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Synthesis, characterization and thermal studies of polyamide esters containing aryl-azo, azomethine and thianthrene units

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New polyamide esters containing aryl-azo, azomethine and thianthrene tetraoxide units in the backbone and also having different aromatic moieties, were synthesized by reacting 4,4′-ozodibenzoyl, 3,3′-ozodibenzoyl, 4,4′[1,4-phenylene *bis*(methylidynenitrilo)] dibenzoyl chlorides, 2,7-dichloroformyl-thianthrene-5-5′,10,10′-tetraoxide, 4,4′-diphenic, isothaloyl and terephthaloyl dichlorides with ethanediamide-*N,N′*-*bis*(2-hydroxyethyl) using the low-temperature solution polycondensation technique. The yields and the values of reduced viscosity of the produced polyamide esters were found to be unaffected by the type of organic solvent used. In order to characterize the polymers, a model compound was prepared from ethanediamide-*N,N′*-*bis*(2-hydroxyethyl) and benzoyl chloride and investigated by infrared, nuclear magnetic resonance and elemental analysis. The synthesized polymers were confirmed by infrared, ultraviolet, nuclear magnetic resonance spectroscopy, elemental analyses and viscosity measurements. The effect of the nature of different units on the thermal properties of polymers was evaluated by thermogravimetric analysis: the data showed that the thermal stabilities of the polymer were remarkably affected by the introduction of these groups.

1. Introduction

Polyoxamides have been studied for many years; they are characterized by high crystallinity, excellent fibre properties and are highly solvent-resistant materials [1–10].

Oxamide-*N,N′*-*bis*(2-hydroxyethyl) has been used in the manufacture of polyamide urethane fibres and films with elastic, heat- and light-resistant properties [11]. This monomer was also applied for the synthesis of copolyether amide urethane and/or copolyester amide urethane polymers which are used in producing artificial leather [12], flame-resistant elastomers [13, 14] and coating materials [15]. Stephen *et al.* [16] in a US Patent, applied the insertion of the *N,N′*-*bis*(2-hydroxyethyl)oxamide for the preparation of hindered phenolic compounds which are useful as stabilizers for polymers in contact with heavy metals such as copper.

Polyester amides are considered to be hybrids of polyesters and polyamides, and have received more attention than any of the other polymer classes. Several patents and reports [17–21] in the field of anisotropic, aromatic polyester amide [22, 23] have been issued in the last few years and recently [24].

The present work deals with the synthesis of new polyamide ester-based *N,N′*-*bis*(2-hydroxyethyl) oxamide and containing aromatic, aromatic-azo, azomethine and thianthrene teteraoxide moieties. The study focused on the effect of the incorporation of these moieties on the thermal behaviour of the polymers. Moreover, the crystallinity, solubility and change in reduced viscosity with change of solvent used in low-temperature polycondensation are discussed.

2. Experimental procedure

2.1. Measurements

Elemental analyses were done using a Perkin–Elmer 240 °C instrument. The infrared spectra were recorded on a Pye Unicam SP3 100 Spectrophotometer using the KBr pellet technique. Proton nuclear magnetic resonance (NMR) spectra were run on a Varian EM-390-90 MHz NMR spectrometer at room temperature in DMSO or $CDCl_3$ and D_2O using TMS as the internal reference. The ultraviolet–visible spectra were scanned on a Varian Cary 219 Spectrophotometer in DMSO. The solution (0.5% wt/vol) in DMSO was determined at 30 °C using a Ubbelohde Suspended Level Viscometer. The solubility of the polymers was examined using 0.02 g polymer in 3–5 ml solvent at room temperature. X-ray diffractographs were obtained with a Philips X-ray PW 1710 diffractometer, using nickel-filtrered CuK_α radiation. Thermogravimetry (TGA) was carried out in air with Du Pont Models 951, 910 and 1090 thermal analysers at a heating rate of 10 °C min^{-1}.

2.2. Reagents and materials

4-4′-Diphenic dichloride was prepared according to the literature [25] are recrystallized twice from tetrachloromethane, m.p. 195 °C. Terephthaloly (Aldrich)

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was recrystallized from *n*-hexane (m.p. 83–84 °C). Isophthaloyl chloride (Aldrich) was recrystallized from *n*-hexane (m.p. 44 °C). 4,4′-Azodibenzoic acid and 3,3′-azodibenzoic acid [26] were obtained from *p*- and *m*-nitrobenzoic acid by the Tomlinson method. 4,4′-Azodibenzoyl and 3,3′-azodibenzoyl dichlorides were prepared as reported in the literature [27]. 4,4′[1,4-Phenylene *bis*(methylidynenitrilo)] dibenzoyl chloride was prepared as reported elsewhere [24]. 2,7-Dichloroformyl-thianthrene-5,5′, 10,10′-tetraoxide was synthesized by the reported method [28]. All other chemicals were highly pure and purified by standard procedures [29].

2.3. Synthesis of the monomer ethanediamide-*N,N′*-*bis*(2-hydroxyethyl)

To a solution of 0.1 mol dimethyl oxalate dissolved in methanol, 0.1 mol ethanolamine was added in a drop-wise manner. After the addition, a white solid precipitate was formed, filtered off, dried and recrystallized from a mixture of ethanol and water (1:1), yielding white needle-shaped crystals, yield 95%, m.p. 165 °C (m.p. 165 °C [26]). ^{1}H-NMR (σ/DMSO) at 3.1–3.6 (t, 4 H of 2-CH_2–O), at 3.6–4 (m, 4 H of 2-CH_2–NH), 8.3 (s, of OH) and at 8.5 (s of NH) p.p.m.

2.4. Synthesis of the model

To a solution of 0.01 mol monomer dissolved in 50 ml NMP , 0.02 mol benzoyl chloride was carefully added at 25 °C. After the addition, the mixture was vigorously stirred for 2 h under a nitrogen atmosphere. At the end of this time, the solid product was separated out, filtered, washed with water and then ethanol, dried and recrystallized from ethanol: yield quantitative, m.p. 220 °C.

Calculated analysis of $C_{20}H_{20}N_2O_6$ gave C 62.50, H 5.20, N 7.29; the analysis found was C 62.70, H 5.18, N 7.35.

Infrared analysis (KBr) showed bands at 3300 cm^{-1} (s, NH), at 1735 cm^{-1} (s, C=O ester), at 1640 cm^{-1} (vs, C=O of amide) and at 1500 cm^{-1}, (vs, C–N band).

^{1}H–NMR (σ $CDCl_3$) at 3.2–3.4 (q, 4 H of O–CH_2–), at 4.3 (t, 4 H of -N–CH_2–) and at 7.1 (complex of 8 H of Ar–H and 2 H of NH) p.p.m.

2.5. Synthesis of the polymer

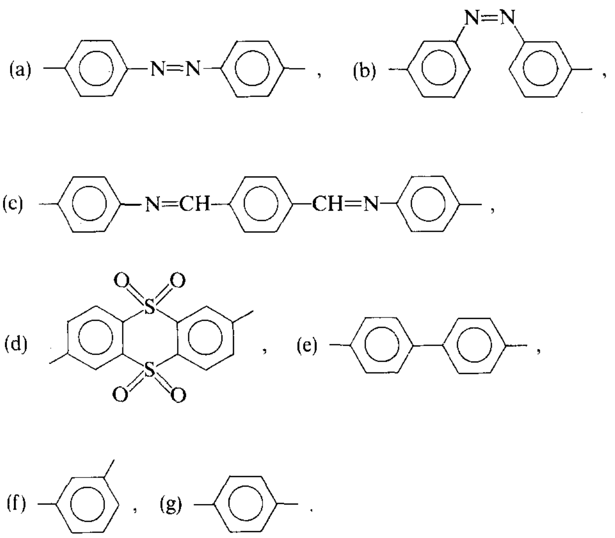
In a three-necked flask, equipped with a mechanical stirrer (2000 r.p.m.), a dry nitrogen inlet and outlet and a dropper, 0.01 mol *N,N′*-*bis*(2-hydroxyethyl)oxamide was dissolved in 50 ml *N*-methyl-2-pyrrolidone. A solution of 0.01 mol acid chloride dissolved in 10 ml THF was added in a drop-wise manner, the reaction temperature was maintained at 25 °C. At the end of the addition, the reaction mixture was stirred for 2 h at ambient temperature and then poured on to a mixture of methanol and water (3:1), whereby a solid polymer was obtained. This was filtered off, washed with water, then ethanol, and dried in a vacuum oven (0.1 mm Hg) for 2 days.

3. Results and discussion

Several patents and papers have reported that *N,N′*-*bis*(2-hydroxyethyl)oxamide has great importance in the synthesis of various types of polymer and copolymer, with a wide industrial application. Furthermore, polyesteramides play important parts in the field of liquid-crystalline polymers (LCP). Consequently, ethanediamide-*N,N′*-*bis*(2-hydroxyethyl) was selected, prepared, and then applied to the synthesis of polyamide esters by interaction with 4,4′-dibenzoyl, 3,3′-dibenzoyl and 4,4′[1,4-phenylene-*bis*-(methylidynenitrilo)] dibenzoyl chlorides, 2,7-dichloroformyl-thianthrene-5,5′,10,10′-tetraoxide, 4,4′-diphenic, isophthaloyl and terephthaloyl dichlorides using a low-temperature polycondensation technique (LTS) as shown in the following Reaction I

$$\begin{aligned} &HO\text{–}(H_2C)_2\text{–}HN\text{–}CO\text{–}CONH\text{–}(CH_2)_2\text{–}OH \\ &+ ClOC\text{–}R\text{–}COCl \xrightarrow[THF]{NMP} [O\text{–}(H_2C)_2\text{–}NH\text{–} \\ &\qquad CO\text{–}CO\text{–}NH\text{–}(CH_2)_2\text{–}O\text{–}CO\text{–}R\text{–}CO]_n \quad (I) \end{aligned}$$

where R is



All of the polyamide esters listed in Table I were prepared by the procedure described in Section 2 in relatively high yields (87%–95%). Additional experiments were carried out where the *N,N′*-dimethylacetamide was substituted for NMP, and no pronounced effects on either polymer yield or viscosity were observed.

The resulting polyamide esters were white in colour, except polymers Ia and Ib which contain azo group and were yellow to orange in colour. The structure of the synthesized polymers was established from elemental and infrared analyses. The infrared spectra showed characteristic absorption bands at 3300 cm^{-1} for the NH group, at 1735 cm^{-1} for C=O of the ester group and at 1640 cm^{-1} for the CO–NH group in addition to other characteristic absorption bands due to specific groups in the various polymers.

The ultraviolet–visible spectra of polymers Ia and Ib in DMSO showed characteristic absorption bands at 305–310 nm, due to π–π* and at 405–420 nm due to n–π* transition.

TABLE I Properties of polyamide esters Ia–Ig

Polymer	Color	Yield %	Red. dL/g	Analysis							
				C(%)		H(%)		N(%)		S(%)	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Ia	Orange	88	0.76	58.53	85.71	4.39	4.40	13.65	13.70		
Ib	Yellow	90	0.66	58.53	58.60	4.39	4.10	13.65	13.81		
Ic	White	86	0.54	65.62	65.50	4.68	4.50	10.93	11.25		
Id	Grey	90	0.70	47.24	47.1	3.14	3.40	5.51	5.30	12.59	13.02
Ie	White	85	0.81	62.28	62.1	4.71	4.90	7.32	7.50		
If	White	96	0.77	54.9	55.1	4.57	4.89	9.15	9.25		
Ig	White	95	0.65	54.9	55.06	5.57	5.80	9.15	9.35		

X-ray diffractograms of some selected polyamide esters were taken. Fig. 1 shows an amorphous halo pattern in the region of $2\theta = 5°–35°$ for polymers Ig and If, and this indicates their low degree of crystallinity. Polymers Ia, Id and Ig showed patterns with a few reflections of sharp peaks intermediate between crystalline and amorphous interferences at $2\theta = 5.35°$. This indicates that there is a large class of structures intermediate in order state between a crystal and an anisotropic liquid with short-range order. Moreover, the presence of oxamide linkage –NH–CO–CO–NH– as the polar group induces some order and mutual attraction between two adjacent chains in the polymer producing crystallinity to some extent [30]. Comparison of the different X-ray patterns proved that the introduction of different moieties in the polyamide esters should induce various degrees of crystallinity.

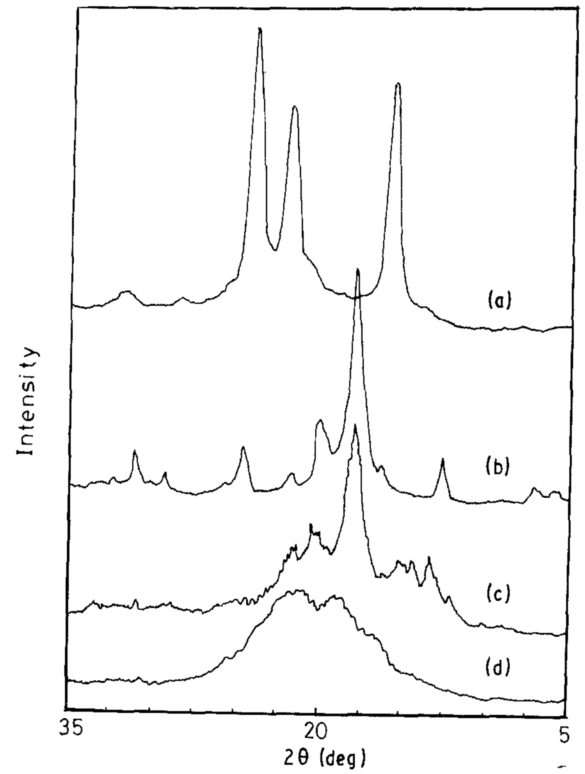


Figure 1 X-ray diffraction patterns of polymers (a) Ia, (b) Id, (c) Ig and (d) If.

Polymers Ia–Ig were insoluble at room temperature in phenol, a mixture of phenol and halogenated solvent such as $CHCl_3$, CCl_4 CH_2Cl_2 in different ratios, and formamide, whereas they were partially soluble in acetone, THF, cyclohexanol and amyl alcohol. The polymers swell in DMF, NMP and dimethylacetamide at 35 °C. In dimethylsulphoxide (DMSO) all polymers dissolved freely at 30 °C. In a protic solvent such as trifluoroacetic acid, H_2SO_4, methanesulphonic acid and dichloroacetic acid, all polymers are easily soluble but undergo a small degradation, which is confirmed by measuring their reduced viscosity. This behaviour may be attributed to the possibility of partial hydrolysis of the ester groups in the main chain of the polymers.

TABLE II Thermal properties of some selected polyamide esters (Ia, Id, If, Ig)

Polymer	Temperature (°C) for various percentages of decomposition					
	5%	10%	20%	30%	40%	50%
Ia	105	200	300	350	370	390
Id	220	250	300	320	340	355
If	205	255	305	330	350	375
Ig	250	290	400	425	450	490

The thermal stabilities of some selected polyamide esters were evaluated by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in air at a heating rate of 10 °C min^{-1}. The TG curves of the polymers are given in Fig. 2, and Table II gives the temperatures for various percentage weight losses. The expected nature of the decomposition of these polyamide esters is an initial loss of adsorbed water below 100 °C, loss of nitrogen from the azo linkage [31], evolution of SO_2, scission of many bonds, all these occurring above 100 °C. The presence of adsorbed water was confirmed from the DTA curve of polyamide ester Id which contains the thianthrene moiety, whereas a sharp endothermic peak is observed at 80 °C in Fig. 3. All polymers showed thermal stability up to 200 °C except polymer Ia, which underwent a remarkable weight loss (about 5%) at 150 °C which may be attributed to the early decomposition of N=N groups with the evolution of nitrogen gas. From Table II, Fig. 2 and using T_{10}, the polymer

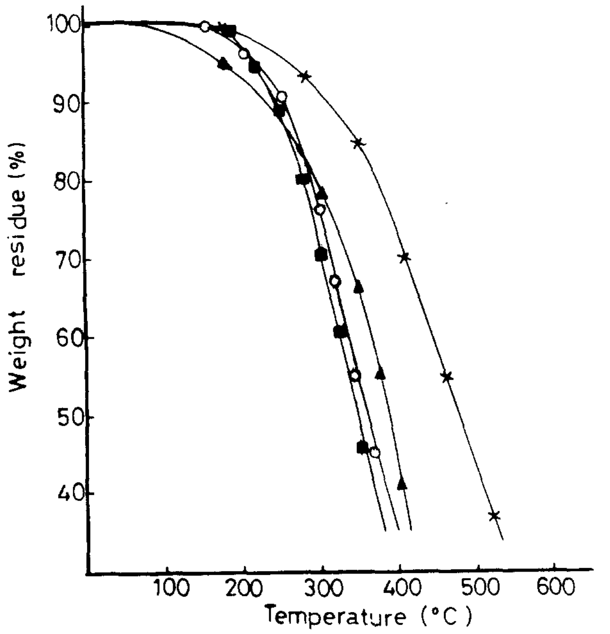


Figure 2 TGA thermograms of polyamide esters (▲) Ia, (■) Id, (○) If and (×) Ig.

decomposition temperature, and comparing the thermal stability of different polymers, it can be inferred that polymer Ig contains the terephthaloyl moiety and is more thermally stable than the other polyamide esters. Therefore, the thermal stability of the polyamide esters could be arranged in the following order: Ig > If > Id > Ia.

References

1. O. VOGL and A. C. KNIGHT, *Macromolecules* **1** (1968) 315.
2. G. S. STAMATOFF and N. K. J. SYMONS, US Pat. 3247168 (1966).
3. S. D. BRUCK, US Pat. 2977 (1961).
4. A. N. ZAV'YALOV, T. A. SOROKINA and T. B. SHABANOVA, *Polym. Sci USSR* **A12** (1970) 2370.
5. S. W. SHALABY, E. M. PEARCE, R. J. FEDERICKS and E. A. TURI, *J. Polym. Sci. Polym. Phys. Ed.* **11** (1973) 1.
6. L. B. SOKOLOV, in "Interfacial Synthesis", Vol. 1, edited by F. Millich and C. E. Carraher Jr (Dekker, New York, 1973).
7. Y. CHATANI, Y. UEDA, H. TADOKORA, W. DEITS and O. VOGL, *Macromolecules* **11** (1978) 636.
8. P. W. MORGAN and T. C. PLETCHER, *J. Polym. Sci. Polym. Chem. Ed.* **18** (1980) 643.
9. J. P. HUMMEL and P. J. FLORY, *Macromolecules* **13** (1980) 497.
10. R. J. GAYMANS, V. S. VENKATRAMAN and J. SCHUIJER, *J. Polym. Sci. Polym. Chem. Ed.* **22** (1984) 1383.
11. S. A. RHONE-POULENE, Fr. Pat. 1371391 (1964); *Chem. Abs.* **62** (1965) 7927 f.

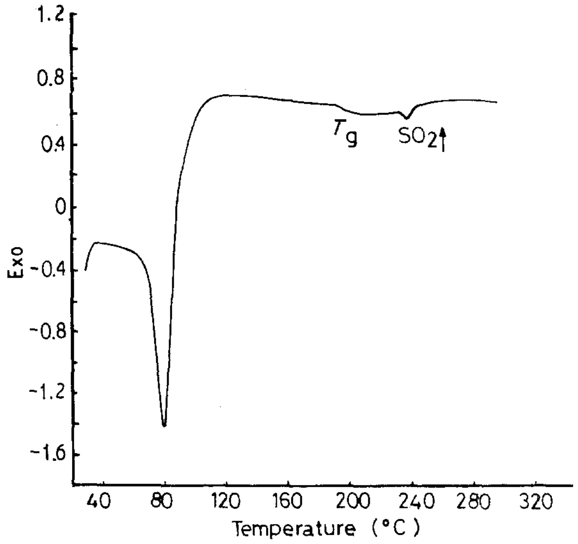


Figure 3 DTA curves of polyamide esters Id.

12. T. A. SAKHAROVA, L. E. KALININA, A. A. AVILOV, L. A. SUKHAREVA, N. I. SERAYA and A. I. ZEMTSEV, *Izv. Vyssh. Ucheb. Zaved., Tekhnol. Legk. Prom.* **6** (1972) 57; *Chem Abs.* **78** (1973) 137166 p.
13. T. REETZ and J. W. BRITIAN, US Pat. 3719639 (1973).
14. H. JUERGEN and M. RLAND, Ger. Offen. 2852785 (1979); *Chem. Abs.* **91** (1979) 158503 e.
15. G. A. YANGOL, G. A. CHERNYAVSKAYA and N. I. SHCHEPETKINA, *Kompoz. Polim. Matter* **7** (1980) 34.
16. F. J. STEPHEN, J. H. SMITH and H. M. MESHREKI, US Pat. 4645853 (1987).
17. A. J. EEAST, L. F. CHARBONNEAU and G. W. CALUNDANN, to Celanese Corporation, US Pat. 4330457 (1982).
18. *Idem., ibid.* 4339375 (1982).
19. *Idem., ibid.* 4351917 (1982).
20. *Idem., ibid.* 4351918 (1982).
21. *Idem., ibid.* 4355132 (1982).
22. A. H. KAHN, J. E. MCINTYRE and H. A. MILBURN, *Polymer* **24** (1983) 1610.
23. M. A. OSMAN, *ibid.* **28** (1987) 713.
24. R. SINTA, R. A. GAUDIANA and H. G. ROGERS, *J. Macromol. Sci. Chem. A* **28** (1989) 773.
25. N. KORBBLUM and D. C. KENDALL, *J. Amer. Chem. Soc.* **74** (1952) 5782.
26. M. L. TOMLINSON, *J. Chem. Soc.* (1946) 756.
27. M. SRINIVASAN and J. GOPAL, *Chem. Ind.* (1985) 339.
28. S. PREMA and M. SRINIVASAN, *Eur. Polym. J.* **23** (1980) 897.
29. D. D. PERRIN, W. L. F. ARMAREGO and D. R. PERRIN, "Purification of Laboratory Chemicals", 2nd Edn (Pergamon Press, New York, 1980).
30. L. MANDELKERN, "Crystallization of Polymers" (McGraw-Hill, New York, 1964).
31. J. E. RIORDAN and H. S. BLAIR, *Polymer* **20** (1979) 196.

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