Iranian Polymer Journal **13** (3), 2004, 205-212

# Synthesis and Characterization of Linear Aromatic Polyester-amides from Diacid Chlorides and Aminophenols

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Received 9 May 2003; accepted 11 January 2004

# ABSTRACT

inear aromatic polyester-amides (PEAs) have been synthesized by interfacial polycondensation of aliphatic and aromatic diacid chlorides (terephthaloyl chloride, isophthaloyl chloride, adipoyl chloride, and sebacoyl chloride) with aminophenols (*p*-aminophenol, *m*-aminophenol) in a chloroform/water system employing phase transfer catalyst. These polymers were characterized by elemental analysis, FTIR, <sup>1</sup>H NMR, solubility studies, intrinsic viscosity and TGA analysis. The polyester-amides so obtained show good thermal stability.

#### Key Words:

polyester-amides; interfacial polycondensation; phase transfer catalyst; physicochemical properties; TGA analysis.

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### **INTRODUCTION**

The development of processable high-performance polymers with increased thermal stability, heat resistance and good mechanical properties has become an important problem [1]. In an attempt to prepare polymers of high glass transition temperature,  $T_g$ , Imai et al. [2,3] synthesized the polyester-amides of high molecular weight and investigated their properties in detail. The PEAs have special structure due to the regular enhancement of ester and amide groups in the same polymer chain, which give them the properties intermediate between the polyester and the polyamide [4]. The rigidity due to the double bond character of the amide group coupled with extensive hydrogen bonding influences the ordering of PEA [5]. Thus, the growth and expansion of aromatic-aliphatic polyester-amides work, both basic and applied over the past few decades has been enormous [6-20]. Apart from high thermal stability, the many PEAs also exhibit liquid crystalline properties [4-9]. The polyester-amides have potential applications as high modulus fibres and engineering polymers [21]. Considering all these important aspects it was decided to undertake the synthesis of new PEAs from polycondensation of aminophenols and diacid chlorides by interfacial method and to evaluate their properties in detail. In this paper we report the synthesis of PEAs by interfacial polycondensation of aliphatic and aromatic diacid chlorides (terephthaloyl chloride, isophthaloyl chloride, adipoyl chloride, and sebacoyl chloride) with aminophenols (p-aminophenol, m-aminophenol) and their characterization through elemental analysis, solubility studies, intrinsic viscosity, FTIR, <sup>1</sup>H NMR, and TGA analysis.

#### EXPERIMENTAL

#### Materials

Adipic acid, sebasic acid, terephthalic acid, isophthalic acid, *p*-aminophenol, *m*-aminophenol, citramide (cetyltriethylammonium bromide), SDS (sodium dodecyl sulphate) and Tween 20 (polyoxyethylene(20) sorbitan monolaurate) were obtained commercially from SRL, Mumbai. Thionyl chloride, pyridine, chloroform, toluene, benzene, cyclohexanone, nitrobenzene, sulphuric acid, hydrochloric acid, dimethyl sulphoxide, dimethylformamide, tetrahydrofuran, dioxane, carbon tetrachloride, *m*-cresol, *o*-chloro phenol, ethyl acetate, methanol, ethanol, iso-propanol, acetone, cyclohexane were also obtained commercially from SRL, Mumbai and used as received.

Adipoyl chloride (ADCl), sebacyl chloride (SECl), terephthaloyl chloride (TPCl), isophthaloyl chloride (IPCl) were obtained from the condensation reaction of their corresponding dicarboxylic acids with excess of thionyl chloride, in the presence of few drops of pyridine as a catalyst. They were purified by crystallization with hexane.

#### Method of Characterization

Elemental analysis (C, H and N) for all PEAs was estimated by "Carlo Erba Elemental Analyzer". Solubility of PEAs was determined for powdery samples in excess of solvent. Viscosity measurements of the polymer solutions were carried out with Ubbelohde Suspended Level Viscometer at 30°C using appropriate set up of the thermostat. FTIR Spectra of the monomer and all polymers have been scanned in KBr pellets on Perkin Elmer IR Spectrometer. <sup>1</sup>H NMR Spectra were taken in DMSO- $d_6$  as a solvent on Bruker DPX-200 spectrometer at 200 MHz (RSIC, CDRI, Lucknow) with a sweep time of 10 min at room temperature. The internal reference used was TMS. Mettler TA 4000 system (Switzerland) was used to obtain the thermograms of the polyester-amide in N<sub>2</sub> atmosphere at a heating rate of 10°C/min in the temperature ranges from 50°C to 700°C.

#### Synthesis of Polyester-amides

Aliphatic and aromatic diacid chlorides and aminophenols were polymerized using interfacial polycondensation technique with chloroform-water interphase system and citramide as phase transfer catalyst. As an example the polycondensation [22,23] of IPC1 with MAP is described in detail.

The reaction was carried out using mechanical stirrer with a switch to control the speed in a 250 mL flask. An initial charge of 0.025 mol of NaOH dissolved in a total of 75 mL of water in a 250 mL flask was stirred at a moderate speed with 0.0125 mol of MAP., 25 mg, citramide (phase transfer catalyst) dissolved in 10 mL of water was added. The organic phase was prepared by dissolving 0.0125 mol IPCl in 35 mL of chloroform. The speed of the stirrer was raised to maximum and the organic phase was introduced rapidly. Mixing was continued thereafter for 5 min. At the end of the 5 min period stirring (which was still in progress) was interrupted and acetone was added to the flask. After 1 min of gentle stirring the polymer was filtered off and washed with acetone and distilled water to remove unreacted monomers, chloroform, excess alkali and salts.

The polymerized product was dried to constant weight in a vacuum oven at 40°C. The polymerization

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HO — Ar — NH<sub>2</sub> + CICO — Ar — COCI room temp.  $\downarrow$  IPC chloroform water  $\bigcirc$  O — Ar — NH — C — Ar' — C — O — O \_ n

reaction is represented as in Scheme I.

Where,



Scheme I

In the similar manner, other PEAs were prepared adopting the parallel procedure outlined above selecting appropriate aliphatic or aromatic diacid chloride and aminophenol. One PEA of MAP with IPCl and four PEAs of PAP with ADCl, SECl, TPCl and IPCl reported in the present investigation have been synthesized.

#### **RESULTS AND DISCUSSION**

The polycondensation of MAP with IPCl leading to polymer was first carried out by the interfacial method. In general, the selection of an adequate solvent in an organic phase is most essential for the production of high-molecular-weight polymers [2]. Therefore, we have carried out polycondensations in (i) chloroform-water, (ii) benzene-water, (iii) toluenewater, (iv) dichloroethane-water, (v) cyclohexanonewater, and (vi) nitrobenzene-water interface systems without catalyst. The use of chloroform-water interface system led to product of higher inherent viscosity. Now we employed three surfactants: (i) citramide as a cationic surfactant, (ii) SDS as an anionic surfactant and (iii) Tween 20 as a non-ionic surfactant for the interfacial polycondensation in the chloroformwater system. Quaternary ammonium salt (citramide) effectively accelerated polycondensation and led to marked increase in inherent viscosity (Table 1). Therefore, interfacial polycondensation in chloroform-water system with citramide as a phase transfer catalyst was then applied to prepare various types of polyesteramides (Table 2).

Yields of the different polymer samples involving aromatic diacid chloride moiety in polymer chain are in the range from 72% to 81%, while those of aliphatic diacid chloride moiety are from 48% to 53%. All the PEAs are solid powders. The one PEA, PPA1 is a black powder and other four PEAs are light to dark brown powders. An examination of inherent viscosities (Table 2) of given PEAs reveals that PPA3 has the highest inherent viscosity and PPA2 the lowest. The inherent viscosities of the investigated PEAs are in the range from 0.141 to 0.238 dL/g and follow the sequence PPA3 > PMA1 > PPA4 > PPA1 > PPA2

The results of elemental analysis of present PEAs are given in Table 3. The observed percentage of C, H and N contents in the present PEAs are fairly in good agreement with those theoretically calculated based on the repeat units in the chain. Relative solubilities of present PEAs in different solvents are summarized in

Table 1	. Effect	of differ	ent sol	vent sy	/stems	and	phase	trans-
fer cata	lyst in ir	nterfacia	l polyc	onden	sation p	oolym	nerizatio	on.

Interphase system	Phase transfer catalyst	η <sub>inh</sub> (dL/g)
Chloroform-water	-	0.133
Toluene-water	-	0.079
Benzene-water	-	0.062
Cyclohexanone-	-	0.114
water		
Dichloroethane-water	-	0.099
Nitrobenzene-water	-	0.103
Chloroform-water	Citramide	0.209
Chloroform-water	Sodium dodecyl sulphate	0.175
Chloroform-water	Tween 20	0.181

Phase volume ratio: 35 mL organic solvent / 85 mL H<sub>2</sub>O; Monomers: IPCI and MAP each 0.01 mol; NaOH: 0.025 mol; phase transfer catalyst: 0.25 mg; Temp.: 30°C; Time: 5 min; stirring: continuous and vigorous.

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Code	Repeat unit	Appearance	Yield (%)	$\eta_{inh}^{*}$ (dL/g)
PPA1	$ \begin{array}{c} O \\ H \\ \hline \\ \hline$	Black powder	48	0.172
PPA2	$ \begin{array}{c} O & O \\ 0 & 0 $	Dark brown powder	53	0.141
PPA3		Brown powder	81	0.238
PPA4		Brown powder	75	0.193
PMA1		Dark brown powder	72	0.209

Table 2. Polyester-amides from diacid chlorides and aminophenols.

(\*) 1% Polymer solution in DMF at 30°C temperature.

#### Table 4.

The formation of PEA is confirmed from the typical characteristic bands observed around 1700-1735 cm<sup>-1</sup> (>C=O stretch in ester) and  $1660\pm15$  cm<sup>-1</sup> (>C=O

**Table 3.** Elemental analysis C, H and N % contents in the polyester-amides.

Polyester-	С (	(%)	Н (	%)	N (%)	
amides	calc.	obs.	calc.	obs.	calc.	obs.
PPA1	72.36	72.25	4.52	4.47	7.04	5.89
PPA2	70.85	70.38	6.27	6.11	5.17	5.12
PPA3	70.29	70.04	3.77	3.71	5.86	5.74
PPA4	70.29	69.92	3.77	3.59	5.86	5.69
PMA1	70.29	70.13	3.77	3.37	5.86	5.65

stretch in amide)[2]. Bands at  $1246\pm25$  cm<sup>-1</sup>,  $1035\pm32$ cm<sup>-1</sup> and 1009±7 cm<sup>-1</sup> correspond to C-O-C symmetric and asymmetric stretch vibration in all the five polyester-amides [24,25]. In all the polymers, the N-H bending and N-H stretching for secondary amide were observed at 1540±5 cm<sup>-1</sup> and 3280±5 cm<sup>-1</sup>, respectively [4]. Few other characteristic absorption frequencies of different involved diacid chlorides can be used to distinguish polyester-amide from each other. The presence of terephthaloyl moiety in PPA3 is indicated by C-H bending vibration of 1,4-substituted benzene at 830 cm<sup>-1</sup> and C=C aromatic at 1610, 1515 and 1435 cm<sup>-1</sup> [24]. The presence of isophthaloyl moiety in PPA4 and PMA1 is confirmed due to bands around 1605±5, 1500±15 and 1440 cm<sup>-1</sup> (C=C stretch, aromatic) and 915±5, 790±15, 690±10 cm<sup>-1</sup> (1,3-substituted benzene). In polyester-amides PPA1

PPA2

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PPA3

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±

PPA4

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PMA1

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Figure 1. FTIR Spectra of PPA1, PPA2, PPA3, PPA4 and PMA1.

and PPA2, the absorption band at 1450 cm<sup>-1</sup> indicates incorporation of -(CH<sub>2</sub>)<sub>n</sub>- of adipoyl and sebacoyl moiety, respectively [26].

<sup>1</sup>H NMR Spectra of four PEAs, PPA1, PPA2, PPA3



Figure 2. <sup>1</sup>H NMR of (a) PPA1 and (b) PPA2.

o-Chlorophenol ± ± ± Ethyl acetate ± ± Carbon tetrachloride Methanol Ethanol Iso-propanol Acetone Benzene Toluene

(++) Soluble at room temperature, (+) soluble on heating, (±) partially soluble on heating, and (-) insoluble.



shown in Figures 2 and 3, which supported the assigned

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Table 4. Relative solubilities of polyester-amides of diacid chlorides + aminophenols.

PPA1

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±

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+

Solvent

H<sub>2</sub>SO<sub>4</sub>

DMSO

DMF

THF

Dioxane

Chloroform

Cyclohexane

Water

m-Cresol

HCI



Figure 3. <sup>1</sup>H NMR of (a) PPA3 and (b) PPA4.

structure of polyester-amides. <sup>1</sup>H of secondary amide group in PPA1 and PPA2 appeared as a singlet at 9.55-9.63 ppm, while at 10.13-10.21 ppm in PPA3 and PPA4. 4H (e) of two central -CH<sub>2</sub>- groups in adipoyl moiety and 8H (e) of central -CH<sub>2</sub>- in sebacoyl moiety appeared in the range  $\delta$  1.48-1.54 ppm. 4H (d,f) of two -CH<sub>2</sub>-C=O groups in adipoyl and sebacoyl moiety appeared around  $\delta$  2.20-2.25 ppm. 2Ar-H (a) ortho to -OOC- group and 2Ar-H (b) ortho to -NH-CO- group showed a doublet at  $\delta$  6.64-6.76 ppm and 7.32-7.61 ppm, respectively, in all four polymers. In PPA3, 2Ar-H (d) ortho to -CO-NH- and 2Ar-H (e) ortho to -COOgroup of terephthaloyl moiety showed  $\delta$  at 8.04-9.28 ppm. In isophthaloyl moiety of PPA4, 1Ar-H (d)  $\delta$ ortho to both -CO-NH- and -COO<sup>-</sup> groups appeared at  $\delta$  9.31 ppm. Multiplet in the range of  $\delta$  8.10 to 8.51 ppm is attributed to the other 3H (e,f) in the isophthaloyl moiety.

Thermograms for three selected PEAs PPA1, PPA3 and PPA4 are shown in Figure 4. The polymer PPA3 degrades in three steps while PPA1 and PPA4 in a single step. The values of  $T_{10}$ ,  $T_{max}$ ,  $T_{50}$  and IPDT are





Figure 4. Thermograms of (a) PPA1, (b) PPA3 and (c) PPA4.

given in Table 5. The values of IPDT (integral proce-

Polymer	Step	T <sub>max</sub> (°C)	T <sub>f</sub> (°C)	T <sub>10</sub> (°C)	T <sub>50</sub> (°C)	IPDT (°C)	Residue (%) at 700°C	E <sub>a</sub> (kcal/mol)
PPA1	I	360	436	278	478	328	35.6	23.94
PPA3	I	332	357	316	563	418	36.2	57.93
	Ш	405	446					78.63
	111	563	620					63.19
PPA4	I	430	565	354	570	447	38.0	63.19

Table 5. Thermal behaviour of polyester-amides in N<sub>2</sub> atmosphere.

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dural decomposition temperature) were obtained by Doyle method [27]. The values of activation energy,  $E_a$ , calculated by Broido method [28] are also given in the last column of Table 5. A comparison of  $T_{10}$ ,  $T_{max}$ ,  $T_{50}$ and IPDT shows, the values of  $T_{max}$ ,  $T_{50}$  and IPDT are somewhat higher for PPA3 and PPA4 than those of PPA1. This indicates that PEAs, PPA3 and PPA4 involving terephthaloyl chloride and isophthaloyl chloride with *p*-aminophenol are comparatively more stable than the PPA1 involving adipoyl chloride with *p*aminophenol.

## CONCLUSION

- All the PEAs are soluble in DMSO, DMF and sulphuric acid at room temperature. PPA3, PPA4 and PMA1 are also easily soluble in dioxane while PPA1 and PPA2 are insoluble. PPA2 is easily soluble, in *m*-cresol PPA1 and PMA1 are soluble on heating while PPA3 is only partially soluble on heating.

- The inherent viscosities of the investigated PEAs are in the range from 0.141 to 0.238 dL/g and follow the sequence: PPA3 > PMA1 > PPA4 > PPA1 > PPA2.

- The PEAs involving terephthaloyl chloride and isophthaloyl chloride are comparatively thermally more stable than involving adipoyl chloride

#### ACKNOWLEDGEMENTS

The authors express their gratitude to the Head, RSIC (CDRI), Lucknow and Director, Mantra, Surat, for providing facilities to scan <sup>1</sup>H NMR and TGA of polymer samples.

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