

# Preparation and Characterization of Novel Poly(ether-imide-urethane)s with Improved Thermal Stability

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Received 12 June 2004; accepted 12 September 2004

## ABSTRACT

In order to prepare polyurethanes with improved thermal stability as well as proper processability, novel poly(ether-imide-urethane)s (PEIUs) were prepared by polycondensation reaction of a diisocyanate containing oxyethylene units and build-in imide rings with ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), respectively. Synthetic procedures for preparation of monomer and polymers were described. The properties of prepared polymers including thermal stability and thermal behaviour were studied by TGA and DSC. Investigation of the results showed that co-presence of oxyethylene groups and imide structures in the polyurethane backbone can improve thermal stability and maintain the processability of final polymers.

### Key Words:

polyurethane;  
poly(ether-imide-urethane);  
thermal stability;  
isocyanate;  
processability.

## INTRODUCTION

Polyurethanes are versatile materials, which can be easily prepared by simple reaction of isocyanates and polyols [1-3]. Despite the possibility of tailoring their properties according to requirements, polyurethanes suffer a serious disadvantage of poor

stability to heat. This low heat resistant is the main reason for limitation in technical application of polyurethanes. Chemical modification of structure by thermally stable heterocyclic groups can improve polyurethanes thermal stability. This

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can be achieved by the introduction of imide groups in polyurethanes.

Various attempts to incorporate polyimide units into polyurethanes can be classified as: (a) reaction of isocyanate or blocked isocyanate terminated polyurethane prepolymers with acid anhydrides [4-10], (b) reaction of amine terminated polyurethane prepolymers with acid anhydride [11-12], (c) reaction of isocyanate terminated polyurethane prepolymers with diols or diacids containing build-in imide groups [13-16], (d) intermolecular Diels-Alder reaction of molecules containing bis(2-furyl-carbamate) units with bis-maleimides [17-19], (e) thermal cross-linking of polyurethane prepolymers containing maleimide functions [20-23], (f) reaction of diisocyanates containing build-in imide groups with different polyols [24-28], (g) reaction of epoxy resins containing imide structure with blocked polyurethane prepolymers [29], (h) reaction of hydroxyl containing polyimides with blocked polyurethane prepolymers [30-31], (i) reaction of polyimide precursor, poly(amic acid), with blocked polyurethane prepolymers [32-33], and (j) blending of thermoplastic polyurethanes with poly(ether imide)s [34].

The present study deals with the preparation and properties of poly(ether-imide-urethane)s based on a diisocyanate containing oxyethylene moieties and build-in imide rings prepared via nonhazardous, non-phosgenation Curtius rearrangement and investigation of their properties.

## EXPERIMENTAL

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

Sodium azide was activated by adding hydrazine hydrate. After keeping overnight, it was dissolved in minimum amount of water, precipitated in acetone, and dried. *N,N*-dimethylacetamide (DMAc) was purified by distillation under reduced pressure over  $\text{CaH}_2$ . Trimellitic anhydride (TMA) was recrystallized from acetic anhydride and sublimed in vacuum before use.

FTIR Spectra were recorded on a Bruker-IFS 48 instrument. NMR Spectra were recorded on a Bruker-Avance DPX 250 MHz instrument. Mass spectra were recorded on a Shimadzu GC-MS QP 1000 EX. TGA

and DSC analyses were performed on a Stanton STA-615 with heating rate  $20^\circ\text{C}/\text{min}$  in air. Melting points were determined in open capillaries with a Buchi 535 instrument. Inherent viscosity of polymers was determined for solution of 0.5 g/dL in DMF at  $30^\circ\text{C}$  using an Ubbelohde viscometer.

### Synthesis of Diacid (I)

Into a three-necked round bottomed flask equipped with a condenser, a dropping funnel, a thermometer, and a magnetic stirrer, trimellitic anhydride (0.1 mol) was dissolved in acetic acid (300 mL) at  $50\text{-}60^\circ\text{C}$ , to obtain a clear solution. Upon cooling at room temperature in a water bath, diamine (0.05 mol) was slowly added in such a way that the temperature of the mixture did not rise over  $25^\circ\text{C}$ . After stirring at this temperature for 1 h, the mixture was stage heated up to  $120^\circ\text{C}$ , and maintained at this temperature for 4 h. The solution was precipitated into water/ice to give the crude diacid-imide as a white powder, which was subsequently thoroughly washed with cold water, dried, and recrystallized from dioxane/hexane (2/1, v/v).

### Synthesis of Diacylchloride (II)

The diacid (I) (0.01 mol) was heated at reflux with thionyl chloride (0.2 mol) for 2 h with catalytic amount of pyridine. Removal of excess thionyl chloride under reduced pressure and recrystallizing from a benzene/dioxane (2/1, v/v) mixture gave diacylchloride.

### Synthesis of Diacylazide (III)

To an ice cold solution of activated sodium azide (0.025 mol) in water (20 mL) was added dropwise a solution of diacylchloride (II) (0.01 mol) in dichloromethane (20 mL) and the solution was stirred vigorously for 2 h at  $0^\circ\text{C}$ . The dichloromethane layer was separated and washed successively with water, 10%  $\text{Na}_2\text{CO}_3$  and finally with water before it was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Removal of the solvent at room temperature under reduced pressure gave the diacylazide.

### Synthesis of Diisocyanate(IV)

Diacylazide(III) (0.01 mol) was dissolved in dry benzene (50 mL) and refluxed for 16 h. Evaporation of the solvent under reduced pressure gave the diisocyanate in pure form.

Elemental analysis,  $C_{24}H_{18}N_4O_8$  (490); calculated: C 58.87, H 3.67, N 11.43; found: C 58.69, H 3.76, N 11.35

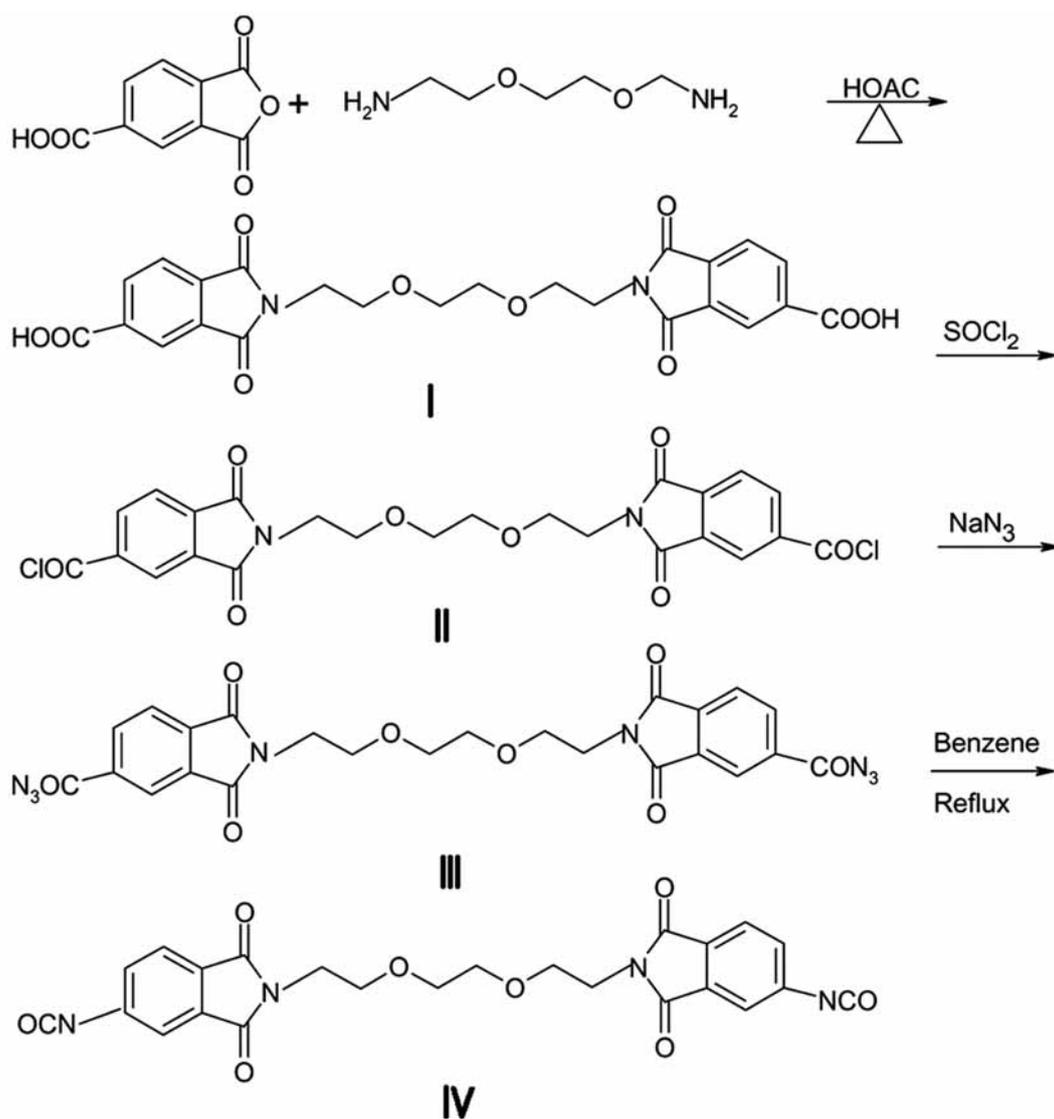
### General Procedure of PEIUs Synthesis

A solution of diisocyanate (IV) (2 mmol) in DMAC (5 mL) was added to a 50 mL four-necked flask equipped with a magnetic stirring bar, a thermometer, a dropping funnel, a condenser and a  $N_2$  inlet. To this, a solution of diol (2 mmol) and dibutyltin dilurate (0.1 mol%) in DMAC (1 mL) was added with vigorous stirring and then, the temperature was raised to  $110^\circ C$  and maintained for 2 h. The pale yellow solution was then poured to 200 mL of water to precipitate the polymer. The precipitate was filtered, redissolved in DMAC,

and the procedure was repeated to isolate the polymers, which was finally dried under vacuum at  $80^\circ C$  overnight.

### RESULTS AND DISCUSSION

The diacid (I) was prepared via imidization of 1,8-diamino-3,6-dioxaoctane with trimellitic anhydride in acetic acid solvent. The diacid was converted to diacylchloride (II) by refluxing with thionyl chloride which was then treated with aqueous sodium azide solution to form the diacylazide (III). The thermal decomposition of the diacylazide via Curtius rearrangement gave corresponding diisocyanate (IV) (Scheme I).



**Scheme I.** Synthetic route to monomer.

**Table 1.** Characteristic data of monomer.

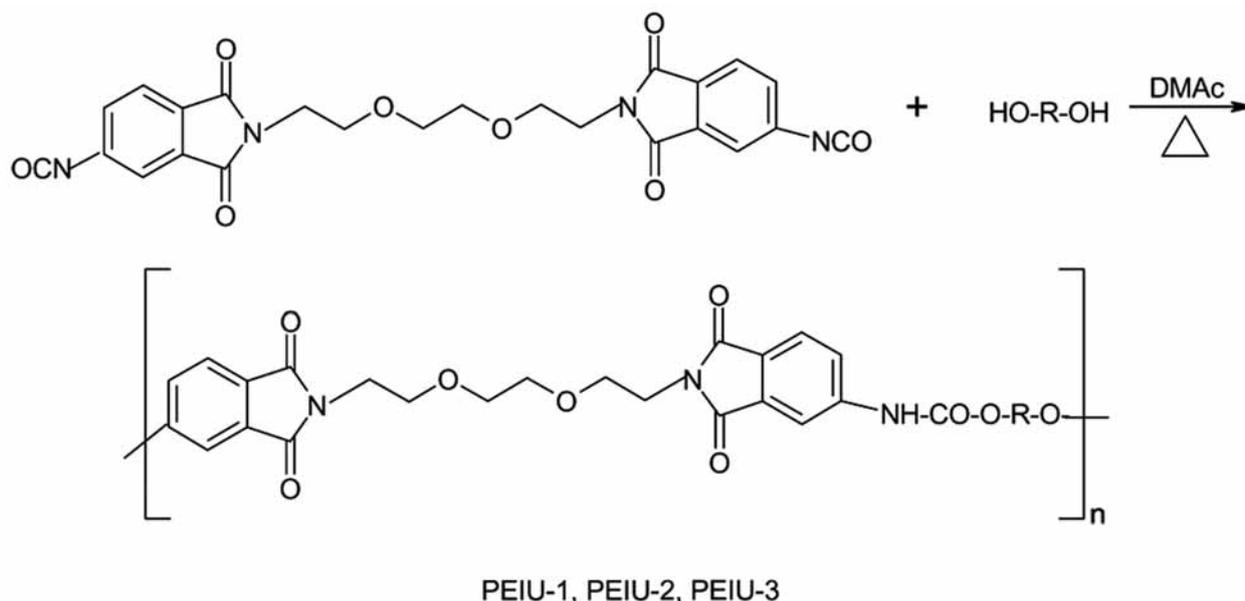
| Code | Yield (%) | mp (°C) | FTIR (cm <sup>-1</sup> )                                  | <sup>1</sup> H NMR (ppm)*   |
|------|-----------|---------|---|---|
| I    | 65        | 209-210 | 3350, 3059, 2881, 1770, 1705, 1685, 1390, 1161, 1080, 744 | 12.05(s, 2H), 8.53(s, 2H), 8.37(d, 2H), 8.08(d, 2H), 3.86 (t, 4H), 3.61(t, 8H). |
| II   | 90        | 88-90   | 3059, 2890, 1805, 1775, 1706, 1396, 1161, 1088, 748       | 8.63(s, 2H), 8.48(d, 2H), 8.20(d, 2H), 3.90(t, 4H), 3.64(t, 8H).                |
| III  | 92        | 90-92   | 3071, 2889, 2145, 1778, 1713, 1396, 1110, 1096, 720       | 8.70(s, 2H), 8.50(d, 2H), 8.22(d, 2H), 3.86(t, 4H), 3.65(t, 8H)                 |
| IV   | 87        | 143-145 | 3071, 2890, 2257, 1774, 1701, 1393, 1196, 1099, 747       | 8.39(s, 2H), 8.21(d, 2H), 7.91(d, 2H), 3.86(t, 4H), 3.62(t, 8H)                 |

(\*) Solvent: CDCl<sub>3</sub>

The IR spectrum of diisocyanate showed absorption band at 2257 cm<sup>-1</sup> due to NCO groups in addition to the four peaks due to cyclic imide rings at 1774, 1393, 1196, 720 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of the diisocyanate showed -O-CH<sub>2</sub> methylene protons as triplet at 3.62 ppm and >N-CH<sub>2</sub> methylene protons as triplet at 3.86 ppm, also aromatic protons of trimellitic rings was observed at 8.39, 8.21, and 7.91 ppm. In addition, molecular ion peak (M<sup>+</sup>= 490) was obvious in mass spectrum of the diisocyanate monomer.

PEIUs were prepared easily via reaction of diisocyanate (IV) with EG, DEG, or TEG, respectively in DMAC solvent at 110°C using catalytic amount of dibutyltin dilurate as catalyst (Scheme II).

The FTIR spectra of PEIUs contained prominent characteristic bands of the urethane, imide and ether groups. The urethane N-H stretching was observed at 3400-3350 cm<sup>-1</sup>. The combination of N-H out-of-plane bending and C-N stretching was observed at 1530 cm<sup>-1</sup> and the bands around 1770 cm<sup>-1</sup> and 1710 cm<sup>-1</sup> were due to imide and imide/urethane carbonyl linkages. The <sup>1</sup>H NMR spectra of PEIUs showed aromatic protons of trimellitimide rings at 8.53, 8.37 and 8.08 ppm. The resonance signals for methylene protons of polymers appeared in the region of 3.6, 3.8 and 4.1 ppm from the neighbouring ether, imide and urethane groups. Also characteristic bands of urethane N-H proton appeared at 8.8 ppm.

**Scheme II.** Preparation of polymers.

**Table 2.** Yield, inherent viscosity and spectroscopic data of polymers.

| Code   | Yield (%) | $\eta_{inh}$ (dL/g) | FTIR (cm <sup>-1</sup> )                                   | <sup>1</sup> H NMR (ppm)*   |
|--------|-----------|---------------------|--|---|
| PEIU-1 | 95        | 0.65                | 3400, 3071, 2924, 1772, 1706, 1558, 1343, 1204, 1099, 747  | 9.1(s, 2H), 8.51(s, 2H), 8.20(d, 2H), 8.02(d, 2H), 4.36(t, 4H), 3.82(t, 4H), 3.62(t, 8H)  |
| PEIU-2 | 95        | 0.71                | 33380, 3071, 2920, 1773, 1706, 1568, 1343, 1204, 1099, 743 | 9.1(s, 2H), 8.51(s, 2H), 8.20(d, 2H), 8.02(d, 2H), 4.25(t, 4H), 3.82(t, 4H), 3.62(t, 12H) |
| PEIU-3 | 94        | 0.67                | 3360, 3071, 2924, 1772, 1707, 1545, 1389, 1217, 1096, 748  | 9.1(s, 2H), 8.51(s, 2H), 8.20(d, 2H), 8.02(d, 2H), 4.20(t, 4H), 3.82(t, 4H), 3.62(t, 16H) |

(\*) Solvent: CDCl<sub>3</sub>**Table 3.** Solubility properties of polymers.

| Code   | NMP | DMF | DMSO | DMAC | Tetrachloroethane | Chloroform | THF |
|--------|-----|-----|------|------|-------------------|------------|-----|
| PEIU-1 | ++  | ++  | ++   | ++   | ++                | +          | -   |
| PEIU-2 | ++  | ++  | ++   | ++   | ++                | +          | -   |
| PEIU-3 | ++  | ++  | ++   | ++   | ++                | +          | -   |

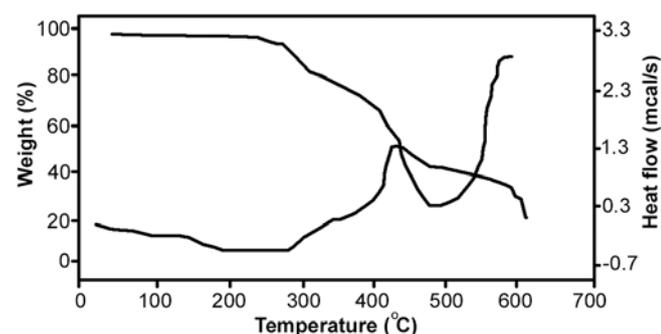
(++) : Highly soluble, (+) : Soluble after heating, (-) : Insoluble

**Table 4.** Thermal property data of polymers.

| Code   | IDT | T <sub>g</sub> | T <sub>10%</sub> | Ch.Y.% |
|--------|-----|----------------|------------------|--------|
| PEIU-1 | 283 | 178            | 340              | 25     |
| PEIU-2 | 276 | 170            | 321              | 19     |
| PEIU-3 | 270 | 165            | 296              | 13     |

IDT: Initial decomposition temperature; T<sub>g</sub>: Glass transition temperature; T<sub>10%</sub>: Temperature of 10% weight loss; Ch.Y.%: Percent of remained polymer at 600°C.

The solubility of PEIUs was studied at different solvents as shown in Table 3. All of PEIUs were soluble in common polar aprotic solvents as well as chlorinated solvent. The good solubility of polymers is a result of high flexibility of oxymethylene units present in polymer backbone.

**Figure 1.** TGA/DSC trace of PEIU-3.

The inherent viscosity of PEIUs measured in DMF at 30°C and 0.5 g/dL concentration was in the range of 0.65- 0.71 dL/g, which showed high molecular weight of polymers (Table 2). So the condition of polymerization reaction was adequate for growing of polymer chains.

The solubility properties of polymers were studied in several solvents. As shown in Table 3 all polymers show excellent solubility in polar aprotic solvents. The films cast from solution of polymers in chloroform was brittle. So it was impossible to study the mechanical properties of polymers. The hardness of compressed disc of polymers was in the range of 68-75 in shore A scale. The hardness of prepared polymers decreases as the length of glycol increases.

Thermal stability of polymers was evaluated by thermal gravimetric analysis. All of polymers showed a two-stage decomposition pattern without considerable weight loss below 270°C. The first stage of decomposition may be attributed to the thermooxidative cleavage of the weak and labile linkages, i.e. methylene and urethane groups, while the second stage being that due to the cleavage of the imide linkages. A 10 % weight loss as a criterion of thermal stability was in the range of 296-340°C, which showed excellent thermal stability of prepared polymers in comparison to common polyurethanes.

In DSC traces of polymers, exotherms due to thermal decomposition of polymers begun around 270°C, and second order transition due to  $T_g$  was observed in the range of 165-178°C, which was much higher than conventional polyurethanes. Thermal characteristic data of polymers were collected in Table 4 and one representative TGA/DSC trace of PEIU-3 is shown in Figure 1.

## CONCLUSION

The synthesis in good yield of a diisocyanate containing oxyethylene linkages and preformed imide rings was carried out by the Curtius rearrangement of the corresponding  $\alpha$ - $\omega$ -diacylazide. The diisocyanate was polycondensed with different diols to give PEIUs. The resulting polymers showed good solubility and thermal stability.

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