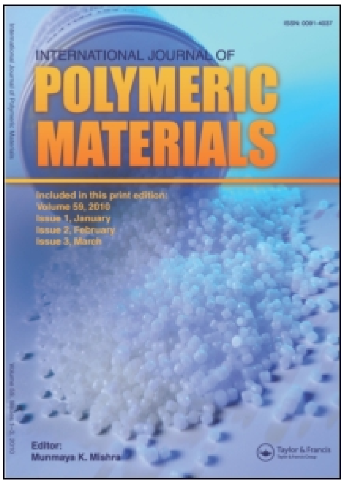

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Polyamides Containing Oxyethylene Linkages: Synthesis and Characterization

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Polyamides Containing Oxyethylene Linkages: Synthesis and Characterization

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New polyamides containing oxyethylene linkages were prepared. The two non-linear diamines containing oxyethylene linkages namely, 1,2-bis(3-aminophenoxy) ethane and bis[2-(3-aminophenoxy)ethyl] ether, were each polymerized by a low temperature solution polycondensation with isophthaloyl chloride and terephthaloyl chloride. The polyamides obtained were characterized by solubility tests, viscosity measurements, IR spectroscopy and by X-ray diffraction studies. The thermal behaviour of the polyamides was studied by thermogravimetric analysis in air.

1. INTRODUCTION

Aromatic polyamides have been universally accepted as high performance polymers because of their high thermal stability.[1] However, insolubility in common solvents and/or high transition temperatures make these polymers difficult to fabricate. Structurally modified polyamides have been synthesized[2–4] with improved solubility and processing characteristics usually with little or no sacrifice in thermo-oxidative or mechanical properties. It has been generally recognized that the introduction of flexible linkages in aromatic polymer chains lowers the glass transition temperature and im-

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proves solubility and other processing characteristics of the polymers.[5–7]

The objective of the present work was to synthesize oxyethylene containing polyamides by the polymerization of the non-linear diamines containing oxyethylene linkages, namely, 1,2-bis(3-aminophenoxy)ethane (BAE) and bis[2-(3-aminophenoxy)ethyl]ether (BAPEE) with aromatic diacid chlorides, isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) and to study the properties of the resulting polyamides.

2. EXPERIMENTAL

2.1 Materials

m-Nitrophenol was recrystallized from water. 1,2-Dibromoethane and 2-chloroethyl ether were purified by distillation. Ethylene glycol was distilled prior to use. 5% Pd/C was used as received. Isophthaloyl chloride and terephthaloyl chloride were prepared by the conventional procedure and purified by recrystallization from dry *n*-hexane. Dimethylacetamide was dried over phosphorus pentoxide for 24 h and distilled under reduced pressure.

2.2. Preparations

2.2.1. *1,2-Bis(3-nitrophenoxy)ethane* A mixture of potassium *m*-nitrophenoxide (35.4 g, 0.20 mol), 1,2-dibromoethane (18.8 g, 0.10 mol) and ethylene glycol (60 ml) was stirred at 130°C for 3 h. The cooled mixture was poured into ice-cold water (600 ml). The solid product obtained was filtered and purified by recrystallization from ethanol. Yield, 60% m.p. 140–141°C (Lit[8] m.p. 139.5–140.5°C).

2.2.2. *Bis[2-(3-nitrophenoxy)ethyl]ether* It was prepared from potassium *m*-nitrophenoxide and 2-chloroethyl ether as per the procedure described above in 55% yield m.p. 132–133°C (Lit[9] m.p. 130–132°C).

2.2.3. *1,2-Bis(3-aminophenoxy)ethane* 1,2-Bis(3-nitrophenoxy)ethane (15.2 g, 0.05 mol), 25 ml of ethanol and 0.02 g of a 5% Pd/C catalyst were placed in a flask fitted with a reflux condenser. Over a period of 0.5 h, 1.5–3.0 ml of 64% hydrazine hydrate were added. The mixture was then refluxed for 16 h. The hot mixture was filtered, cooled and the solid obtained was recrystallized from ethanol. Yield, 85%, m.p. 136–137°C (Lit[8] m.p. 134–135°C). IR (Nujol): 3400 (NH_2); 3320 (NH_2) cm^{-1}. NMR (DMSO-d_6): $\delta = 4.1$ (s, 4H, —OCH_2CH_2O—); 5.0(bs, 4H, NH_2, Exchanges with D_2O); 6.0–6.4(m, 6H, Aromatic); 6.8(t, 2H, Aromatic). MS [*m/e*: 244 (M^+)]. Elemental Analysis: Calculated for $C_{14}H_{16}N_2O_2$: C, 68.85%; H, 6.56%; N, 11.48%. Found: C, 68.78%; H, 6.51%; N, 11.52%.

2.2.4. *Bis[2-(3-aminophenoxy)ethyl]ether* It was obtained by the reduction of bis[2-(3-nitrophenoxy)ethyl]ether. Yield, 80%, m.p. 104–105°C. IR (Nujol): 3400 (NH_2); 3320 (NH_2) cm^{-1}. NMR (DMSO-d_6): $\delta = 3.6$–4.1 (m, 8H, —OCH_2CH_2O—); 5.0 (bs, 4H, NH_2, Exchanges with D_2O); 5.9–6.3 (m, 6H, Aromatic); 6.8 (t, 2H, Aromatic). MS [*m/e*; 288 (M^+)]. Elemental Analysis: Calculated for $C_{16}H_{20}N_2O_3$: C, 66.67%; H, 6.94%; N, 9.72%. Found: C, 66.56%; H, 6.90%; N, 9.82%.

2.2.5. *Preparation of polyamides* In a 100 ml three necked flask fitted with a nitrogen inlet and thermometer were placed 20 ml of dimethylacetamide containing 5 wt % of lithium chloride. 1,2-Bis(3-aminophenoxy)ethane (1.22 g, 0.005 mol) was added and the solution stirred for a few minutes under nitrogen. The flask was cooled to 0–5°C and isophthaloyl chloride (1.015 g, 0.005 mol) was added all at once. Stirring was continued for about half an hour at this temperature and for 3 h at room temperature. The polymerization mixture was poured into water to precipitate the polymer. The polymer obtained was filtered, washed several times with water and finally with methanol. It was dried under vacuum at 100°C for 8 h.

Similar procedure was followed to prepare other polyamides.

2.3. Measurements

The IR spectra were recorded on a Pye Unicam SP-3 300 spectrophotometer.

The NMR spectra were recorded on a Varian FT-80 instrument.

Mass spectra were run on AEI MS 30 double beam mass spectrometer.

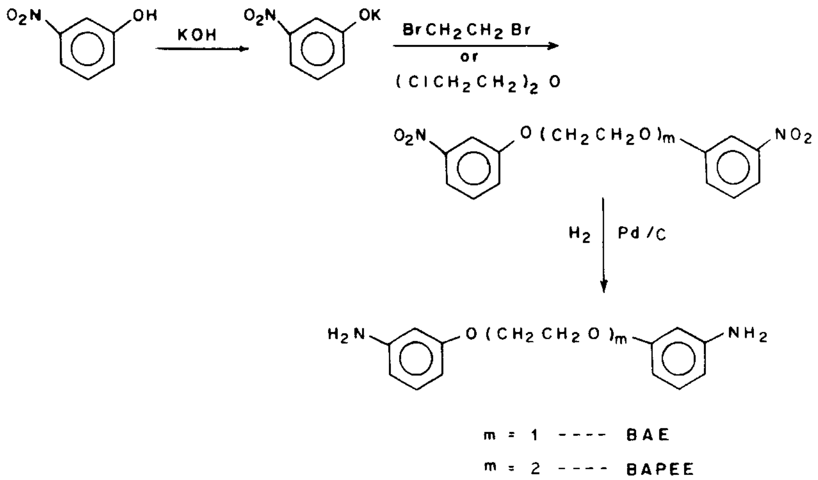
Viscosity measurements were made with 0.5% (w/v) solutions of polymers in concentrated sulphuric acid at 30°C using Ubbelhode suspended level viscometer.

The X-ray diffractograms of polymers were obtained with a Phillips X-ray unit (Phillips generator, PW-1730) and a Nickel filtered CuK$_\alpha$ radiations.

Thermogravimetric analyses were made with a NETZSCH 409 thermal analyzer. The measurements were recorded in air at a heating rate of 10°C/minute.

3. RESULTS AND DISCUSSION

The non-linear diamine monomers containing oxyethylene linkages were prepared by the following route.

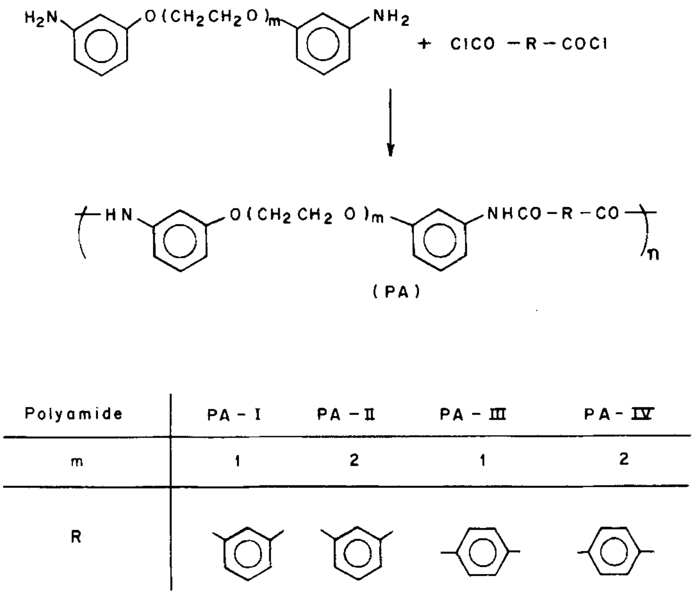


SCHEME I Preparation of diamines.

The reaction of potassium salt of *m*-nitrophenol with 1,2-dibromoethane and 2-chloroethyl ether yielded 1,2-bis(3-nitrophenoxy) ethane and bis[2-(3-nitrophenoxy)ethyl] ether, respectively. Reduction of the dinitro compounds to the desired diamines was accomplished chemically with hydrazine hydrate and a

5% Pd/C catalyst.[5] The diamines were characterized in detail by elemental analysis and by IR, NMR and mass spectra.

Polyamides containing oxyethylene linkages were obtained by the low-temperature solution polycondensation of oxyethylene-containing diamines with IPC and TPC.



SCHEME II Preparation of polyamides.

Dimethylacetamide containing 5 wt% of lithium chloride was used as a reaction medium. The resulting polyamides were isolated as white fibrous or powdery materials in excellents yields with inherent viscosities in the range of 0.40–0.48 dL/g, as summarized in Table I.

The IR spectrum of a typical polyamide is shown in Figure 1. The IR spectra of all the polymers showed the N—H stretching frequency as a broad band around 3300 cm^{-1}. This lowering of frequency could be attributed to the involvement of —NH groups in hydrogen bonding. The amide-I band, associated with stretching vibration of the carbonyl group appears at 1660 cm^{-1}. The amide-II

TABLE I

Preparation of polyamides

Polymer	Diamine	Diacid chloride	Yield (%)	η inh[a] (dL/g)
PA-I	BAE	IPC	98	0.46
PA-II	BAPEE	IPC	97	0.48
PA-III	BAE	TPC	98	0.44
PA-IV	BAPEE	TPC	98	0.40

[a] Measured at a concentration of 0.5% (W/V) in concentrated sulphuric acid at 30°C.

band, ascribed to the coupling of N—H bending and C—N stretching of the C—N—H group, appears around 1525 cm^{-1}. The C—O—C asymmetric stretching vibration is observed around 1250 cm^{-1}.

The solubility characteristics of the polyamides are summarized in Table II. All the polyamides were insoluble in common organic solvents but soluble in dimethyl acetamide containing 5 wt% of lithium chloride and concentrated sulphuric acid. Polyamides derived from IPC showed better solubility than those derived from TPC, which may be attributed to their amorphous nature.

The X-ray diffraction patterns of the polyamides are given in Figure 2. Polyamides PA-I and PA-II, derived from the non-linear diamines and *meta*-oriented aromatic diacid chloride (IPC) exhibited a pattern typical of amorphous materials. On the other hand, polyamides PA-III and PA-IV obtained from *para*-oriented diacid chloride (TPC) showed some degree of crystallinity.

The thermal behaviour of the polyamides was evaluated by means of thermogravimetric analysis in air. Figure 3 illustrates a typical TG curve for the representative polyamide PA-I. All the polyamides showed similar patterns of decomposition with no weight loss below 380°C in air. From the traces, the decomposition temperature where 10% of the polymer weight was lost (T_{10}) were noted and the values are documented in Table III. A comparison of the T_{10} values of the polyamides indicated that the polyamides derived from BAPEE were comparatively less thermally stable than the polyamides derived from BAE, which may be attributed to the increased chain length of the aliphatic linkage in the former diamine.

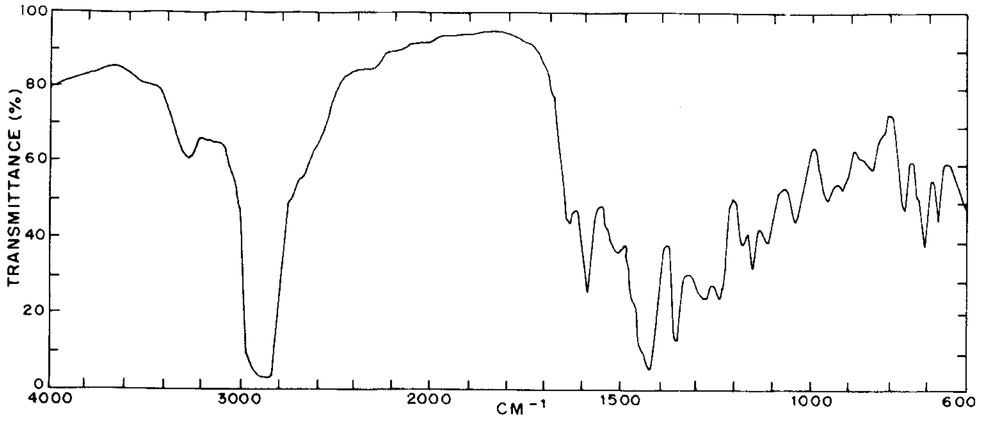


FIGURE 1 IR Spectrum of polyamide PA-I.

TABLE II

Solubility of polyamides[a,b]

Polymer	DMAC	DMAC+ 5% LiCl	NMP	HMPA	*m*-Cresol	H_2SO_4
PA-I	+	+ +	+ +	+ +	−	+ +
PA-II	+ +	+ +	+ +	+ +	−	+ +
PA-III	−	+ +	−	−	−	+ +
PA-IV	−	+ +	−	−	−	+ +

[a] + +, soluble; +, moderately soluble; −, insoluble.

[b] DMAC, dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone, HMPA, hexamethylphosphoramide.

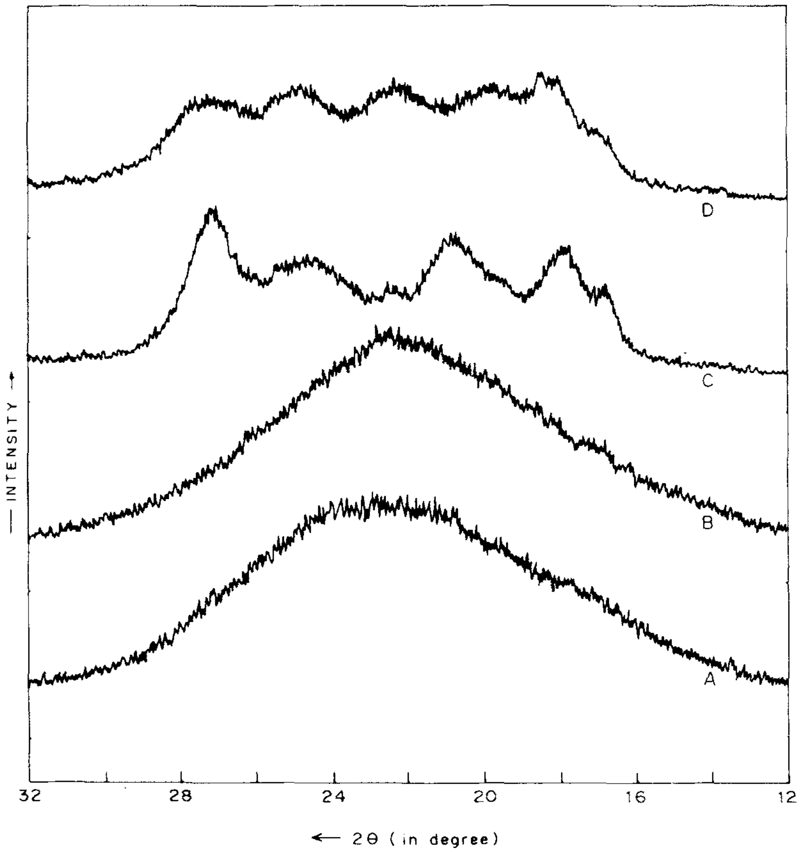


FIGURE 2 X-Ray diffraction patterns of the polyamides (A), PA-I (B), PA-II (C), PA-III and (D), PA-IV.

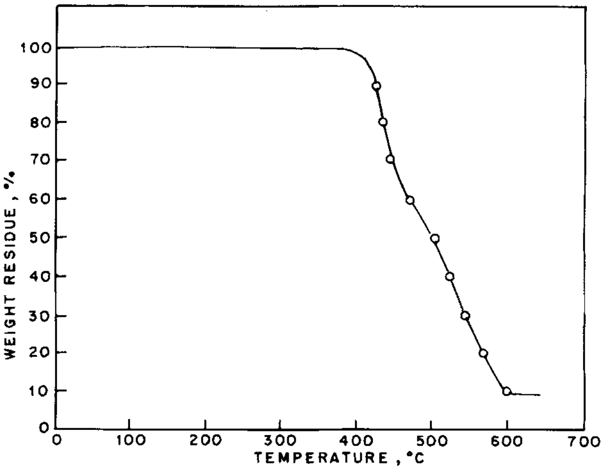


FIGURE 3 TG curve of polyamide PA-I in air heating rate 10°C/min.

TABLE III

Thermal behaviour data of polyamides

Polymer	T_{10}, °C[a]
PA-I	425
PA-III	400
PA-III	430
PA-IV	400

[a] T_{10}, temperature at which 10% weight loss was recorded by TG at a heating rate of 10°C/minute in air.

References

1. P. E. Cassidy, *Thermally Stable Polymers—Syntheses and properties,* Marcel Dekker, New York, 1980.
2. V. Guidotti and N. J. Johnston, Paper Presented at the American Chemical Society 167th National Meeting, Los Angeles, California, April 6–11, 1974.
3. Y. Imai, N. N. Maldar and M. Kakimoto, *J. Polym. Sci., A-1,* **23,** 1797 (1985).
4. K. J. Scariah, V. N. Krishnamurthy, K. V. C. Rao and M. Srinivasan, *Makromol. Chem.,* **186,** 2427 (1985).
5. W. A. Feld, B. Ramalingam and F. W. Harris, *J. Polym. Sci., A-1,* **21,** 319 (1983).

6. F. W. Harris, M. W. Beltz, S. Das and R. K. Gupta, *Polym. Preprints,* **25(1),** 160 (1984).
7. F. W. Harris, A. J. Karnavas, C. N. Cucuras and S. Das, *Polym. Preprints,* **26(2),** 287 (1985).
8. CIBA Ltd. Fr. 1, 562, 336 (1969), *Chem. Abstr.* **73,** 57142*j* (1970).
9. J. Hackel, G. Adamska and J. Rusek, *Biul. Wojskowej Akad. Tech.*, **10(108),** 81 (1961), *Chem. Abstr.* **57,** 11074g (1962).