Liquid crystalline polyureas with oligo(ethylene glycol) sequences

Shahram Mehdipour-Ataei,* Leila Akbarian-Feizi

*Iran Polymer and Petrochemical Institute, P.O. Box 14965/115, Tehran 14977, Iran; fax: +9821 44580023; e-mail: s.mehdipour@ippi.ac.ir

(Received: 16 December, 2009; published: 12 November, 2010)

Abstract: A diamine monomer containing ester, amide and ether functional groups was prepared and its polymerization reaction with different diisocyanates to give main chain poly(ester amide ether urea)s was investigated. The monomer was synthesized via reaction of terephthaloyl chloride with 4-hydroxybenzoic acid and subsequent reaction of the resulted diacid with 1,8-diamino-3,6-dioxaoctane. The polymers were characterized by FT-IR and 1H-NMR spectroscopic method and elemental analysis. The resulting polymers exhibited excellent solubility in polar solvents. Crystallinity of the resulted polymers was evaluated by wide-angle X-ray diffraction (WXRD) method, and they exhibited semi-crystalline patterns. The glass transition temperatures (Tg) of the polymers determined by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were in the range of 88-112 °C. The temperatures for 10% weight loss (T10) from their thermogravimetric analysis (TGA) curves were found to be in the range of 297–312 °C in air. Also the prepared polyureas showed liquid crystalline character.

Keywords: polyurea; liquid crystal; thermally stable; properties.

Introduction

Polyureas have been widely used during the past three decades as industrial cast elastomers [1-5]. Aromatic polyureas are generally termed as valuable thermoplastics because of their reasonably high glass-transition temperature (Tg), relative high decomposition temperature, good mechanical properties, hydrolytic stability, chemical resistance and unique nonlinear optical properties [6-14].

These properties are the result of hydrogen bonding between the polymer chains from different sides. However, potentially more useful polyureas are those containing other functional groups such as urea–formaldehyde resins, poly(urethane-urea)s, poly(ether-urea)s, and poly(amide-urea)s [15-20].

Although polyureas have been used for many applications, including the encapsulation of pharmaceuticals, inks, dyes, and the modification of wool fibers by interfacial grafting techniques [21-28] and many related fields, not too much attention has been paid on the synthesis of polyureas because wholly aromatic polyureas were found to be infusible and insoluble and hence were difficult to process [29].

Therefore, preparation of soluble polyureas without perceptible loss of favorable properties has been the main research interest, and a great deal of attempts has been made to improve the processing characteristics of this class of polymers. A number of methods have been used to increase solubility and decrease Tg of polyureas. One approach to increase their solubility in organic solvents is the
introduction of bulky groups in the polymer backbone. Introduction of flexible groups in the backbone and copolymerization are also efficient methods in this regard [30, 31].

In this work a diamine was designed and prepared in such a way that in addition to ester and amide rigid groups, oligo ethylene glycol sequences as flexible group in the backbone were introduced for increasing solubility while maintaining the thermal stability of resulting polyureas. Other properties of these polymers including thermal, physical, and liquid crystallinity properties were also investigated.

**Results and discussion**

The aim of this study was preparation of new polyureas with specific properties and increasing fusibility and solubility of them with incorporation of flexible groups such as oligo ethylene glycol sequences in the structure of polymer. For this purpose, a diamine (TABE) was designed. TABE was synthesized via two steps: nucleophilic reaction of 4-hydroxybenzoic acid with terephthaloyl chloride in the presence of NaOH resulted in preparation of TOBA and then reaction of TOBA with 1,8-diamino-3,6-dioxaoctane (DADO) via Yamazaki method in the presence of pyridine, NMP, triphenylphosphite and CaCl₂ led to TABE (scheme 1). Thus, a diamine containing ester and amide groups and oligo ethylene glycol sequences was produced.

![Scheme 1. Preparation of TABE diamine.](image)

**Tab. 1. Characterization of TOBA and TABE.**

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>IR (KBr, cm⁻¹)</th>
<th>NMR (DMSO-d₆, δ)</th>
<th>Calculated</th>
<th>Found</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOBA</td>
<td>3250 (O-H)</td>
<td>13.11S (2H, COOH)</td>
<td>65.02, 3.45, -</td>
<td>65.27, 3.19, -</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>1748 (COOH)</td>
<td>8.28S (4H, aromatic)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1688 (COOH)</td>
<td>8.14 d (4H, aromatic)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1425 (C=C)</td>
<td>7.79d (CH, aromatic)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1285(C-O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3298(N-H)</td>
<td>8.63 S(2H, NH), 8.19 d(4H, aromatic), 7.90d(4H, aromatic)</td>
<td>61.26, 6.30, 8.40</td>
<td>60.85, 6.16, 8.28</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>3076( Ar-H)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2870,2921(CH₂)</td>
<td>7.40d(O-H-4H, aromatic),</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1740 (COOH)</td>
<td>3.16t(4H, O-CH₂), 3.52t(4H, O-CH₂), 3.42t (8H, O-CH₂-CH₂),</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1630 (CONH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1547(NH,CN)</td>
<td>3.36t(4H, CH₂NH), 2.54 t(4H, CH₂NH)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1281 (C-O )</td>
<td>CH₂NH), 1.23S(4H, NH₂)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Scheme 2. Synthesis of polyurea.

Structures of the TOBA and TABE were characterized and confirmed using FT-IR and $^1$H-NMR, and elemental analysis. The results are collected in Table 1.

Polymerization reaction of TABE with different diisocyanates produced new polyureas with improved fusibility and solubility and preserved thermal properties (scheme 2).

This reaction is step-growth addition reaction of amine across the carbon–nitrogen double bond without any by products. In this way, new types of polyureas with built-in ester, amide, and ether linkages and also methylene groups were synthesized. Polyureas were characterized with FT-IR, $^1$H-NMR, and elemental analysis.

**Tab. 2.** Characterization of polymers.

<table>
<thead>
<tr>
<th>Product</th>
<th>IR (KBr cm$^{-1}$)</th>
<th>NMR (DMSO-d$_6$ δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TABE-PPDI</td>
<td>3395,3047,2912,2870, 1752,1656,1633, 1547, 1500,1398,</td>
<td>8.67( S, 2H,NH), 8.59( S,2H,NH), 8.26(d,4H,phenyl), 8.06(S,2H,NH), 7.96(d,4H,phenyl), 7.64(d,4H,phenyl), 7.36(d,4H,phenyl), 3.62(t,4H, -O-CH$_2$-), 3.44(t,4H, -O-CH$_2$-), 3.41(t,8H, -CH$_2$-CH$_2$-), 3.36(4H, -CH$_2$-NH-), 3.32(4H, -CH$_2$-NH-)</td>
</tr>
<tr>
<td>TABE-NDI</td>
<td>3392,3078,2922,2870, 1735,1657,1635,1545, 1499,1379,</td>
<td>8.66(S,2H,NH), 8.5(S,2H,NH), 8.24(d,4H,phenyl), 8.06(S,2H,NH), 7.97(d,4H,phenyl), 7.35(4H,phenyl), 7.15(m,4H,naphthyl), 6.54(d,2H,naphthyl), 3.63(t,4H, -O-CH$_2$-), 3.43(4H, -O-CH$_2$-), 3.40(t,8H, -CH$_2$-CH$_2$), 3.36(4H, -CH$_2$-NH-), 3.31(4H, -CH$_2$-NH-)</td>
</tr>
<tr>
<td>TABE-MDI</td>
<td>3394,3109,2937,2864, 1750,1655, 1634,1544, 1476,1550,</td>
<td>8.65(S,2H,NH), 8.55(S,2H,NH), 8.21(d,4H,phenyl), 8.03(S,2H,NH), 7.91(d,4H,phenyl), 7.42(d,4H, phenyl), 7.34(d,4H,phenyl), 7.09(d,4H,phenyl), 3.79(S,2H, -CH$_2$-), 3.55(t,4H, -O-CH$_2$-), 3.42(t,4H, -O-CH$_2$-), 3.40(t,8H, -CH$_2$-CH$_2$), 3.30(4H, -CH$_2$-NH-), 3.23(t,4H, -CH$_2$-NH-)</td>
</tr>
<tr>
<td>TABE-TDI</td>
<td>3395,3078,2922,2866, 1729,1650, 1628,1524, 1497,1378,</td>
<td>8.64(S,2H,NH), 8.56(S,2H,NH), 8.25(d,4H,phenyl), 8.03(S,2H,NH), 7.95(d,4H,phenyl), 7.51(d,1H,phenyl), 7.34(d,4H,phenyl), 7.04(d,1H,phenyl), 6.89(d,1H, phenyl), 3.61(t,4H, -O-CH$_2$-), 3.45(t,4H, -O-CH$_2$-), 3.42(t,8H, -CH$_2$-CH$_2$), 3.35(t,4H, -CH$_2$-NH-), 3.32(4H, -CH$_2$-NH-), 2.34(3,3H,CH$_3$)</td>
</tr>
<tr>
<td>TABE -H$_2$MDI</td>
<td>3388,3069,2920,2862, 1765,1729,1656, 1544, 1472,1348,</td>
<td>8.62(S,2H,NH), 8.53(S,2H,NH), 8.20(d,4H,phenyl), 8.01(S,2H,NH), 7.90(d,4H,phenyl), 7.30(d,4H, phenyl), 3.52(t,4H, -O-CH$_2$-), 3.40(t,4H, -O-CH$_2$-), 3.36(m,10H, CH$_2$-CH$_2$-CH cyclic), 3.30(t,4H, -CH$_2$-NH-), 3.22(t,4H, -CH$_2$-NH-), 1.64(m,8H, -CH$_2$-cyclic), 1.42(m,2H,CH cyclic), 1.39(m,8H, -CH$_2$-cyclic), 1.20(d,2H, CH$_3$)</td>
</tr>
</tbody>
</table>

The FT-IR spectrum of polyureas showed a strong peak at 3388-3395 cm$^{-1}$ and 3047-3109 cm$^{-1}$ for the N-H bond, strong peaks at 2912-2937 and 2862-2870 cm$^{-1}$ for the aliphatic C-H bounds, also three strong peaks in the range of 1628-1765 cm$^{-1}$. 
for three different carbonyl groups, other strong peaks at 1500-1547 cm⁻¹ for N-H out of plane bending and C-N, and also 1472-1500 cm⁻¹ for C=C (Table 2 and Fig. 1).

Fig. 1. FT-IR spectrum of TABE-MDI.

The ¹H-NMR spectra of polymers showed peaks that confirmed structure of different polyureas (Table 2) and also elemental analyses validated them (Table 3).

Tab. 3. Structures, elemental analysis, inherent viscosities and yields of polymers.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Elemental analysis (%)</th>
<th>Inherent Viscosity (dl/g)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>TABE-PPDI</td>
<td>Calcd: C 60.97, H 5.56, N 10.16</td>
<td>60.49, 5.78, 10.01</td>
<td>0.835</td>
</tr>
<tr>
<td></td>
<td>Found:</td>
<td></td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>TABE-NDI</td>
<td>Calcd: C 62.98, H 5.47, N 9.58</td>
<td>61.89, 5.16, 9.88</td>
</tr>
<tr>
<td></td>
<td>Found:</td>
<td></td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>TABE-TDI</td>
<td>Calcd: C 64.16, H 5.67, N 9.16</td>
<td>63.87, 5.86, 8.99</td>
</tr>
<tr>
<td></td>
<td>Found:</td>
<td></td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>TABE-MDI</td>
<td>Calcd: C 61.38, H 5.71, N 9.99</td>
<td>61.04, 5.54, 10.21</td>
</tr>
<tr>
<td></td>
<td>Found:</td>
<td></td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>TABE-H₂MDI</td>
<td>Calcd: C 63.33, H 6.89, N 9.04</td>
<td>64.86, 6.65, 8.86</td>
</tr>
<tr>
<td></td>
<td>Found:</td>
<td></td>
<td>89</td>
</tr>
</tbody>
</table>

The inherent viscosity of the polymers, as a criterion for estimation of molecular weight, was measured at a concentration of 0.5 g/dL in DMF at 30 °C. The viscosity
of polyureas was in the range of 0.802–0.835 dL/g that revealed reasonable molecular weights (Table 3). The inherent viscosity of the TABE-H$_{12}$MDI was lower than others which is in line with the lower molecular weight compared with other polyureas because cycloaliphatic structure and methyl linkage segment in diisocyanate structure increased negative charge of NCO group that reduced nucleophilic attack of diamine to NCO group and led to decreased molecular weight of polyurea.

Fig. 2. DMTA curve of TABE–MDI.

The inherent viscosity of the TABE-PPDI was highest because aromatic ring in the structure of diisocyanate increased positive charge of NCO group and affinity of diamine for attack to NCO. The solubility of the polyureas in dipolar aprotic solvents such as NMP, DMAc, DMF, and DMSO was about 4.2–5.6 g/dL. Presence of flexible groups including oligo ethylene glycol sequences in polymer chain was an effective factor in improving the solubility of the polyureas.

Fig. 3. DSC curve of TABE–MDI.
The thermal behavior and stability of polyureas was studied by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and thermal gravimetry analysis (TGA) techniques. The glass transition temperature of polyureas ($T_g$) were found in the range of 88-112 °C based on decreasing in storage modulus with increasing of tan δ in DMTA (Fig. 2).

Also the midpoint of the change in slope of the baseline in DSC curve confirmed it (Fig 3).

TABE–PPDI showed highest $T_g$ among the polymers due to highest molecular weight and rigidity of main chain. Generally, $T_g$ of these polymers was lower than conventional polyureas that show effect of flexible linkage in the structure of polymers. Also two endothermic peaks were observed in the DSC plots of each polymer. They could be attributed to liquid crystalline nature of the polymers. This property was validated by the polarized light microscopy (PLM) technique.

Thermal stability of the polymers was evaluated by TGA in air at a heating rate of 10°C/min and the results are summarized in Table 4.

**Tab. 4. Thermal analysis data.**

<table>
<thead>
<tr>
<th>Product</th>
<th>$T_g$ (°C)</th>
<th>$T_0$ (°C)</th>
<th>$T_{10}$ (°C)</th>
<th>$T_{max}$ (°C)</th>
<th>Char Yield at 600°C(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TABE-PPDI</td>
<td>112</td>
<td>220</td>
<td>312</td>
<td>385</td>
<td>32</td>
</tr>
<tr>
<td>TABE-NDI</td>
<td>109</td>
<td>218</td>
<td>309</td>
<td>365</td>
<td>31</td>
</tr>
<tr>
<td>TABE-MDI</td>
<td>104</td>
<td>217</td>
<td>307</td>
<td>360</td>
<td>30</td>
</tr>
<tr>
<td>TABE-TDI</td>
<td>93</td>
<td>209</td>
<td>303</td>
<td>354</td>
<td>26</td>
</tr>
<tr>
<td>TABE-H$_{12}$MDI</td>
<td>88</td>
<td>200</td>
<td>297</td>
<td>342</td>
<td>21</td>
</tr>
</tbody>
</table>

$T_g$: glass transition temperature
$T_0$: initial decomposition temperature
$T_{10}$: temperature for 10% weight loss
$T_{max}$: maximum decomposition temperature

![TGA curve of TABE–MDI.](image)

The initial decomposition temperatures ($T_0$) were about 200–220 °C and the temperatures for 10% gravimetric loss ($T_{10}$), which is an important evidence for
thermal stability, were in the range of 297–312 °C. The highest values were obtained with polymer bearing more aromatic segment TABE-PPDI. Also char yields of the polyureas at 600 °C were about 21–32%. Typical TGA curve is shown in Fig. 4.

Obviously, factors such as incorporation of phenyl moieties, amide and ester groups were effective factors in increasing the thermal stability. However, it should be mentioned that presence of flexible linkages in the structure of polymers (oligo ethylene glycol units) led to lower thermal stability of these polyureas in comparison to conventional fully aromatic polyureas. For instance, $T_{10}$ in the polyureas have been prepared from 2,6-bis(4-aminophenoxy)pyridine and similar diisocyanates was in the range of 312-328 °C, and their char yields at 600 °C were about 40-44%. Also, the amounts of $T_{10}$ and char yield for polyureas have been prepared from 2,6-bis(5-amino-1-naphthoxy)pyridine were about 292-316 °C and 37-45%, respectively [17].

To evaluate the crystallinity of the polyureas, wide-angle X-ray diffraction pattern of the polyureas in the region of $2\theta = 5$-70 ° at room temperature were studied. They showed semi-crystalline patterns with about 20-32 % crystallinity. The representative wide-angle X-ray diffractogram of the polymers is shown in Fig. 5. Existence of the rigid planar segments in the macromolecular backbones led to a better packing of polymer chains but presence of flexible groups attached to the central aromatic structure, induced a looser chain packing and reduced crystallinity. It is worth to mention that, the crystallinity of all polymers was reflected in their solubility behavior, which is in agreement with the general rule that the solubility increases with decreasing crystallinity.

![Fig. 5. X-ray diffractogram of TABE–MDI](image)

Liquid crystalline behaviors of the polymers were studied using polarizing light microscopy (PLM) analysis with a temperature-controlled hot stage. The polymers were heated to melting at 10 °C/ min and isothermally kept for 3 min (dark appearance) and the melt was subsequently cooled under control at 10 °C/min. Throughout cooling from the melt and also in the subsequent heating cycle, nematic LC phases were distinguished. Different features for the LC phases of the MDI-based polyurea at different range of temperatures are shown in Figure 6. The polymer was completely melted at 228 °C, and it was maintained at this temperature for 3 min [Fig. 6(a)]. Presence of small nucleation sites and subsequently a uniform pattern during cooling at 195 °C was confirmed Fig. 6(b). The pattern became more uniform and the...
texture remained almost identical upon further cooling at 146 °C (Fig. 6c). In the second heating (at 10 °C/min), the LC phases initially disappeared, rapidly reappeared at 144 °C (Fig. 6d) and gradually flowed at 212 °C (Fig. 6e).

Fig. 6. Polarized light microscopy photographs of TABE-MDI, (a) at 228 °C (isotropic phase), (b,c) cooling from the isotropic phase at 10 °C/min [(b) 195, (c) 146 °C], and (d,e) second heating at 10 °C/min [(d) 144, (e) 212 °C].
Conclusions

New polyureas containing ester, amide and oligo ethylene glycol sequences were synthesized. Introduction of different structural units into the polyurea backbone led to nice and unique balance of properties in these polymers. Presence of aromatic, ester, and amide groups induced thermal stability to the final polymers, whereas aliphatic oligo ethylene glycol units induced solubility to the polymers. Combination of these factors resulted in preparation of new thermally stable liquid crystalline polyureas with improved solubility.

Experimental part

Materials

All chemicals were purchased either from Merck or Aldrich Chemical Co. Commercial 4,4’-dicyclohexylmethane diisocyanate (H12MDI), methylene-bis(4-phenylisocyanate) (MDI) and toluene diisocyanate (TDI) were purified by distillation. p-Phenylene diisocyanate (PPDI), and 1,5-naphtalene diisocyanate (NDI) were used after sublimation. Commercial solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP) were purified by vacuum distillation over calcium hydride.

Instruments

The IR spectra of the polymers were recorded with Bruker- IFS 48 FTIR spectrometer (Ettlingen, Germany). The H-NMR spectra were recorded in dimethyl sulfoxide (DMSO-d6) solution using a Bruker Avance DPX 250-MHz instrument (GmbH, Germany). A CHN-O-Rapid Heraeus elemental analyzer performed elemental analyses (Wellesley, MA). Differential scanning calorimetry (DSC) was recorded on a Stanton Redcraft STA-780 (London, UK). Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) traces were recorded on a Polymer Lab TGA-1500 (London, UK). The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model MK-II) over a temperature range of 25-200 ºC at 1 Hz and a heating rate of 5 ºC /min (Surrey, UK). The value of tan δ and the storage modulus versus temperature were recorded for each sample. Inherent viscosities were measured by using an Ubbelohde viscometer in a concentration of 0.5 g/dL in DMF at 30 ºC. Wide angle X-ray diffraction patterns were performed at room temperature on an X-ray diffractometer (Siemens model D 5000) using Ni-filtered Cu Kα radiation (40 kV, 25 mA) with scanning rate of 3 º/min. The liquid crystalline texture of the polymers was studied with an optical microscope (Zeiss) fitted with crossed polarizers. The temperature was controlled to ± 1 ºC by means of a computerized Linkam TMS 94 heat controller.

Monomer synthesis

Terephthaloyl bis (4-oxybenzoic) acid (TOBA) and terephthalic acid bis(4-{(2-(2-amino ethoxy)ethoxy)ethyl carbamoyl}phenyl) ester (TABE) were synthesized in our laboratory as reported [32].

Polymer synthesis
Polyureas were synthesized from reactions of MDI, PPDI, NDI, TDI and H12MDI with TABE via solution polymerization route. A typical procedure for preparation of polyureas was as follows: A round-bottomed flask equipped with N2 inlet tube, condenser, and thermometer was charged with 2 mmol of diamine and 5 mL of dry NMP. Then a solution containing 2 mmol of diisocyanate in 5 mL of dry NMP was added in one lot to the flask contents. The solution was stirred for 1 h at room temperature and 2 h at 60 °C then the mixture was precipitated in water. The polymer was filtered, washed with hot water and methanol, and dried at vacuum oven at 100 °C. Yields about 88-92% were obtained.

References