Synthesis and Characterization of Novel Polyureas with 4-Phenylurazole Moieties in the Chain

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ABSTRACT

The reaction of 4-phenylurazole (PHU) 1 with n-isopropylisocyanate 3 was performed at room temperature and the resulting bis-urea derivative 4 was obtained in high yield and it was finally used as a model compound for the polymerization reaction. The step-growth polymerization reactions of monomer 1 with hexamethylene diisocyanate (HMDI) 5, isophorone (IPDI) 6 and toluene-2,4-diisocyanate (TDI) 7 were performed in DMAc in the presence of pyridine or triethylamine as a catalyst. The resulting novel polyureas have an inherent viscosity in a range of 0.04–0.23 g dL\(^{-1}\) in DMF at 25 °C. These polyureas were characterized by IR, \(^1\)H NMR and elemental analysis. The resulting polymers are soluble in most organic solvents. Some physical properties and structural characterization of these novel polyureas are reported.

Key Words: 4-phenylurazole, polyureas, solution polymerization, inherent viscosity, step-growth polymerization

INTRODUCTION

4-Alkyl and aryl substituted urazoles (e.g., structure 1) are important class of heterocyclic compounds. One of its main application is for the synthesis of 4-substituted-1,2,4-triazoline-3,5-dione 2. The compound 2 is an exceptionally strong electron acceptor and, thus, is among the most powerful dienophiles, enophiles as well as electrophiles [1–4]. Although the above substituted urazoles (1) are very stable molecules and their shelf life time extends for many years, but they can be readily oxidized to compound 2 with a wide variety of oxidizing reagents [5].

(1) \( R = \text{Alkyl} \)
(2) \( R = \text{Aryl} \)

The compound 1 has also two N–H protons which are acidic. The urazole derived from the ene reaction of triazolinediones with alkenes and polydiynes has one N–H proton, which seems to be very acidic. The acidity of this proton has been measured.

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and is quite acidic with pKa of 4.71 which is almost the same as that of acetic acid [6]. The compounds 1 have the potential to undergo N-acylation. 4-Substituted-urazoles were converted to 1-acyl derivatives by acylation reaction with a series of carboxylic acid anhydrides [7]. A simplified procedure for the N-acylation of oxazolidin-2-one chiral auxiliaries has also been reported [8].

Recently we have been able to take advantage of these acidic N—H in a compound, 1-methyl-2,5-bis(4-phenylurazolyl)pyrrole and to synthesize novel polymers via N-alkylation and N-acylation reactions [9, 10].

Polymerization of 4-phenylurazole (PHU) 1, where R : phenyl, with phosgene, terephthaloyl chloride, and epichlorohydrin has been reported to give insoluble polymers [11]. The step-growth polymerization of compound PHU with aliphatic dicarboxylic acids gave soluble polyamides with inherent viscosity of 0.59 dLg⁻¹ [12]. The step-growth polymerization of 4-cyclohexylurazole (CHU) and copolymerization of PHU/CHU with aliphatic dicarboxylic acids also gave soluble polyamides with inherent viscosity in a range of 0.10—0.17 dLg⁻¹ [13].

The polymerization reactions of monomer 1 with diisocyanates. In the present paper we report on the first successful step-growth polymerization where PHU as a novel monomer is used for the synthesis of soluble polyureas.

**EXPERIMENTAL**

**Materials and Equipment**

Reagents were purchased from Fluka Chemical Co. and Aldrich Chemical Co. and Riedel-deHaen AG. The compound PHU 1 was synthesized according to published procedure [5]. N,N-dimethylacetamide (DMAc) was dried over BaO and then was distilled under reduced pressure. Chloroform was purified by washing with water, drying with CaCl₂ and subsequent distillation under normal pressure.

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

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. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TGA-50. Elemental analyses were performed by Research Institute of Petroleum Industry, Tehran, I.R.Iran.

**Reaction of Compound PHU 1 with n-Isopropylisocyanate**

Into a 25 mL round bottom flask, compound PHU 1 (0.20 g, 1.129×10⁻³ mol), and 0.01 mL of pyridine were dissolved in 2 mL of DMAc. To this mixture, a solution of 0.4 mL (4.516×10⁻³ mol) of n-isopropylisocyanate 3 in 2 mL of chloroform was added dropwise. The solution was stirred for 24 h. The excess isocyanate was removed under reduced pressure and the residue was precipitated in 50 mL of distilled water. The white solid was filtered off and dried to give 0.34 g (87.0%). The solid was recrystallized from THF and gave the model compound 4 as white crystal, mp 120—121 °C; IR (KBr): 3400 (m), 3350 (m) 2950 (m), 2850 (w), 1780 (s, sh), 1740 (s, br), 1520 (s), 1460 (w), 1420 (w), 1420 (s), 1380 (w), 1260 (s), 1200 (s), 1160 (w), 1070 (w), 1050 (w), 1020 (m), 830 (w), 750 (s), 750 (m), 690 (w), 580 (w) cm⁻¹; 'H NMR (DMSO-d₆, TMS): 8 0.90 (t, 6H), 1.62 (m, 4H), 3.40 (q, 4H), 6.90 (t, br, 2H), 7.60 (s, 5H).

The elemental analysis results obtained as follows:

<table>
<thead>
<tr>
<th>C₁₆H₂₁O₄N₅</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>55.32</td>
<td>6.09</td>
<td>20.16</td>
</tr>
<tr>
<td>Found</td>
<td>55.10</td>
<td>6.10</td>
<td>20.50</td>
</tr>
</tbody>
</table>

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Polymerization of PHU 1 with HMDI 5

Method A

Into a 25 mL round bottom flask was placed a solution of PHU (0.20 g, 1.129$x10^{-3}$ mol) in 1.3 mL of DMAc and 0.1 mL of pyridine was added. To this solution, HMDI (0.18 mL, 1.129$x10^{-3}$ mol) was added dropwise. The mixture was stirred for 40 h at room temperature and a very viscous solution was formed, which was heated with a heating gun. The mixture was stirred at room temperature for additional 45 h and was precipitated in 50 mL of ether. The white solid was filtered off, and dried to give 0.385 g (98.7%), mp 115 °C; IR(KBr): 3350 (m), 3050 (w), 2900 (m), 2250 (m), 1790 (m, sh), 1740(s), 1640 (w), 1520 (s), 1460 (w), 1420 (s), 1410 (s), 1270 (s), 1200 (s), 1170 (w), 1060 (w), 1020 (w), 830 (w), 750 (m), 690 (w), cm$^{-1}$; $^1$H NMR (DMSO-$d_6$, TMS): 8 1.20-1.85 (s, br, 8H), 3.10—3.55 (m, 4H), 7.60 (s, 5H), 8.00 (s, br, 2H).

Method B

The above procedure was repeated except triethylamine was used in replacing pyridine and the resulting polymer was precipitated in water. The yield is 74.4% and mp 100 °C.

Method C

The procedure A was repeated except the amount of DMAc was reduced from 1.3 to 1 mL and the resulting polymer was precipitated in ether. The yield is 100% and mp 117 °C.

Polymerization of PHU 1 with IPDI 6

Method A

Into a 25 mL round bottom flask was placed a solution of PHU (0.20 g, 1.129$x10^{-3}$ mol) in 1.4 mL of DMAc and 0.1 mL of pyridine was added. To this solution, IPDI (0.24 mL, 1.129$x10^{-3}$ mol) was added dropwise. The mixture was stirred for 92 h at room temperature and a very viscous solution was formed, which was precipitated in 50 mL of ether. The white solid was filtered off, and dried to give 0.400 g (88.8%), mp 102 °C; IR(KBr): 3250 (m), 3050 (w), 2950 (m), 2250 (m), 1790 (m, sh), 1740(s), 1650 (w), 1600 (w), 1500 (s), 1460 (w), 1410 (s), 1360 (w), 1300 (w), 1240 (s), 1200 (s), 1060 (w), 740 (m), 690 (w), cm$^{-1}$; $^1$H NMR (DMSO-$d_6$, TMS): 81.00 (m, br, 13H), 1.70 (m, br, 2H), 2.00 (s, DMAc), 3.90 and 3.20 (s, DMAc), 3.30 (m, br, 2H), 4.10 (m, br, 1H), 7.00 (m, br, 2H), 7.60 (s, 5H).

The elemental analysis results obtained as follows:

<table>
<thead>
<tr>
<th>C$<em>{26}$H$</em>{25}$O$<em>{4}$N$</em>{5}$</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>60.14</td>
<td>6.31</td>
<td>17.53</td>
</tr>
<tr>
<td>Found</td>
<td>59.00</td>
<td>6.80</td>
<td>17.00</td>
</tr>
</tbody>
</table>

Method B

The above procedure was repeated except triethylamine was used in replacing pyridine. The yield is 60.0% and mp105 °C.

Method C

The procedure A was repeated except the amount of reaction time was reduced from 92 h to 73 h. The yield is 44.4% and mp 106 °C.

Method D

The procedure C was repeated except the amount of DMAc was reduced from 1.4 mL to 1 mL. The yield is 90.0% and mp 125 °C.

Polymerization of PHU 1 with TDI 7

Into a 25 mL round bottom flask was placed a solution of PHU (0.20 g, 1.129$x10^{-3}$ mol) in 1.4 mL of DMAc and 0.1 mL of pyridine was added. To this solution, TDI (0.16 mL, 1.129$x10^{-3}$ mol) was added dropwise. The mixture was stirred for 72 h at room temperature and a very viscous solution was formed, which was precipitated in 50 mL of ether. The white solid was filtered off, and dried to give 0.398 g (100%), mp 137 °C; IR(KBr): 3250 (m, br), 3050 (w), 2950 (m), 2250 (m), 1790 (m, sh), 1740(s), 1600 (s), 1540 (s), 1500 (s), 1460 (m), 1400 (s), 1360 (m), 1220 (s, br), 1050 (m), 1020 (m), 870 (w), 810 (w), 760 (m), 720 (m), 690 (w), 640 (w), 590 (w), cm$^{-1}$; $^1$H NMR (DMSO-$d_6$, TMS): 8 2.00 (s, DMAc), 2.30 (s, br, 3H), 2.90 (s, DMAc), 3.00 (s, DMAc), 7.30 (m, br, 2H), 7.70 (m, br, 6H), 9.90 (s, br, 2H).

The elemental analysis results obtained as
Synthesis and Characterization of Novel Polyureas with 4-Phenylurazoles

follows:

<table>
<thead>
<tr>
<th>C₂₀H₂₅O₂N</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>58.12</td>
<td>3.73</td>
<td>19.94</td>
</tr>
<tr>
<td>Found</td>
<td>59.80</td>
<td>4.00</td>
<td>19.10</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Model Compound Studies
Compound 1 was allowed to react with n-propylisocyanate 3 in DMAc solution and gave the model compound 4 in high yield (Scheme I). The compound 4 was characterized with IR, ¹H NMR, and elemental analysis. The IR spectrum of 4 showed two strong peaks at 1780 and 1740 cm⁻¹ for the carbonyl groups. These are characteristic patterns for the urazole moiety. The ¹H NMR spectrum of 4 showed all peaks which are consistent with the assigned structure of 4.

Polymerization Reactions
Since bis-urea 4 as a model compound was synthesized in high yield and purity, we became interested to perform this type of the reaction for the formation of the novel polyureas. Thus (HMDI) 5, (IPDI) 6 and (TDI) 7 were selected as diisocyanates. The reaction of monomer 1 with HMDI was performed by three methods via solution polycondensation reaction.

In method A, the reaction was carried out in DMAc solution with pyridine as a catalyst and the resulting polymer (8A) was obtained in quantitative yield (Scheme II). This polymer was also characterized by IR, ¹H NMR spectra and elemental analysis which are in agreement with structure (9A). In method B the step-growth solution polymerization was carried out in DMAc in presence of triethylamine which gave lower yield of polyurea (9B). In method C the polymerization reaction time was reduced from 92 to 73 h and the resulting polymer (9C) was obtained as a white solid, lower yield and lower inherent viscosity.

In method D the polymerization reaction was carried out in more concentrated solution and the resulting polymer (9D) was obtained as a white solid with higher yield and higher inherent viscosity.

The reaction of monomer 1 with IPDI was performed by four methods via solution polycondensation reaction. In method A, the reaction was carried out in DMAc solution with pyridine as a catalyst and the resulting polymer (8A) was obtained in high yield (Scheme II). This polymer was also characterized by IR, ¹H NMR spectra and elemental analysis which are in agreement with structure (9A). In method B the step-growth solution polymerization was carried out in DMAc in presence of triethylamine which gave lower yield of polyurea (9B). In method C the polymerization reaction time was reduced from 92 to 73 h and the resulting polymer (9C) was obtained as a white solid, lower yield and lower inherent viscosity.

In method D the polymerization reaction was carried out in more concentrated solution and the resulting polymer (9D) was obtained as a white solid with higher yield and higher inherent viscosity.

The reaction of monomer 1 with TDI was carried out in DMAc solution and the resulting polymer 10 was obtained in quantitative yield. This polymer peak at 2250 cm⁻¹ for isocyanate group and strong peaks at 1790 and 1740 cm⁻¹ for the carbonyl groups. The ¹H NMR spectrum of this polymer showed peaks of 8.00 ppm for N–H, 7.60 ppm for phenyl protons and 1.40, 3.30 ppm for hexamethylene protons.

In method B the step-growth solution polymerization was carried out in DMAc in presence of triethylamine which gave lower yield and the resulting polyurea (8B) is insoluble materials.

In method C the polymerization reaction was performed in more concentrated solution and the resulting polymer (8C) was obtained as a white solid high yield and higher inherent viscosity.

The reaction of monomer 1 with IPDI was performed by four methods via solution polycondensation reaction. In method A, the reaction was carried out in DMAc solution with pyridine as a catalyst and the resulting polymer (9A) was obtained in high yield (Scheme II). This polymer was also characterized by IR, ¹H NMR spectra and elemental analysis which are in agreement with structure (9A). In method B the step-growth solution polymerization was carried out in DMAc in presence of triethylamine which gave lower yield of polyurea (9B). In method C the polymerization reaction time was reduced from 92 to 73 h and the resulting polymer (9C) was obtained as a white solid, lower yield and lower inherent viscosity.

In method D the polymerization reaction was carried out in more concentrated solution and the resulting polymer (9D) was obtained as a white solid with higher yield and higher inherent viscosity.

The reaction of monomer 1 with TDI was carried out in DMAc solution and the resulting polymer 10 was obtained in quantitative yield. This polymer peak at 2250 cm⁻¹ for isocyanate group and strong peaks at 1790 and 1740 cm⁻¹ for the carbonyl groups. The ¹H NMR spectrum of this polymer showed peaks of 8.00 ppm for N–H, 7.60 ppm for phenyl protons and 1.40, 3.30 ppm for hexamethylene protons.

In method B the step-growth solution polymerization was carried out in DMAc in presence of triethylamine which gave lower yield and the resulting polyurea (8B) is insoluble materials.

In method C the polymerization reaction was performed in more concentrated solution and the resulting polymer (8C) was obtained as a white solid high yield and higher inherent viscosity.

The reaction of monomer 1 with IPDI was performed by four methods via solution polycondensation reaction. In method A, the reaction was carried out in DMAc solution with pyridine as a catalyst and the resulting polymer (9A) was obtained in high yield (Scheme II). This polymer was also characterized by IR, ¹H NMR spectra and elemental analysis which are in agreement with structure (9A). In method B the step-growth solution polymerization was carried out in DMAc in presence of triethylamine which gave lower yield of polyurea (9B). In method C the polymerization reaction time was reduced from 92 to 73 h and the resulting polymer (9C) was obtained as a white solid, lower yield and lower inherent viscosity.

In method D the polymerization reaction was carried out in more concentrated solution and the resulting polymer (9D) was obtained as a white solid with higher yield and higher inherent viscosity.
was also characterized by IR, $^1$H NMR spectra and elemental analysis which are in agreement with structure 10.

The polymers (8A–C) are soluble in most of the organic solvents such as DMSO, DMF, and CHCl$_3$ and they are insoluble in solvents such water, methanol, acetone and nonpolar solvents such as cyclohexane, $n$-hexane. The polymers (9A–D) are also soluble in most of the organic solvents such as DMSO, DMF, THF, acetone and CH$_2$Cl$_2$ and they are insoluble in solvents such water, methanol, acetone and nonpolar solvents such as cyclohexane, $n$-hexane.

The polymer (10) shows lower solubility and is soluble in DMSO and DMF. The reaction conditions, some physical properties for these novel polyureas are summarized in Tables 1 and 2.

**Table 1.** Reaction conditions for the polymerization of monomer 1 with diisocyanates in DMAC and some physical properties for polyureas (8A, 8B, 8C, 9A, 9B, 9C, 9D and 10).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Diisocyanate</th>
<th>Catalyst</th>
<th>Reaction time (h)</th>
<th>Non-solvent</th>
<th>Yield (%)</th>
<th>$\eta_{inh}$ $^a$</th>
<th>mp $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8A</td>
<td>HMDI</td>
<td>Py</td>
<td>90</td>
<td>ether</td>
<td>98.7</td>
<td>0.193</td>
<td>115</td>
</tr>
<tr>
<td>8B</td>
<td>HMDI</td>
<td>TEA</td>
<td>92</td>
<td>ether</td>
<td>74.4</td>
<td>0.235</td>
<td>100</td>
</tr>
<tr>
<td>8C</td>
<td>HMDI</td>
<td>Py</td>
<td>72</td>
<td>ether</td>
<td>100</td>
<td>0.078</td>
<td>105</td>
</tr>
<tr>
<td>9A</td>
<td>IPDI</td>
<td>Py</td>
<td>92</td>
<td>ether</td>
<td>88.8</td>
<td>0.071</td>
<td>106</td>
</tr>
<tr>
<td>9B</td>
<td>IPDI</td>
<td>TEA</td>
<td>92</td>
<td>ether</td>
<td>60.0</td>
<td>0.043</td>
<td>125</td>
</tr>
<tr>
<td>9C</td>
<td>IPDI</td>
<td>Py</td>
<td>73</td>
<td>ether</td>
<td>44.4</td>
<td>0.097</td>
<td>137</td>
</tr>
<tr>
<td>9D</td>
<td>IPDI</td>
<td>Py</td>
<td>72</td>
<td>ether</td>
<td>90</td>
<td>0.086</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>TDI</td>
<td>Py</td>
<td>72</td>
<td>ether</td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) inherent viscosity dL/g, measured at a concentration of g dl$^{-1}$ in DMF at 25 $^\circ$C, (b) Measured by melting point apparatus, (c) Py=Pyridine, (d) Due to insolubility the viscosity was not measured.
Table 2. Solubilities of polymers 8, 9, and 10 in different solvents.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>(8)</th>
<th>(9)</th>
<th>(10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>DMF</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>THF</td>
<td>-</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>++</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>-</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>++</td>
<td>++</td>
<td>±</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>+</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Acetone</td>
<td>-</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Toluene</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ether</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Concentration: 5 mg mL⁻¹; (++) soluble within 1h at room temperature; (+) slightly soluble; (+) soluble at boiling point of water; (-) insoluble even heated up to 100 °C.

weight loss at 240, 200 and 240 °C, respectively.

CONCLUSION

The present work has shown that 4-phenylurazole 1 is an interesting monomer for the formation of novel polyureas. The compound 1 has two acidic N-H groups and it readily reacts with two moles of n-propylisocyanate. This reaction gives bis-urea 4 in quantitative yield and high purity. Thus compound 1 can act as a bifunctional monomer and its step-growth polymerization reaction with diisocyanates gave novel polyureas 8-10 with 4-phenylurazole linkages. The resulting polymers are soluble in most organic solvents and can be used as thermoplastic materials.

Since the 4-position of the urazole group can readily be substituted with a wide variety of the functional groups, one can readily achieve the properties such a supramolecular aggregation by hydrogen bonding, optically active and liquid crystals polymers.

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