

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

Shantilal L. Oswal* and Ashesh K. Pandya

Department of Chemistry, South Gujarat University, Surat-395 007, India

Received 9 May 2003; accepted 11 January 2004

ABSTRACT

Linear 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, ¹H 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.

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

(*)To whom correspondence should be addressed.
E-mail: oswalsl@satyam.net.in

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 sebacyl chloride) with aminophenols (*p*-aminophenol, *m*-aminophenol) and their characterization through elemental analysis, solubility studies, intrinsic viscosity, FTIR, ^1H NMR, and TGA analysis.

EXPERIMENTAL

Materials

Adipic acid, sebacic 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. ^1H 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_2 atmosphere at a heating rate of 10°C/min in the temperature ranges from 50°C to 700°C.

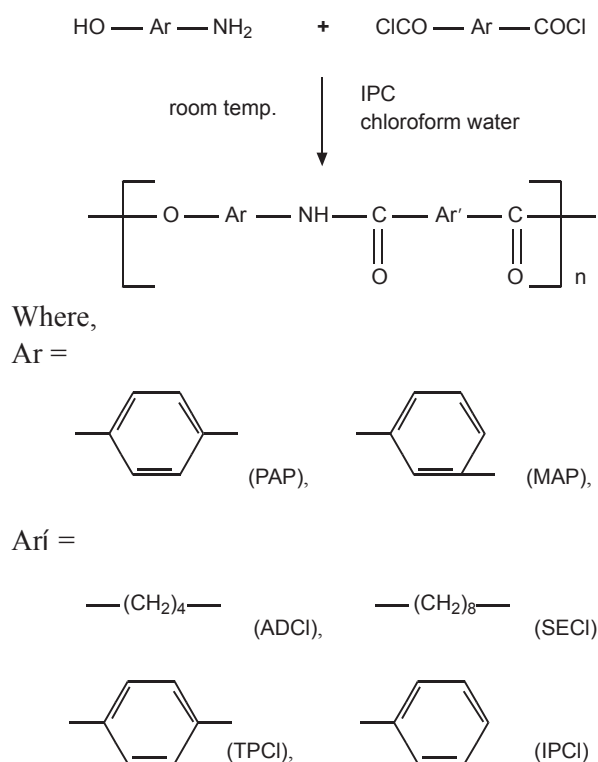
Synthesis of Polyester-amides

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 IPCl 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

reaction is represented as in Scheme I.



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 IPCI and four PEAs of PAP with ADCI, SECI, TPCI and IPCI reported in the present investigation have been synthesized.

RESULTS AND DISCUSSION

The polycondensation of MAP with IPCI 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) toluene-water, (iv) dichloroethane-water, (v) cyclohexanone-water, 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 surfac-

tant and (iii) Tween 20 as a non-ionic surfactant for the interfacial polycondensation in the chloroform-water 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 polyester-amides (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 different solvent systems and phase transfer catalyst in interfacial polycondensation polymerization.

| Interphase system | Phase transfer catalyst | η_{inh} (dL/g) |
|----------------------|-------------------------|---------------------|
| Chloroform-water | - | 0.133 |
| Toluene-water | - | 0.079 |
| Benzene-water | - | 0.062 |
| Cyclohexanone-water | - | 0.114 |
| 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 H₂O; 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.

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

| Code | Repeat unit | Appearance | Yield (%) | η_{inh}^* (dL/g) |
|------|-------------|-------------------|-----------|-----------------------|
| PPA1 | | Black powder | 48 | 0.172 |
| PPA2 | | 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 |

(*) 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^{-1} ($>\text{C}=\text{O}$ stretch in ester) and 1660 \pm 15 cm^{-1} ($>\text{C}=\text{O}$

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

| Polyester-amides | C (%) | | H (%) | | N (%) | |
|------------------|-------|-------|-------|------|-------|------|
| | 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 \pm 25 cm^{-1} , 1035 \pm 32 cm^{-1} and 1009 \pm 7 cm^{-1} 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 \pm 5 cm^{-1} and 3280 \pm 5 cm^{-1} , 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^{-1} and C=C aromatic at 1610, 1515 and 1435 cm^{-1} [24]. The presence of isophthaloyl moiety in PPA4 and PMA1 is confirmed due to bands around 1605 \pm 5, 1500 \pm 15 and 1440 cm^{-1} (C=C stretch, aromatic) and 915 \pm 5, 790 \pm 15, 690 \pm 10 cm^{-1} (1,3-substituted benzene). In polyester-amides PPA1

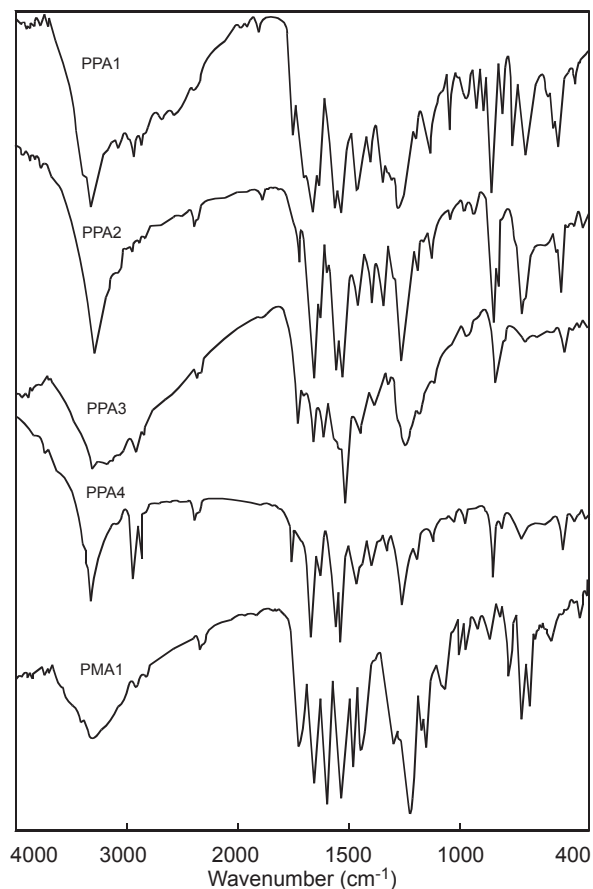
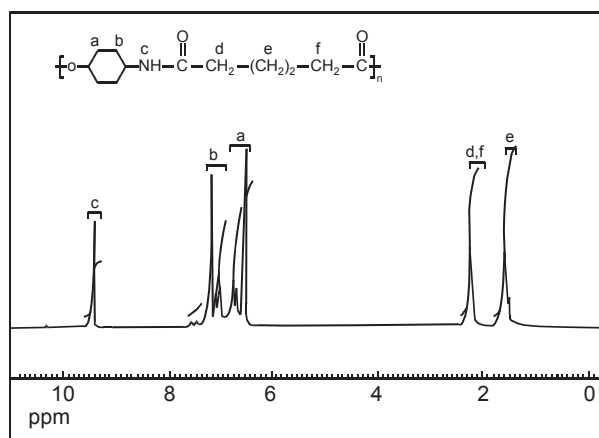


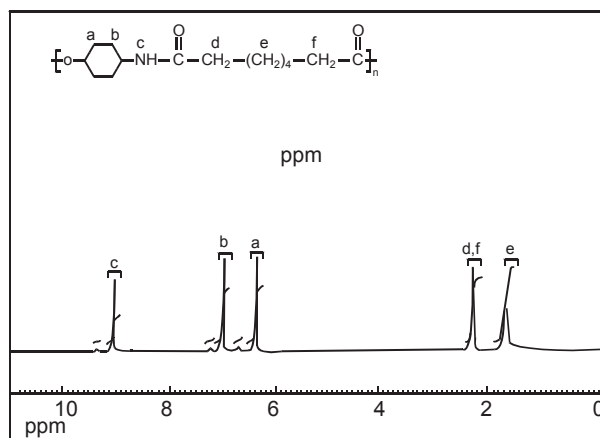
Figure 1. FTIR Spectra of PPA1, PPA2, PPA3, PPA4 and PMA1.

and PPA2, the absorption band at 1450 cm^{-1} indicates incorporation of $-(\text{CH}_2)_n-$ of adipoyl and sebacoyl moiety, respectively [26].

^1H NMR Spectra of four PEAs, PPA1, PPA2, PPA3



(a)



(b)

Figure 2. ^1H NMR of (a) PPA1 and (b) PPA2.

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

| Solvent | PPA1 | PPA2 | PPA3 | PPA4 | PMA1 |
|--------------------------------|------|------|------|------|------|
| H ₂ SO ₄ | ++ | ++ | ++ | ++ | ++ |
| HCl | ± | - | ± | - | - |
| DMSO | ++ | ++ | ++ | ++ | ++ |
| DMF | ++ | ++ | ++ | ++ | ++ |
| THF | - | + | - | - | ++ |
| Dioxane | - | - | ++ | ++ | ++ |
| Chloroform | - | - | - | - | - |
| <i>m</i> -Cresol | + | ++ | ± | - | + |
| <i>o</i> -Chlorophenol | ± | ± | ± | - | + |
| Ethyl acetate | - | ± | - | - | ± |
| Carbon tetrachloride | - | - | - | - | - |
| Methanol | - | - | - | - | - |
| Ethanol | - | - | - | - | - |
| Iso-propanol | - | - | - | - | - |
| Acetone | - | - | - | - | - |
| Benzene | - | - | - | - | - |
| Toluene | - | - | - | - | - |
| Cyclohexane | - | - | - | - | - |
| Water | - | - | - | - | - |

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

and PPA4 obtained in DMSO-*d*₆ at 200 MHz were shown in Figures 2 and 3, which supported the assigned

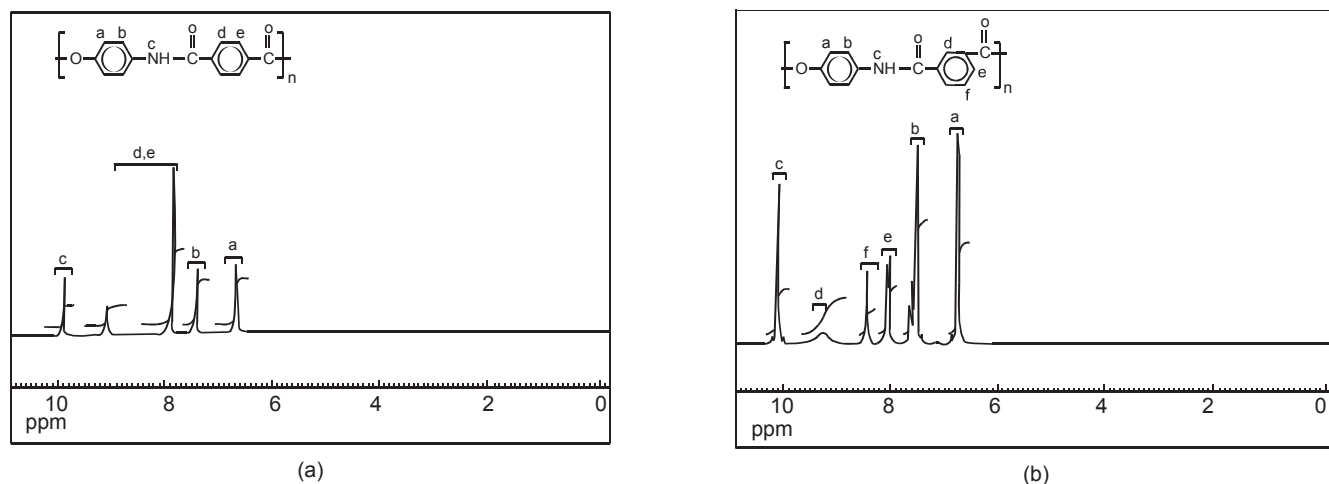


Figure 3. ¹H NMR of (a) PPA3 and (b) PPA4.

structure of polyester-amides. ¹H 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 -CH₂- groups in adipoyl moiety and 8H (e) of central -CH₂- in sebacoyl moiety appeared in the range δ 1.48-1.54 ppm. 4H (d,f) of two -CH₂-C=O groups in adipoyl and sebacoyl moiety appeared around δ 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 δ 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 -COO- group of terephthaloyl moiety showed δ at 8.04-9.28 ppm. In isophthaloyl moiety of PPA4, 1Ar-H (d) δ *ortho* to both -CO-NH- and -COO⁻ groups appeared at δ 9.31 ppm. Multiplet in the range of δ 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 T₁₀, T_{max}, T₅₀ and IPDT are

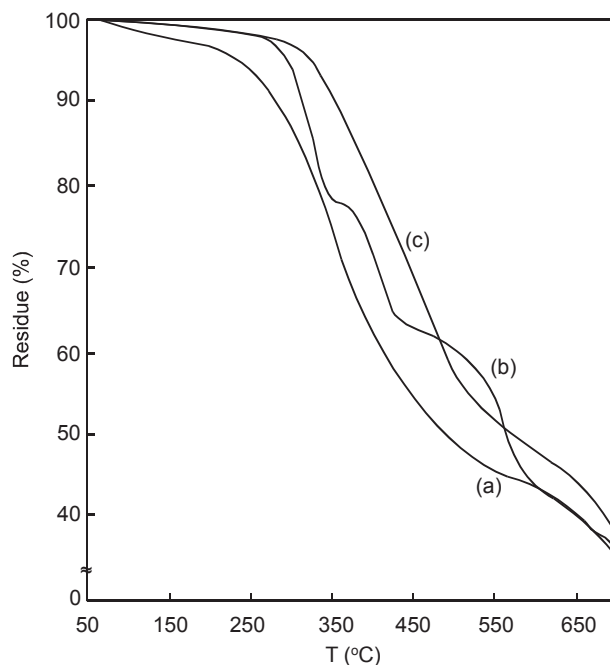


Figure 4. Thermograms of (a) PPA1, (b) PPA3 and (c) PPA4.

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

Table 5. Thermal behaviour of polyester-amides in N₂ atmosphere.

| Polymer | Step | T _{max} (°C) | T _f (°C) | T ₁₀ (°C) | T ₅₀ (°C) | IPDT (°C) | Residue (%) at 700°C | E _a (kcal/mol) |
|---------|------|-----------------------|---------------------|----------------------|----------------------|-----------|----------------------|---------------------------|
| PPA1 | I | 360 | 436 | 278 | 478 | 328 | 35.6 | 23.94 |
| PPA3 | I | 332 | 357 | 316 | 563 | 418 | 36.2 | 57.93 |
| | II | 405 | 446 | | | | | 78.63 |
| | III | 563 | 620 | | | | | 63.19 |
| PPA4 | I | 430 | 565 | 354 | 570 | 447 | 38.0 | 63.19 |

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 ^1H NMR and TGA of polymer samples.

REFERENCES

1. Critchley J.P., Knight G.J., and Wright W.W., *Heat Resistant Polymers*, Plenum, New York, Ch.3 (1983).
2. Imai Y., Abe S., and Ueda M., Preparation and properties of aromatic polyamide-esters from aminophenols and aromatic diacid chlorides, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 3285-3291 (1981).
3. Kakimoto M.A., Nagi Y.S., and Imai Y., Synthesis and characterization of aromatic polyesters and polyamide-esters from bisphenols and aromatic aminophenols, and 2,5-bis(4-chloroformyl)-3,4-diphenylthiophene, *J. Polym. Sci., Part A, Polym. Chem.*, **34**, 1511-1517 (1986).
4. Sudha J.D., Synthesis and characterization of hydrogen-bonded thermotropic liquid crystalline aromatic-aliphatic poly(ester-amide)s from amido diol, *J. Polym. Sci. Part A: Polym. Chem.*, **38**, 2469-2486 (2000).
5. Kalyvas V. and McIntyre J.E., Thermotropic liquid crystal behaviour in some aromatic esteramides, *Mol. Cryst. Liq. Cryst.*, **80**, 105-118 (1982).
6. Aharoni S.M., Hydrogen bonded highly regular strictly alternating aliphatic-aromatic liquid crystalline poly(ester-amides), *Macromolecules*, **21**, 1941-1961 (1988).
7. Gaudiana R.A., Pickens N., and Sinta R., An X-ray diffraction study of glassy, rodlike polymers, *Mol. Cryst. Liq. Cryst.*, **243**, 149-160 (1994).
8. Sudha J.D., Ramamohan T.R., Pillai C.K.S., and Scariah K.J., Lyotropic behaviour of liquid crystalline poly(ester amide) containing diamide links, *Eur. Polym. J.*, **35**, 1637-1646 (1996).
9. McCarthy T.F., Lenz R.W., Kantor S.W., and Curran S., Liquid crystalline poly(ester amide)s based on *N,N*-dimethyldiamines and aromatic ester triad, *Macromolecules*, **30**, 2825-2838 (1997).
10. Paredes N., Rodriguez-Galan A., and Puiggali J., Synthesis and characterization of a family biodegradable poly(ester amide)s derived from glycine, *J. Polym. Sci. Part A: Polym. Chem.*, **36**, 1271-1282 (1998).
11. Pascale C., Jean-Claude S., Jean-Claude B., and Manfred G., Synthesis of poly(amide-ester)s from 2,6-pyridine dicarboxylic acid and ethanolamine derivatives: Investigation of the polymer sorption behaviour towards heavy metal ions, *React. Funct. Polym.*, **42**, 129-146 (1999).
12. Li L., Seino H., Yonetake K., and Ueda M., Synthesis and characterization of ordered poly(amide-ester)s from isophthaloyl chloride and 4-(2-aminoethyl) phenol, *Macromolecules*, **32**, 3851-3858 (1999).
13. Wang C.S. and Lin C.H., Synthesis and properties of phosphorus containing polyester-amides derived from 1,4-bis(3-aminobenzoyloxy)-2-(6-oxido-6H-

- dibenz(c,e)(1,2) oxaphosphorin-6-yl) phenylene, *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 891-899 (1999).
14. Bruch M., Burgath A., Loontjens T., and Mulhaupt R., Synthesis and characterization of polyesteramides derived from an oxazoline-functional alcohol and dicarboxylic acid anhydrides, *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 3367-3376 (1999).
15. Tuominen J. and Seppälä J.V., Synthesis and characterization of lactic acid based poly(ester-amide), *Macromolecules*, **33**, 3530-3535 (2000).
16. Fan Y., Kobayashi M., and Kise H., Synthesis and specific biodegradation of novel polyesteramides containing amino acid residues, *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 1318-1328 (2001).
17. Khan A.R., Mathew J., Al-Shayji K., and Sari M., Copolyesteramides: Synthesis and kinetic analysis, *Eur. Polym. J.*, **38**, 1013-1023 (2002).
18. Botines E., Rodríguez-Galan A., and Puiggali J., Poly(ester amide)s derived from 1,4-butanediol, adipic acid and 1,6-aminohexanoic acid: characterization and degradation studies, *Polymer*, **43**, 6073-6084 (2002).
19. Ferré T., Franco L., Rodríguez-Galán A., and Puiggali J., Poly(ester amide)s derived from 1,4-butanediol, adipic acid and 6-aminohexanoic acid. Part II: Composition changes and fillers, *Polymer*, **44**, 6139-6152 (2003).
20. Sang-Il H., Byung-Soo K., Sun-Woong K., Hirofusa S., and Seung S. I., Cellular interactions and degradation of aliphatic poly(ester amide)s derived from glycine and/or 4-amino butyric acid, *Biomaterials*, **24**, 3453-3462 (2003).
21. Roggero A., In *Thermotropic Liquid Crystal Polymer Blends*, La Mantia F.P.E.d., Technomic, **6**, 157 (1993).
22. Morgan P.W., *Condensation Polymers by Interfacial and Solution Methods*, Interscience, New York, Ch.4 (1965).
23. Cassasa E.Z., Chao D.Y., and Henson M., Cationic surfactants in interfacial synthesis of linear aromatic polyester, *J. Macromol. Sci. Chem.*, **A-15**, 799-813 (1981).
24. Jeong H.J., Kakimoto M.A., and Imai Y., Synthesis and characterization of novel polyarylates from 2,5-bis(4-hydroxyphenyl)-3,4-diphenylfuran and aromatic diacid chlorides, *J. Polym. Sci. Part A. Polym. Chem.*, **29**, 1293-1299 (1991).
25. Liaw D.J. and Chen P.S., Preparation and properties of polyesters derived from 4,4'-sulfonyldibenzoyl by solution polycondensation, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 885-891 (1996).
26. Silverstein R.M., Basseler G.C., and Marill T.C., *Spectrometric Identification of Organic Compounds*, John Wiley, New York, 4th ed., Ch.3 (1981).
27. Doyle C.D., Estimating thermal stability of experimental polymers by empirical thermogravimetric analysis, *Anal. Chem.*, **33**, 77-83 (1961).
28. Broido A., A simple, sensitive graphical method of treating thermogravimetric analysis data containing 4-methoxy-4'-hydroxy-a-methylstilbene based mesogenic groups, *J. Polym. Sci.*, **A2**, 1761-1773 (1969).