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Synthesis and Characterization of Pyridine-Based Polyurethanes

Kakarla Raghava Reddy*, Anjanapura V. Raghu a,b, Han Mo Jeong b
and Siddaramaiah c

a Department of Chemistry, University of Ulsan, Ulsan 680-749, South Korea
b Department of Fuel Cell, Dhirubhai Ambani Life Sciences Centre, Rabale, Navi Mumbai 400-701, India
c Department of Polymer Science and Technology, S. J. College of Engineering, Mysore, India

Abstract
A series of novel linear segmented polyurethanes (PUs) containing a pyridine unit in the main chain have been synthesized by polycondensation reaction of various diisocyanates, 4,4′-diphenyl-methane diisocyanate (MDI), toluene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI), with 4,4′-{pyridine-2,6-diylbis[nitrilomethylene]}diphenol-based diol. The structure of the diol and segmented PUs were established by NMR, Fourier transform infrared (FT-IR), ultraviolet-visible (UV-Vis) and fluorescence spectroscopic methods. The thermal behavior of the synthesized PUs was further characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All PUs were soluble in polar aprotic solvents.

Keywords
Polyurethanes, pyridine-Schiff base based polymers, spectral study, solubility, thermal properties

1. Introduction
Polyurethanes (PUs) are unique polymeric materials with a wide range of physical and chemical properties [1, 2]. Because a wide range of monomeric materials is now commercially available and tailor-made properties can be obtained from well-designed combinations of monomeric materials, PUs can be extensively used to meet the highly diversified demands of modern technologies such as automobile, medicine, coating, adhesive, fiber, foam, thermoplastic elastomers and packaging [1]. Their properties depend on several factors and can be varied in a wide range by the proper selection of components, composition and preparation conditions. To introduce functionalities within the PU materials, few possibilities can be considered. The wide range of starting compounds leads to the synthesis of materi-
als with different and unique properties. More recently, much attention is shown for the development of functional PUs because it is expected that they lead to applications that are outside of the PU market, thus giving rise to additional functionality to the end-materials [3, 4].

Polymers containing Schiff base units in the main chain display many special properties, such as excellent mechanical strength, high thermal stability, semiconducting, good optoelectronic properties and thermotropic liquid crystalline behavior [5, 6]. Hard segmented PUs show poor solubility in common organic solvents due to their rigid backbones [7, 8], which limits their application and makes it difficult to process them. In order to overcome such difficulties, the polymer structure modification is necessary, wherein one can introduce the bulky or asymmetric groups on the polymer backbone or incorporate the non-coplanar structural units on the main polymer chain [9, 10]. In this study, we attempted to increase the solubility in polar solvents of novel linear segmented PUs prepared by the reaction of 4,4′-{pyridine-2,6-diylbis[nitrilomethyllylidene]}diphenol with 4,4′-diphenyl methane diisocyanate (MDI), toluene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), or hexamethylene diisocyanate (HDI). The structures of 4,4′-{pyridine-2,6-diylbis[nitrilomethyllylidene]}diphenol and PUs were established by FT-IR, 1H-NMR, 13C-NMR, UV-Vis and fluorescence spectral methods. The PUs were further characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

2,6-Diaminopyridine, 4-hydroxy benzaldehyde, IPDI, dibutyltin dilaurate (DBTL), MDI, TDI and HDI were purchased from Aldrich (Milwaukee, WI, USA) and were used without further purification. Methanol, ethanol, dimethyl sulphoxide, dichloromethane, dimethyl formamide, dimethyl acetamide, 4-methyl-2-pentanone and hydrochloric acid were all purchased from Fluka (Milwaukee, WI, USA).

2.2. Characterization

1H-NMR and 13C-NMR spectra in DMSO-d6 were recorded at 25°C with a Bruker 300 spectrometer. FT-IR spectral measurements were scanned between 400 and 4000 cm⁻¹ using Nicolet (Varian) spectrophotometer. UV-Vis spectra (Secomam) were recorded in the wavelength range of 200–600 nm using a dilute PU solution (5 × 10⁻⁴ M) prepared in a spectroscopic grade DMF solvent. Fluorescence spectra (Varian) were also recorded in the wavelength range of 200–600 nm. TGA and DSC were performed using Perkin-Elmer Diamond analyzer under nitrogen atmosphere at a heating rate of 20°C/min. The TGA and DSC thermograms were recorded in the temperature range ambient to 800°C and ambient to 450°C, respectively.
2.3. Synthesis of 4,4′-[pyridine-2,6-diylbis[nitrilomethylidylen]]Diphenol (PBNMD)

To a stirred solution of 2,6-diaminopyridine (5.45 g, 0.05 mol) in hot (70°C) methanol (50 ml) was added drop-wise a solution of 4-hydroxy benzaldehyde (12.21 g, 0.1 mol) in methanol (75 ml). The mixture was refluxed for 8 h. After cooling, the resultant product was filtered, washed with distilled water and recrystallized from ethanol. Thereafter the sample was dried in air (yield 13.0 g (76%)). The characteristic FT-IR spectral absorption bands of PBNMD are 3425, 3155, 1640, 1583, 1455, 1339, 1247, 1166, 1010 and 899 cm⁻¹.

2.4. Synthesis of Polyurethanes

The general procedure used to synthesize PUs involves the reaction in a three-necked 100-ml round bottom flask equipped with a stirrer, condenser and a dropping funnel. 4,4′-[pyridine-2,6-diylbis[nitrilomethylidylen]]Diphenol (0.005 mol) was dissolved in 10 ml dry DMF in the presence of 0.2 ml DBTL under nitrogen atmosphere with constant stirring. Then, an equimolar quantity of diisocyanates (MDI, TDI, IPDI or HDI) with respect to diol taken in 10 ml dry 4-methylpentanone was added once with constant stirring. The reaction mixture was heated for 10 h at 80°C to obtain the solid. The obtained PUs were cooled, poured into distilled water and then filtered. The recrystallization of the obtained solid product was done using dry DMF. The formation of PUs is shown in Scheme 1.

Scheme 1. Reaction pathways for the formation of PU-1 to PU-4.
2.4.1. Poly[4,4′-{pyridine-2,6-diylbis[nitrilomethylylidene]}diphenyl, 4,4′-Methylene Di-phenyl Diurethane] (PU-1)
PU-1 was prepared using 1.25 g MDI and 1.73 g PBNMD, with a yield of 2.75 g (92%). FT-IR (KBr): 3355, 3021, 2922, 2854, 1655, 1603, 1542, 1443, 1307, 1224, 1102 and 813 cm$^{-1}$.

2.4.2. Poly[4,4′-{pyridine-2,6-diylbis[nitrilomethylylidene]}diphenyl, Toluene-2,4-di-urethane] (PU-2)
PU-2 was prepared using 0.84 g TDI and 1.73 g PBNMD, with a yield of 2.50 g (96%). FT-IR (KBr): 3369, 3013, 2960, 2924, 2858, 1659, 1611, 1544, 1512, 1451, 1387, 1227, 1173 and 833 cm$^{-1}$.

2.4.3. Poly[2,2′-{4,4′-{pyridine-2,6-diylbis[nitrilomethylylidene]}diphenyl, Isophorone Di-urethane}] (PU-3)
PU-3 was prepared from 1.11 g IPDI and 1.73 g PBNMD, with a yield of 2.71 g (95%). FT-IR (KBr): 3370, 2952, 2930, 1663, 1618, 1594, 1451, 1382, 1239, 1095 and 887 cm$^{-1}$.

2.4.4. Poly[4,4′-{pyridine-2,6-diylbis[nitrilomethylylidene]}diphenyl, Hexamethylene Di-urethane] (PU-4)
PU-4 was prepared from 0.82 g HDI and 1.73 g PBNMD, with a yield of 2.48 g (96%). FT-IR (KBr): 3339, 2930, 2846, 1657, 1620, 1574, 1512, 1446, 1386, 1253, 1170, 1100 and 829 cm$^{-1}$.

3. Results and Discussion

3.1. Spectral Data

UV-Vis and florescence spectra of the PBNMD and PUs were recorded in DMF at ambient temperature. The electronic absorption and emission spectral data of both the diol monomer and PUs are listed in Table 1. In the spectra of the Schiff base PUs, the aromatic bands at 265 and 267 nm are attributed to $\pi$–$\pi^*$ transitions of benzene. The bands at 312 and 322 nm are assigned to –C=O, $\pi$–$\pi^*$ transitions. The emissions from these diol and PUs appear around 367–378 nm and 466–490 nm, and the excitations at 265 and 320 nm, respectively. From the absorption and emission spectra, it is concluded that there is no significant difference in the monomer and the PUs prepared.

The FT-IR spectrum of each PU shows several characteristic stretching vibration modes due to N–H, C=O, CH=N and C–H bands, as shown in Fig. 1. The FT-IR spectra of the PUs indicated the disappearance of hydroxyl (no absorption at 3425 cm$^{-1}$) and isocyanate groups (no absorption at 2270 cm$^{-1}$), which indicates its utilization during polymerization. In all the PUs, the broad bands appearing between 3339 and 3370 cm$^{-1}$ are due to the presence of a hydrogen-bonded N–H group [11]. However, the hydrogen-bonded carbonyl groups of urethane are shown in the region from 1655 to 1663 cm$^{-1}$. The imine bands appeared in the region from 1603 to 1620 cm$^{-1}$.
Table 1.
Absorption and emission spectral peaks for PBNMD and different PUs

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Peak λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>Absorption</th>
<th>Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBNMD</td>
<td>267, 312</td>
<td>378, 490</td>
<td></td>
</tr>
<tr>
<td>PU-1</td>
<td>265, 320</td>
<td>367, 473</td>
<td></td>
</tr>
<tr>
<td>PU-2</td>
<td>266, 322</td>
<td>370, 495</td>
<td></td>
</tr>
<tr>
<td>PU-3</td>
<td>265, 319</td>
<td>371, 485</td>
<td></td>
</tr>
<tr>
<td>PU-4</td>
<td>266, 315</td>
<td>370, 466</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. FT-IR spectra of polyurethanes PU-1 to PU-4.

NMR analysis allows the observation of disappearance of –OH and –NCO groups and the formation of an urethane polymer chain (Table 2). The <sup>1</sup>H-NMR spectra of the diol and PUs show characteristic signals. The <sup>1</sup>H-NMR spectrum of PU-1 is shown in Fig. 2. Resonance peaks in the region of δ = 0.87–3.79 ppm correspond to the methyl/methylene/isophorone protons of the PUs. The hydroxyl proton of the diol is observed at δ of 9.91 ppm. The resonance peaks of imine protons appear in the region of δ = 8.73–9.20 ppm. The multiplet due to aromatic protons occurs in the region of δ = 6.48–8.96 ppm.
Table 2.
Data obtained from $^1$H-NMR spectra for PBNMD and PUs

<table>
<thead>
<tr>
<th>Sample code</th>
<th>OH/NH protons</th>
<th>Aromatic protons</th>
<th>Methyl/methylene/isophorone protons</th>
<th>CH=NX protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBNMD</td>
<td>9.91</td>
<td>6.53–7.79</td>
<td>–</td>
<td>8.73</td>
</tr>
<tr>
<td>PU-1</td>
<td>9.79</td>
<td>6.48–8.56</td>
<td>3.79</td>
<td>9.14</td>
</tr>
<tr>
<td>PU-2</td>
<td>9.11</td>
<td>6.53–8.98</td>
<td>2.86</td>
<td>9.08</td>
</tr>
<tr>
<td>PU-3</td>
<td>9.77</td>
<td>6.55–7.94</td>
<td>0.87–3.65</td>
<td>9.12</td>
</tr>
</tbody>
</table>

Figure 2. $^1$H-NMR spectrum of PBNMB.

The $^{13}$C-NMR spectra of all PUs show the characteristic signals and data are presented in Table 3. The $^{13}$C-NMR spectra of PU-1 are shown in Fig. 3. The chemical shift ranging between 17.55 and 46.61 ppm is due to methyl/methylene/isophorone carbons. Resonance signals observed in the region between 110.67 and 159.19 ppm are due to aromatic carbons. Peaks observed in the region from 190.89 to 191.26 ppm were ascribed to urethane carbonyl carbons. Imine carbon peaks appeared in the region between 162.30 and 162.52 ppm.

3.2. Solubility Study

We have examined the solubility of the PUs by using polar and non-polar solvents. PUs are soluble in polar solvents like dichloromethane, dimethylformamide, N-methyl-2-pyrrolidone and dimethyl sulfoxide. However, they were insoluble in methanol, ethanol, methylene chloride, toluene, carbon tetrachloride, ethyl acetate,
dioxane, tetrahydrofuran, ethyl methyl ketone, n-hexane and chloroform. Due to the presence of intermolecular hydrogen-bonding they are insoluble in low-boiling-temperature solvents.

3.3. Thermal Properties

The thermal properties of all the PUs were evaluated using DSC and TGA. The DSC-derived curves are displayed in Fig. 4. The existence of multiple endotherm peaks has been documented in several studies of the thermal behavior of segmented polyurethane block copolymers [10–14]. Koberstein and Galambos [15] suggested that the origin of multiple endotherm peaks in PUs is dependent upon the specimen preparation procedure. Martin et al. [16] indicated that the five endotherms were possibly due to melting of various hard segment length populations. Van Bogart et al. [17] have identified three endothermic transitions associated with the ordering of
MDI/1,4-butane diol hard segments in materials subjected to a third thermal cycle. Blackwell and Lee [18] studied the multiple melting in MDI-based PUs that had been oriented and thermally annealed. In the light of the above information, it is clear that the melting behavior of PUs is highly dependent on the procedure adopted for sample preparation. Indeed, the origins of multiple melting may be inherently different for materials prepared under varying conditions.

In the present work, it was noticed that the multiple melting phenomena occurred in identical PUs prepared from only hard segments in the main chain. In all the PUs, $T_g$ is not clearly shown due to alternative hard segment [19]. The DSC data indicates the two endotherm peaks for PU-1 and PU-2, and three endothermic peaks for PU-3 and PU-4. In PU-1 the intermediate temperature endothermic peak ($T_2$) observed at 329°C is related to the melting of microcrystalline regions within hard microdomains. A higher melting temperature ($T_3$) was observed at 384°C. In PU-2, the intermediate temperature endotherm ($T_2$) was observed at 330°C. The melting of microcrystalline regions within hard microdomains is also observed, at 370°C. In PU-3 the lowest endotherm ($T_1$) observed at 134°C is due to a local restructuring of hard-segment units within the hard microdomains. The intermediate temperature
endotherm observed at 326°C is related to the melting of microcrystalline regions within hard microdomains. A higher melting temperature was observed at 382°C. In PU-4, the intermediate temperature endotherm has displayed two peaks, one at 206°C and another at 216°C. The melting of microcrystalline regions within hard microdomains is also observed at 375°C.

The TGA thermograms for all the PUs are shown in Fig. 5 and the obtained weight loss data are presented in Table 4. The results suggest that 10% weight loss occurs at 156–180°C, while the curves show major weight loss in the region 234–482°C. The residual weight remaining at 800°C was about 23–38%. This variation in weight loss is due to the differences in the structure of diisocyanates in PUs. In PU-1, the 10% weight loss begins at 180°C, but major weight loss occurs in the temperature range around 234–482°C. In PU-2, 10% weight loss begins at 170°C and major weight loss occurs at 203–450°C. In PU-3, 10% weight loss begins at 156°C and major weight loss occurs at 285–434°C. In PU-4, 10% weight

Figure 5. TGA thermograms of polyurethanes PU-1–PU-4.

Table 4. Thermal properties of PUs

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Decomposition temperature (°C)</th>
<th>Major weight loss transition (°C)</th>
<th>Residual weight loss at 800°C (%)</th>
<th>Onset temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{10}$a</td>
<td>$T_{50}$b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PU-1</td>
<td>180</td>
<td>458</td>
<td>234–482</td>
<td>38</td>
</tr>
<tr>
<td>PU-2</td>
<td>170</td>
<td>419</td>
<td>203–450</td>
<td>34</td>
</tr>
<tr>
<td>PU-3</td>
<td>156</td>
<td>379</td>
<td>285–434</td>
<td>23</td>
</tr>
<tr>
<td>PU-4</td>
<td>206</td>
<td>400</td>
<td>237–480</td>
<td>28</td>
</tr>
</tbody>
</table>

a Temperature at which 10% of weight loss was observed by TGA.
b Temperature at which 50% of weight loss occurred in TGA.
c Residual weight observed by TGA at 800°C in N₂.
loss begins at 106°C and the major weight loss occurs around 234–480°C. TGA data indicate that PU-1 exhibit good thermal stability compared to other PUs and this is attributed to an increase in the phenyl rings of MDI, which is attributed to the presence of biphenyl on the main chains. TGA measurements established that the incorporated pyridine-based diol in the PU backbone strongly improves the final char yield [20]. The abrupt variation of weight loss of PUs may be due to the different diisocyanate segments in the main chain.

4. Conclusions
Novel PUs containing Schiff base moieties like 4,4′-[pyridine-2,6-diylbis[nitrilomethylylidene]]diphenol in the main chain have been prepared using MDI, TDI, IPDI and HDI via polycondensation. The structures of 4,4′-[pyridine-2,6-diylbis[nitrilomethylylidene]]diphenol and PUs have been confirmed by FT-IR, 1H-NMR and 13C-NMR spectral data. TGA data indicated that the incorporated pyridine based diol in the PU backbone strongly improves the final char yield. DSC displayed multiple endotherms peaks. PUs are soluble in polar aprotic solvents. Utilization of this novel PUs for suitable applications is currently under way.

References