Novel Imide-modified Polyurethanes, Synthesis and Thermal Characteristics

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ABSTRACT

New (polyurethane-imide)s (PUIs) were synthesized by polyaddition reaction of two different diisocyanates with three different imide containing diols. The reactions were performed in DMAc solvent at 100 °C using dibutyltin dilaurate as a catalyst. The structure of diols and PUIs were characterized by conventional methods including \(^1\)H NMR, FTIR, and mass spectroscopies. and physical properties such as solution viscosity, solubility property, thermal stability and thermal behaviour were studied for PUIs. These polymers showed excellent solubility in polar aprotic and chlorinated solvents. Their inherent viscosities were in the range of 0.28–0.35 dL/g. Also their 10% weight loss were in the temperature range of 323–358 °C.

Key Words: polyurethane, polyimide, poly(urethane-imide), thermal stability, diol

INTRODUCTION

Polyurethanes (PUs), a well-known class of polymers, can be mainly prepared by polyaddition of diols with diisocyanates. The tailor made properties from supersoft flexible foam to tough elastomers and to high-resistant coatings have resulted in many end applications [1–4]. However, PUs are generally known to offer little resistance to heat, which cause their properties to disappear from about 80–90 °C and largely accounts for their relatively limited technical applicability. Thus, thermal stability of PU has received extensive attention. One accepted approach for the improvement of thermal stability of PUs is the chemical modification of their structure by blending or copolymerization with more thermally stable polymers [5]. More attention has been paid to modifications of these polymers by heterocyclic groups such as isocyanurate [6–8], oxazolidone [9–11], and imide [12–14] groups into the backbone of PUs. Among these groups PUs containing imide structures show remarkable heat resistance and superior mechanical, electrical and durable properties.

In our previous works we reported the preparation of novel PUIs using diisocyanates containing build-in imide structure [15], and also explored the possibility of introducing the imide function in the PUs backbone through the reaction of imide containing diol chain extenders with isocyanate terminated PU prepolymer [16].

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This study presents an investigation undertaken to use imide-containing diols for making non-segmented polyurethanes.

EXPERIMENTAL

Chemicals were purchased from either Merck and Fluka Co. Toluene diisocyanate (TDI mixture of 80% 2,4 and 20% 2,6 isomers) and hexamethylene diisocyanate (HDI) were vacuum distilled before use. \(N,N'-\text{Dimethyl acetamide (DMAc)}\) and \(N\)-methyl pyrrolidone (NMP) were vacuum distilled from CaH\(_2\) and stored over 4 Å molecular sieves. Trimellitic anhydride was purified by recrystallization from acetic anhydride. 4,4'-Diaminodiphenyl ether was purified by vacuum drying at 50–60 °C. Ethylene glycol (EG), diethylene glycol (DEG), and 1,3-propylene glycol (1,3-PG) were dried under vacuum at 90 °C. Other chemicals and solvents were used as received.

FTIR spectra were recorded on a Bruker-IFS 48 instrument. \(^1\)H NMR spectra were obtained using a Jeol-Japan GNM-EX at 90 MHz instrument. TGA and DSC analyses were performed on a Stanton STA-615 with heating rate of 20 °C/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 °C using a ubbelohde viscometer.

Synthesis of \(N,N'-(4,4'-\text{Diphenyl ether) bis Trimellitimide (I)}\)

The reaction of trimellitic anhydride dissolved in NMP and 4,4'-diaminodiphenyl ether was carried out according to the full procedure described earlier [16] by the authors.

Synthesis of Imide Containing Diols (II, III, IV)

Diacid I (6 g, 0.011 mol) was reacted with either EG, DEG or 1,3-PG according to the detailed procedure described in full as in ref. [16].

Preparation of Poly(urethane-imide)

A solution of diisocyanate (2 mmol) in DMAc (5 mL) and two drops of dibutyltin dilaurate was added to a 50 mL four-necked flask equipped with a magnetic stirring bar, a thermometer, a dropping funnel, a condenser and a nitrogen inlet. To this, a solution of diol (2 mmol) in DMAc (5 mL) was added with vigorous stirring and then, the temperature was raised to 100 °C and maintained for 2 h. The pale yellow solution was then poured into 200 mL of water to precipitate the polymer. The precipitate was filtered, redissolved in DMAc, and the procedure was repeated to isolate PUI. Finally it was dried under vacuum.

RESULTS AND DISCUSSION

Scheme I depicts the synthesis routes of the imide containing diols. Diacid I was conveniently prepared by the condensation of two equivalents of trimellitic anhydride with 4,4'-diaminodiphenyl ether in NMP. The diacid I was subjected to the reaction with excess amount of EG, DEG, 1,3-PG and the resulting diols (II–IV) were prepared in excellent yields. Mass spectrum of diacid I showed \(m/z= 548\), corresponding to molecular ion peak. IR Spectrum of diacid I showed characteristic imide group absorption peak at 1780, 1720, 719 cm\(^{-1}\), acid carbonyl group at 1693 cm\(^{-1}\) and aromatic ether group at 1225 cm\(^{-1}\). \(^1\)H NMR spectra of the diols were in accordance with the proposed structures. All spectral data of compounds I–IV were indicated in Table 1 [16].

PUIs were prepared easily through reaction of diols with TDI or HDI in DMAc solvent at 100 °C (Scheme II). The IR spectra of all PUIs contained prominent characteristic bands of the imide and urethane groups. The bands around 1780–1770 cm\(^{-1}\) and 1740–1710 cm\(^{-1}\) were due to imide and ester carbonyl linkages and N–H stretching band.
of urethane group was observed around 3400-3350 cm⁻¹. The ¹H NMR spectra of polymers showed the aromatic ring protons in the region 7.10-7.56 ppm and aromatic protons of trimellitimide rings at 8.08-8.53 ppm. The resonance signals for methylene protons of the polymers appeared in the region 1.68-4.48 ppm depending on the position of the methylene groups from the neighbouring ester, ether and

![Scheme 1](image1)

![Scheme II](image2)

\[
\text{Scheme I}
\]

<table>
<thead>
<tr>
<th>( R )</th>
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<tbody>
<tr>
<td>II   (-\text{CH}_2\text{CH}_2)</td>
</tr>
<tr>
<td>III  (-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)</td>
</tr>
<tr>
<td>IV   (-\text{CH}_2\text{CH}_2\text{CH}_2)</td>
</tr>
</tbody>
</table>

![Scheme II](image3)

\[
\text{Scheme II}
\]

<table>
<thead>
<tr>
<th>( R )</th>
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<tbody>
<tr>
<td>V ((\text{CH}_2)_2)</td>
</tr>
<tr>
<td>VI ((\text{CH}_2\text{CH}_2)_2\text{O})</td>
</tr>
<tr>
<td>VII ((\text{CH}_2)_3)</td>
</tr>
<tr>
<td>VIII ((\text{CH}_2)_2\text{OCH}_2\text{CH}_2)</td>
</tr>
<tr>
<td>IX ((\text{CH}_2\text{CH}_2)_2\text{O})</td>
</tr>
<tr>
<td>X  ((\text{CH}_2)_3)</td>
</tr>
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Table 1. Spectral and physical data of compounds I-IV [16].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
<th>mp (°C)</th>
<th>IR (cm⁻¹)</th>
<th>°H NMR (ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>80</td>
<td>380</td>
<td>3600, 3100, 1780, 1720, 1693, 1600, 1580, 1390, 1225, 1110, 719</td>
<td>8.53 (s, 2H), 8.37 (d, 2H), 8.08 (d, 2H), 7.56 (d, 4H), 7.31 (d, 4H)</td>
</tr>
<tr>
<td>II</td>
<td>82</td>
<td>128</td>
<td>3450, 2925, 2858, 1780, 1720, 1380, 1160, 729</td>
<td>8.53 (s, 2H), 8.37 (d, 2H), 8.08 (d, 2H), 7.56 (d, 4H), 7.31 (d, 4H), 4.85 (t, 4H), 4.65 (t, 4H), 4.32 (s, 2H)</td>
</tr>
<tr>
<td>III</td>
<td>83</td>
<td>111</td>
<td>3452, 2925, 2863, 1780, 1720, 1380, 1120, 734</td>
<td>8.53 (s, 2H), 8.37 (d, 2H), 8.08 (d, 2H), 7.56 (d, 4H), 7.31 (d, 4H), 4.85 (t, 4H), 4.65 (t, 4H), 4.32 (s, 2H), 3.56 (t, 8H)</td>
</tr>
<tr>
<td>IV</td>
<td>82</td>
<td>119</td>
<td>3452, 2930, 2860, 1784, 1723, 1380, 1120, 728</td>
<td>8.53 (s, 2H), 8.37 (d, 2H), 8.08 (d, 2H), 7.56 (d, 4H), 7.31 (d, 4H), 4.85 (t, 4H), 4.65 (t, 4H), 4.32 (s, 2H), 1.68 (m, 4H)</td>
</tr>
</tbody>
</table>

*S Solvent: DMSO-d₉

Table 2. Yield, inherent viscosity, and spectral data of PUIs.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield (%)</th>
<th>Inh (dL/g)</th>
<th>IR (cm⁻¹)</th>
<th>°H NMR (ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>93</td>
<td>0.35</td>
<td>3345, 2925, 2857, 1780, 1728, 1523, 1380, 1250, 1080, 730</td>
<td>9.61 (s, 2H), 9.43 (s, 2H), 8.92 (s, 2H), 8.72 (s, 2H), 8.55 (s, 2H), 8.37 (d, 2H), 8.08 (d, 2H), 7.1–7.5 (m, 11H), 4.85 (t, 4H), 4.32 (t, 4H), 2.13 (s, 3H)</td>
</tr>
<tr>
<td>VI</td>
<td>92</td>
<td>0.32</td>
<td>3345, 2923, 2850, 1780, 1725, 1520, 1380, 1252, 1120, 1080, 735</td>
<td>9.61 (s, 2H), 9.43 (s, 2H), 8.92 (s, 2H), 8.72 (s, 2H), 8.37 (d, 2H), 8.08 (d, 2H), 8.55 (s, 2H), 7.1–7.5 (m, 11H), 4.85 (t, 4H), 4.30 (t, 4H), 3.62 (t, 8H), 2.13 (s, 3H)</td>
</tr>
<tr>
<td>VII</td>
<td>92</td>
<td>0.33</td>
<td>3343, 2920, 2860, 1782, 1722, 1523, 1380, 1250, 1080, 730</td>
<td>9.61 (s, 2H), 9.43 (s, 2H), 8.92 (s, 2H), 8.72 (s, 2H), 8.55 (s, 2H), 8.37 (d, 2H), 8.08 (d, 2H), 7.1–7.5 (m, 11H), 4.85 (t, 4H), 4.30 (t, 4H), 2.13 (s, 3H), 1.68 (m, 4H)</td>
</tr>
<tr>
<td>VIII</td>
<td>90</td>
<td>0.30</td>
<td>3344, 2930, 2857, 1780, 1720, 1523, 1380, 1250, 1080, 732</td>
<td>9.61 (s, 2H), 9.43 (s, 2H), 8.92 (s, 2H), 8.72 (s, 2H), 8.55 (s, 2H), 8.37 (d, 2H), 8.08 (d, 2H), 7.1–7.5 (m, 11H), 4.85 (t, 4H), 4.32 (t, 4H), 4.1 (t, 4H), 1.2–1.7 (m, 8H)</td>
</tr>
<tr>
<td>IX</td>
<td>89</td>
<td>0.29</td>
<td>3345, 2925, 2857, 1780, 1728, 1523, 1380, 1250, 1120, 1080, 738</td>
<td>9.61 (s, 2H), 9.43 (s, 2H), 8.92 (s, 2H), 8.72 (s, 2H), 8.55 (s, 2H), 8.37 (d, 2H), 8.08 (d, 2H), 7.1–7.5 (m, 11H), 4.85 (t, 4H), 4.30 (t, 4H), 4.1 (t, 4H)</td>
</tr>
<tr>
<td>X</td>
<td>91</td>
<td>0.28</td>
<td>3340, 2925, 2860, 1780, 1728, 1523, 1384, 1250, 1080, 727</td>
<td>9.61 (s, 2H), 9.43 (s, 2H), 8.92 (s, 2H), 8.72 (s, 2H), 8.55 (s, 2H), 8.37 (d, 2H), 8.08 (d, 2H), 7.1–7.5 (m, 11H), 4.85 (t, 4H), 4.32 (t, 4H), 4.1 (t, 4H), 1.2–1.7 (m, 10H)</td>
</tr>
</tbody>
</table>

*S Solvent: DMSO-d₉
The peak due to methyl group of TDI in polymers V–VII appeared at 2.13 ppm. Also characteristic bands of urethane N–H proton appeared at 9.60, 9.43, 8.90 and 8.72 ppm. The spectral data of all polymers were collected in Table 2.

The inherent viscosities of the polymers were measured in DMF solvent at 30 °C and results were presented in Table 2. The results revealed that the polymers were of moderate to high molecular weight. However the films casted from the solution of polymers in DMF solvent were hard and brittle.

The solubility properties of PUIs were studied using several solvents. As shown in Table 3 all polymers showed excellent solubility in polar aprotic solvents and chlorinated solvents such as tetrachloroethane, but less efficient solvents such as toluene and xylene could not solve the polymers.

The thermal stability of PUIs was evaluated by thermal gravimetric analysis. 10% Weight losses of polymers as a criterion of thermal stability of polymers were in the range of 323–358 °C. Compared to the conventional polyurethanes, the decomposition temperature of PUIs was improved. It seems that increased domain cohesion, because of strong dipole-dipole interaction of imide groups present in the polymers backbone are responsible for improvement of thermal properties.

Thermal behaviours of PUIs were studied by DSC. The glass transition temperatures of PUIs were observed around 82–98 °C that is higher than typical polyurethanes. This behaviour can be attributed to incorporation of rigid imide rings in PUIs. Also the exotherm due to the thermal decomposition of PUIs, which indicate the upper limit for use of these polymers were begun around 310 °C. The temperature of various transitions concerning thermal stability and thermal behaviour of prepared PUIs, are presented in Table 4.

**CONCLUSION**

The new aromatic aliphatic non-segmented PUIs composed of TDI or HDI disiocyanate and three different imide containing diols were produced via polyaddition reactions with excellent yields.

Simultaneous presence of flexible methylene or oxyethylene groups and also imide structure in PUI, backbone caused improved solubility in polar aprotic solvents and improved thermal stability up to 360 °C, respectively.

Compared to corresponding segmented PUI [16], the non-segmented PUIs show higher thermal
stability but lower rubber like flexibility.

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REFERENCES