

NOTES

Synthesis and Properties of Polyamides Derived from 2,2-Bis[4-[2-(4-aminophenoxy)ethoxy]phenyl]propane by Direct Polycondensation

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Wholly aromatic polyamides (aramids) are high performance materials with excellent thermal stability and mechanical properties.¹ However, aramids have a fabrication problem due to limited solubility and high melt or softening temperature. Therefore, a great deal of effort has made for improving the processability of polyamides.

The incorporation of bulky substituents and/or flexible linkages, such as arylene ether (–O–), methylene (–CH₂–), sulfone (–SO₂–), isopropylidene [–C(CH₃)₂–], siloxane (–Si–O–), and perfluoroisopropylidene [–C(CF₃)₂–] into the polymer backbone increases the overall chain flexibility.^{2–7}

This polymer structural modification is usually done by the insertion of flexible segments into the diamine monomer. In previous work⁸ the diamine, 2,2-bis[4-[2-(4-aminophenoxy)ethoxy]phenyl]propane (BAEPP), containing softening oxyethylene and isopropylidene linkages was prepared by reaction of [2,2-bis(4-β-hydroxyethoxy)phenyl]propane with *p*-chloronitrobenzene, followed by reduction. Polyimides derived from such flexible diamine exhibit good solubility and moderate glass transition temperatures. One showed melt-moldability. Obviously, the introduction of flexible oxyethylene and isopropylidene linkages into the polymer backbone leads to significant improvement in processability. Therefore, beneficial effects on polyamide processability such as enhanced solubility and thermoplasticity are expected.

In the present study, BAEPP was used for the preparation of polyamides by direct polycondensation with various aromatic dicarboxylic acids. Solubility, crystallinity, mechanical properties and thermal properties of the polyamides were investigated.

EXPERIMENTAL

Polymerization

A mixture of 2.0 mmol of diamine BAEPP, 2.0 mmol of diacid, 0.64 g of calcium chloride, 1.3 mL of triphenyl phosphite, 0.8 mL of pyridine, and 6 mL of NMP was heated with stirring at 100°C for 3 h. After cooling, the reaction mixture was poured into methanol (500 mL) with constant stirring, to produce a fibrous precipitate

that was washed thoroughly with methanol and hot water, collected on a filter and dried at 100°C under vacuum.

RESULTS AND DISCUSSION

Preparation of Polyamides

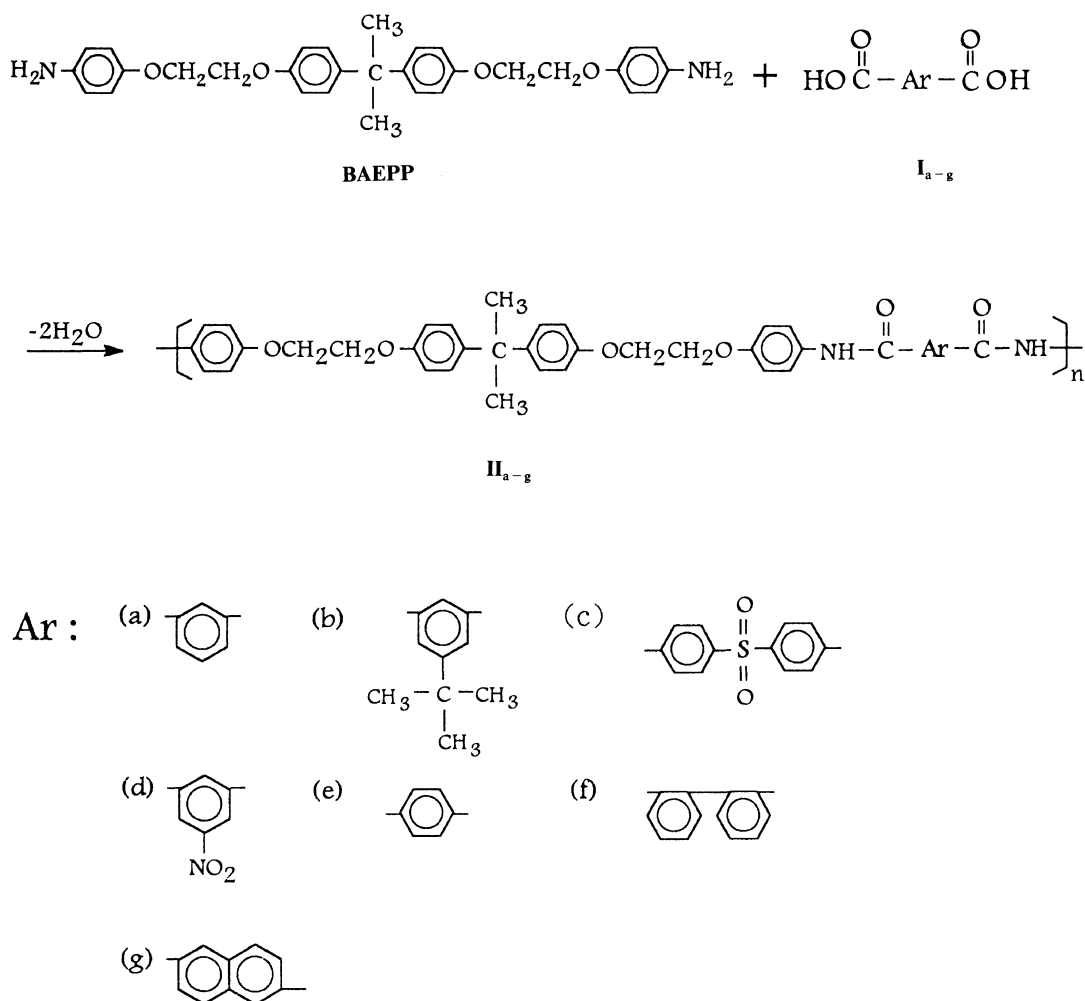
The direct polycondensation of diamine with aromatic dicarboxylic acids using triphenyl phosphite and pyridine as condensing agents is a convenient method for the preparation of polyamides on a laboratory scale.⁹ This method was utilized here to prepare flexible linkages-containing polyamides **II**_{a–g} from diamine BAEPP and various aromatic diacids **I**_{a–g} (Scheme 1). Table I summarizes the results of the polymerization. All reactions proceeded readily in homogeneous solutions to give quantitative yields of polyamides with inherent viscosities between 0.41 and 1.05 dL g^{–1}.

The polymers were identified by elemental analysis, and IR and NMR spectra. Elemental analysis of the polyamides showed carbon values smaller than those calculated for proposed structures. These discrepancies are attributed to hygroscopic characteristics of the amide group. The amount of absorbed water of these polyamides was in the range 1.49–3.35%. Corrected values agreed satisfactorily with those calculated after correction. These polyamides showed characteristic amide absorptions at 3242–3438 cm^{–1} (N–H) and 1637–1685 cm^{–1} (C=O) in IR spectra, supporting the formation of the polyamides. It is of interest that the IR data of the polyamides showed N–H stretching bands of **II**_e and **II**_g compounds with lower wave numbers than other polyamides, thus indicating stronger hydrogens bond in **II**_e and **II**_g than others.¹⁰ Figure 1 shows the ¹H and ¹³C NMR spectra of polyamide **II**_b. Each carbon and proton of **II**_b were assigned and the results further provided clear evidence that the polyamides prepared in this study are consistent with proposed structures.

Properties of Polyamides

Crystallinity of the polymers was examined by wide-angle X-ray diffraction diagrams. Polyamides **II**_e and **II**_g derived from rigid diacids showed crystalline patterns with reflection peaks around 2θ = 22°, corresponding to poor solubility. All other polymers were amorphous and afforded flexible and tough polyamide films.

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Scheme 1.

Table I. Preparation of polyamides from diamine BAEPP and various diacids^a

Diacid	Polymer			
	Code	Yield/ %	$\eta_{inh}^b/$ dL g^{-1}	Aspect
I_a	II_a	99	1.02	String
I_b	II_b	98	1.05	String
I_c	II_c	97	0.63	String
I_d	II_d	96	0.77	String
I_e	II_e	99	0.41 ^c	Powder
I_f	II_f	97	0.50	Powder
I_g	II_g	99	0.78 ^c	String

^a Polymerization was carried out using 2 mmol of diamine BAEPP and 2 mmol of diacids with 1.3 ml of triphenyl phosphite and 0.8 ml pyridine in 8 ml of NMP containing 0.64 g of calcium chloride at 100°C for 3 hours. ^b Measured in DMAc at a concentration of 0.5 g dL⁻¹ at 30°C. ^c Measured in DMAc-5% LiCl at a concentration of 0.5 g dL⁻¹ at 30°C.

The solubility of the polyamides was tested qualitatively in various solvents. All polyamides, except **II_e** and **II_g**, were soluble in polar solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc), *N*-methylpyrrolidone (NMP), dimethyl sulfoxide (DMSO) at room temperature or on heating. Polyamides **II_e** possessing a *p*-phenylene unit and **II_g** with a naphthalene group

were almost insoluble in organic solvents but dissolved in DMAc containing 5 wt% LiCl. The poor solubility of **II_e** and **II_g** may be accounted for by the more rigid diacid moieties and crystallinity. Interestingly, polyamide **II_f** showed excellent solubility at room temperature even in common organic solvents like tetrahydrofuran (THF). This is reasonable because the less symmetric 1,2-unit linked through diacid hinders the close packing of polymer chains, leading to decrease of crystallinity and enhanced solubility.

Transparent, tough, and flexible films of the polyamides, except **II_e** and **II_g**, were obtained by casting from DMAc solutions. The tensile properties of the polyamide films are summarized in Table II. The films had tensile strength of 54–89 MPa, elongation at a break of 6–13%, and initial modulus of 1.68–2.32 GPa. The molar mass of the polyamides influenced markedly tensile values, *i.e.*, the polyamides having higher inherent viscosities afforded films having better mechanical properties.

The thermal behavior of the polyamides was evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) and is summarized in Table III. The glass transition temperatures (T_g 's) of the polyamides, except **II_g**, could be determined from second heating traces of DSC after quenching the samples from elevated temperatures. T_g 's of the polyamides were in the

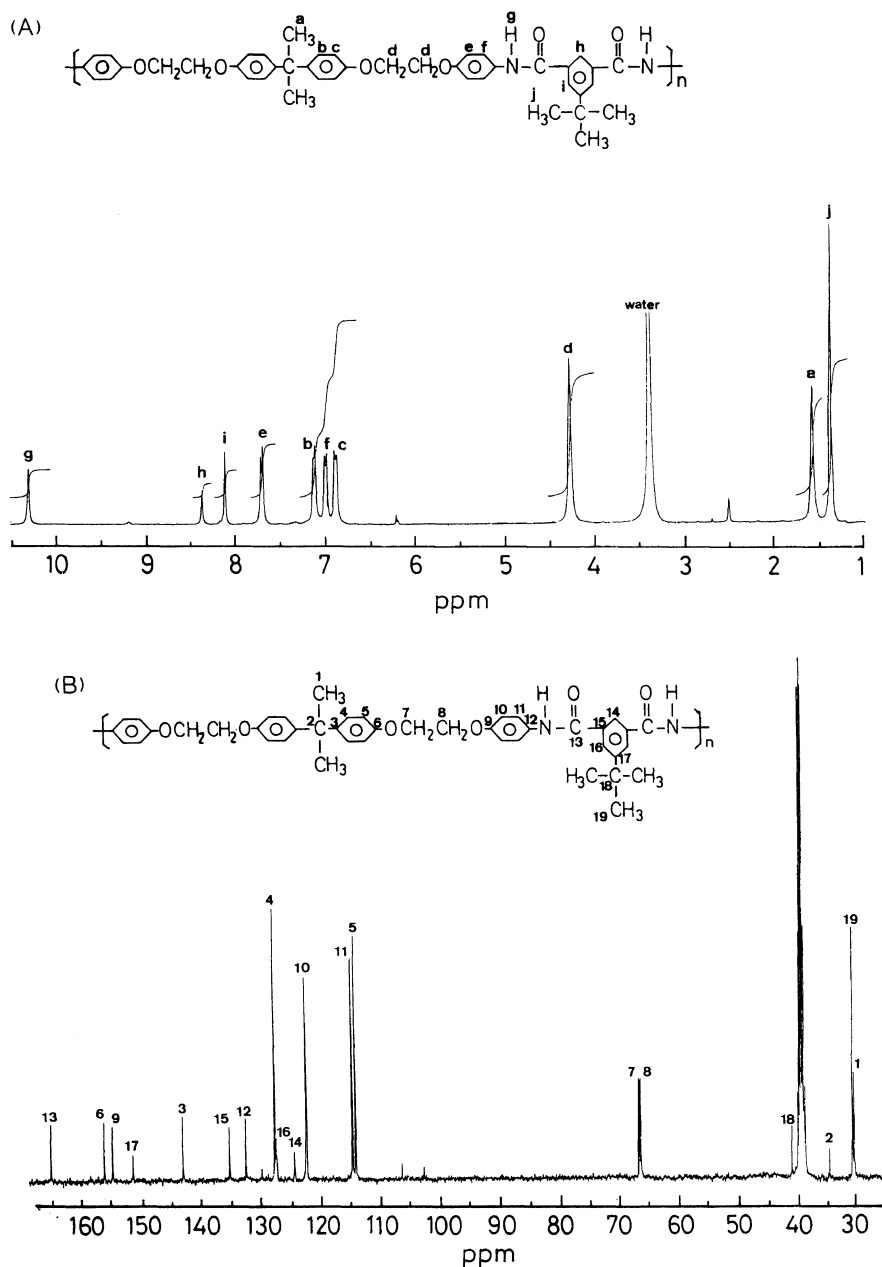


Figure 1. NMR spectra of polymer II_b . Use $\text{DMSO}-d_6$ as solvent in 10% solution: (A) ^1H NMR; (B) ^{13}C NMR.

Table II. Mechanical properties of BAEPP-based polyamides

Polymer	Tensile strength	Elongation at break	Initial modulus
	MPa	%	GPa
II_a	89	8	2.12
II_b	86	7	2.32
II_c	67	13	1.68
II_d	77	12	1.78
II_f	54	6	1.79

Table III. Thermal properties of BAEPP-based polyamides

Polymer	DSC		TGA		
	T_g^a	T_m^b	$T_{10}^c/^\circ\text{C}$		R_{800}^d
	$^\circ\text{C}$	$^\circ\text{C}$	In N_2	In air	%
II_a	239	—	461	436	32.9
II_b	279	—	443	423	32.9
II_c	264	—	459	432	36.3
II_d	249	—	448	402	41.0
II_e	310	340 (336) ^a	464	436	41.2
II_f	271	—	455	430	41.0
II_g	—	333, 347 (313, 335) ^a	466	460	46.1

^a From second heating traces of DSC measurements conducted at a heating rate of $20^\circ\text{C min}^{-1}$. ^b From the first heating traces of DSC measurements conducted at a heating rate of $20^\circ\text{C min}^{-1}$. ^c Temperature at 10% mass loss recorded on TG at a heating rate of $20^\circ\text{C min}^{-1}$. ^d Residual mass % at 800°C in nitrogen.

range of $239\text{--}310^\circ\text{C}$. As expected, polyamide derived from isophthalic acid (I_a) possessing nonlinear meta-link had the lowest T_g . 5-*t*-Butylisophthalamide (polyamide II_b) and 5-nitroisophthalamide (polyamide II_d) groups in place of isophthalamide (polyamide II_a) increased T_g of the resulting polymer. Polyamides with crystallinity

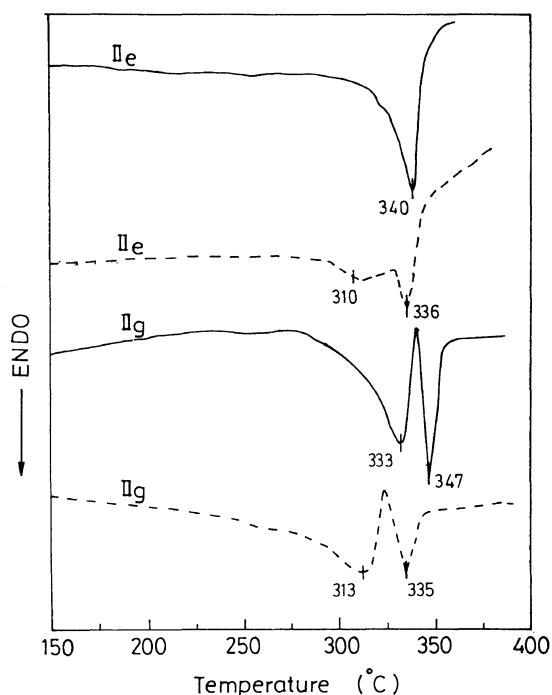


Figure 2. DSC curves for polyamide II_e and II_g at a heating rate of $20^\circ\text{C min}^{-1}$: (—) first heating; (---) second heating.

such as II_e and II_g showed melting endotherms in DSC traces as shown in Figure 2. Polyamide II_e showed one endotherm at 340°C during the first scan while II_g , two discrete endotherms at 333 and 347°C . After being quenched in liquid nitrogen, the endotherm of II_e was minimized and a glass transition signal appeared at 310°C in the second run. Polyamide II_f crystallized so quickly that after quenching, two endotherms were measured at 313 and 335°C on the second heating.

The thermal stability of the polyamides was characterized by TGA at a heating rate of $20^\circ\text{C min}^{-1}$. All polyamides indicated no mass loss below 350°C in air or nitrogen atmosphere. Decomposition temperatures of 10% mass loss were in the range of 443 – 466°C in nitrogen and 402 – 460°C in air. Char yields of the polyamides at 800°C in nitrogen atmosphere were above 32.9%. II_g containing a naphthalene group had the highest 10% mass loss temperature and highest char yield. Polyamides II_b and II_d having *tert*-butyl and nitro substituents had lower 10% mass loss temperature than the other polyamides, and showed less thermal stability.

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