

Aliphatic-aromatic poly(ester-imide)s from diisocyanates containing ester groups and aromatic dianhydrides*

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SUMMARY

Four new ester group containing diisocyanates, viz., 3,3'-(glutaryldioxy)diphenyl diisocyanate, 4,4'-(glutaryldioxy)diphenyl diisocyanate, 3,3'-(adipoyldioxy)diphenyl diisocyanate, and 4,4'-(adipoyldioxy)diphenyl diisocyanate were synthesized from the corresponding dicarboxylic acids via the Curtius rearrangement reaction. These diisocyanates were polycondensed with pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) in dimethylacetamide to yield eight aliphatic-aromatic polyimides containing ester groups in the backbone with inherent viscosities in the range 0.25-0.70 dL/g. These poly(ester-imide)s were semicrystalline in nature and exhibited no weight loss below 300°C in air.

INTRODUCTION

Wholly aromatic poly(ester-imide)s are an important class of thermally stable polymers.^{1,2} Poly(ester-imide)s are generally prepared by the direct polycondensation of (i) trimellitic anhydride with a mixture of a diamine and a diol³ (ii) a dicarboxylic acid^{2,4} containing preformed imide group(s) with a diol, (iii) a diphenol containing imide groups with a diacid chloride,⁵ (iv) a dianhydride containing ester group(s) with a diamine^{6,7} or a diisocyanate⁸, and (v) a diamine containing ester linkages with a dianhydride.⁹

Aromatic poly(ester-imide)s suffer from being infusible and insoluble in organic solvents and pose processing difficulties limiting their widespread utility.¹⁰ Approaches taken to improve upon the processing characteristics of thermally stable polymers include incorporation of flexibilizing linkages, bulky groups, and meta-catenation.¹¹

Flexibilizing groups such as, oxyethylene¹², sulfone,¹³ silane,¹⁴ etc., have been incorporated conveniently into the polymers via the diisocyanates containing respective functional groups. Diisocyanates having ester groups may be polycondensed with dianhydrides to obtain poly(ester-imide)s. Consequently, in this paper we report on the synthesis of ester group containing diisocyanates, viz., (alkanedioxyldioxy) diphenyl diisocyanates. The polycondensation of these diisocyanates with PMDA and BTDA to obtain aliphatic-aromatic

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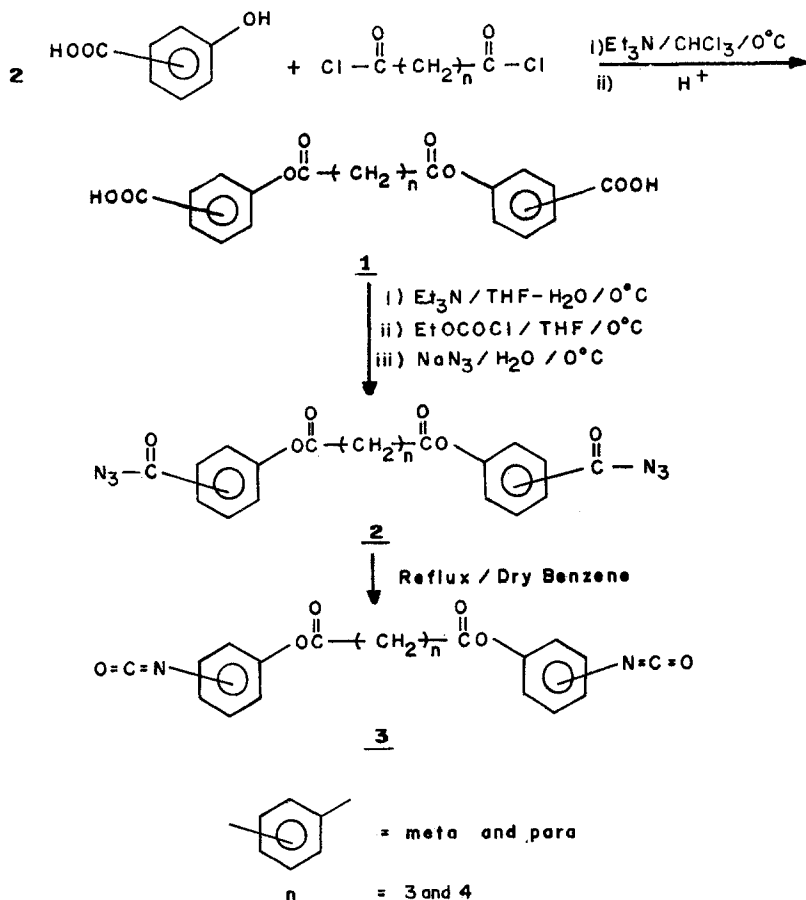
poly(ester-imide)s is also described.

EXPERIMENTAL

Materials: 3- and 4-Hydroxybenzoic acids, glutaric acid, adipic acid, and dimethylacetamide (DMAC) were purified by known procedures.¹⁵ Sodium azide was activated by trituration with hydrazine hydrate. Thionyl chloride, triethylamine, and ethyl chloroformate were distilled before use. Pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) were sublimed prior to use.

Glutaric acid and adipic acid were refluxed with thionyl chloride in presence of a catalytic amount of pyridine. Removal of thionyl chloride and distillation of the residue gave glutaryl dichloride (bp 92°C/10 mm Hg) and adipoyl chloride (bp 112°C/10 mm Hg), respectively.

The diisocyanates were synthesized from the corresponding dicarboxylic acids as illustrated in Scheme 1.



Scheme 1: SYNTHESIS OF (ALKANEDIOYLDIOXY) DIPHENYL DIISOCYANATES, 3a-3d.

**Synthesis of (alkanedioyldioxy)dibenzoic acids (1 a - 1 d)
(eg., 3,3'-(Glutaryldioxy)dibenzoic acid, 1 a)**

To a well stirred solution of 3-hydroxybenzoic acid (13.8g, 0.1 mol) in 50 mL of chloroform at 0 °C was added triethylamine (22.0g, 0.22 mol) dropwise over a period of 30 min. After stirring for 1 1/2 h at 0 °C, glutaryl dichloride (8.45g, 0.05 mol) was added dropwise over 30 min and the reaction mixture was stirred overnight. After the chloroform was removed under vacuum, the residue was dissolved in water, and acidified with dilute hydrochloric acid. The resulting dicarboxylic acid was filtered and washed with water and methanol and then dried.

**Synthesis of (alkanedioyldioxy)dibenzoyl diazides (2 a - 2 d)
(eg., 3,3'-(glutaryldioxy)dibenzoyl diazide, 2 a)**

To a well agitated suspension of dicarboxylic acid, 1 a, (3.72g, 0.01 mol) in 20 mL of THF-water (1:1) mixture maintained at 0 °C was added triethylamine (2.5g, 0.022 mol) in 5 mL of THF dropwise over a period of 30 min and stirred for 1 1/2 h. Ethyl chloroformate (2.39g, 0.022 mol) in 5 ml of THF was added dropwise over 30 min and maintained for 1 h at 0 °C. Next, activated sodium azide (1.65g, 0.025 mol) solution in 20 mL of water was added over 30 min and stirred at 0 °C for 1 1/2 h. Water (100 mL) was added dropwise and the mixture was gradually allowed to attain ambient temperature. The white solid that separated out was filtered, washed with water and dissolved in 25 mL of dichloromethane. The dichloromethane solution was dried over anhydrous sodium sulfate and concentrated by the removal of solvent at room temperature under reduced pressure. The solution was poured into a large excess of petroleum ether to afford the pure diacylazide, 2 a.

**Synthesis of (alkanedioyldioxy)diphenyl diisocyanates
(3 a - 3 d)**

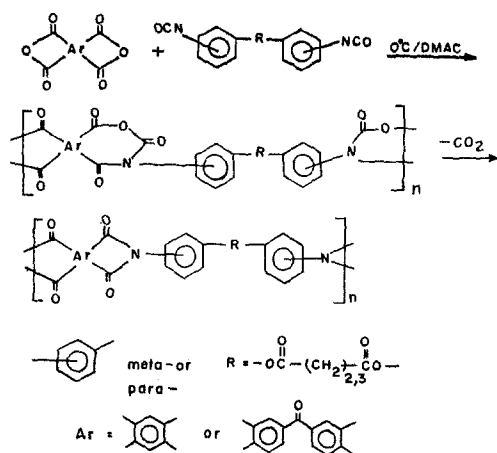
(eg., 3,3'-(glutaryldioxy)diphenyl diisocyanate, 3 a)

The diacylazide, 2 a, (4.23g, 0.01 mol) was dissolved in 50 mL of dry benzene and refluxed for 12 h. The benzene was removed under vacuum and the crude product was recrystallized from a mixture of petroleum ether - benzene to afford the diisocyanate, 3 a in pure form.

Synthesis of Poly(ester-imide)s (A - H)

(eg., poly(ester-imide) D)

A solution of 3,3'-(glutaryldioxy)diphenyl diisocyanate, 2 a (0.366g, 0.001 mol) in 10 ml of DMAc was taken in a 100 mL three-necked flask equipped with a thermowell, a nitrogen gas inlet and a calcium chloride guard tube and stirred at 0 °C when BTDA (0.322g, 0.001 mol) was added in small portions over a period of 1 h. The reaction mixture was stirred at that temperature for 30 min and then gradually heated to 40 °C, at which temperature it was held for 2 1/2 h. Then the reaction temperature was slowly raised to 90 °C and finally to 130 - 140 °C and held at that temperature for 24 h. The polymer was isolated by pouring the reaction mixture into a large excess of methanol, filtered, washed well with methanol, and then dried under vacuum at 100 °C for 3 h.



SCHEME 2: SYNTHESIS OF POLY (ESTER-IMIDE)S, A-H.

RESULTS AND DISCUSSION

The synthesis of diisocyanates is depicted in Scheme 1. Ester group containing dicarboxylic acids (**1 a - 1 d**) were prepared by the reaction of triethylamine salts of 3- or 4-hydroxybenzoic acids with alkanedioylchlorides in 65-70% yields as detailed in experimental section.

Melting points of the dicarboxylic acids (**1 a - 1 d**) in °C

1 a	1 b	1 c	1 d
200	218	265	(Lit. ¹⁶ 245-250)

IR spectra of the dicarboxylic acids showed absorption bands at 1750 cm^{-1} (ester carbonyl) and 1700 cm^{-1} (acid carbonyl). Satisfactory microanalyses were obtained for all the dicarboxylic acids.

The diacyl azides (**2 a - 2 d**) were synthesized via the elegant 'one pot' Weinstock modification of the Curtius reaction in 80-85% yields. The diacyl azides were refluxed in dry benzene to get the corresponding diisocyanates (**3 a - 3 d**).

The IR spectra of the diacyl azides showed characteristic absorption bands at 1700 cm^{-1} (azido carbonyl), 1750 cm^{-1} (ester carbonyl), and 2120 cm^{-1} (N_3), while those of the diisocyanates exhibited strong bands at 1750 cm^{-1} (ester carbonyl) and 2260 cm^{-1} ($\text{N}=\text{C}=\text{O}$). The $^1\text{H-NMR}$ spectral values of the diacyl azides (**2 a - 2 d**) and diisocyanates (**3 a - 3 d**) and the molecular ion peak (M^+) of the diisocyanates confirmed the structures proposed (Tables I a and b).

Eight aliphatic-aromatic poly(ester-imide)s were synthesized by the polycondensation of the diisocyanates (**3 a - 3 d**) with PMDA and BTDA (Scheme 2 and Table II).

The inherent viscosities of the poly(ester-imide)s (**A - H**) ranged from 0.25-0.70 dL/g in sulfuric acid at $30\text{ }^\circ\text{C}$.

All the poly(ester-imide)s were insoluble in the polar solvents such as DMAc, dimethylformamide, dimethylsulfoxide, hexamethylphosphoramide, and m-cresol.

TABLE I
(a) Physical and Spectral Data of (Alkanedioyldioxy)dibenzoyl Diazides (2 a - 2 d).

$$\text{N}_3\text{OC}-\text{C}_6\text{H}_4-\text{OCO}-\left(\text{CH}_2\right)_n-\text{COO}-\text{C}_6\text{H}_4-\text{CON}_3$$

Product ¹ 2	n	Yield (%)	m.p. °C	¹ H-NMR (CDCl ₃) (δ, ppm)
a	3	80	107	2.18 (quintet, 2 H), 2.68 (t, 4 H), 7.25 - 7.90 (m, 8 H)
b	4	84	98	1.89 (quintet, 4 H), 2.68 (t, 4 H), 6.81 - 7.48 (m, 8 H)
c	3	85	122	2.20 (quintet, 2 H), 2.76 (t, 4 H), 7.24 (d, 4 H), 8.11 (d, 4 H)
d	4	81	108	1.89 (quintet, 4 H), 2.68 (t, 4 H), 7.20 (d, 4 H), 8.07 (d, 4 H)

(b) Physical and Spectral Data of (Alkanedioyldioxy)diphenyl Diisocyanates (3 a - 3 d).

$$\text{OCN}-\text{C}_6\text{H}_4-\text{OCO}-\left(\text{CH}_2\right)_n-\text{COO}-\text{C}_6\text{H}_4-\text{NCO}$$

Product ^{1,2} 3	n	Yield (%)	m.p. °C	¹ H-NMR (CDCl ₃) (δ, ppm)	M ⁺ (70 ev)
a	3	92	71	2.18 (quintet, 2 H), 2.75 (t, 4 H), 6.87 - 7.51 (m, 8 H)	366
b	4	94	65	1.89 (quintet, 4 H), 2.68 (t, 4 H), 6.81 - 7.48 (m, 8 H)	380
c	3	95	95	2.20 (quintet, 2 H), 2.77 (t, 4 H), 6.98 - 7.40 (m, 8 H)	366
d	4	93	88	1.89 (quintet, 4 H), 2.64 (t, 4 H), 7.70 - 7.44 (m, 8 H)	380

1 a and b are meta- and c and d are para-linked

2 Satisfactory elemental analysis obtained

TABLE II
Synthesis of Poly(Ester-Imide)s (A - H)

Polymer	Diisocyanate (0.001 mol)	Dianhydride (0.001 mol)	Yield (%)	$[\eta]_{inh}^+$ (dL/g)
A	3 a	PMDA	92	0.25
B	3 a	BTDA	95	0.33
C	3 b	PMDA	94	0.45
D	3 b	BTDA	94	0.57
E	3 c	PMDA	95	0.32
F	3 c	BTDA	95	0.42
G	3 d	PMDA	94	0.55
H	3 d	BTDA	95	0.70

+ Measured at a concentration of 0.5 g/dL in sulfuric acid at 30 °C.

The IR spectra of the poly(ester-imide)s (A-H) showed characteristic bands at 1780 cm^{-1} and 1720 cm^{-1} (imide-I), 1370 cm^{-1} (imide-II), 1120 cm^{-1} (imide-III), 720 cm^{-1} (imide-IV), and 1745 cm^{-1} (ester carbonyl).

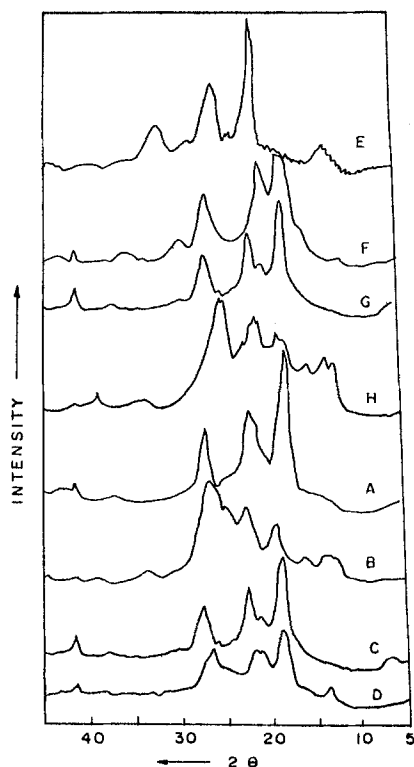


FIG. 1. X-RAY DIFFRACTOGRAMS OF POLY (ESTER-IMIDE)S, A-H.

X-Ray diffractograms (Fig. 1) taken by the powder method using Nickel filtered $\text{CuK}\alpha$ radiations on a Phillips X-Ray Unit (Phillips Generator, PW 1730) indicated that the poly(ester-imide)s (E - H) derived from para-linked diisocyanates (3 c and 3 d) were more crystalline than the poly(ester-imide)s (A - D) based on meta-linked diisocyanates (3 a and 3 b). The PMDA based poly(ester-imide)s were more crystalline than those based on BTDA.

Thermogravimetric analysis (TGA) of the poly(ester-imide)s (A - H) was carried out on a Netzsch 409 Thermal Analyzer in air at a heating rate of $10^\circ\text{C}/\text{min}$. Representative TGA curves of poly(ester-imide)s (A, E, G and H) are shown in Fig. 2. Table III incorporates thermal characteristics, such as, IDT, T_{10} , and T_{max} , i.e., initial decomposition temperature, temperature at 10% weight loss, and at maximum rate of decomposition. T_{max} was determined from the DTG curve. A comparison of the IDT values indicated that poly(ester-imide)s derived from PMDA were more stable than the corresponding poly(ester-imide)s derived from BTDA. The poly(ester-imide)s (E - H) based on the para-linked diisocyanates were thermally more stable than those (A - D) based on the meta-oriented diisocyanates.

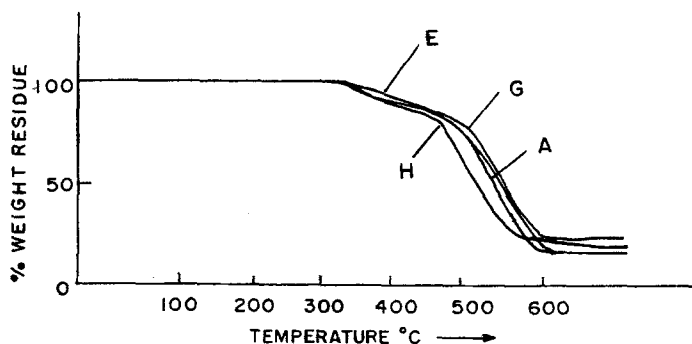


FIG. 2: TGA CURVES OF POLY (ESTER-IMIDE)S, A, E, G AND H.

TABLE III
Thermal Characteristics of Poly(Ester-Imide)s (A - H)^a.

Poly(ester imide)s	A	B	C	D	E	F	G	H
T _g	-	200	-	-	-	210	185	140
IDT	335	320	305	300	370	345	335	335
T ₁₀	420	400	390	375	450	430	405	380
T _{max}	575	550	560	550	590	555	565	565

a All temperatures in $^\circ\text{C}$
 IDT - Initial decomposition temperature,
 T_g - Glass transition temperature, T₁₀ and T_{max} are temperatures at 10% weight loss and maximum rate of decomposition, respectively.

The glass transition temperatures (T_g) of some of the poly(ester-imide)s were examined. Amongst these, the T_g value of poly(ester-imide) (B) based on meta-oriented diisocyanate (3 a) was lower than that of poly(ester-imide) (F) derived from para-oriented diisocyanate (3 c). The T_g value for poly(ester-imide) (G) based on PMDA was higher than that of poly(ester-imide) (H) derived from BTDA.

CONCLUSION

Four new ester group containing diisocyanates were synthesized via the Curtius rearrangement reaction. These diisocyanates paved a convenient route to the insertion of ester linkages in the polyimide backbone by their polycondensation with PMDA and BTDA. These poly(ester-imide)s were semicrystalline in nature and exhibited good thermal stability.

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