

# Synthesis and Characterization of Formal-Group-Containing Diisocyanates and Polyimides Therefrom\*

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## SYNOPSIS

Four new formal-group-containing diisocyanates, namely, bis(3-isocyanatophenoxy) methane, bis(4-isocyanatophenoxy) methane, bis[2-(3-isocyanatophenoxy) ethyl] formal, and bis[2-(4-isocyanatophenoxy)ethyl] formal, were synthesized by the Curtius rearrangement from the corresponding dicarboxylic acids. The diisocyanates were polycondensed with pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) in dimethylacetamide (DMAc) to obtain formal-group-containing polyimides. These polyimides were characterized by viscosity measurements, IR spectroscopy, X-ray diffraction, and thermogravimetric analysis.

## INTRODUCTION

Aromatic polyimides exhibit exceptional thermooxidative stability and mechanical properties.<sup>1</sup> However, they have poor solubility and processing characteristics. One approach to this problem has been to modify these wholly aromatic polyimides by incorporating various flexibilizing linkages in the backbone.<sup>2,3</sup> Polyimides containing various flexible groups, such as ether,<sup>4-6</sup> sulfone,<sup>7,8</sup> silane,<sup>9</sup> etc., have been reported.

Polyformals are known to exhibit good thermal stability and yet have comparatively lower glass transition temperatures than most polyimides.<sup>10</sup> Introduction of formal groups into the polyimides is thus expected to lower their  $T_g$ . In the present work, we report the synthesis of four new aromatic diisocyanates containing formal groups and their solution polycondensation with pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) to give polyimides containing formal groups in the polymer backbone. These polymers ranged from completely amorphous to semicrystalline in nature and showed good thermal stability.

## EXPERIMENTAL

### Materials

Dibromomethane, bis(2-chloroethyl) formal, triethylamine, ethyl chloroformate, and tetrahydrofuran (THF) were distilled prior to use. 3- and 4-Hydroxybenzoic acids were recrystallized from water. Sodium azide was "activated" by trituration with hydrazine hydrate. Dimethylacetamide (DMAc) was kept standing over  $P_2O_5$  for 24 h and then distilled under reduced pressure. PMDA and BTDA were recrystallized from freshly distilled acetic anhydride and sublimed *in vacuo* prior to use.

The synthesis of formal-group-containing diisocyanates from the corresponding dicarboxylic acids is illustrated in Scheme 1.

### Synthesis of Dicarboxylic Acids (1a-1d)

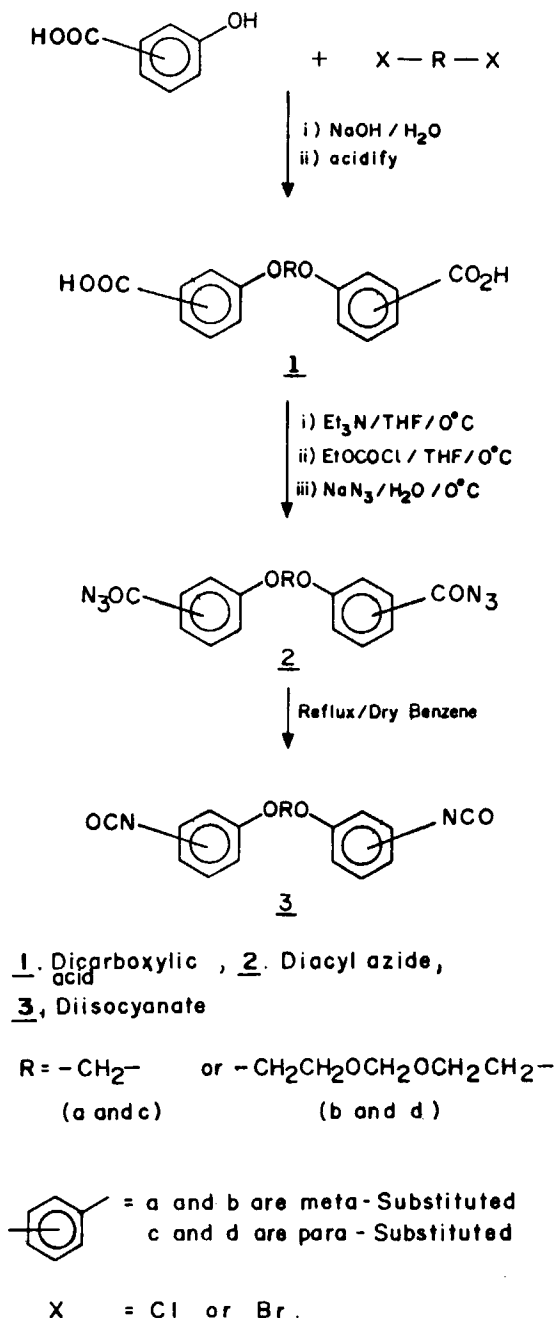
The preparation of dicarboxylic acids (1a-1d) was carried out as per the procedure reported earlier.<sup>11</sup>

The melting points of dicarboxylic acids ( $^{\circ}C$ ) for 1a and 1b were 267 (lit.<sup>12</sup> mp 264-267) and 183, respectively, and for 1c and 1d 285 (lit.<sup>12</sup> mp 288-289) and 240, respectively.

The general procedure for the synthesis of diacylazides (2a-2d) (Table I) and diisocyanates (3a-3d) (Table II) is given below.

\* NCL Communication No. 5104.

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**Scheme 1** Synthesis of formal-group-containing diisocyanates.

### Synthesis of Diacylazides (2a–2d)

A suspension of dicarboxylic acid (0.01 mol) in 15 mL THF–water (1 : 1) mixture was stirred at 0°C when triethylamine (0.022 mol) in 5 mL THF was added dropwise over 30 min. To the clear solution formed was added ethyl chloroformate (0.022 mol) in 5 mL THF dropwise over 30 min and stirred for

2 h at 0°C. Next, sodium azide (0.025 mol) solution in 15 mL water was added dropwise over 30 min and the reaction mixture stirred for 2 h at 0°C. One hundred mL water was added dropwise and the reaction mixture was gradually allowed to attain ambient temperature. The solid that separated out was filtered, washed with water, and then dissolved in 25 mL dichloromethane. The dichloromethane solution was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent under reduced pressure at room temperature afforded the diacylazide in yields above 85%. All these aromatic diacylazides were found to be quite safe to handle in the laboratory. However, it is recommended to observe normal safety precautions while handling them because of their known potential hazards.

### Synthesis of Diisocyanates (3a–3d)

The diacylazide (0.01 mol) was dissolved in 50 mL dry benzene and refluxed for 12 h. Evaporation of the solvent and recrystallization of the crude product from benzene–pet ether mixture gave the corresponding diisocyanate in pure form in quantitative yields. The thermal Curtius rearrangement took place smoothly.

### Synthesis of Polyimides (I–VIII)

Polyimides were prepared by the solution polycondensation of the diisocyanates (3a–3d) with PMDA and BTDA as illustrated in Scheme 2 and Table III. In a 100 mL three-necked flask equipped with a thermowell, a nitrogen gas inlet, and a  $\text{CaCl}_2$  guard tube was placed a solution of the diisocyanate (0.01 mol) in 10 mL DMAc. To this solution at 0°C was added the solid dianhydride (0.01 mol) in small portions over a period of 1 h.

The reaction mixture was stirred at this temperature for 30 min and then heated to 40°C at which temperature it was held for 2.5 h. The temperature of the reaction mixture was gradually raised to 90°C and finally to 130–140°C and held at that temperature for 24 h. The reaction mixture was then poured into a large excess of water and the polymer was isolated by filtration. It was washed with methanol and dried at 150°C *in vacuo* for 3 h.

## RESULTS AND DISCUSSION

The dicarboxylic acids (1a–1d) were prepared by the procedure reported earlier.<sup>11</sup> The diacylazides

**Table I Physical and Spectral Data of Formal-Group-Containing Diacylazides (2a-2d)**

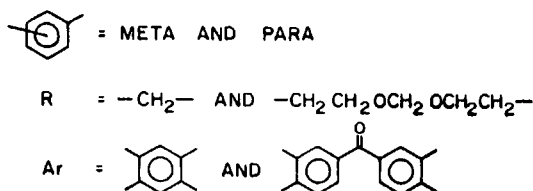
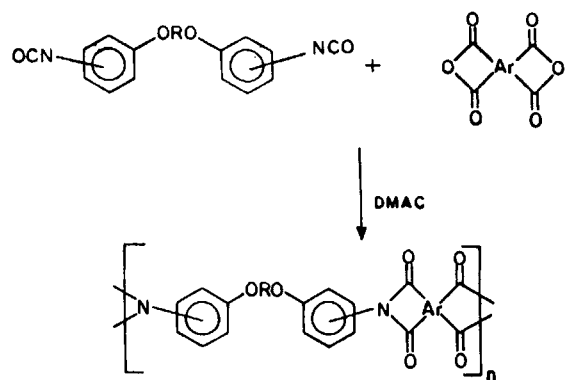
Product <sup>a</sup> 2	R	Yield (%)	mp (°C)	<sup>1</sup> H-NMR/CDCl <sub>3</sub> (δ, ppm)
a	—CH <sub>2</sub> —	85	98	5.75 (s, 2 H); 7.26–7.40 (m, 6 H); 7.60–7.76 (m, 2 H)
b	—CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> —	87	83	3.89 (m, 4 H); 4.10 (m, 4 H); 4.77 (s, 2 H); 7.10 (m, 6 H); 7.60 (m, 2 H)
c	—CH <sub>2</sub> —	88	112	5.79 (s, 2 H); 7.08 (d, 4 H); 7.95 (d, 4 H)
d	—CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> —	87	103	3.53 (m, 4 H); 4.12 (m, 4 H); 4.61 (s, 2 H); 6.77 (d, 4 H); 7.89 (d, 4 H)

<sup>a</sup> a and b are metasubstituted and c and d are parasubstituted.

**Table II Physical and Spectral Data of Formal-Group-Containing Diisocyanates (3a-3d)**

Product <sup>a</sup> 3	R	Yield (%)	mp (°C)	<sup>1</sup> H-NMR/CDCl <sub>3</sub> (δ, ppm)	M <sup>+</sup> (70 eV)
a	—CH <sub>2</sub> —	95	85	5.75 (s, 2 H); 7.29–7.47 (m, 8 H)	282
b	—CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> —	97	65	3.78 (m, 4 H); 4.22 (m, 4 H); 4.80 (s, 2 H); 6.50–6.77 (m, 6 H); 7.00–7.24 (m, 2 H)	370
c	—CH <sub>2</sub> —	96	100	5.63 (s, 2 H); 6.77–7.24 (m, 8 H)	282
d	—CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> —	97	97	3.56 (m, 4 H); 4.07 (m, 4 H); 4.61 (s, 2 H); 6.37 (d, 4 H); 6.72 (d, 4 H)	370

<sup>a</sup> a and b are metasubstituted and c and d are parasubstituted. Satisfactory microanalyses obtained.



**Scheme 2** Synthesis of formal-group-containing polyimides.

(2a–2d) were prepared via the elegant “one-pot” Weinstock modification of the Curtius reaction. The diacylazides were then refluxed in dry benzene to yield the corresponding diisocyanates (3a–3d), as detailed in the experimental section. While the diacylazides were characterized by infrared (IR) and  $^1\text{H}$ -nuclear magnetic resonance (NMR) spectroscopy, the diisocyanates were characterized by IR,  $^1\text{H}$ -NMR, mass spectroscopy, and elemental analysis. The IR spectra of all diacylazides showed strong absorptions at  $1230\text{ cm}^{-1}$  (C—O—C),  $1660\text{ cm}^{-1}$

(C=O), and  $2130\text{ cm}^{-1}$  ( $\text{N}_3$ ). The IR spectra of all diisocyanates showed strong bands at  $1230\text{ cm}^{-1}$  (C—O—C) and  $2250\text{ cm}^{-1}$  ( $\text{N}=\text{C}=\text{O}$ ). The  $^1\text{H}$ -NMR spectral values of the diacylazides (2a–2d) and diisocyanates (3a–3d) were in accordance with the structures proposed (Tables I and II).

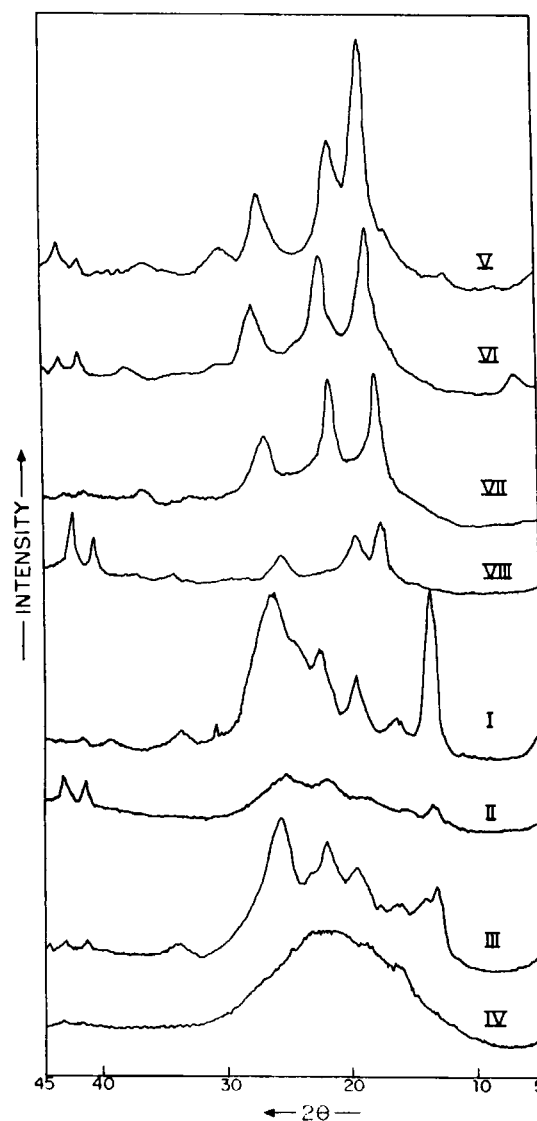
All four diisocyanates were polycondensed with PMDA and BTDA in DMAC to yield eight formal-group-containing polyimides (Scheme 2 and Table III).

Inherent viscosities of the polyimides (I–VIII) were determined in sulfuric acid at a concentration of  $0.5\text{ g/dL}$  at  $30^\circ\text{C}$ . The viscosity values varied from

**Table III** Preparation of Polyimides and Their Inherent Viscosities<sup>a</sup>

Polyimide	Diisocyanate (0.01 mol)	Dianhydride (0.01 mol)	$[\eta]_{\text{inh}}$ (dL/g)
I	3a	PMDA	0.23
II	3a	BTDA	0.28
III	3b	PMDA	0.43
IV	3b	BTDA	0.48
V	3c	PMDA	0.31
VI	3c	BTDA	0.35
VII	3d	PMDA	0.63
VIII	3d	BTDA	0.65

<sup>a</sup> Inherent viscosities were determined at a concentration of  $0.5\text{ g/dL}$  in concentrated sulfuric acid at  $30 \pm 0.01^\circ\text{C}$ .



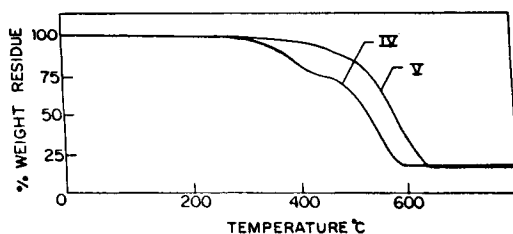
**Figure 1** XRD curves of formal-group-containing polyimides.

0.23–0.65 dL/g (Table III). Except for polyimide IV, which was soluble in polar solvents like DMAc, DMF, DMSO, HMPA, NMP, and *m*-cresol, all other polyimides were insoluble in these solvents.

The IR spectra of all polyimides showed peaks at 1780  $\text{cm}^{-1}$  (imide-I), 1370  $\text{cm}^{-1}$  (imide-II), 1120  $\text{cm}^{-1}$  (imide-III), 720  $\text{cm}^{-1}$  (imide-IV), and 1240  $\text{cm}^{-1}$  (C—O—C). Imide-I band is attributed to the stretching vibrations of the two weakly coupled carbonyl groups. Imide-II, -III, and -IV bands are due to the axial, transverse, and out-of-plane vibrations of the cyclic imide structure.<sup>13</sup>

X-ray diffraction patterns (Fig. 1) of the polyimides were determined by the powder method using Nickel-filtered  $\text{CuK}\alpha$  radiations on a Phillips X-Ray Unit (Phillips Generator, PW 1730). These indicate that the polyimides ranged from completely amorphous to semicrystalline in nature. Polyimides derived from PMDA were more crystalline than the corresponding polymers obtained from BTDA. Polyimides based on para-oriented diisocyanates (3c and 3d) were more crystalline than those derived from the meta-oriented diisocyanates (3a and 3b). Also, polyimides containing short (methylene) spacer were more crystalline than those containing long (bis[ethyl] formal) spacer.

Thermogravimetric analysis (TGA) of the polyimides (I–VIII) was carried out on a Netzsch 409 Thermal Analyzer in air at a heating rate of 10°C/min. Illustrative TGA curves of polyimides IV and V are given in Figure 2. Thermal characteristics such as  $T_{10}$ ,  $T_{30}$ ,  $T_{50}$ , and  $T_{\text{max}}$ , i.e., temperatures at 10%, 30%, 50%, and maximum rate of decomposition are incorporated in Table IV.  $T_{\text{max}}$  was determined from the DTG curve. A comparison of the  $T_{10}$  values of the polyimides indicated that polyimides containing aromatic formal grouping [derived from diisocyanates containing short (methylene) spacer] were comparatively more thermally stable than the corresponding polyimides containing aliphatic formal



**Figure 2** TGA curves of formal-group-containing polyimides.

**Table IV** Thermal Characteristics of Polyimides<sup>a</sup>

	Polyimide							
	I	II	III	IV	V	VI	VII	VIII
$T_g$	—	196	155	147	209	—	—	—
$T_{10}$	465	407	366	357	471	420	385	377
$T_{30}$	517	487	452	440	530	502	494	455
$T_{50}$	547	525	535	509	555	545	550	535
$T_{\text{max}}$	562	552	560	532	582	567	572	547

<sup>a</sup> All temperatures in °C.  $T_{10}$ ,  $T_{30}$ ,  $T_{50}$ , and  $T_{\text{max}}$  are temperatures corresponding to 10%, 30%, 50%, and maximum decomposition, respectively.

grouping [derived from diisocyanates containing long (bis[ethyl] formal) spacer].

The glass transition temperatures ( $T_g$ ) of some polyimides were determined on a Mettler DSC 30 S. The  $T_g$  values are incorporated in Table IV. Among the polymers examined, the  $T_g$  values were higher for polyimides containing short (methylene) spacer as compared to those containing long (bis[ethyl] formal) spacer. The polyimide derived from PMDA (III) exhibited higher  $T_g$  value as compared to the polyimide derived from BTDA (IV).

## CONCLUSIONS

The synthesis of formal-group-containing diisocyanates was achieved via the Curtius rearrangement. These diisocyanates were polycondensed with PMDA and BTDA to yield formal-group-containing polyimides. The polyimides were semicrystalline except for polyimide IV, which was amorphous in nature. The polyimides showed good thermal stability with relatively low  $T_g$  values.

The authors thank Dr. S. Sivaram, Deputy Director and Head, Division of Polymer Chemistry, National Chemical Laboratory, Pune, India, for encouragement during the course of this work and Dr. V. G. Gunjekar for the thermogravimetric analyses.

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*Received June 5, 1991*

*Accepted August 28, 1991*