

Preparation of Polyesteramides Based on Aliphatic Amine-Containing Phenol Derivatives via Interfacial Polymerization

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Abstract: A series of polyesteramides with randomly introduced ester/amide group ratio of 50/50 were newly synthesized by reacting terephthaloyl chloride, isophthaloyl chloride and sebacoyl chloride with tyramine and tyrosine. The polymerization was carried out by interfacial polymerization in two phase solvent systems, which gave various polyesteramides with moderate molecular weights in good yields. The chemical structures of the polymers were confirmed by ^1H NMR, IR and elemental analysis. Tyrosine based polyesteramide was degraded thermally around 290°C to give the polyesteramide, which was obtainable from tyramine. Thermal stability and degradation behaviors were examined by differential scanning calorimetry and thermogravimetric analyses.

Keywords: polyesteramide, tyramine, tyrosine, decarboxylation, interfacial polymerization.

Introduction

Polyesteramides combine the good properties of polyester and polyamide, such as high melting temperature, fast crystallization, good mechanical properties, good solvent resistance and low water absorption.^{1,2}

The interesting properties of polyarylateamides as a building block for the construction with arylate and aliphatic amide unit have been long appreciated. Polyarylateamides prepared from tyramine and tyrosine deserve special attention because they are easily accessible via interfacial condensation polymerization and display a desirable pattern of thermal and mechanical properties.³⁻⁵ These polyarylateamides can be distinguished from conventional polyesteramide in undergoing appreciable degradation under high temperature.⁶⁻⁸

Polyesteramides with mixture of poly(tetramethylene oxide) and 1,5-pentanediol as soft segments were prepared from *N,N*-bis(*p*-carbomethoxybenzoyl)butadienediamine as crystalline segments and their thermal properties were evaluated.⁹ Also the polyesteramides based on *L*-tartaric acid were obtained using 1,6-hexanediamine, 1,6-hexanediol and 2,3-dimethoxy-*L*-tartaric acid, and succinic acid as building blocks. They were degraded by aqueous buffer of pH 7.4.¹⁰

As pointed out by Wallenfels,¹¹ a $>\text{C}=\text{C}(\text{CN})_2$ group can be considered structurally equivalent to a $>\text{C}=\text{O}$ group in reaction where oxygen is exerting an electron-withdrawing effect. By this analogy, poly(enamino-enaryloxynitriles)s are

considered analogous to polyesteramides. As a part of our studies addressed to the development of new polyenamino-nitriles and polyenaryloxynitriles based on aliphatic amine-containing phenol derivatives, we have already reported on poly(enamino-enaryloxynitriles)s.¹²⁻¹⁷

This article deals with new polyesteramides obtained by reaction of tyramine and tyrosine with aromatic and aliphatic acid chloride via interfacial polymerization. The study of thermal behaviors of new polyesteramides is presented.

Experimental

Materials. Tyramine and tyrosine (Aldrich Chem. Co.) were purified by recrystallization from ethanol/water (2/1) solution. Terephthaloyl chloride and isophthaloyl chloride were purified by sublimation. Sebacoyl chloride was purified by vacuum distillation. 1,2-Dichloroethane was purified by distillation after drying with calcium hydride. Nitrobenzene and *n*-tetrabutyl ammonium chloride (TBAC) was used without further purification.

Instruments. ^1H NMR spectra were recorded on a Varian Gemini 2000 spectrometer. Fourier-transform infrared (FT-IR) spectra were taken on a Midac model M-1200 spectrometer. Elemental analysis data were obtained with Yanaco MT-3 CHN analyzer. Differential scanning calorimetry measurements were performed on a Perkin-Elmer DSC 7 under nitrogen at a heating rate of $10^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) measurements were carried out on a Shimadzu TGA 50 thermal analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen.

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Preparation of *p*-[2-(Benzoylamino)ethyl]phenyl benzoate (1). In a stainless steel jar, was placed a solution of benzoyl chloride (0.70 g, 5 mmol) and TBAC (5 mol% of benzoyl chloride) dissolved in 1,2-dichloroethane (20 mL). A solution of tyramine (0.34 g, 2.5 mmol) and sodium hydroxide (0.24 g, 6 mmol) dissolved in water (20 mL) was added dropwise with vigorous stirring under nitrogen. The reaction mixture was moved to a round bottomed flask and maintained at 50°C for 2 h with vigorous stirring. After the solvent was evaporated, the powdery product was washed with distilled water several times and recrystallized from acetonitrile to give pale yellow powder, and dried under vacuum at 50°C for 12 h.

1: Yield 86%. mp 158. IR (KBr, cm^{-1}) 3340 (s, amide *N-H*), 3080 (aromatic *C-H*), 2925-2880 (aliphatic *C-H*), 1735 (s, arylate *C=O*), 1685 (s, amide *C=O*), 1260-1110 (*C-O* and *C-N*). $^1\text{H NMR}$ (DMSO- d_6 + CDCl_3): δ 9.35 (br, 1 H, *N-H*), 7.72-7.25 (m, 10 H, 2 *Ph*), 7.21-6.87 (m, 4 H, -*Ph-O*-), 3.23 (m, 2 H, - $\text{CH}_2\text{-NH}$ -), 2.42 (t, 2 H, - Ph-CH_2 -). *Anal.* Calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_3$ (345.40): C, 76.50%; H, 5.54%; N, 4.06%. Found: C, 76.36%; H, 5.60%; N, 4.02%.

Preparation of *p*-[2-(Benzoylamino-1-carboxyethyl)phenyl benzoate (2). In a stainless steel jar, was placed a solution of benzoyl chloride (0.70 g, 5 mmol) and TBAC (5 mol% of benzoyl chloride) dissolved in 1,2-dichloroethane (20 mL). A solution of tyrosine (0.45 g, 2.5 mmol) and sodium hydroxide (0.40 g, 10 mmol) dissolved in water (20 mL) was added dropwise with vigorous stirring under nitrogen. The reaction mixture was moved to a round bottomed flask and maintained at 50°C for 2 h with vigorous stirring. After the solvent was evaporated, the resulting slurry was neutralized with excess 0.1 N HCl. The powdery product was washed with distilled water several times and recrystallized from acetonitrile to give pale yellow crystals, and dried under vacuum at 50°C for 12 h.

2: Yield 82%. mp 263°C(dec.). IR (KBr, cm^{-1}) 3385 (br, *OH*), 3320 (br, *N-H*), 3060 (aromatic *C-H*), 2890 (aliphatic *C-H*), 1735, 1705 (s, *C=O*), 1678 (amide *C=O*), 1250-1100 (*C-O* and *C-N*). $^1\text{H NMR}$ (DMSO- d_6 + CDCl_3) δ 10.8 (br, 1 H, *OH*), 9.26 (br, 1 H, *N-H*), 7.75-7.20 (m, 10 H, 2 *Ph*-), 7.21-6.85 (m, 4 H, -*Ph-O*-), 3.54 (s, br, 1 H, - $\text{CH}(\text{COO-})\text{-NH}$ -), 2.47 (t, 2 H, - Ph-CH_2 -). *Anal.* Calcd for $\text{C}_{23}\text{H}_{19}\text{N}_1\text{O}_5$ (389.41): C, 69.99%; H, 4.92%; N, 3.60%. Found: C, 70.06%; H, 4.89%; N, 3.57%.

Representative Interfacial Polymerization of Tyramine with Terephthaloyl chloride. A solution of terephthaloyl chloride (2.00 g, 9.84 mmol) and TBAC (10 mol% of terephthaloyl chloride) in 20 mL of nitrobenzene was transferred to a blender. Tyramine (1.35 g, 9.84 mmol) and sodium hydroxide (0.80 g, 20 mmol) in 20 mL of water was added quickly to the blender at full speed and maintained for 3 min. After the reaction, 100 mL of *n*-hexane was added to the reaction mixture, and the precipitate was filtered and washed with water. The resulting polymer was purified by

Soxhlet extraction with boiling methanol for a day and dried under vacuum at 80°C for 12 h.

Similar synthetic procedures were applied to the other polyesteramides using isophthaloyl chloride and sebacoyl chloride.

3: Yield 86%. IR (KBr, cm^{-1}) 3340 (*N-H*), 3070 (aromatic *C-H*), 2970 (aliphatic *C-H*), 1735 (*C=O*), 1684 (amide *C=O*), 1280-1100 (*C-O* and *C-N*). *Anal.* Calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_3$ (267.28): C, 71.90%; H, 4.90%; N, 5.24%. Found: C, 71.65%; H, 4.82%; N, 5.31%.

4: Yield 92%. IR (KBr, cm^{-1}) 3335 (*N-H*), 3080 (aromatic *C-H*), 2980 (aliphatic *C-H*), 1735 (*C=O*), 1685 (amide *C=O*), 1260-1100 (*C-O* and *C-N*). $^1\text{H NMR}$ (DMSO- d_6 + CDCl_3): 9.19 (br, 1 H, *N-H*), 8.64-7.62 (m, 4 H, - CO-Ph-CO -), 7.22-6.86 (m, 4 H, -*Ph-O*-) 3.20 (br, 2 H, - $\text{CH}_2\text{-NH}$ -), 2.42 (br, 2 H, - Ph-CH_2 -). *Anal.* Calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_3$ (267.28): C, 71.90%; H, 4.90%; N, 5.24%. Found: C, 71.59%; H, 4.80%; N, 5.29%.

5: Yield 94%. IR (KBr, cm^{-1}) 3340 (*N-H*), 3080 (aromatic *C-H*), 2980 (s, aliphatic *C-H*), 1735 (*C=O*), 1685 (amide *C=O*), 1260-1110 (*C-O* and *C-N*). $^1\text{H NMR}$ (DMSO- d_6 + CDCl_3): 9.25 (br, 1 H, *N-H*), 7.23-6.86 (m, 4 H, -*Ph-O*-), 3.34 (br, 2 H, - $\text{CH}_2\text{-NH}$ -), 2.40 (br, 2 H, - Ph-CH_2 -), 2.3 (m, 4 H, 2 CO-CH_2 -), 1.82 (m, 12 H, -(CH_2) $_6$ -). *Anal.* Calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_3$ (303.40): C, 71.26%; H, 8.31%; N, 4.62%. Found: C, 71.37%; H, 8.11%; N, 4.55%.

Representative Interfacial Polymerization of Tyrosine with Terephthaloyl chloride. A solution of terephthaloyl chloride (2.0 g, 9.84 mmol) and TBAC (10 mol% of terephthaloyl chloride) in 20 mL of nitrobenzene was transferred to a blender. Tyrosine (1.35 g, 9.84 mmol) and sodium hydroxide (1.60 g, 40 mmol) in 20 mL of water was added quickly to the blender at full speed and maintained for 3 min. The reaction mixture was moved to a round bottomed flask and maintained at 50°C for 2 h with vigorous stirring. After the solvent was evaporated, the resulting slurry was neutralized with excess 0.1 N HCl. The resulting polymer was purified by Soxhlet extraction with boiling hexane for a day and dried under vacuum at 80°C for 12 h. Similar synthetic procedures were applied to the other polyesteramides using isophthaloyl chloride and sebacoyl chloride.

6: Yield 91%. IR (KBr, cm^{-1}), 3380 (s, br, *OH*), 3325 (br, *N-H*), 3015 (aromatic *C-H*), 2980 (aliphatic *C-H*), 1735 (s, *C=O*), 1715 (s, *C=O*), 1680 (s, amide *C=O*), 1250-1080 (*C-O* and *C-N*). $^1\text{H NMR}$ (DMSO- d_6 + CDCl_3) δ 10.41 (br, 1 H, *OH*), 9.18 (br, 1 H *N-H*), 7.83 (m, 4 H, -*Ph*-), 7.21-6.85 (m, 4 H -*Ph-O*-), 3.67 (br, 1 H, - $\text{CH}(\text{COO-})\text{-NH}$ -), 2.46 (br, 2 H - Ph-CH_2 -). *Anal.* Calcd for $\text{C}_{17}\text{H}_{13}\text{NO}_5$ (311.29): C, 65.60%; H, 4.21%; N, 4.50%. Found: C, 65.42%; H, 4.23%; N, 4.48%.

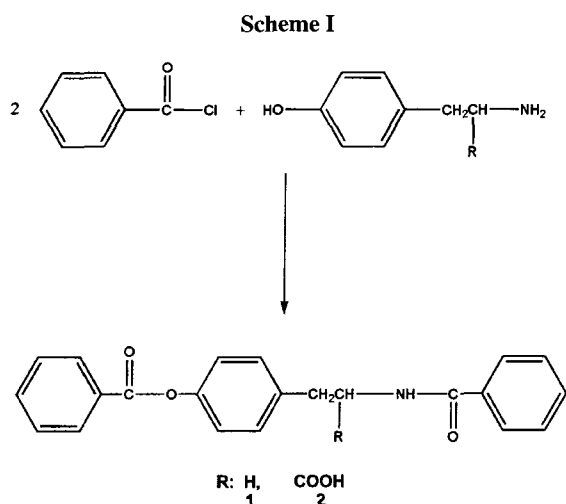
7: Yield 96%. IR (KBr, cm^{-1}), 3385 (s, br, *OH*), 3340 (br, *N-H*), 3010 (aromatic *C-H*), 2980 (aliphatic *C-H*), 1735 (s, *C=O*), 1715 (s, *C=O*), 1685 (s, amide *C=O*), 1260-1100 (*C-O* and *C-N*). $^1\text{H NMR}$ (DMSO- d_6 + CDCl_3) δ 10.38 (br, 1 H, *OH*), 9.21 (br, 1 H *N-H*), 8.61-7.64 (m, 4 H, -*Ph*-), 7.22-

6.84 (m, 4 H *-Ph-O-*), 3.64 (br, 1 H, *-CH(COO-)-NH-*), 2.42 (br, 2 H *-Ph-CH₂-*). *Anal.* Calcd for C₁₇H₁₃NO₅ (311.29): C, 65.60%; H, 4.21%; N, 4.50%. Found: C, 65.47%; H, 4.18%; N, 4.45%.

8: Yield 89%. IR (KBr, cm⁻¹) 3400 (br, *COOH*), 3340 (br, *N-H*), 3020 (aromatic C-H), 2970 (s, aliphatic C-H), 1735 (s, *C=O*), 1716 (s, *C=O*), 1685 (amide *C=O*), 1250-1110 (C-O and C-N). ¹H NMR (DMSO-*d*₆+CDCl₃): 10.12 (s, 1 H, *COOH*), 9.35 (br, 1 H, *N-H*), 7.20-6.86 (m, 4 H, *-Ph-O-*), 3.68 (br, 2 H, *-CH(COOH)N-*), 2.42 (br, 2 H, *-Ph-CH₂-*), 2.31 (m, 4 H, 2 CO-*CH₂-*), 1.82 (m, 12 H, *-(CH₂)₆-*). *Anal.* Calcd for C₁₉H₂₅NO₅ (347.41): C, 65.69%; H, 7.25%; N, 4.03%. Found: C, 65.13%; H, 7.16%; N, 4.09%.

Results and Discussion

Model Reaction. A model compound study was performed before polymer synthesis to obtain information regarding the feasibility of the reaction for polymer formations and to obtain model compounds for comparison with the polymers as shown in Scheme I. The reactions of benzoyl chloride with tyramine and tyrosine were carried out in the presence of sodium hydroxide. The model reaction was based on the procedure for the interfacial technique, and proceeded rapidly



in a two phase solvent system leading to the formation of good yields of *p*-[2-(benzoylamino)ethyl]phenyl benzoate (**1**) and *p*-[2-(benzoylamino-1-carboxyethyl)]phenyl benzoate (**2**).

The reactivity of aliphatic amine (RNH₂) toward acid chloride was similar to phenoxide (PhO⁻) as an ability of the conjugated base.¹⁸

Polymerization. Polymerization of corresponding acid chloride with tyramine and tyrosine was carried out by the interfacial polymerization technique, *n*-tetrabutyl ammonium chloride being used as a phase transfer agent in a two phase solvent system as shown in Scheme II.¹⁹⁻²² At this point it was thought that it might be possible to prepare polymers by reacting aminoalkyl-containing phenol derivatives with acid chlorides. However, it has possibility that acid chloride may be attacked by two phenoxides or two amines. At the present time, it is difficult, according to NMR and IR spectra, to determine the structures of polymers **3**, **4**, and **5**, obtained by both phenoxide and aliphatic amine attack.

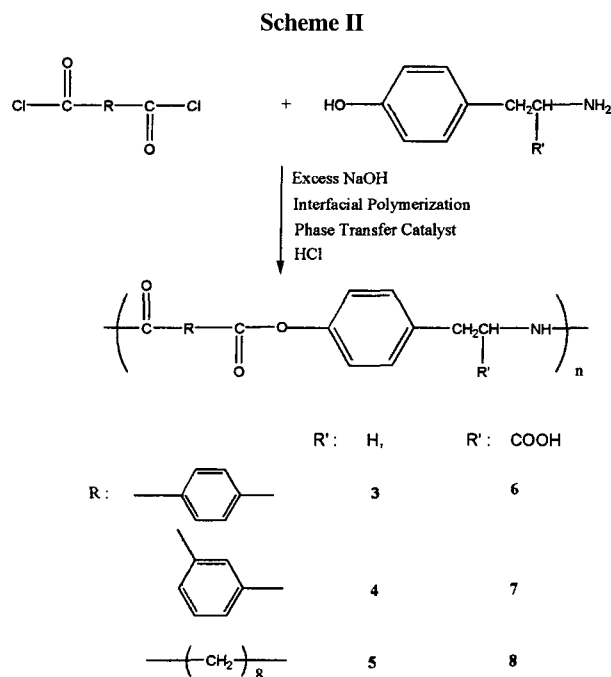


Table I. Results of Polymerization of Various Acid Chlorides and Alkyamine-Containing Phenol Derivatives

Polymers	Monomers ^a	MW ($\times 10^{-4}$) ^b	MWD	η_{inh}^c	Yield (%)
3	TC, tyramine	1.05	1.8	-	86
4	IC, tyramine	1.47	1.7	0.56	92
5	SC, tyramine	2.10	1.5	0.92	94
6	TC, tyrosine	1.98	1.6	0.84	91
7	IC, tyrosine	2.23	1.9	0.81	96
8	SC, tyrosine	1.25	1.8	0.46	89

^aTC, terephthaloyl chloride; IC, isophthaloyl chloride; SC, sebacoyl chloride.

^bMolecular weights were measured with Waters HPLC using Three columns (3, 4 and 5 Å) by using THF as eluent at 30 °C.

^cInherent viscosity was determined by Cannon-Ubbelode viscometer in 1.0 gL⁻¹ in DMF at 20 °C.

The results of polymerizations are summarized in Table I along with viscosity and molecular weight. The polymers obtained here were identified as polyesteramides by comparing IR spectra with those of model compound **1** (Figure 1(a)) and **2**. In the IR spectra of the polymers, **3-8**, characteristic absorption bands of N-H, C=O, amide C=O and C-O were exhibited at 3420, 1735, 1680 and 1250-1100 cm^{-1} , respectively as shown in Figure 1(b). Polyesteramide **6-8** showed an additional strong carbonyl absorption band at 1715 cm^{-1} corresponding to carboxyl group (Figure 1(c)). In the ^1H NMR spectrum of polymer in the Figure 2, alkyl protons exhibited broad peaks at 3.20 and 2.48 ppm. In the cases of model compound **1** and polymer **4**, the phenyl proton in the fragment of acid chloride appeared at 8.64-7.62 ppm, whereas those of tyramine were present at 7.21-6.82 ppm. Elemental analysis also supported the formation of the model compounds, and polymers **3-8** matched well with the calculated data.

Solubility. The solubility of polymers was investigated. Table II presents the solubility of polyesteramide. Most polymers exhibited solubility in polar aprotic solvents such as *N*-methyl pyrrolidinone (NMP), *N,N*-dimethylformamide, dimethylsulfoxide and *N,N*-dimethylacetamide, with the exception of **3** which remained insoluble in NMP. Upon comparison of the structures of polymers **3** and **4**, we notice that the polymer **3** has 1,4-entrainment about the benzene ring, which can lead to better packing of the chains. Another reason for the lack of this solubility in the polymer **3** is more crystalline and consequently the polymer chains are less mobile. Especially, all the polyesteramides showed fairly good solubility in NMP-LiCl. Alkyl-containing polyarylateamide displayed better solubility than previously reported rigid aromatic polyarylate and polyamide.¹⁹ But the polymers **6**, **7** and **8** exhibited solubility in acetone, chloroform, THF and 1,2-dimethoxyethane and fairly good solubility in polar aprotic solvents at ambient temperature or on slight heating. But the polyesteramides **6**, **7** and **8** were dissolved or swelled in aqueous alkaline solution.

Interfacial polymerization gave the polymers of moderate molecular weights judging from the data of viscosity and GPC. The polymers obtained from interfacial polymerization possessed inherent viscosity of 0.46-0.92 dL/g. Average

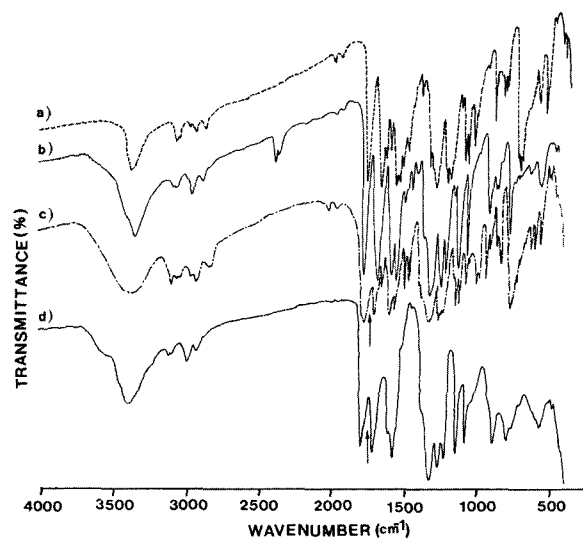


Figure 1. IR spectra of a) **1**, b) polymer **3**, c) polymer **6**, and d) polymer **6** after curing at 290 °C.

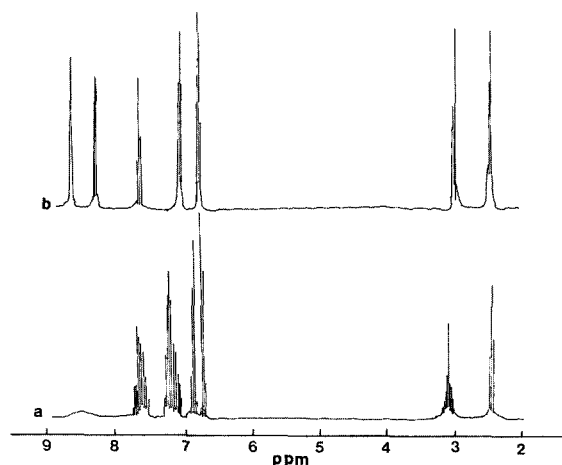


Figure 2. NMR spectra of a) **1** and b) polymer **4**.

molecular weight was 10,500-22,300. The alkyl-containing polymer **5** showed high molecular weight of 21,000. Tough films of polymers **3** and **5**, which were somewhat resilient,

Table II. Solubility Properties of Polymers in Various Solvents

Solvents Polymers	NMP	DMSO	EtOH	<i>m</i> -Cresol	THF	Acetone	Toluene
3	--	--	--	--	-	-	-
4	++	++	--	++	-	-	-
5	-	-	--	+	-	-	-
6	++	++	--	+	-	-	-
7	++	++	--	-	-	-	-
8	++	++	++	++	++	+	-

--, insoluble; -, slightly soluble; +, soluble; ++, very soluble.

could be cast from its solution in these solvents. When the films were cast by allowing the solvents to evaporate from solution on a glass plate, films of polymer **5** adhered very strongly to glass surface.

Thermal Properties. Differential scanning calorimetry was used as a tool in characterizing the thermal behaviors of polyesteramides prepared in this experiment. The DSC data are summarized in Table III. When the model compounds **1** and **2** were heated in a capillary tube, model compound **1** melted at about 157-159°C, and the model compound **2** melted and decomposed at around 263°C.

In a series of tyramine polymers, a melting transition occurred without decomposition as shown in Figure 3(a). In the case of DSC traces of polymer **3**, endothermic peak around 282°C was coincident with the resulting temperature determined in a capillary tube. The polymer **5** derived from long-chain aliphatic moiety exhibited well-defined melting transition around 150°C as shown in Figure 4(a). Polymers **3-5** showed a glass transition temperature as well as melting temperature. Higher transition temperature was observed for polymers incorporating aromatic units. We observed higher values of glass transition temperature for polymer **3** and **4** than **5**.

Polymer **6** derived from tyrosine showed a different thermal behavior as seen in Figure 2. At a temperature of the exotherm, detectable weight loss of the polymer was observed (Figure 3(b), (d)). The polymers began to lose weight at 230-238°C in nitrogen. Carbon dioxide was evolved and the weight loss was about 25% according to the TGA traces (Figure 4(d)).

When the polymer **6** was heated at 290°C in nitrogen atmosphere, the IR spectrum of the heat-treated polymer showed a decrease of relative intensity of the carbonyl band at 1715 cm⁻¹ as shown in Figure 1(d). This phenomenon could be associated with changes of carbonyl band caused by the decarboxylation reaction during heating. The chemical structure of resulting decomposition product was analogous to polymer **3**, which is obtainable from terephthaloyl chloride and tyramine.²³

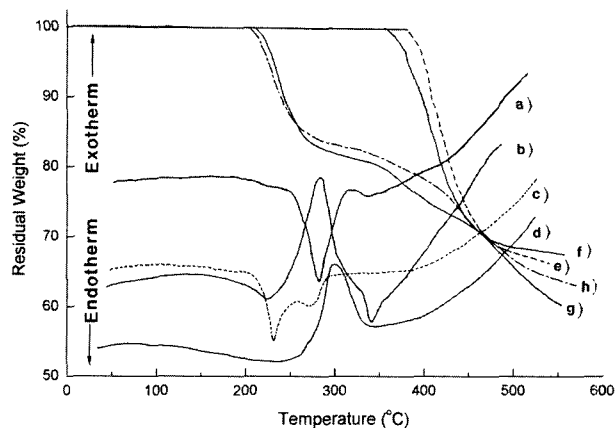


Figure 3. DSC thermograms of a) polymer **3**, b) **6**, c) **4** and d) **7**, and TGA traces of e) **3**, f) **4**, g) **6**, and h) **7**.

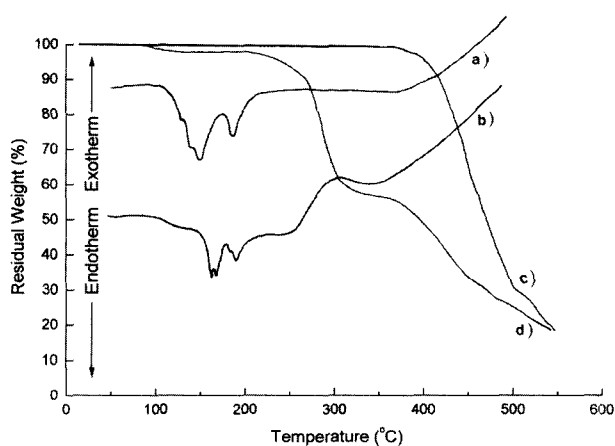


Figure 4. DSC thermograms of a) polymer **5** and b) **8**, and TGA traces of c) polymer **5**, and d) polymer **8**.

Thermal stability data are listed in Table III and TGA traces in Figure 3. The initial decomposition temperature followed a similar trend regardless of the chemical structure

Table III. Thermal Properties of Polyesteramides Obtained by Interfacial Polymerization Technique

Polymers	T_{exo}^a	T_m^b	T_d^c	$T_{10\%}^d$	T_g^e	Residual Weight (%)	
						400°C	500°C
3	-	282	349	398	221	90.1	68.4
4	286	232	371	411	187	96.0	67.9
5	-	150	362	418	114	95.1	30.1
6	314	298	249	286	-	78.1	67.8
7	284	220	242	290	-	75.5	65.9
8	311	162	247	274	147	50.9	26.2

^a T_{exo} : temperature of exotherm. ^b T_m : temperature of endotherm. ^c T_d : initial decomposition temperature.

^d $T_{10\%}$: temperature determined at a weight loss of 10%. ^e T_g : glass transition temperature.

of the polymers 3-5. Polymers 3, 4 and 5 sustained a 10% weight loss at 398, 411 and 418 °C at a heating rate of 10 min⁻¹, and gave residual weight varying from 30 to 68% at 500 °C in nitrogen (Figure 3(e) and (f)). On the other hand the initial decomposition temperature of tyrosine based polymers 6, 7 and 8 showed lower temperature of 10% weight loss than those of tyramine, but gave residual weight varying from 26 to 67% at 500 °C in nitrogen (Figure 3(g) and (h)). Such susceptibility toward degradation has been related to the carboxyl groups attached to the tyramine upon decarboxylation. When Comparing to the data in Table III, polymer 4 showed improved thermal stability over polymer 3, which was caused by the molecular weights of the polymers. The rigid structured polymers had comparatively lower molecular weight. The polymer 3 obtained from terephthaloyl chloride possess comparatively lower molecular weight than that obtained from isophthaloyl chloride. The rigid rod shaped structure prevented the polymers from growing.

Conclusions

A series of polyarylateamides with randomly introduced ester/amide group ratio of 50/50 were newly prepared by interfacial polymerization from aminoalkyl-containing phenol derivatives and various diacid chlorides. The interfacial polymerization gave various polyesteramides with moderate molecular weights in good yields. They showed enhanced solubility in common organic solvents. Tyrosine based polyesteramide was degraded thermally around 290 °C to give the polyesteramide, which was obtainable from tyramine. Although the polyarylateamide possess an alkyl moiety, they displayed good thermal stability.

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