Synthesis of Novel Polyurethanes with Fluorescein Linkages

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ABSTRACT

The reaction of n-propylisocyanate with fluorescein (FLU) has been performed in N,N-dimethylacetamide (DMAc) in the presence of triethylamine and the resulting bis-adduct has been obtained in high yield and finally was used as a model compound for the polymerization reactions. The step-growth polymerization reaction of the monomer FLU with hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI), and toluene-2,4-diisocyanate (TDI) was carried out in DMAc solution and in the presence of pyridine as a catalyst. The above polymerization reactions lead to the formation of novel aromatic-aliphatic polyurethanes having fluorescein moieties in the main chain. The resulting novel polyurethanes have an inherent viscosity in a range of 0.08—0.23 dLg"¹ and show light-violet fluorescence property and could be used as photoactive polymers for labeling materials. These polyurethanes were characterized by IR, "H NMR, TGA/DTG, DSC and elemental analyses. Some physical properties of this novel polymers are reported.

Key Words: fluorescein, polyurethanes, solution polymerization, inherent viscosity, photoactive polymers

INTRODUCTION

Polyurethanes are a class of synthetic polymers which have a wide variety of applications because their properties can be tailored by changing the components from which they are constructed: rigid diols, flexible polyols, and polyisocyanate [1]. Polyurethanes are used as foams, fibres, elastomers, coating and adhesives.

Polymers with fluorescent properties have been investigated in recent years. These polymers include chromophore in the backbone and polymers having chromophore as a pendant group. They are used as fluorescent label and photo-harvesters [2—4].

Fluorescent labeling has been used to study specific interactions between macromolecules in polyelectrolytes, water soluble polymers, homopolymers, block and random copolymers [5—10] and water soluble polymers with aromatic chromophores which sensitize photochemical reactions [11].

Novel polymers containing fluorescein moieties have been reported recently [12, 13]. They are

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soluble in most organic solvents and give film with excellent transparency when casted from solutions. The polymers show intense yellow luminescence in solution and as films. Acrylfluorescein polymer and rigid diol fluorescein used as chain extender have also been reported [14, 15]. A number of novel polymers containing arylene vinylidene ethylene groups were also synthesized via the Heck reaction [16]. The resulting polymers are amorphous and soluble in most common organic solvents. Some showed strong blue luminescence in the region of 380-480 nm. Another interesting class of photoactive polymers is anthracene containing polymers. They show intense blue fluorescence and photoconductive properties [17]. Various polymers of vinyl type anthracene-containing have been reported [18].

In previous articles the novel monomer 7,12-bis(2-hydroxyethyl)benzo[k]fluoranthate (BHBF) I was synthesized and its polyesterrification reactions with aromatic diacids chloride were investigated [19]. Although these polyesters containing benzo[k]-fluoranthenes moieties have low inherent viscosities, but they showed strong violet fluorescence. This monomer BHBF (Scheme I) was also reacted with aromatic and aliphatic diisocyanates for the formation of novel polyurethanes with photoactive properties [20].

In this paper we wish to report the polycondensation reactions of FLU (1), a diol tautomer, with diisocyanates for the formation of photoactive polyurethanes.

### EXPERIMENTAL

#### Materials and Equipment

Reagents were purchased from Aldrich Chemical Co., Fluka Chemical Co and Riedel-deHaen AG. DMAC (N,N'-dimethylacetamide) was dried over BaO, then it was distilled under reduced pressure.

IR Spectra were recorded on Shimadzu 435 IR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm⁻¹). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). The fluorescence spectra were recorded on Shimadzu RF-5000 spectrofluorophotometer.

Proton nuclear magnetic resonance (¹H NMR, 90MHz) spectra were recorded on a Varian EM-390 instrument. Multiplicities of proton resonances are designated as multiplet (m) and broad (br). Tetramethylsilane (TMS) was used as an internal reference.

All melting points were taken with a Gallenkamp melting point apparatus and are uncorrected. Inherent viscosities were measured by standard procedure using a Cannon Fensk Routine viscometer. Differential scanning calorimetry (DSC) data for polymers were recorded on a Mettler DSC-30 instrument under N₂ atmosphere at a rate of 20 °C/min. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TGA-50. Elemental analyses on CHNO⁻ Rabid-Hereaus were performed by Research Institute of petroleum Industry, Tehran.

#### Model Compound Synthesis

**Reaction of FLU (I) with n-Propylisocyanate**

FLU (1) of 0.30 g (9.028×10⁻⁴ mol) with 1 mL of DMAC and a magnetic bar were placed into a 25 mL of round-bottomed flask. The stirrer was started and 0.40 mL (0.36 g, 4.267×10⁻³ mol) of n-propylisocyanate and 0.25 mL of triethylamine were added. The reaction mixture was stirred at room temperature for 36 h. Then it was precipitated in 30 mL of water.

The solid was collected, dried to give 0.35 g (77.8%) orange solid. Recrystallization from ethanol gave orange crystals, mp 151-153 °C. IR (KBr):
The elemental analysis results for the model compound obtained are as follows:

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>66.92</td>
<td>5.22</td>
<td>5.58</td>
</tr>
<tr>
<td>Found</td>
<td>67.00</td>
<td>5.10</td>
<td>5.70</td>
</tr>
</tbody>
</table>

**Polymer Synthesis**

*Reaction of 1,6-Hexamethylene Diisocyanate (HMDI) with Monomer FLU (1)*

Into a 25 mL of round bottomed flask 0.20 g (6.02x10^-4 mol) of monomer FLU (I), 1 mL of chloroform, 0.2 mL of pyridine and 0.1 mL (0.10 g, 6.02x10^-4 mol) of HMDI were added. The mixture was stirred at 60 °C for 6 days, which during this time the reaction mixture became gel. The light-red viscous solution was precipitated in 50 mL of water. The resulting polymer (PU1) was filtered off, and dried to give 0.27 g (89.7%) of light orange solid, mp>160 °C (dec). IR (KBr): 3350 (m,br), 3100 (w,br), 2950 (m), 2900 (br), 1740 (s,br), 1620 (s,br), 1550 (m, br), 1490 (m), 1460 (m), 1420 (m), 1380 (w), 1320 (w), 1280 (m), 1220 (s,br), 1170 (s), 1110 (s), 990 (m), 860 (m,br), 760 (w), 690 (w), 600 (w) cm^-1.

The elemental analysis results for PU1 obtained as follows:

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>69.30</td>
<td>5.27</td>
<td>5.05</td>
</tr>
<tr>
<td>Found</td>
<td>68.50</td>
<td>6.40</td>
<td>6.30</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

*Reaction of Isophoron Diisocyanate (IPDI) with Monomer FLU (1)*

The above solution polymerization was carried out by the reaction of FLU with IPDI and the mixture was heated for 6 days. The orange-red polymer solution was precipitated in water. The polymer (PU2) was filtered off, and dried to give 0.22 g (65.9%) of light-orange solid, mp>191 °C (dec). IR (KBr): 3350 (s,br), 3100 (w,br), 2950 (m), 2900 (s,br), 1740 (s,br), 1620 (s,br), 1550 (m, br), 1490 (m), 1460 (m), 1420 (m), 1380 (w), 1320 (w), 1280 (m), 1220 (s,br), 1170 (s), 1110 (s), 990 (m), 860 (m,br), 760 (w), 690 (w), 600 (w) cm^-1.

The elemental analysis results for PU2 are obtained as follows:

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>68.77</td>
<td>3.58</td>
<td>5.53</td>
</tr>
<tr>
<td>Found</td>
<td>65.30</td>
<td>4.70</td>
<td>6.40</td>
</tr>
</tbody>
</table>

**Model Compound Studies**

FLU 1 was allowed to react with excess n-propylisocyanate in DMAc solution in the presence of triethylamine as a catalyst and gave fluorescein di-n-propylurethane (2) in good yield (Scheme II).

Compound 2 was characterized by IR and elemental analysis. The IR spectrum of 2 showed peaks at 3350 and 3300 cm^-1 for N–H stretching and strong peaks at 1770, 1750 and 1715 cm^-1 for carbonyl groups. The other peaks are consistent with
the proposed structure of 2. The elemental analysis is also in agreement with the structure 2.

Polymerization Reactions
Fluorescein structure 2 as a model compound was synthesized in good yield and purity; therefore we were interested in performing this type of reaction for the formation of novel polyurethanes. Thus, HMDI, IPDI and TDI were selected as diisocyanates. The monomer FLU (1) was reacted with HMDI in DMAc solution in the presence of pyridine as a catalyst and resulting polymer, PU1, obtained in high yield (Scheme III). Polymer PU1 was characterized by IR and elemental analysis. The IR spectrum showed strong peaks for N–H and carbonyl groups. This polyurethane is partially soluble in solvents such as DMSO, DMF, and DMAc and insoluble in solvents such as acetic acid, THF, methanol, acetone, chloroform and etc., the solubility was measured at a concentration of 5 mg mL\(^{-1}\). The low solubility of the polymer PU1 precluded any NMR measurements.

The polycondensation reaction of monomer FLU (1) with IPDI was carried out in a similar manner and the resulted polymer PU2 was obtained in moderate yield (Scheme III). The polymer PU2 was characterized by IR, \(^1\)H NMR and elemental analysis. The IR spectrum showed peaks for N–H and carbonyl groups and other peaks are in agreement with the

\[
\text{FLU (1)} + \text{O} = \text{C} = \text{N} - \text{R} - \text{N} = \text{C} = \text{O} \quad \text{Solvent} \rightarrow \text{PU1}
\]

\[
\text{R} = -(\text{CH}_2)_{6}-(\text{HMDI}), -\text{CH}_2-(\text{IPDI}), -\text{CH}_3-(\text{TDI})
\]

Scheme III
Table 1. Reaction conditions for the polymerization of FLU (1) with diisocyanates in DMAc in the presence of pyridine and some physical properties of polyurethanes (PU1 and PU2).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Diisocyanate</th>
<th>Reaction time at 60 °C (days)</th>
<th>Yield (%)</th>
<th>Non-solvent</th>
<th>$\eta_{\text{inh}}$</th>
<th>D.P$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU1</td>
<td>HMDI</td>
<td>6</td>
<td>89.7</td>
<td>water</td>
<td>0.228</td>
<td>&gt;160</td>
</tr>
<tr>
<td>PU2</td>
<td>IPDI</td>
<td>6</td>
<td>65.9</td>
<td>water</td>
<td>0.077</td>
<td>&gt;191</td>
</tr>
<tr>
<td>PU3</td>
<td>TDI</td>
<td>6</td>
<td>98.4</td>
<td>water</td>
<td>0.170</td>
<td>&gt;260</td>
</tr>
</tbody>
</table>

a) Inherent viscosities, measured at a concentration of 0.5 g dm$^{-1}$ in DMSO at 25 °C.

b) Decomposition points in °C, measured by melting point apparatus.

The polymer structure. The $^1$H NMR spectrum of the polymer PU2 in DMSO-$d_6$ showed a broad peak at 10.50 ppm for N–H proton, peaks between 6.30–8.40 (m) ppm for aromatic protons and peaks between 0.75–4.00 (m) for aliphatic protons. This polyurethane is soluble in most organic solvents such as DMSO, DMAc, DMF, and THF and it is insoluble in solvents such as chloroform, dichloromethane, acetone, water and non-polar solvents.

The polymerization reaction of monomer FLU (1) with TDI was also performed in DMAc solution in the presence of pyridine catalyst. The resulting polymer PU3 was obtained in quantitative yield (Scheme III). The polymer PU3 was characterized by IR, and elemental analysis. The IR spectrum of the polymer PU3 showed peaks which are in agreement with the structure of the resulting polyurethane PU3 (Scheme III). This polymer has low solubility in solvents such as DMSO, DMF and DMAc and is insoluble in most organic solvents.

Although the elemental analysis of the model compound (2) is in excellent agreement with the theoretical values, but in the case of the resulting polyurethanes (PU1–PU3) the elemental analyses have some differences with the theoretical values. These differences are due to the presence of small amount of unreacted monomers and as well as DMAc in the polymer. Reaction conditions and physical properties of the novel polyurethanes (PU1–PU3) are summarized in Table 1.

The fluorescence excitation and emission spectra data for the model compound 2 and polyurethanes (PU1–PU3) in DMSO are summarized in Table 2. For excitations, the wavelengths inducing the maximum emission were employed (maximum excitation wavelength).

**Thermal Properties**

The thermal properties of the polymers (PU1–PU3) were measured by DSC and TGA/DTG at a rate of 20 °C min$^{-1}$ in nitrogen. The DSC curve of the polymer PU1 showed an endothermic baseline shift around 175 °C which it corresponds to the glass transition temperature ($T_g$). This polymer also showed three endotherm peaks with the maximum at 350 °C, 470 °C and 570 °C which are related to the melting temperature ($T_m$) and decomposition temperature ($T_d$), respectively. Furthermore, the endotherm peaks appearing at 470 °C and 570 °C in the DSC thermogram should not be associated with the polymer (PU1) melting temperature. TGA trace of this polymer indicates that such endothermic behaviour in DSC thermogram should be attributed to the polymer’s thermal decomposition, since the peaks occurred at temperatures at which the corresponding

Table 2. Fluorescence excitation and emission spectra of model compound (2) and polyurethanes (PU1–PU3) in DMSO$^a$.

<table>
<thead>
<tr>
<th>Polyurethane/Model comp.</th>
<th>$\lambda_{\text{Ex}}$ (nm)</th>
<th>$\lambda_{\text{Em}}$ (nm)</th>
<th>$\Phi_{\text{FLU}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>523</td>
<td>536</td>
<td>787.13</td>
</tr>
<tr>
<td>PU1</td>
<td>540</td>
<td>549</td>
<td>578.24</td>
</tr>
<tr>
<td>PU2</td>
<td>535</td>
<td>548</td>
<td>512.70</td>
</tr>
<tr>
<td>PU3</td>
<td>360</td>
<td>437</td>
<td>197.31</td>
</tr>
</tbody>
</table>

a) Measured at a concentration of 1.00×10$^{-5}$ mol/L.

b) Fluorescence intensity (arbitrary unit)
TGA traces exhibited rapid weight loss (Figures 1 and 2), therefore, these temperatures are associated with thermal decomposition. The DSC curve of the polymer PU2 showed an endothermic baseline shift around 195 °C which corresponds to the glass transition temperature (T_g). This polymer also showed an endotherm peak with the maximum at 380 °C, which is related to the decomposition temperature (T_d). The DSC curve of the polymer PU3 showed two endotherm peaks with the maximum at 300 °C and 450 °C which are related to the decomposition temperature (T_d).

The TGA/DTG traces of these novel polyure-
thanates (Figures 2–4) provide additional information regarding their thermal stability and thermal degradation behaviour. An examination of the data reveal that all of the above polymers are thermally stable up to 200 °C in nitrogen. The polymers (PU1–PU3) show 5% weight loss at 260 °C, 270 °C and 245 °C, respectively. The residual weight for these polymers at 550 °C are 37.7, 35.5 and 52.2%, respectively.

CONCLUSION

This investigation has shown that FLU (1) is an interesting monomer for the polycondensation reactions. Its step-growth polymerization reactions with diisocyanates give novel polyurethanes with fluorescein linkages. Although the polyurethane PU2 has good solubility in polar organic solvents, but the polymers PU1 and PU3 have low solubility. Therefore increasing viscosity of the above polyurethane decreases the solubility properties and would not be useful. These novel polymers show light violet fluorescence photoactivity and can be used as fluorescent labeling materials.

ACKNOWLEDGEMENTS

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REFERENCES