

## Synthesis and Characterization of Polyesteramides

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### Summary

Polyesteramides have been synthesized from N,N'-bisoxalamide, p-aminophenol, iso- and tere-phthaloyl chlorides. Through ring-opening addition reaction, a bisphenolamide was first formed; it was then polycondensed with acid chlorides to produce polyesteramides, with an ordered sequence. The polymers were fully characterized by elemental analysis, infrared and electronic spectra, solubility in various solvents as well as inherent viscosity measurements. Thermal behaviour of the polymers were determined by thermogravimetric analysis in nitrogen atmosphere.

### Introduction

Polycondensation reaction between a diacid chloride and a hydroxyamine generally results in the formation of polyesteramides. Laakso and Reynolds (1) have demonstrated the synthesis of polyesteramides through ester interchange between glycol and diesteramides. Recently, random, aliphatic polyesteramides have been synthesized from hexanedioyl chloride, 1,6 - diaminohexane, and 1,10-decanediol (2). Panaitov (3) reported the synthesis of both random and ordered polyesteramides from aminophenols and diacid chlorides through interfacial polycondensation; the more reactive amine group, in this case, reacts with an acid chloride to produce first an intermediate containing amide linkage. The fact that the difference in reactivity of an acid chloride towards aminophenol can be used preferentially in the preparation of amides, was indicated by Lyman and Jung (4); hence, ordered polyamides could be easily prepared by this route. Malescot and Jasse (5-7) introduced 11-aminoundecanoic acid, in part, along with the dibasic acid in the synthesis of polyester precursor leading to the formation of polyesteramides; polyesteramides have also been reported by the ring - opening polyaddition reaction of bisoxazolines with dicarboxylic acids or aminoacids (8-10). Imai (11) and Preston (12) have reported the synthesis of ordered polyesteramides through the initial formation of bisphenolamides, and then polycondensation with diacid chlorides, by both solution and interfacial techniques. Literature (13) presents a report on the synthesis of unsaturated polyesteramides from fumaroyl chloride and aminophenols. In this article we report and discuss the synthesis and characterization of two polyesteramides from N,N'-bisoxalamide, p-aminophenol and iso- and tere-phthaloyl chlorides.

### Experimental

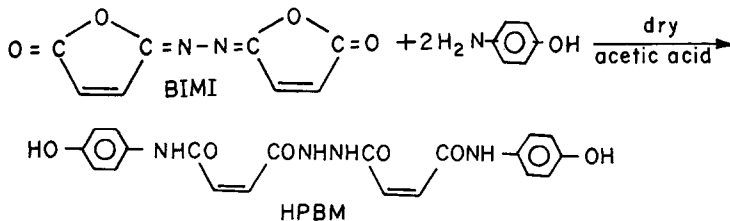
Maleic anhydride, hydrazine hydrate, trifluoroacetic anhydride, all AnalaR BDH samples, were used without further purification. Methylene chloride, acetic acid, tetrahydrofuran (THF), N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), N,N-dimethyl-formamide (DMF), chloroform, triethylamine and thionyl chloride were purified by employing standard procedures.

Iso-and tere- phthaloyl chlorides (IPC and TPC) were prepared by refluxing respective phthalic acids (25 g) with thionyl chloride (100 mL) in presence of a few drops of pyridine to get a clear solution. The unused thionyl chloride was removed by distillation under reduced pressure. The products IPC and TPC on recrystallization from dry hexane afforded white crystals with m.p. 43 and 74°C, respectively.

N,N'-Bis(isomaleimide) (BIMI) was prepared from hydrazine hydrate and maleic anhydride; the yellow crystallines after recrystallization from DMF, had an m.p. 260°C (lit. m.p. 260°C) (14). BIMI in acetonitrile has  $\lambda_{\max}$  at 292 nm. BIMI (9.6 g, 0.05 mol) was then stirred with p-aminophenol (10.9 g, 0.1 mol) in dry acetic acid (300 mL) for 24 h under nitrogen at room temperature. The dark, yellow product was collected, washed with ethanol, ether, and air-dried. The resulting compound, 1,2-bis [(p-hydroxyanilide) of 3-carboxyacryloyl] hydrazine (HPBM) was recrystallized from aqueous DMF (m.p. 203°C).

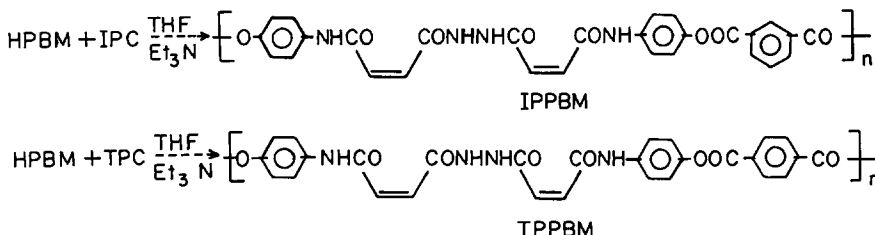
Anal. Calc. for  $C_{20}H_{18}N_4O_6$  : C, 58.54%; H, 4.39%; N, 13.66%

Found: C, 59.02%; H, 4.35%; N, 13.75%.



### Polymerization

Both solution and interfacial methods were adopted for polycondensation reaction between HPBM and IPC/TPC, as shown below.



### Solution Method

A two-necked polymerization kettle with a side nitrogen inlet was fitted with a mechanical stirrer and a drying tube. Into the kettle were placed HPBM (1.23 g, 0.003 mol), triethylamine (0.66 g, 0.0066 mol) and THF (20 mL) which had been deaerated and maintained under nitrogen. The contents were slowly stirred and were cooled to 0°C in an ice-bath, and to this was added IPC (0.609 g, 0.003 mol). The ice-bath was removed after 5 min and the stirring was continued for 24 h at room temperature to complete the polymerization. The reaction mixture was poured into 500 mL of water with stirring and the precipitated polyester maleamide was collected by filtration and dried on the filter. The drying was completed in vacuum at 65-70°C for 3 days. A similar procedure was employed for TPPBM using TPC in place of IPC.

### Interfacial method

Into a two-necked kettle with a side nitrogen inlet fitted with a mechanical stirrer was placed HPBM (2.05 g, 0.005 mol) and dissolved in NaOH (5 mL of 1 N) and diluted with water (40 mL). A solution of IPC (1.015 g, 0.005 mol) in chloroform (7 mL) was added to the aqueous solution and the mixture was stirred rapidly for 15 min. The polymer was precipitated by the removal of chloroform under reduced pressure and dried in vacuum at 65-70°C. The same procedure was followed for TPPBM with TPC.

### Characterization

Elemental analysis was carried out in a Perkin-Elmer 240 B analyzer. The infrared (KBr) and electronic spectra (concentrated sulfuric acid solution) were recorded on Perkin-Elmer 598 IR spectrophotometer and Carl Zeiss UV-VIS specord. The solubilities of the polymers (0.005 g in 1 mL) in various solvents were determined. The inherent viscosity ( $\eta_{inh}$ ) was measured using a modified Ubbelohde viscometer at 25 ± 0.1°C having a flow time for the solvent exceeding hundred seconds. Thermal behaviour of the polymers was followed by thermogravimetry using a Perkin-Elmer TGS-2 instrument under nitrogen at a heating rate of 20°C/min.

### Results and Discussion

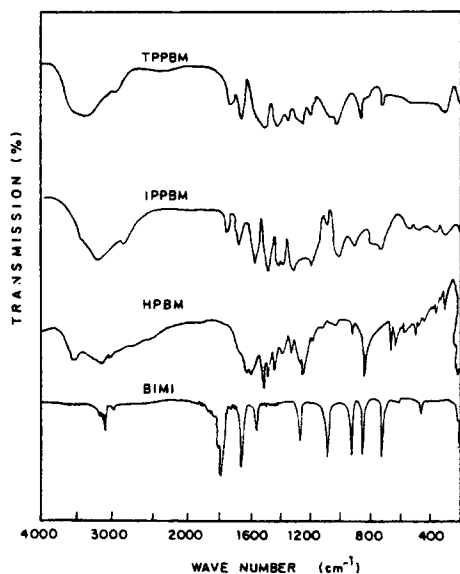
BIMI undergoes nucleophilic attack at the carbonyl function by the amine group of p-aminophenol, the isoimide ring breaks up producing an amide and imidol; the latter immediately tautomerizes to another amide group and thus a diphenolamide (HPBM) results. HPBM is soluble in NaOH but not in hydrochloric acid indicating the presence of free phenol and not amine groups in it.

In the polymerization process the free phenolic groups present in HPBM have been converted into ester moieties by condensation with iso- and tere- phthaloyl chlorides. The experimental results are summarized in Table 1.

Table 1. Yield, Viscosity, and Elemental Analysis Data on Poly-termaleamides

Polymer	Yield %	$\eta^e$ dl/g	Repeat unit	Elemental Analysis
IPPBM				
(a)	92	0.13	$C_{28}H_{20}N_4O_8$	Calc., %: C, 62.22; H, 3.70; N, 10.37
(b)	85	0.12		Found, %: C, 61.95; H, 3.72; N, 10.50
TPPBM				
(a)	95	0.15	$C_{28}H_{20}N_4O_8$	Calc., %: C, 62.22; H, 3.70; N, 10.37
(b)	90	0.14		Found, %: C, 62.70; H, 3.71; N, 10.32

- (a) Solution polymerization was carried out with 0.003 mol of each monomer and 0.0066 mol of triethylamine in 20 mL of THF at 25°C.
- (b) Interfacial polymerization was carried out with 0.005 mol of HPBM in 5 mL of 1N NaOH and 0.005 mol of diacid chloride in 7 mL chloroform.
- <sup>e</sup> Inherent viscosity measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 25°C.



The structures of the compounds are elucidated primarily by IR spectra. On ring-opening reaction the characteristic IR frequencies (Figure 1) at  $1790\text{ cm}^{-1}$  (five-membered lactone ring) and  $1665\text{ cm}^{-1}$  (C=N) of BIMI have disappeared and new peaks at  $1600\text{ cm}^{-1}$  (assigned to the overlap of C=C and C=O stretchings),  $3125\text{ cm}^{-1}$  (N-H stretching) and  $3560\text{ cm}^{-1}$  (O-H stretching) for HPBM have been observed instead.

Fig. 1. Infrared absorption spectra of BIMI, HPBM, IPPBM, & TPPBM.

The polymers were obtained in moderate to excellent yields and the  $\eta_{inh}$  ranges from 0.12 to 0.15. The results of elemental analysis are consistent with the expected structures.

Table 2. Solubility of Polyestermaleamides in various solvents

Solvent Polymer	H <sub>2</sub> SO <sub>4</sub>	NMP	DMSO	DMF	HCOOH	m-Cresol	THF	EtOH	Me <sub>2</sub> CO
IPPBM(s)	++	+	+	+	-	-	±	-	-
IPPBM(i)	++	+	+	+	-	-	±	-	-
TPPBM(s)	++	+	+	+	-	-	±	-	-
TPPBM(i)	++	+	+	+	-	-	±	-	-

's' refers to solution method; 'i', interfacial method; '++', soluble at room temperature; '+', soluble on heating; '±', swells; '-', insoluble.

Table 2 shows the data on solubility of polymers in various solvents. These polymers are found to be insoluble in common organic solvents such as THF, formic acid, ethanol, and acetone but freely soluble only in concentrated sulfuric acid. The IR spectra of the polymers are presented in Figure 1. Both the polymers have absorptions at 3400 - 3200, 1730 and  $\sim$ 1660 cm<sup>-1</sup>, respectively for amide-NH, ester-carbonyl and amide-carbonyl stretchings (15). The absorptions at  $\sim$ 720 cm<sup>-1</sup> (C-H bending deformation) indicates the presence of cis-configuration about the C-C double bond and the absence of absorption at  $\sim$ 970 cm<sup>-1</sup> (for trans-form) also corroborates this view (15,16).

In the electronic spectra the following absorptions ( $\lambda_{max}$  in nm) have been observed: IPPBM (195, 220, 360) and TPPBM (198, 234, 357). It is to be pointed out that TPPBM (234 nm), absorbs at higher wavelength compared to IPPBM (220 nm); this can be attributed to the extension of conjugation through the para oriented phenylene rings in TPPBM, which is not possible to the same extent in IPPBM.

Thermogravimetric curves for IPPBM and TPPBM are shown in Figure 2. The integral procedural decomposition temperatures (ipdt's) T\*<sub>A</sub>, Characteristic end of volatilization temperature and T\*, half-volatilization temperature, were computed following the procedure of Doyle (17). The data on initial decomposition, 10%-weight-loss, and rapid-weight-loss temperatures and T\*<sub>A</sub> and T\* are listed in Table 3. From the table it is seen that all these values for IPPBM are less compared to those for TPPBM. This indicates the higher stability of tere-phthalic acid-derived polyestermaleamide over the iso-phthalic acid-derived polymer (18) and the higher stability of TPPBM may be attributed to its para orientation of aromatic ring substituents in the right-end portion of the repeat unit. This conclusion is further strengthened by  $\lambda_{max}$  values.

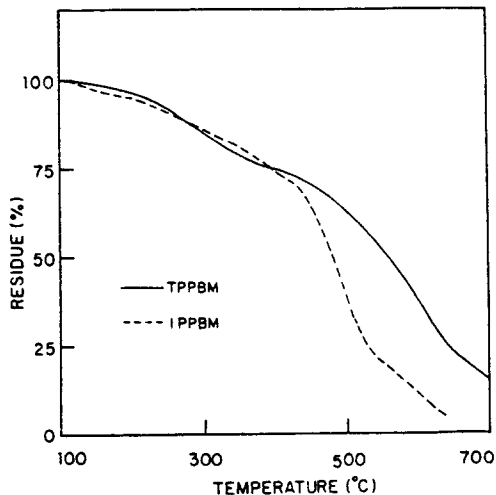


Fig. 2. Thermogravimetric curves for IPPBM and TPPBM in nitrogen atmosphere.

Table 3. Thermal Analysis Data on Polyesteramideamides in Nitrogen Atmosphere

Polymer	Initial decomposition temperature, °C	10%-weight-loss temperature, °C	Rapid Weight-loss temperature, °C	ipdt T* <sub>A</sub> , °C	T*, °C
IPPBM	125	260	500	452.4	399.3
TPPBM	130	265	550	517.8	439.6

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