Synthesis, Characterization and Properties of Novel Poly(Ester-Amide-Urethane)s

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Summary: A diacid (TOBA) containing an ester group was synthesized by reaction of terephthaloyl chloride with 4-hydroxybenzoic acid. Reaction of the obtained diacid with thionyl chloride resulted in preparation of the related diacid chloride (TOBC). Nucleophilic substitution reaction of 4-aminophenol and also 5-amino-1-naphthol with the prepared diacid chloride afforded two aromatic diols containing ester and amide groups, respectively. Aromatic and semi-aromatic poly(ester-amide-urethane)s were prepared via addition polymerization of different diisocyanates with novel diols. The prepared polyurethanes showed improved thermal stability.

Keywords: addition polymerization; copolymerization; polyurethanes; synthesis; thermal properties

Introduction

Polyurethanes comprise a class of versatile materials that have excellent abrasion resistance and the properties of both rubber and plastics. They are becoming more important as engineering materials.[1] In spite of their extended applications, the main drawback of polyurethanes is their poor heat resistance. Their acceptable mechanical properties disappear at about 80-90°C and thermal degradation takes place above 200°C. [2]

Attempts to improve the thermal stability of polyurethanes have been made over a long period. One important method by which to improve the thermal stability of polyurethanes is chemical modification of their structure by copolymerization with highly thermally-stable polymers. This can be achieved by incorporation of an amide and ester moiety into the polyurethane chain. Polyamides and polyesters are important classes of high performance polymers that have remarkable high temperature resistance and superior physical and mechanical properties. [3-5]

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Pursuing our continued interest in synthesizing thermally stable polymers, [6-15] here we describe the synthesis of novel diols with preformed ester and amide structures. Addition polymerization of diols with six different diisocyanates led to the preparation of twelve different aromatic and semi-aromatic poly(ester-amide-urethane)s. The presence of urethane, ester, and amide linkages in the polymer chain may alter the properties of polymers to an even greater extent. Hence it was thought interesting to synthesize and characterize poly(ester-amide-urethane)s.

Experimental

Materials

All the required chemicals were purchased either from Merck or Aldrich Chemical Co. Terephthaloyl chloride, p-phenylene diisocyanate (PPDI), naphthalene diisocyanate (NDI), and cyclohexane diisocyanate (CHDI) were purified by sublimation. Diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI), and dicyclohexylmethane diisocyanate (H_{12}MDI) were purified by distillation. NMP, DMAc, and toluene were purified by vacuum distillation over CaH_2.

Analytical Instruments

Infrared measurements were performed on a Bruker IFS-48 FT-IR spectrometer. The ^{1}H-NMR spectra were recorded in dimethyl sulfoxide (DMSO-d_6) solution, using a Bruker Avance DPX 500-MHz instrument. Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780. Differential thermogravimetric (DTG) traces were recorded on a Polymer Lab TGA-1500. The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model MK-II) over a temperature range of −100 to 200 °C at 1 Hz and a heating rate of 5 °C /min. The value of tan δ and the storage modulus versus temperature were recorded for each sample. Inherent viscosities were measured using an Ubbelohde viscometer.

Monomer Synthesis

Synthesis of terephthaloyl bis (4-oxybenzoic)acid (TOBA):

4-Hydroxybenzoic acid (23.14g) was dissolved in 350 ml of a 0.1 M aqueous solution of sodium hydroxide. After cooling the solution to 10°C, 11.58g of terephthaloyl chloride dissolved in 115 ml of tetrachloroethane and was added drop-wise to the mixture with stirring. The reaction mixture was stirred at room temperature for 6 h. The mixture was soaked in 430 ml of 3M HCl for 14h.

The product was obtained by filtration and washed with water, ether, and ethanol. Then it was vacuum dried at 60°C overnight (yield 85%).

[IR (KBr): υ 3250 (O-H); 1748 (-COOR); 1688 (-COOH); 1425 (C=C); and about 1285 cm^{-1} (C-O); ^{1}H-NMR (ppm) (DMSO-d_6): δ 13.11 s (2H, COOH); 8.04-8.27 m (8H, aromatic); 7.45-7.80m (4H, aromatic)].

Synthesis of terephthaloyl dioxydibenzoylchloride (TOBC):

TOBA (7.0 g) was refluxed with thionyl chloride (87.5ml) and two drops of dry DMF for 4 h. Excess thionyl chloride was removed from the mixture by distillation. The crude product was recrystallized from ether and vacuum dried at 50°C. (Yield 89%). [IR (KBr): υ 1780 (-COCl); 1745 (-COOR); 1600 (C=C); 1408 (C=C); 1265 cm^{-1} (C-O).

Synthesis of diol (AP-diol):

4-Aminophenol (0.048 mole) was dissolved in 60 ml of dry NMP. The mixture was cooled to 0°C and 5 ml of propylene oxide was added. TOBC (0.0153 mole) was added to the mixture and stirred at 0°C for 0.5 h. The mixture was further stirred for 4 h at room temperature. The product was obtained by pouring the flask content into 300 ml of H_2O. It was then filtered and washed with methanol. (Yield 88%). [IR (KBr): υ 3320-3345 (NH, OH); 1734 (-COOR), 1643 (-CONH), 1250 cm^{-1}(C-O); ^{1}H-NMR(ppm) (DMSO-d_6): δ 10.10 s (2H, NH); 9.22 s (2H,OH); 8.06-8.29 m (8H, aromatic); 7.49-7.56 m (8H, aromatic); 6.76-6.78 m (4H, aromatic).

The same procedure was performed to prepare AN-diol. In this case, 5-amino-1-naphthol was used instead of 4-aminophenol. (Yield 86%). [IR (KBr): υ 3198-3250 (NH, OH); 1736(-COOR), 1641 (-CONH), 1263 cm^{-1} (C-O); ^{1}H-NMR (ppm) (DMSO-d_6): δ 10.16 s (2H, NH); 9.40 s (2H, OH); 8.07-8.30 m (8H, aromatic); 7.20-7.57 m (12H, aromatic); 6.58-6.62 m (4H, aromatic).

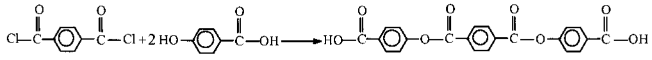
Polyurethane Synthesis

The synthesis of a polyurethane was typically carried out as follows: Diisocyanate (0.0012 mole) was dissolved in 5 ml of dry NMP under a nitrogen atmosphere. Two drops of dibutyltin dilaurate was added to the mixture and heated to 110°C . Then 0.0012 mole of the prepared diol (AP or AN diol) was dissolved in 5 ml of dry NMP, added to the mixture and heated for 4 h. The mixture was cooled, poured into 200 ml of H_2O and filtered. Then the polymer was purified using DMF and H_2O as a solvent-non solvent system. The obtained polymer was vacuum dried at 70°C for 5 h. Yield of the reactions was about 73-95%.

Results and Discussion

Improving the thermal stability of polyurethane was the main aim of this study. This was achieved by the following structural modifications: (a) introduction of thermally stable amide and ester groups into the polymer backbone; (b) phenylation of the backbone; (c) retention of regularity and symmetry of units.

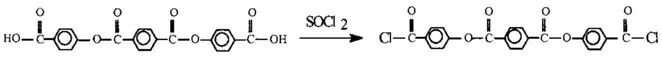
Thus, preparation of two novel, fully aromatic diols with preformed ester and amide groups was considered. In this way, by condensation reaction of 4-hydroxybenzoic acid with terephthaloyl chloride, according to the Schotten-Baumann reaction, a diacid (TOBA) was prepared (Scheme 1).



TOBA

Scheme 1. Synthesis of TOBA

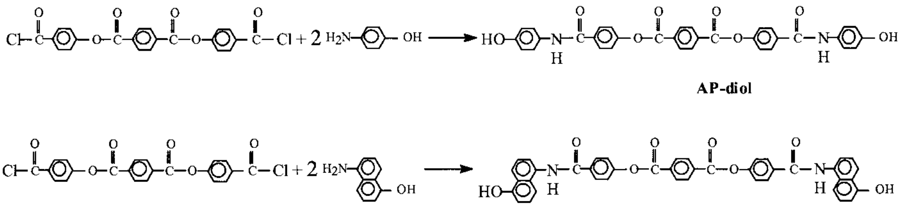
Conversion of the diacid to the corresponding diacid chloride (TOBC) was achieved by $SOCl_2$ in the presence of catalytical amount of dry DMF (Scheme 2).



TOBC

Scheme 2. Synthesis of TOBC

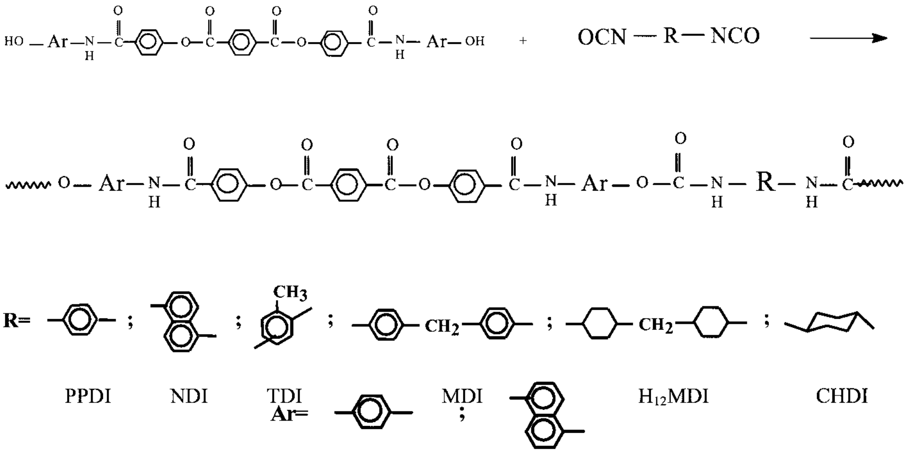
Two novel aromatic diols containing built in ester and amide units were obtained by the nucleophilic substitution reaction of TOBC with 4-aminophenol and also 5-amino-1-naphthol (Scheme 3).



AP-diol

AN-diol

Scheme 3. Preparation of diols with preformed groups

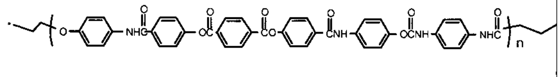
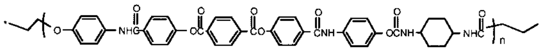
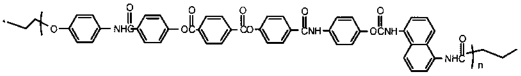
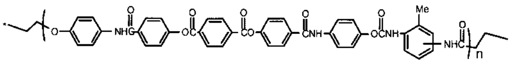
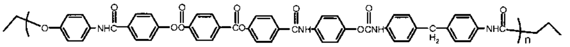
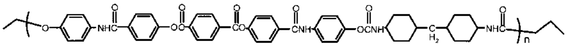
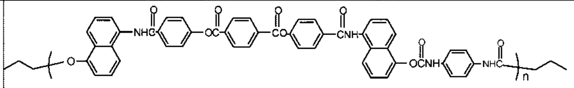
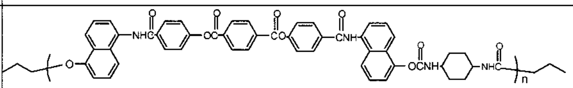
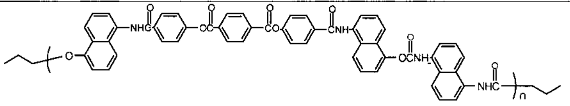
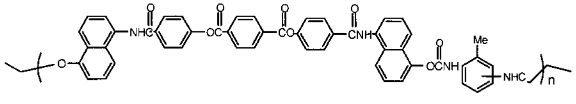


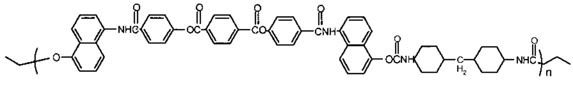
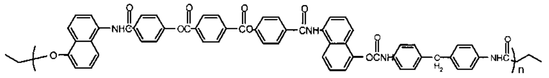
Scheme 4. Preparation of poly (ester-amide-urethane)s

Addition polymerization of the prepared diols with aromatic and aliphatic diisocyanates afforded 12 different poly(ester-amide-urethane)s. (Scheme 4).

Structures of the prepared polyurethanes and yields of the reaction are tabulated in Table 1.

Table 1. Structures of the poly (ester-amide-urethane)s

Reactants	Structures of the polymers	Yield (%)
1. Diol- AP+ PPDI		86
2. Diol- AP+ CHDI		90
3. Diol- AP+ NDI		76
4. Diol- AP+ TDI		97
5. Diol- AP+ MDI		90
6. Diol- AP+ H_{12}MDI		94
7. Diol- AN+ PPDI		80
8. Diol- AN+ CHDI		84
9. Diol- AN+ NDI		73
10. Diol- AN+ TDI		88

11. Diol- AN+ MDI		90
12. Diol- AN+ H_{12} MDI		95

The polyurethanes were characterized by spectroscopic methods and the results are tabulated in Table 2.

Table 2. Spectroscopic analysis of the polyurethanes

Polyurethane	IR(KBr)cm^{-1}	^1H-NMR(DMSO-d_6) δ
1)AP+PPDI	3323, 1734, 1643, 1610, 1541, 1252, 866	10.47 (amide,2H), 10.30 (urethane,2H), 6.71-8.32 (aromatic,24H)
2) AP+ CHDI	3327,2928, 1730, 1643, 1539, 1514, 1252, 827	10.18 (amide,2H), 9.30 (urethane,2H), 6.76-8.29 (aromatic,20H) 3.28-3.30 (CH,2H), 2.18-2.20 (CH_2,8H)
3)AP + NDI	3325, 1736, 1644, 1539, 1516, 1254, 834	10.45 (amide,2H), 10.31 (urethane,2H), 6.70-8.51 (aromatic,26H)
4) AP + TDI	3321, 2935,1735, 1646, 1537, 1323, 1252, 826	10.46 (amide,2H), 10.30 (urethane,2H), 6.72-8.39 (aromatic,23H) 1.78 (CH_3,3H)
5) AP + MDI	3329,2920, 1738, 1643, 1609, 1544, 1250, 864	10.16 (amide,2H), 9.29 (urethane,2H), 6.75-8.52 (aromatic,28H) 3.90 (CH_2,2H)
6) AP+H_{12}MDI	3325,2922, 1732, 1647, 1530, 1517, 1253, 866	10.21 (amide,2H), 9.27 (urethane,2H), 6.72-8.26 (aromatic,20H) 3.17 (aliphatic,2H), 2.09-2.13 (aliphatic,18H), 1.30(CH_2,2H)
7) AN + PPDI	3302, 1736, 1641, 1597, 1514, 1406,1269, 826	10.46 (amide,2H), 10.27 (urethane,2H), 6.70-8.35 (aromatic,28H)
8) AN+CHDI	3319,2928, 1745, 1642, 1597, 1531, 1268, 861	10.19 (amide,2H), 9.29 (urethane,2H), 6.70-8.51 (aromatic,24H) 3.29-3.32 (CH,2H), 2.18-2.20 (CH_2,8H)
9) AN+ NDI	3320, 1731, 1644, 1538,	10.47 (amide,2H), 10.30 (urethane,2H), 6.71-8.53 (aromatic,30H)

	1510, 1252, 836	
10) AN + TDI	3306,2972, 1742, 1643, 1597, 1531, 1267, 869	10.47 (amide,2H), 10.32 (urethane,2H), 6.71-8.61 (aromatic,27H) 1.78 (CH_3,3H)
11) AN+ MDI	3300,2968, 1736, 1648, 1611, 1511, 1257, 856	10.15 (amide,2H), 9.30 (urethane,2H), 6.73-8.53 (aromatic,32H) 3.87 (CH_2,2H)
12) AN+H_{12}MDI	3323, 2922,1732, 1642, 1539, 1513, 1250, 865	10.33 (amide,2H), 9.97 (urethane,2H), 6.72-8.26 (aromatic,24H) 3.20 (aliphatic,2H), 2.11-2.17 (aliphatic,18H), 1.32(CH_2,2H)

The results of elemental analysis were in good agreement with the calculated amounts and, therefore, confirmed the structures. (Table 3).

Table 3. Elemental analysis of the polyurethanes

Polyurethane		Calculated			Found		
		C	H	N	C	H	N
1.	AP-PPDI: $C_{42} H_{28} N_4 O_{10}$	67.38	3.74	7.49	67.17	3.65	7.62
2.	AP-CHDI: $C_{42} H_{34} N_4 O_{10}$	66.84	4.51	7.43	66.75	4.23	7.56
3.	AP-NDI: $C_{46} H_{30} N_4 O_{10}$	69.17	3.76	7.02	69.10	3.66	7.08
4.	AP- TDI: $C_{43} H_{30} N_4 O_{10}$	63.54	3.69	6.90	63.59	3.51	6.98
5.	AP-MDI: $C_{49} H_{34} N_4 O_{10}$	70.17	4.06	6.68	70.15	4.10	6.53
6.	AP-H_{12}MDI: $C_{49} H_{46} N_4 O_{10}$	69.18	4.00	6.59	69.01	3.95	6.72
7.	AN-PPDI: $C_{50} H_{32} N_4 O_{10}$	70.75	3.77	6.60	70.60	3.68	6.73
8.	AN-CHDI: $C_{50} H_{38} N_4 O_{10}$	70.26	4.45	6.56	70.30	4.51	6.67
9.	AN-NDI: $C_{54} H_{34} N_4 O_{10}$	72.16	3.79	6.24	72.09	3.85	6.20
10	AN-TDI: $C_{51} H_{34} N_4 O_{10}$	70.99	3.94	6.50	70.81	3.85	6.63

11	AN-MDI: $C_{57} H_{38} N_4 O_{10}$	72.92	4.05	5.97	73.01	4.09	6.01
12	AN-H_{12}MDI: $C_{57} H_{50} N_4 O_{10}$	72.00	5.26	5.89	71.92	5.20	5.98

The inherent viscosity of the polymers measured at a concentration of 0.5 g/dl in DMAc at 30°C (Table 4) was about 0.35-0.42 dl/g, indicating acceptable molecular weights.

Solubility of the prepared polyurethanes in dipolar aprotic solvents was about 0.5-1.3 g/dl.

Thermal properties and thermal behavior of the polymers was studied using DSC, TGA, and DMTA techniques. The T_g of the polymers was in the range of 155-179°C, the 10% weight loss was in the range of 278-299°C, and the char yields of the polymers at 550°C were about 24-48% (Table 4).

According to the results, the thermal stabilities of the prepared polyurethanes are higher than the conventional polyurethanes. This can be mainly attributed to the incorporation of ester and amide groups into the polymer backbone.

Thus, polyurethanes derived from AP-diol are more heat resistant and less soluble than the AN-diol derived polyurethanes. This is a result of symmetry and close packing of the aminophenol unit in comparison with the bulky aminonaphthol unit.

On the other hand, polyurethanes derived from fully aromatic diisocyanates are more heat resistant and less soluble than the polyurethanes derived from aliphtic diisocyanates.

Table 4. Thermal analysis and viscosity of the polymers

Polyurethane	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Char Yield (at 550°C)	Inherent Viscosity (dL/g)
1)AP+PPDI	179	190	299	327	33	0.42
2) AP+ CHDI	170	180	287	325	28	0.41
3)AP + NDI	176	188	290	309	39	0.37
4) AP + TDI	171	179	288	306	29	0.38
5) AP + MDI	172	185	293	322	34	0.40
6) AP+H_{12}MDI	168	177	284	315	24	0.40
7) AN + PPDI	177	189	297	322	48	0.38
8) AN+CHDI	158	175	282	323	37	0.35
9) AN+ NDI	172	185	289	310	38	0.35
10) AN + TDI	166	177	284	300	26	0.36
11) AN+ MDI	169	183	287	317	33	0.37
12) AN+H_{12}MDI	155	169	278	303	25	0.39

In general, more aromatic, more symmetric and less bulky polyurethanes have high thermal stability and low solubility. Also, more aliphatic, more bulky and less symmetric polyurethanes have high solubility and low thermal stability.

Conclusions

To improve the thermal stability of polyurethanes, introduction of thermally stable units into the polymer backbone was considered. In this way, two aromatic diols with preformed ester and amide groups were prepared. Polyaddition reactions of the two diols with different diisocyanates afforded poly(ester-amide-urethane)s. The polymers were characterized and their physical properties were examined. All the polyurethanes showed improved thermal stability in comparison with conventional polyurethanes.

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