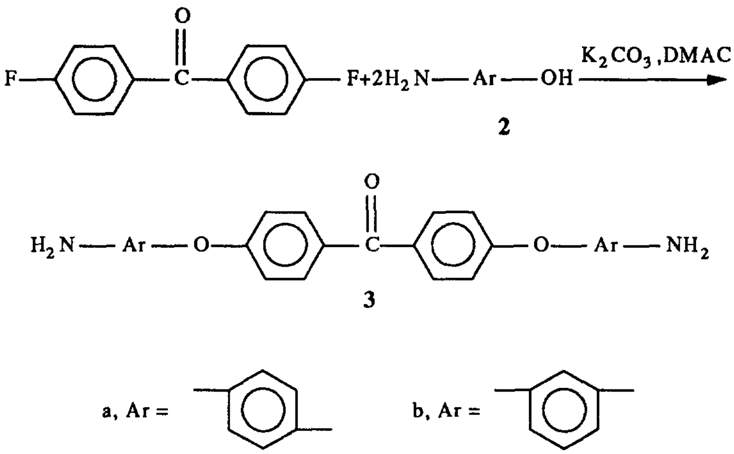
*To whom all correspondence should be addressed.

Characterization

Infrared spectra of the polymers were recorded with KBr pellets using a Perkin–Elmer 283 spectrophotometer over the range of 200–4000 cm^{-1}. Inherent viscosities were obtained for 0.4% solutions in NMP (except for polymer **5a, c** where conc. H_2SO_4 was used) at 30°C using an Ubbelohde suspension level viscometer. Wide angle X-ray scattering data were obtained on pellet samples of the polymer using a Philips X-ray unit PW 1710 diffraction counting unit, and PW 1729 X-ray generator with Ni filtered CoKα radiation at 30 kV and 20 mA over the 2θ angular range of 10 to 40°C Thermal analysis of the polymer was carried out under N_2 using Dupont thermal analyser system 2000 in combination with Dupont 951 thermogravimetric analyser at a heating rate of 10°C/min. T_gs were determined by using Mettler thermal analyser 3000 coupled with DSC 20 at a heating rate of 10°C/min. Elemental analyses were obtained by a Perkin–Elmer 2400 CHN analyser.

RESULTS AND DISCUSSION

Ether ketone diamines were prepared by the aromatic nucleophilic displacement of fluorine from an activated substrate (DFBP) by aminophenol in the presence of potassium carbonate in DMAc medium according to the scheme.



Polyamides (**5**) were prepared by direct polycondensation of the aromatic dicarboxylic acid (**4**) with ether ketone diamines (**3**) via the phosphorylation route by the procedure described by Higashi *et al.* [18].

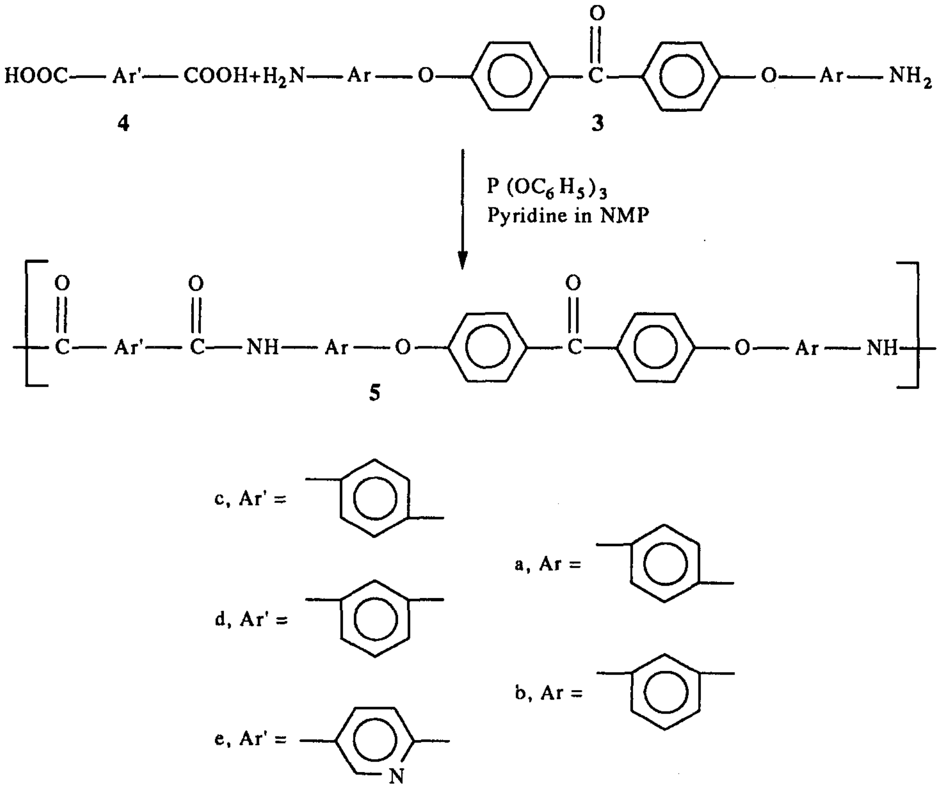


Table 1. Some properties of polyamides

Polyamide	η_{inh}[a] (dl g^{-1})	Yield (%)	Elemental analyses[b]		
			C (%)	H (%)	N (%)
5a, c	0.68[c]	95	74.35 (75.28)	4.10 (4.18)	5.18 (5.32)
5a, d	0.48	90	74.65 (75.28)	4.07 (4.18)	5.12 (5.32)
5a, e	0.62	92	71.96 (72.86)	3.92 (3.98)	7.85 (7.96)
5b, c	0.37	90	74.82 (75.28)	4.12 (4.18)	5.23 (5.32)
5b, d	0.32	85	74.45 (75.28)	4.08 (4.18)	5.21 (5.32)
5b, e	0.39	87	71.85 (72.86)	3.90 (3.98)	7.87 (7.96)

[a] Inherent viscosity determined at 30°C for 0.4% solution in NMP.
[b] Values in parentheses are calculated values.
[c] Inherent viscosity determined at 30°C for 0.4% solution in conc. H_2SO_4.

The properties of the polyamides are summarized in Table 1. The polymers were obtained in high yields. The carbon, hydrogen and nitrogen contents are in close agreement with the calculated values.

Infrared spectra

Infrared spectra of all the compounds show the N—H stretching at 3300 cm^{-1}. The presence of absorption bands at 1650 cm^{-1} due to amide I C=O, at 1600 cm^{-1} due to amide II N—H bend and at 1410 cm^{-1} due to amide III C—N stretch confirms the structure of the polyaramides.

Solubility

All the polymers are soluble in conc. H_2SO_4 and all, except **5a, c**, are soluble in dipolar aprotic solvents such as NMP, DMSO etc. The insolubility of polymer **5a, c** is due to the high order of crystallinity as indicated by X-ray diffraction (Fig. 1). The polymers were insoluble in acetone, chloroform, methanol, carbon tetrachloride and tetrahydrofuran. These results clearly show that ether and carbonyl groups between the aromatic moieties of the diamines, and *meta* structures of diamines and dicarboxylic acids increase the solubility and lead to better processability at the cost of little thermal stability.

Inherent viscosity

Inherent viscosities are given Table 1. The values for the *para* linked polyamides are higher than those for the *meta* linked polyamides as might be expected from structural considerations. Both poly(terephthalamides) and poly(isophthalamides) prepared from meta amine (**3b**) have the lowest inherent viscosities; this effect may be due to B_3ABP being less reactive than B_4ABP towards dicarboxylic acid.

Glass transition temperature

Values of T_g were determined by DSC (see Table 2). Samples were heated to 200°C for 20 min at the heating rate of 10°C/min in static air then cooled to room temperature and subsequently rerun to obtain T_g. The results show that T_gs for the *para* linked

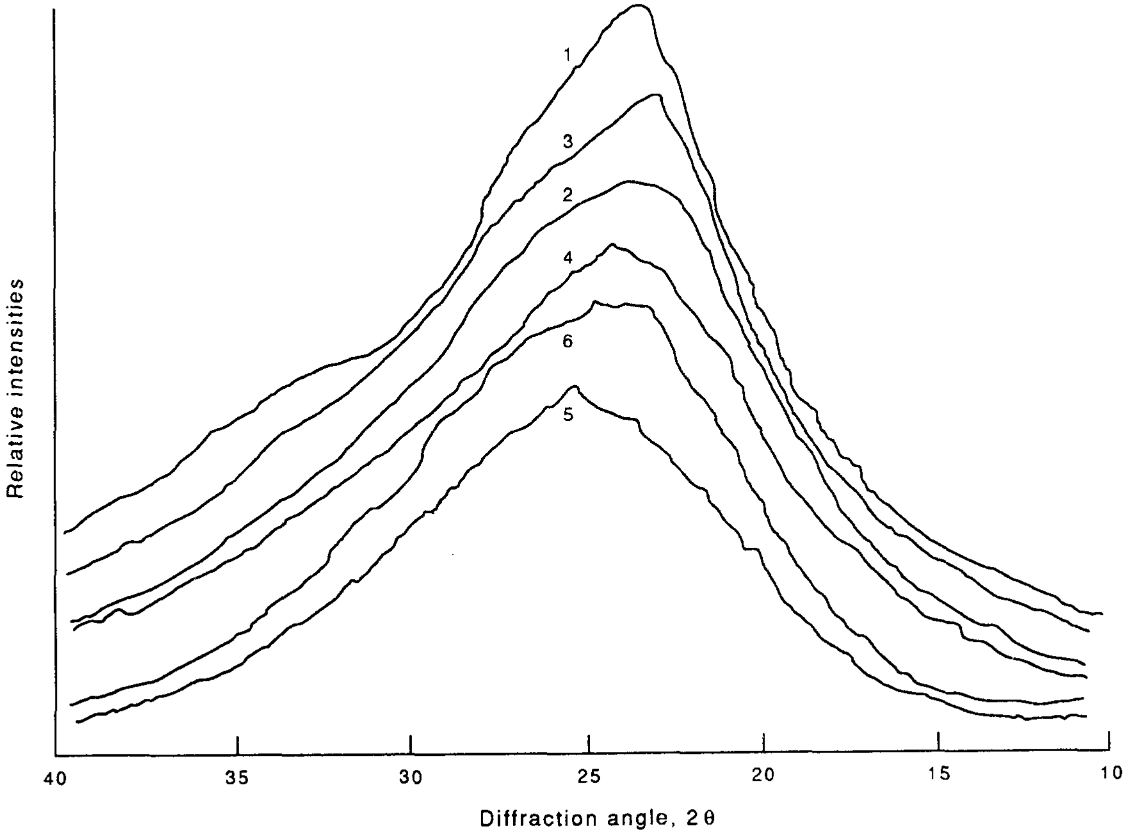


Fig. 1. X-ray diffraction patterns of polyamides. 1, Polymer **5a, c**; 2, polymer **5a, d**; 3, polymer **5a, e**; 4, polymer **5b, c**; 5, polymer **5b, d**; 6, polymer **5b, e**.

Table 2. Thermal properties of polyamides

Polyamide	IDT (°C)[a]	% Char residue 500°C	700°C	900°C	D_{max} (°C)[b]	IPDT (°C)[c]	T_g (°C)[d]
5a, c	420	84	64	50	580	749	160
5a, d	390	84	66	52	575	759	145
5a, e	410	82	61	49	570	730	170
5b, c	380	80	65	55	542	754	126
5b, d	360	78	67	57	540	757	114
5b, e	350	73	62	53	550	735	154

[a] IDT = Initial decomposition temperature.
[b] D_{max} = Maximum decomposition temperature.
[c] IPDT = Integral procedural decomposition temperature.
[d] T_g = Glass transition temperature.

polyamides are slightly higher than those for the *meta* linked, probably because of the closer packing of the chains in the former, as confirmed from X-ray diffraction (Fig. 1).

X-ray diffraction

Wide angle X-ray diffractions were obtained on pellet samples and diffractograms are shown in Fig. 1. Polyamides obtained from B_4ABP monomer (**5a, c** and **5a, e**) exhibit higher crystallinity than those from B_3ABP monomer (**5b, c** and **5b, e**) confirming that the polymeric chains in the *para–para* system are more highly ordered.

Thermogravimetric analyses (TGA)

Thermal degradation of the polyamides was studied by TGA in N_2 (Table 2 and Fig. 2). From the TG trace, initial decomposition temperature (IDT), maximum decomposition temperature (D_{max}) integral procedural decomposition temperature (IPDT) and percentage char residue at 500, 700 and 900°C were determined. All polymers were stable up to 350°C. Maximum decomposition temperature was observed between 540 and 580°C. All polymers gave a char residue of about 50–55% at 900°C. They also showed the lower percent weight loss at higher temperatures. Similar results were obtained by us [13] and others [16, 17].

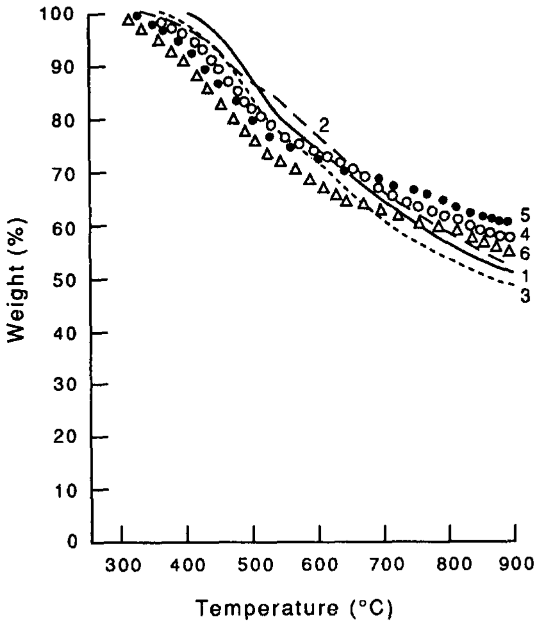


Fig. 2. Thermogravimetric analyses of polyamides. 1, (——) polymer **5a, c**; 2, (– – –) polymer **5a, d**; 3, (- - - -) polymer **5a, e**; 4, (○) polymer **5b, c**; 5, (●) polymer **5b, d**; 6, (△) polymer **5b, e**.

Acknowledgements—The authors thank Dr V. N. Krishnamoorthy (Deputy Director, Propellants, Polymers and Chemicals); Dr K. N. Ninan (Group Head, Propellants and Special Chemicals Group); Dr R. Ramaswamy (Head, Polymers and Special Chemicals Division); Dr M. M. Singh Bisht and Dr S. Venkatachalam for constant encouragement; Dr K. Krishnan; Mr G. Viswanathan Achary for recording TG curves; and Mr N. S. Babu (Metallography Section) for recording X-ray spectra.

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