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Preparation and Properties of Poly(urethane-imide)s Derived from Diisocyanates Containing Build-in Imide Rings

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ABSTRACT ,

Poly(urethane-imide)s were prepared by polycondensation reaction of four imides containing diisocyanates with poly(tetramethylene oxide)glycol. Synthetic procedures for the preparation of the diisocyanates were described. The chemical structures of the monomers and polymers obtained were characterized by IR, ¹H NMR, and mass spectroscopies. The physical properties of polymers including solution viscosity, solubility properties, thermal stability and thermal behaviour were studied as well. The polymers showed excellent solubility in polar aprotic solvents such as DMF, DMAc and NMP. Their inherent viscosities were in the range of 0.50-0.55 dL/g. T_{10} % obtained as a criterion of thermal stability was in the range of 316-335 °C for the polymers.

Key Words: poly(urethane-imide), polyurethane, diisocyanate, curtius rearrangement, thermal stability

INTRODUCTION

Among various classes of condensation monomers used in polymer synthesis, diisocyanates are very valuable [1]. The salient feature of the diisocyanates is their high reactivity towards nucleophiles, cycloadditions to unsaturated systems, Diels-Alder reaction, and so on [2–4]. The increasing interest in the diisocyanates, can be attributed to their applications in polyurethane coatings, adhesives, and rubber vulcanizates. In light of the ever-expanding spectrum of diisocyanate applications, the quest for and therefore the synthesis of novel diisocyanates becomes attractive [5–8].

Typical polyurethanes are known to exhibit small resistance to heat. This low heat resistance is the

main reason of relatively limited technical applicability of these polymers. One of the reported methods to improve the thermal stability of these polymers is a chemical modification of their structure by introduction of heterocyclic groups; e.g. isocyanurate [9–11], oxazolidone [12–14], and imide groups [15–19].

In an effort to prepare new phase-segregated polyurethanes having high thermal stability and retaining their flexibility at the same time, we synthesized four diisocyanates containing aromatic and aliphatic moieties with the aim to obtain polyurethanes having rigid imide ring as the hard segment and aliphatic methylene groups as the soft segment. The monomers and polymers were characterized by conventional methods and their physical properties

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were studied.

EXPERIMENTAL

All needed chemicals were purchased from Fluka, Merck or Aldrich chemical companies.

Sodium azide was activated by adding hydrazine hydrate. After keeping it overnight, it was dissolved in minimum amount of water, precipitated in acetone, and dried. N_iN' -Dimethylacetamide (DMAc) and N_iN' -dimethylformamide (DMF) were purified by distillation under reduced pressure over CaH₂. Pyromellitic dianhydride (PMDA), trimellitic anhydride (TMA) were recrystallized from acetic anhydride and sublimed in vacuum before use.

Poly(tetramethylene oxide)glycol, PTMEG, of molecular weight 1000 (BASF) was dried at 70 °C under vacuum overnight.

FTIR spectra were recorded on a Bruker-IFS 48 instrument. ¹H NMR spectra were recorded on a Bruker-Avance DPX 250 MHz instrument. Mass spectra were recorded on a Shimadzu GC-MS QP 1000 EX, and TGA and DSC analyses were performed on a Stanton STA-615 with heating rate 20 °C/min in air. Melting points were determined in open capillaries with a Buchi 535 instrument. Inherent viscosities of polymers were determined for solution of 0.5 g/dL



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Table 1. Monomer characterization data.

Comp.	Structure		mp	IR (cm ⁻¹)	¹ H NMR (ppm)	Ms. 70
No.		(%)	(°C)			eV
1a	<u>0 0 </u>	82	254	3040, 2937, 2850, 2600,	_	444
		}		1780, 1705, 1310, 1115,		
	HU2C 1CH2/5/1			725		
	Ö O					
1b	0 0 ·	83	194	3035, 2935, 2850, 2605,	~	584
				1780, 1707, 1320, 1120,		}
				730		
20		92	197	3020 2937 2849 1774	-	305
20				1711, 1302, 1115, 729		
	N-1CH275CO2H					
2b	Q	90	156	3020, 2926, 2850, 1774,	-	375
				1717, 1390, 1306, 1190,		
				733		
1						
3a	C C	95	158	3040, 2935, 2858, 2272,	1.3–1.8 (m, 12H), 3.3	438
1				1771, 1705, 1578, 1369,	(t, 4H) 3.8 (t, 4H), 8.3	1
				1123, 729	(s, 2H)	
	ÖÖ					
36		94	132	3037, 2935, 2854, 2773,	1.4–1.8 (m, 32H), 3.2	574
	OCN-1CH2toN N-1CH2toNCO		ļ	1772, 1707, 1580, 1370,	(t, 4H) 3.9 (t, 4H), 8.4	•
				1120, 730	(s, 2H)	
4a		89	141	3030, 2935, 2860, 2272,	1.3–1.8 (m, 6H), 2.9	299
	N-1CH ₂₇₅ NCO			1767, 1701, 1396, 1210,	(t, 2H) 3.5 (t, 2H),	
	OCN ~ 0			/48	1 7.5-8.3 (M, 3H)	
4h) N	89	119	3080, 2930, 2856, 2259,	1.4-1.8 (m, 16H). 2.9	369
				1771, 1713, 1396, 1188,	(t, 2H) 3.5 (t, 2H),	
	OCN (CIT2710)	1		748	7.5–8.3 (m, 3H)	
	ö					

* Solvent: DMSO-d6

in DMF at 30 °C using an Ubbelhode viscometer.

acid was conducted according to ref. 20.

Synthesis of *N*,*N*-Bis (Carboxylatoalkyl)-1,2,4,5benzenetetracarboxylic-1,2:4,5-diimides (1a,b) The reaction of pyromellitic dianhydride and ω -amino

Synthesis of N-(Carboxylatoalkyl)-1,2,4-benzenetricarboxylic-1,2 Imide (2a,b) The synthesis of N-(carboxylatoalkyl)-1,2,4-benzene-

Archive of SID tricarboxylic-1,2 imide was conducted according to ref. 21.

Synthesis of N,N-Bis (Isocyanatoalkyl)-1,2,4,5-, beuzenetetracarboxylic-1,2:4,5-diimides (3a,b)

The synthesis was carried out as detail described in ref. 20.

Synthesis of N-(Isocyanatoalkyl)-1,2,4-benzenetricarboxylic-1,2 Imides (4a,b)

The above procedure was repeated for the preparation of this compound, but the intermediate diacylazide was separated as oil, which was extracted with benzene. dried over sodium sulphate and then refluxed for 8 h, as in ref. 21.

Preparation of Poly(urethane-imide)

A solution of diisocyanate (5 mmol) in DMAc (5 mL) was placed in a 50 mL three-necked flask equipped with a magnetic stirring bar, a dropping funnel, a condenser and a nitrogen inlet. To this, a solution of PTMEG (5 mmol) in DMAc (5 mL) and a few drops of stannous octoate catalyst were added with vigorous stirring, and then the temperature was raised to 110 °C and maintained for 2 h. The pale yellow solution was then poured into 200 mL of water to precipitate the polymer. The precipitation was filtered, redissolved in DMAc, and the procedure was repeated to isolate the polymer. Finally it was dried under vacuum at 50 °C for 24 h.

RESULTS AND DISCUSSION

Diisocyanates can serve as backbones for a host of polyurethanes and these diisocyanates can be synthesized by a variety of methods of which the most important ones are phosgenation of diamine and Curtius rearrangements of diacylazides. In the present work, Weinstock modification of Curtius rearrangement was chosen for the preparation of diisocyanates as shown in Scheme L

Condensation of ω -amino acid with either pyromellitic dianhydride or trimellitic anhydride gave diacids 1a,b and 2a,b, respectively. These diacids were converted to corresponding diisocyanates via action of sodium azide. ethylchloroformate. triethylamine reagents and subsequent heating of intermediate diacylazides.

IR spectra of diisocyanates 3a,b and 4a,b showed characteristic bands of imide rings at 1780 cm⁻¹ (imide I), 1370 cm⁻¹ (imide II), 1120 cm⁻¹ (imide III), 720 cm⁻¹ (imide IV) and band at 2980 cm⁻¹ due to aliphatic methylene groups. Also characteristic NCO stretching band at 2260 cm⁻¹ was observed in IR spectra of diisocyanates.

All of these diisocyanates showed molecular ion peaks in their mass spectra. ^tH NMR spectra of diisocyanates showed aromatic proton resonance signals at about 8 ppm and aliphatic methylene group proton resonance at 1.4-3.8 ppm depending on the position of neighbouring imide or isocyanate groups. Spectroscopic data of all monomers were collected in Table 1.

Four poly(urethane-imide)s were prepared by the reaction of diisocyanates with PTMEG in DMAc solvent (Scheme II).

The IR spectra of all polymers contained prominent characteristic bands of the imide and urethane groups. The bands around 1780 cm⁻¹ and 1740-1710 cm⁻¹ were due to imide and imide/urethane carbonyl linkages, respectively and N-H stretching band of urethane group was observed around 3350 cm⁻¹. Also C-O-C stretching of the PTMEG segment was observed at 1110 cm⁻¹. In ¹H NMR spectra of polymers, aromatic protons resonance signals were observed at 8.05-8.5 ppm. The methylene protons of >N-CH₂ at 3.8 ppm, of -CH₂-O- at 3.3 ppm, of -CH2-OCONH- at 4.3 ppm and central CH2 groups of aliphatic part of diisocyanate or PTMEG at 1.3-1.8 ppm were also obvious at ¹H NMR spectra.

Spectroscopic data of all polymers were collected in Table 2.

The inherent viscosities of the polymers were measured in DMF solvent at 30 °C and the results were presented in Table 2. The results revealed the high molecular weight of the polymers. All of these polymers produced clear, flexible and tough films, which could be cast from solution of polymers in DMF solvent. This showed good mechanical strength

Table 2. Spectroscopic data, yield and viscosity of polymer.

Comp.	Structure	Yield	ղ Inh	IR (cm ⁻¹)	¹ H NMR (ppm)*
No.		(%)	(dL/g)		
5a	<u>ဂူ ဂူ</u>	92	0.55	3356, 2935,	1.3–1.8 (m, 16H),
				2860, 1770,	3.6-3.8 (t, 8H), 4.1-
				1712, 1540,	4.3 (t, 4H), 8.3 (s,
	0			1340, 1110,	2H), 8.5 (s, 2H), 9.1
				730	(s, 2H)
5b		91	0.51	3352, 2935,	1.3–1.8 (m, 36H),
				2860, 1770,	3.6–3.8 (t, 8H), 4.1–
	ö ö			1705, 1550,	4.3 (t, 4H), 8.3 (s,
				1346, 1115,	2H), 8.5 (s, 2H), 9.1
				735	(s, 2H)
6a		93	0.52	3360, 2930,	1.4–1.8 (m, 10H),
				2850, 1769,	3.6-3.8 (t, 4H), 4.1-
				1707, 1546,	4.3 (t, 4H), 7.5–8.3
				1359, 1120,	(m, 3H), 8.5 (s, 2H),
1				740	9.1 (s, 2H)
6b		92	0.50	3366, 2930,	1.4-1.8 (m, 20H),
				2856, 1765,	3.6–3.8 (t, 4H), 4.1–
	+C-N			1705, 1545,	4.3 (t, 4H), 7.5–8.3
	L "Ö]n			1370, 1130,	(m, 3H), 8.5 (s, 2H),
				750	9.1 (s, 2H)

* Solvent DMSO-d6

of the films.

The solubility properties of polymers were studied in several solvents. As shown in Table 3 all polymers show excellent solubility in polar aprotic solvents.

Thermal stability of polymers was evaluated by

thermal gravimetric analysis. All of the polymers showed a two-stage decomposition pattern without considerable weight loss below 250 °C. The first stage of decomposition may be attributed to the thermooxidative cleavage of the weak and labile linkages, methylene and urethane groups, while the second

Table 3. Solubility of bolythers in different solven
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Polymer	DMF	DMAc	NMP	DMSO	m-Cresol	THF	Toluene
5a	+	+	+	+	+ -		-
5b	+	+	+	+	+	-	-
6a	+	+	+	+	+-	-	-
6b	+	+	+	+	+	_	-

+ Soluble; - Insoluble; + - Soluble after heating to 60 °C.



Scheme II

stage being as in due to the cleavage of the imide linkages. Also in DSC traces of polymers, the exotherm due to thermal decomposition of polymers begin around 250 °C. Thermal characteristic of polymers were collected in Table 4.

Table 4. Thermal	property	/ of	polymers.
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Polymers	IDT	T ₁₀ (%)	T _{max}	Ch. Y	Tg
5a	261	335	402	20	99
5b	257	325	391	18	92
6a	250	317	386	15	112
6b	250	316	380	13	100

IDT: Initial decomposition temperature; T₁₀%: Temperature of 10% weight loss; T_{max}. Maximum Decomposition temperature, Ch.Y: Percent weight of polymer remained at 600 °C, T_a; Glass transition temperature.

CONCLUSION

The facile synthesis of four diisocyanates with preformed imide rings was achieved via the nonphosgenation, Weinstock modification of Curtius rearrangement reaction. New soluble, and thermally stable poly(urethane-imide)s were derived using these diisocyanates and PTMEG diol. Poly(urethaneimide)s derived from 3a and 3b diisocyanates have higher thermal stability and lower glass transition temperatures than polymers based on 4a and 4b isocyanates. There were also no considerable difference between solubility properties and inherent viscosity of these two classes of polymers.

Compared to the conventional polyurethanes, these polymers showed improved the relation showed improved the relation of the re

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seems that increased phase separation and domain cohesion because of strong dipole-dipole interaction of imide groups, present in the hard segment, were responsible for the improvement of thermal properties.

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