Polymer Bulletin 23, 163–169 (1990)

Polymer Bulletin

Synthesis and characterization of imide containing diisocyanates and poly(imide-urethane)s therefrom*

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SUMMARY

A facile synthesis of eight novel diisocyanates, viz. N,N-bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides and N,N-bis(isocyanatoalkyl)-3,3',4,4'-benzophenonetetracarboxylic-3,3':4,4'-diimides, containing built-in imide rings, which serve as intermediates for the preparation of polyurethanes containing imide rings in the main chain, is reported. The solution polyaddition reaction of four representative diisocyanates with polytetramethylene glycol is also described. The resulting amorphous, thermally stable poly(imide-urethane)s are soluble with inherent viscosities ranging from 0.36 - 0.83 dL/g in m-cresol.

INTRODUCTION

Diisocyanates are reactive and versatile materials used for the synthesis of polyurethanes, polyamides, polyimides, foams, adhesives, curing agents, etc. There has been a constant need and hence an unceasing quest for the synthesis of novel monomers containing various functional groups such as $-SO_2-$, $-O-$, $-SiR_2-$, etc [1-5]. Imide groups are known for their thermal stability and their presence in polymers improves physical properties [6]. However, imide group containing aliphatic diisocyanates are not known to our knowledge, though imide group containing aromatic diisocyanates have been synthesized by the reaction of dianhydride with excess toluene diisocyanate to give isomeric mixtures [7-9].

In this paper we report the unequivocal synthesis and characterization of eight new aliphatic diisocyanates with pre-formed imide rings by the Curtius rearrangement reaction. The polyaddition reaction of four representative diisocyanates with polytetramethylene glycol (PTMG) to form amorphous, thermally stable poly(imide-urethane)s (PIUs) is also described. These PIUs with inherent viscosities in the range 0.36 - 0.83 dL/g in m-cresol were characterized by IR spectroscopy, x-ray diffraction and thermogravimetry.

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EXPERIMENTAL

Glycine, β-alanine, 4-aminobutyric acid, and 6-aminocaproic acid were of reagent grade and were used as such. Thionyl chloride, m-cresol, acetic anhydride, and N,N-dimethylformamide were distilled prior to use. Sodium azide was 'activated' by trituration with hydrazine hydrate. Benzophenonetetracarboxylic dianhydride (BTDA) and pyromellitic dianhydride (PMDA) were recrystallized from acetic anhydride and freshly sublimed in vacuum before use. Polytetramethylene glycol (PTMG) (Mol.Wt.1000, OH No.113.8) was dried till constant weight at 80 °C in vacuum.

Synthesis of N,N-Bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides (4 a - 4 d) and N,N-Bis(isocyanatoalkyl)-3,3', 4,4'-benzophenonetetracarboxylic-3,3':4,4'-diimides (4 e - 4 h).

The synthesis of diisocyanates (**4 a** - **4 h**) from the corresponding diacids (**1 a** - **1 h**) is illustrated in Scheme 1. The diacids (**1 a** - **1 h**) were synthesized by reacting 1.0 mol of either PMDA or BTDA with 2.0 mol of ω-aminoacids, such as, glycine, β-alanine, 4-aminobutyric acid, and 6-aminocaproic acid in m-cresol [10]. The general procedure for the synthesis of diacylazides (**3 a** - **3 h**) and diisocyanates (**4 a** - **4 h**) is given below.

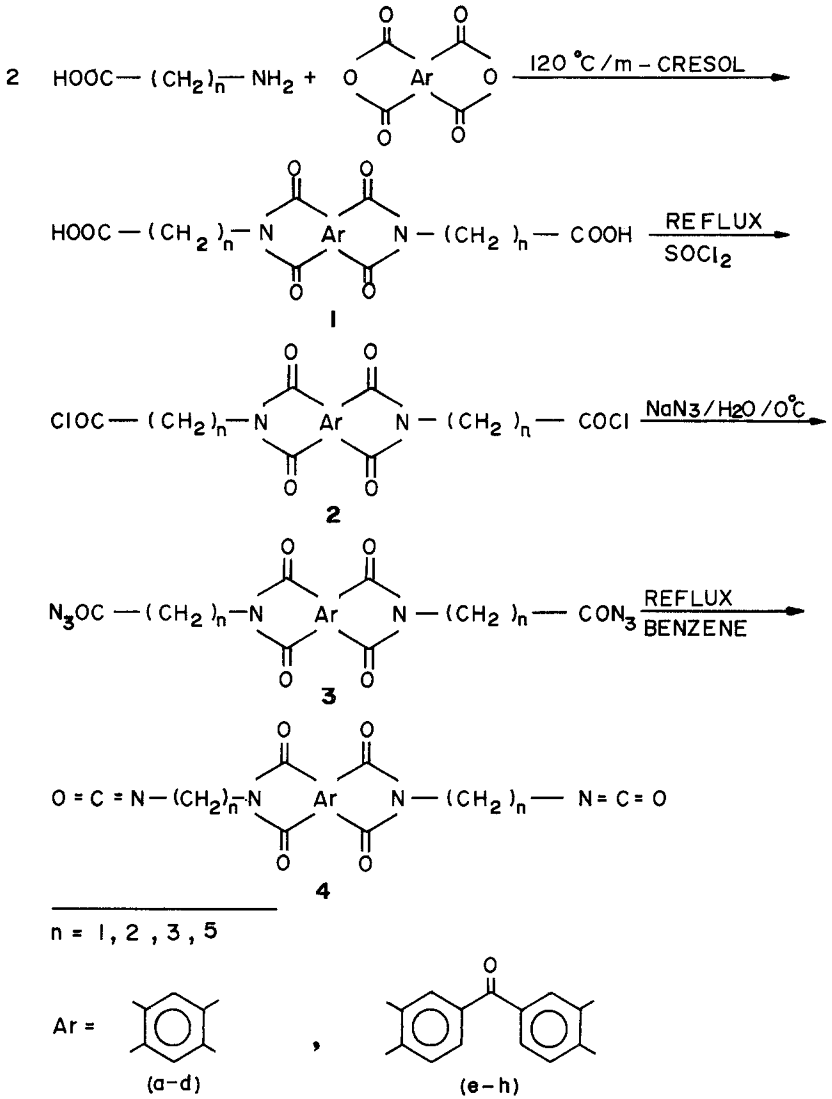
Synthesis of N,N-bis(azidocarbonylalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides (3 a - 3 d) and N,N-bis(azidocarbonylalkyl)-3,3'-4,4'- benzophenonetetracarboxylic-3,3':4,4'-diimides (3 e - 3 h).

The diacids (**1 a** - **1 h**) (0.01 mol) were refluxed with thionyl chloride (0.2 mol) for 4 h with a catalytic amount of pyridine. Removal of excess thionyl chloride under reduced pressure and recrystallization of the residue from pet ether - benzene mixture gave the diacylchlorides (**2 a** - **2 h**) in yields above 95 %.

Melting points of diacylchlorides in °C.

2 a	2 b	2 c	2 d	2 e	2 f	2 g	2 h
240	165	180	148	150	172	152	96

To ice cold solutions of 'activated' sodium azide (0.025 mol) in 20 mL water were added dropwise solutions of diacylchlorides (**2 a** - **2 h**) (0.01 mol) in 20 mL dichloromethane and stirred vigorously for 2 h at 0 °C. The dichloromethane layers were washed successively with water, 5% Na_2CO_3, and finally with water before they were separated and dried over anhydrous Na_2SO_4. Removal of the solvent at room temperature under reduced pressure gave diacylazides (**3 a** - **3 h**), with yields above 90 %. Melting points are incorporated in Table 1.



SCHEME.1. SYNTHESIS OF DIISOCYANATES 4a-4h

Synthesis of N,N-bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides (4 a - 4 d) and N,N-bis(isocyanatoalkyl)-3,3′, 4,4′-benzophenonetetracarboxylic-3,3′:4,4′-diimides (4 e - 4 h).

The diacylazides (**3 a** - **3 h**) (0.01 mol) were dissolved in 50 mL dry benzene and refluxed for 8 h. Evaporation of solvent and recrystallization from pet ether - benzene mixture gave the diisocyanates (**4 a** - **4 h**) with yields above 95 % (in case of diisocyanate **4 a**, a solid separated out during decomposition giving only 75 % yield). Melting points are incorporated in Table 2.

Spectral data of diacylazides (**3 a** – **3h**) and diisocyanates (**4 a** – **4 h**) are given in Tables 1 and 2 below.

Table 1.

Physical and spectral values of diacylazides (**3 a** – **3 h**)

Product **3**	m.p. °C	^{1}H-NMR ($CDCl_3$) (δ ppm)
a	129	4.48 (s, 4 H), 8.30 (s, 2 H)
b	125	2.79 (t, 4 H), 3.98 (t, 4 H), 8.27 (s, 2 H)
c	147	1.84-2.12 (m, 4 H), 2.56 (t, 4 H), 3.82 (t, 4 H), 8.23 (s, 2 H)
d	112	1.14-1.98 (m, 12 H), 2.32 (t,4 H) 3.72 (t, 4 H), 8.23 (s, 2 H)
e	120	4.48 (s, 4H), 7.91-8.27 (m, 6H)
f	152	2.80 (t, 4 H), 4.40 (t, 4 H), 7.91-8.27 (m, 6 H)
g	140	1.84-2.20 (m, 4 H), 2.62 (t, 4 H), 3.83 (t, 4 H), 7.93-8.22 (m, 6 H)
h	85	1.11-1.90 (m, 12 H), 2.36 (t,4 H), 3.73 (t, 4 H), 7.96-8.27 (m. 6 H)

Table 2.

Physical and spectral values of diisocyanates (**4 a** – **4 h**)

Product **4**	m.p. °C	^{1}H-NMR ($CDCl_3$) (δ ppm)	Mass (70 eV) (M^+)
a	142	5.24 (s, 4 H), 8.37 (s, 2 H)	326
b	182	3.66 (t, 4 H), 3.99 (t, 4 H), 8.33 (s, 2 H)	354
c	162	1.84-2.20 (m, 4 H), 3.44 (t, 4 H), 3.89 (t, 4 H), 8.24 (s, 4 H)	382
d	158	1.23-1.84 (m, 12 H), 3.31 (t, 4 H), 3.73 (t, 4 H), 8.22 (s, 2 H)	438
e	145	5.20 (s, 2 H), 8.07-8.33 (m,6 H)	430
f	155	3.66 (t, 4 H), 4.07 (4 H), 8.10-8.31 (m, 6 H)	458
g	132	1.89-2.20 (m, 4 H), 3.42 (t, 4 H), 3.86 (t, 4 H), 7.89-8.27 (m, 6 H)	486
h	82	1.33-1.87 (m, 4 H), 3.31 (t, 4 H), 3.74 (t, 4 H), 7.89-8.82 (m, 6 H)	514

Synthesis of Poly(imide-urethane)s (PIUs) (I -IV).

PIUs were prepared by the solution polyaddition reaction of representative diisocyanates, **4 a, 4 d, 4 e, and 4 h** with PTMG as illustrated (Table 3).

In a dry 100 mL three-necked flask fitted with a thermowell, nitrogen gas inlet and $CaCl_2$ guard tube, were placed the diisocyanates (0.01 mol) in 15 mL DMF. To these was added an equivalent amount of PTMG. The reaction mixtures were stirred at 70 °C for 6 h after which they were cooled and poured into a large excess of methanol. The powdery polymers that precipitated were filtered and dried in vacuum at 100 °C.

RESULTS AND DISCUSSION

Conventional polyurethanes loose their mechanical properties above 90 °C and undergo thermal degradation at processing temperatures above 200 °C. To improve upon their properties, heterocyclic imide groups have been incorporated in the main chain by reacting isocyanate terminated polyimides (obtained by the reaction of dianhydride with excess diisocyanate) with a diol [2-4].

In the present paper we report the unequivocal synthesis of eight new aliphatic diisocyanates with pre-formed imide rings via the Curtius reaction. The solution polyaddition reaction of representative diisocyanates with PTMG to form poly(imide-urethane)s with built-in imide rings in the backbone is also described and are characterized by IR spectroscopy, x-ray diffraction and thermogravimetric analysis.

The synthesis of diisocyanates (**4 a** - **4 h**) from the corresponding ω-aminoacids and PMDA and BTDA is illustrated in Scheme 1. The diacids (**1 a** - **1 h**) were converted to the diacylchlorides (**2 a** - **2 h**) (by refluxing with thionyl chloride) which were then treated with aqueous sodium azide solutions to form the diacylazides (**3 a** - **3 h**). These were decomposed in solution to the diisocyanates (**4 a** - **4 h**) as detailed in experimental section.

Table 3.
Preparation and inherent viscosities of poly(imide-urethane)s (**I** - **IV**).

Polymer	Diisocyanate	Diol[a]	η_{inh}[b]
I	**4 a**	PTMG	0.58
II	**4 d**	PTMG	0.83
III	**4 e**	PTMG	0.36
IV	**4 h**	PTMG	0.39

[a] Diol:Polytetramethylene glycol (Mol.Wt.1000. OH No.113.8)
[b] Measured at a concentration of 0.5 g/dL in m-cresol at 30 °C.

Table 4.

Thermal characteristics of Poly(imide-urethane)s (I - **IV**)^{a}.

Polymer ->	I	II	III	IV
IDT	215	217	219	216
T_{10}	290	289	291	306
T_{30}	350	341	382	410
T_{50}	397	444	583	512
T_{max}	580	558	610	593

[a] All temperatures in ^{o}C
IDT - Initial Decomposition temperature
T_{10}, T_{30}, T_{50}, and T_{max} are temperatures at T_{10} %, T_{30} %, T_{50} %, and maximum decomposition, respectively.

A solid that separated out in case of diisocyanate **4 a** is being identified.

The IR spectra of diacylazides (**3 a - 3 h**), showed absorption bands at 1630 cm^{-1} (C = O), 2130 cm^{-1} (N_3), 1780 cm^{-1} (imide-I), 1370 cm^{-1} (imide-II), 1120 cm^{-1} (imide-III), and 720 cm^{-1} (imide-IV). The IR spectra of diisocyanates showed absorption band at 2260 cm^{-1} (N=C=O) in addition to the above four peaks due to cyclic imide rings. ^{1}H-NMR spectra of diacylazides and ^{1}H-NMR and mass spectra of diisocyanates are in accordance with the proposed structure (Tables 1 and 2).

Four new PIUs were synthesized by the reaction of representative diisocyanates (**4 a, 4 d, 4 e,** and **4 h**) with PTMG as detailed in experimental section. These were soluble in polar aprotic solvents like DMSO, DMF, DMAc, HMPA, m-cresol, and in H_2SO_4. The solubility increase with increase in the aliphatic chain of the diisocyanates. The PIUs derived from BTDA showed better solubility than those obtained from PMDA. The inherent viscosities were determined in m-cresol at a concentration of 0.5 g/dL which varied from 0.36 - 0.83 dL/g at 30 ^{o}C (Table 3).

X-Ray diffraction patterns (Fig. 1) of PIUs were determined by the powder method using nickel filtered CuK α on Phillips PW-1730 Unit. These indicate that the PIUs were semicrystalline in nature. The polymers derived from diisocyanates **4 a** and **4 d** (ie. derived from PMDA) were more crystalline than those derived from diisocyanates **4 e** and **4 h** (ie. derived from BTDA).

The thermal analysis of PIUs (**I - IV**) was carried out on a Netzsch 409 Thermal Analyzer in air at a heating rate of 10 ^{o}C/min. All the polymers showed a two stage decomposition pattern without any weight loss below 215 ^{o}C (Fig. 1). The first stage of decomposition may be attributed to the thermooxidative cleavage of the weak and labile linkages while the second stage being that due to the cleavage of the imide linkage. Thermal characteristics,

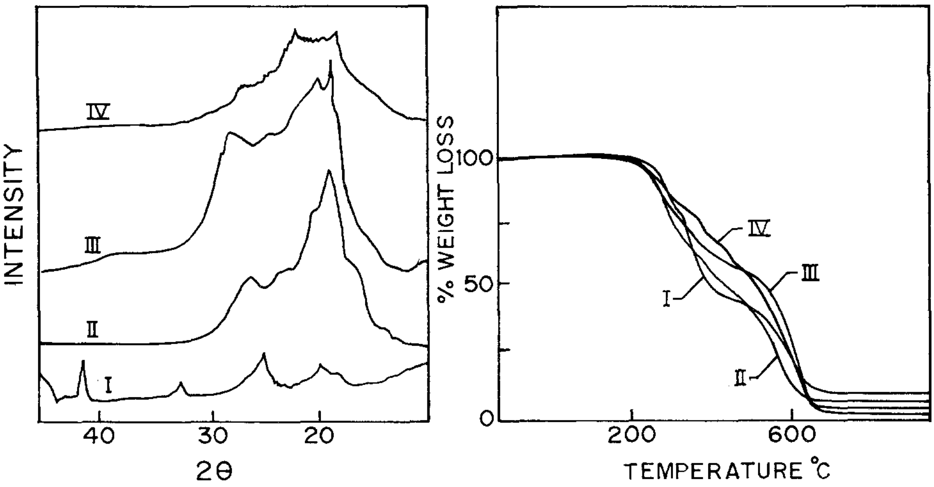


FIG.1: X-RAY DIFFRACTION AND TGA CURVES OF PIUs (I-IV)

such as, initial decomposition temperature (IDT), T_{10}, T_{30}, T_{50}, and T_{max}, ie. temperatures at 10 %, 30 %, 50%, and maximum decomposition, respectively, are incorporated in Table 4. T_{max} was determined from the DTG curves.

CONCLUSIONS

The facile synthesis of eight diisocyanates with pre-formed imide rings was achieved via the non phosgenation Curtius rearrangement reaction. New, soluble, semicrystalline and thermally stable poly(imide-urethane)s were prepared by the reaction of representative diisocyanates with PTMG.

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Accepted December 9, 1989 S