

# Polymeric Azo Dyes Derived from 4-[4'-(4-Dimethylamino-1-phenylazo) phenyl]-1,2,4-triazolidine-3,5-dione and Diisocyanates

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## ABSTRACT

4-[4'-(4-Dimethylamino-1-phenylazo)phenyl]-1,2,4-triazolidine-3,5-dione **1** was reacted with excess amount of *n*-propylisocyanate in DMF (*N,N*-dimethylformamide) solution at room temperature. The reaction proceeded with moderate yield and involved reaction of both N-H of the urazole group. The resulting bis-urea derivative **2** was characterized by IR, <sup>1</sup>H NMR, elemental analysis and UV-vis spectra and it was finally used as a model compound for the polymerization reaction. Solution polycondensation reactions of monomer **1** with hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI) and tolylene-2,4-diisocyanate (TDI) were performed in DMF in the presence of pyridine as a catalyst and lead to the formation of novel aliphatic and aromatic azo-containing polyurea dyes which are soluble in polar solvents. These novel polyureas have inherent viscosities in a range of 0.15–0.27 dLg<sup>-1</sup> in DMF at 25 °C. Some structural characterization and physical properties of these novel polymers are reported.

**Key Words:** polymeric dyes, polyurea, step-growth polymerization, inherent viscosity, 4-[4'-(4-dimethylamino-1-phenylazo)phenyl]-1,2,4-triazolidine-3,5-dione

## INTRODUCTION

Among the photoresponsive materials, azo compounds are of great interest, because of *cis/trans* isomerization about the diazo bond, which is responsible for the immediate optical properties observed, especially the absorption spectra [1–5]. Photoresponsive polymers especially azo containing polymers have attracted a great deal of interest for variety of applications [6–19].

Polymeric dyes are prepared by using either inert or reactive monomeric dyes. In the first case, the dye is dissolved in molten polymer and a physical blend of the macromolecule and dye is obtained. In the second case, the dye becomes part of the macromolecule [20], as the main chain [9, 20, 21] or side chain [22–25], both via polymerization of monomeric dye [9, 21] or chemical modification of colourless polymers [11, 17, 26, 27].

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Polymerization of monomeric dyes could be performed via polycondensation of bifunctional dyes [9, 20, 21] or polyaddition of vinyl containing dyes [10, 15, 28]. Concerted colour formation polymerization is also reported [29].

Recently we have been able to take advantage of acidic N-H in a compound, 1-methyl-2,5-bis(4-phenylurazoyl) pyrrole and synthesis novel polymers via *N*-alkylation and *N*-acylation reactions [30, 31]. Polymerization of compound 4-phenylurazole (PHU) with phosgene, terephthaloyl chloride, and epichlorohydrine has been reported to give insoluble polymers [32]. Polymerization of compound PHU with aliphatic diacid chlorides gave soluble polyamides with inherent viscosity of  $0.39 \text{ dLg}^{-1}$  [33].

Copolymerization of 4-cyclohexylurazole (CHU) with aliphatic diacid chlorides gave soluble polyamides [34]. We have also reported the reaction of PHU with diisocyanates [35]. The resulting novel polyureas have inherent viscosities in a range of 0.04–0.23  $\text{dLg}^{-1}$ .

The aim of this investigation was to examine the step-growth polymerization reactions of 4DPAPT as a monomer with diisocyanates. In the present paper we wish to report on the successful polycondensation reaction where 4DPAPT as a novel monomer is used for the synthesis of soluble novel polyurea dyes.

## EXPERIMENTAL

### Materials

Reagents were purchased from Fluka Chemical Co., Alderich Chemical Co. and Riedel-de Haen AG, and were used without further purification. 4-[4'-(4-Dimethylamino-1-phenylazo)phenyl]-1,2,4-triazolidine-3,5-dione (4DPAPT) was synthesized according to our previous report [36].

### Techniques

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR, 90 MHz) spectra were recorded on a Varian EM-390 instrument. 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 ( $\text{cm}^{-1}$ ). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fensk Routine Viscometer (Germany).

Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TGA-4000 in nitrogen atmosphere at a rate of  $10^\circ\text{C}/\text{min}$ . Elemental analyses were performed by Research Institute of Petroleum Industry, Tehran.

### Preparation of 1,2-bis(*n*-propylamidocarbonyl)-4-[4'-(4-dimethylamino-1-phenylazo)phenyl]-1,2,4-triazolidine-3,5-dione (model compound 2)

Into a 25 mL round bottom flask, *n*-propylisocyanate (0.52 mL,  $6.17 \times 10^{-3}$  mol) and compound 4DPAPT 1 (0.200 g,  $6.17 \times 10^{-4}$  mol) were dissolved in 1 mL of DMF. The solution was stirred for 48 h at room temperature. The excess *n*-propylisocyanate was removed under reduced pressure and the residue was precipitated in 25 mL of diethyl ether. The resulting solid was filtered off, dried to give 0.16 g (52%) of orange solid 2. This solid was recrystallized from water-acetone mixture, mp  $194\text{--}195^\circ\text{C}$ ; IR(KBr): 3350 (m), 3120 (m), 2960 (m), 2920 (m), 1780 (m), 1720 (s), 1680 (m), 1600 (s), 1515 (s, sh), 1500 (s), 1410 (s), 1362 (s), 1310 (w), 1280 (m), 1240 (m, br), 1138 (s), 1060 (w), 1008 (w), 940 (w), 840 (w), 820 (m), 740 (w, br), 640 (w, br), 550 (w)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ , TMS):  $\delta$  0.9 (t, 6H, J = 6.25 Hz), 1.5 (m, 4H), 2.9–3.4 (m, 6H), 3.1 (s, 6H), 6.9 (d, 2H,  $J_1 = 7.5$  Hz), 7.85 (m, 6H).

The elemental analysis results obtained as follows:

$\text{C}_{24}\text{H}_{30}\text{N}_8\text{O}_4$	C (%)	H (%)	N (%)
Calculated	58.29	6.11	22.66
Found	59.26	5.89	23.03

### Polymerization of 4DPAPT with HMDI

Into a 25 mL round bottom flask, compound 4DPAPT (0.2017 g,  $6.22 \times 10^{-4}$  mol), compound HMDI 3 (0.1046 g,  $6.22 \times 10^{-4}$  mol) and pyridine (0.1 mL,  $1.24 \times 10^{-3}$  mol) were dissolved in 0.5 mL of DMF. The solution was stirred for 24 h at room temperature.

then for 24 h at 85 °C. The viscous solution was precipitated in 50 mL of methanol. The solid was filtered off, dried to give 0.16 g (52%) of orange polyurea PU1 with mp >180 °C; inherent viscosity (0.5 dLg<sup>-1</sup> DMF, 25 °C) = 0.19; IR (KBr): 3310 (m), 2900 (m), 2820 (w), 1725 (s, sh), 1650 (w), 1595 (s), 1510 (s, br), 1395 (s, br), 1360 (s), 1310 (w), 1245 (m, br), 1130(s), 1060 (w), 1005 (w), 940 (m), 840 (m), 820 (m), 760 (m, br), 640 (m, br), 550 (m, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub> TMS): δ 1.35 (m, 8H), 3.0 (br, 4H), 3.1 (s, 6H), 4.1 (m, 2H), 6.85 (d, 2H, J=7.5 Hz), 7.8 (m, 6H). Thermal analysis: T<sub>5</sub> 181 °C, T<sub>10</sub> 281 °C, char yield at 600 °C: 29.1%.

The elemental analysis results obtained as follows:

C <sub>24</sub> H <sub>28</sub> N <sub>8</sub> O <sub>4</sub>	C (%)	H (%)	N (%)
Calculated	58.53	5.73	22.75
Found	57.27	5.98	22.15

#### Polymerization of 4DPAPT with IPDI

Into a 25 mL round bottom flask, compound 4DPAPT (0.2046 g, 6.31×10<sup>-4</sup> mol), compound IPDI 4 (0.1402 g, 6.31×10<sup>-4</sup> mol) and pyridine (0.1 mL, 1.26×10<sup>-3</sup> mol) were dissolved in 0.5 mL of DMF. The solution was stirred for 24 h at room temperature, then for 24 h at 85 °C. The solution was precipitated in 50 mL of methanol. The solid was filtered off, dried to give 0.23 g (68%) of orange polyurea PU2, mp >240 °C; inherent viscosity (0.5 dLg<sup>-1</sup> DMF, 25 °C) = 0.27; IR (KBr): 3340 (m), 2940 (m), 2900 (m), 1730 (s, sh), 1600 (m), 1515 (s, br), 1405 (s, br), 1360 (s, br), 1310 (w), 1240 (m, br), 1140 (s), 1060 (w), 1010 (w), 940 (w), 840 (m), 820 (m), 760 (m, br), 640 (w), 550 (w, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub> TMS): δ 1.1 (m, 12H), 1.6 (m, 3H), 3.1 (s, 6H), 4.0 (m, 5), 7.0 (d, 2H, J = 7.5 Hz), 7.9 (m, 6H). Thermal analysis: T<sub>5</sub> 140 °C, T<sub>10</sub> 247 °C, char yield at 600 °C: 23.3%.

The elemental analysis results obtained as follows:

C <sub>28</sub> H <sub>34</sub> N <sub>8</sub> O <sub>4</sub>	C (%)	H (%)	N (%)
Calculated	61.52	6.27	20.50
Found	60.59	6.57	20.43

#### Polymerization of 4DPAPT with TDI

Into a 25 mL round bottom flask, compound 4DPAPT (0.2063 g, 6.36×10<sup>-4</sup> mol), compound TDI 5 (0.1108 g, 6.36×10<sup>-4</sup> mol) and pyridine (0.1 mL, 1.27×10<sup>-3</sup> mol) were dissolved in 0.5 mL of DMF. The solution was stirred for 24 h at room temperature, then for 24 h at 85 °C. The solution was precipitated in 50 mL of methanol. The solid was filtered off, dried to give 0.16 g (50%) of orange polyurea PU3, mp >300 °C; inherent viscosity (0.5 dLg<sup>-1</sup> DMF, 25 °C) = 0.15; IR (KBr): 3270 (s, br), 1780 (m, br), 1690 (s, br), 1640 (s, br), 1595 (s), 1510 (s, br), 1400 (s), 1360 (s), 1305 (s, br), 1220 (s, br), 1140 (s), 1060 (w), 1005 (w), 90 (w), 820 (m), 750 (w), 640 (w), 550 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub> TMS): δ 2.15 (s, 3H), 3.05 (s, 6H), 3.5 (br, 2H), 6.9 (d, 2H, J=7.5 Hz) 7.2 (m, 3H), 7.9 (m, 6H). T<sub>5</sub> 200 °C, T<sub>10</sub> 250 °C, char yield at 600 °C: 35.2%.

The elemental analysis results obtained as follows:

C <sub>25</sub> H <sub>27</sub> N <sub>8</sub> O <sub>4</sub>	C (%)	H (%)	N (%)
Calculated	60.24	4.45	22.48
Found	60.11	4.40	22.59

## RESULTS AND DISCUSSION

### Model Compound Studies

4DPAPT 1 was allowed to react with excess n-propylisocyanate in DMF solution, and gave 1,2-bis(n-propylamidocarbonyl)-4-[4'-(4-dimethylamino-1-phenyl-azo)phenyl]-1,2,4-triazolidine-3,5-dione 2 in good yield (Scheme 1). The compound 2 was characterized by IR, <sup>1</sup>H NMR, elemental analysis and UV-vis spectra. The IR spectrum of 2 showed a medium peak at 3350 cm<sup>-1</sup> for the N-H bond, two medium peaks at 2960 and 2920 cm<sup>-1</sup> for the methylene and methyl C-H bond, also three peaks at 1780, 1720 and 1680 cm<sup>-1</sup> for the carbonyl groups. The first two peaks are characteristic pattern for the urazole moiety. <sup>1</sup>H NMR spectrum of 2 showed a triplet at 0.9 ppm for the two methyl groups, a multiplet at 1.5 ppm for the two methylene groups attached to the methyl groups, a multiplet at 2.9–3.4 ppm for the other two methylene groups attached to the amide groups

and two N–H of the amide groups, a singlet at 3.1 ppm for the methyl groups of the dimethylaniline moiety, a doublet at 6.9 ppm for the two aromatic protons which are in ortho position to the dimethylamine group and a multiplet at 7.85 ppm for other aromatic protons. The elemental analysis results are in good agreement with the structure of model compound 2.

### Polymerization Reactions

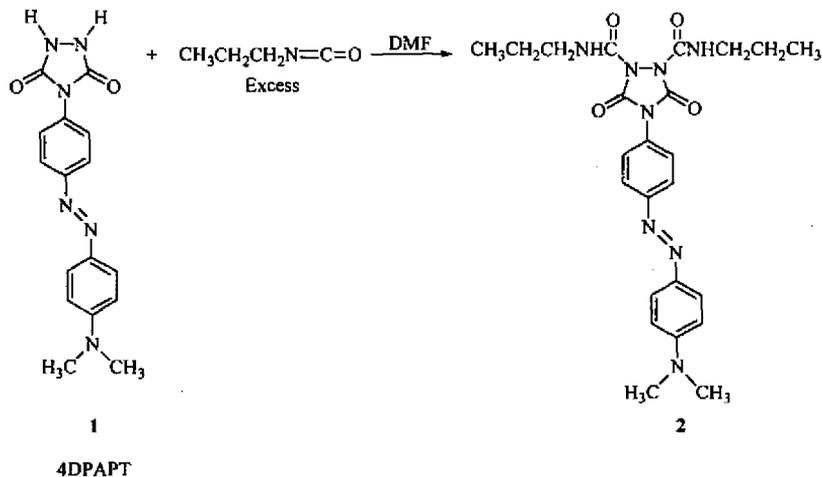
As 1,2-bis(*n*-propylamidocarbonyl)-4-[4'-(4-dimethylamino-1-phenylazo)phenyl]-1,2,4-triazolidine-3,5-dione **2** as a model compound was synthesized in good yield and purity we became interested to perform this type the reaction for the formation of the novel azo-containing polyureas.

Thus HMDI **3**, IPDI **4** and TDI **5** were selected as diisocyanates. The reaction of monomer **1** with these diisocyanates was performed via solution polymerization. The reactions were carried out in DMF solution in the presence of pyridine as a catalyst and the resulted polyureas PU1–PU3 were obtained as orange solids in good yield (Scheme II).

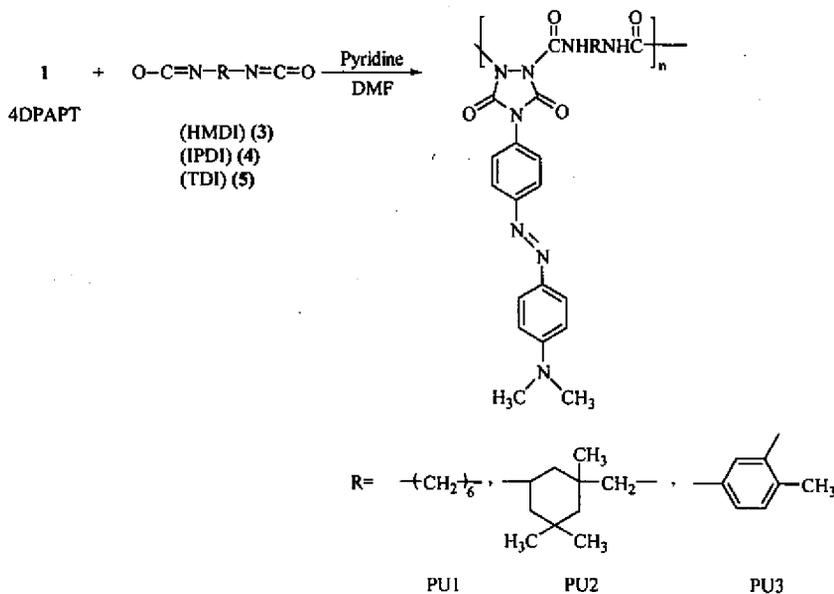
The resulting polymers were characterized by IR, <sup>1</sup>H NMR, elemental analysis, UV-vis and TGA. The IR spectrum of polymer PU1 showed a medium peak at 3310 cm<sup>-1</sup> for the N–H bond, a medium peak

at 2900 cm<sup>-1</sup> for the aliphatic C–H bonds, also a strong broad peak with two shoulders at 1725 cm<sup>-1</sup> for the carbonyl groups. These peaks are characteristic pattern for the urazole moiety. The <sup>1</sup>H NMR spectrum of PU1 showed a multiplet at 1.35 ppm for the four central methylene groups, a multiplet at 3.0 ppm for the other two methylene groups attached to the amide groups. A singlet at 3.1 ppm for the methyl groups of the dimethylaniline moiety, a broad peak at 4.1 ppm for the two N–H of the amide groups, a doublet at 6.85 ppm for the two aromatic protons which are in ortho position to the dimethylamin group and a multiplet at 7.8 ppm for other aromatic protons. The elemental analysis results are also in good agreement with the structure of PU1.

The IR spectrum of polymer PU2 showed a medium peak at 3340 cm<sup>-1</sup> for the N–H bond, two medium peaks at 2940 and 2900 cm<sup>-1</sup> for the methylene and methyl C–H bond, also a strong broad peak with two shoulders at 1730 cm<sup>-1</sup> for the carbonyl groups. The <sup>1</sup>H NMR spectrum of PU2 showed a multiplet at 1.0 ppm for the two methyl and methylene groups of the isophorone moiety, a multiplet at 1.6 ppm for the methylene methyldene groups attached to the amide groups, a singlet at 3.1 ppm for the methyl groups of the dimethylaniline moiety, a



Scheme 1



Scheme II

broad peak at 4.0 ppm for the two N-H of the amide groups and other methyl group of the isophorone moiety, a doublet at 7.0 ppm for the two aromatic protons which are in ortho position to the dimethylamin group and a multiplet at 7.9 ppm for other aromatic protons. The elemental analysis results are also in good agreement with calculated percentages for carbon, hydrogen and nitrogen contents in polymer repeating unit of PU2.

Table 1. UV-vis spectra of model compound 2 and polymers PU1-PU3 in DMF.

Code	Colour	$\lambda_{\text{max}}$ (A, $\epsilon \text{ M}^{-1} \text{ cm}^{-1}$ )
Compound 2	Orange	272 (0.717, 29550)
		425 (1.033, 42573)
PU1	Orange	271 (0.509, 12535)
		425 (1.229, 30267)
PU2	Orange	271 (0.537, 11290)
		425 (1.228, 25818)
PU3	Orange	271 (0.859, 38928)
		426 (0.482, 21843)

The IR spectrum of polymer PU3 showed a strong broad peak at  $3270 \text{ cm}^{-1}$  which covers the area

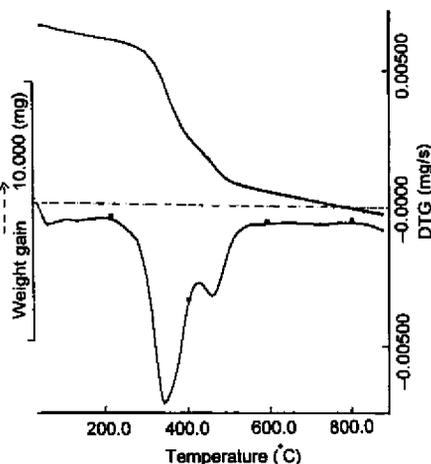


Figure 1. TGA and DTG thermograms of polymer PU1 under nitrogen atmosphere.

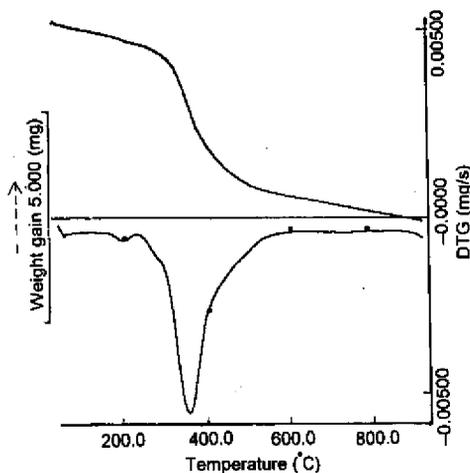


Figure 2. TGA and DTG thermogram of polymer PU2 under nitrogen atmosphere.

for the N-H, aromatic C-H and aliphatic C-H bonds, and two broad peaks at 1780 and 1690  $\text{cm}^{-1}$  for the carbonyl groups. The  $^1\text{H}$  NMR spectrum of PU3

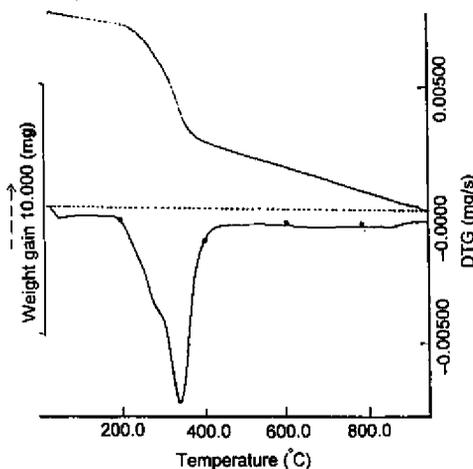


Figure 3. TGA and DTG thermogram of polymer PU3 under nitrogen atmosphere.

showed a singlet at 2.15 ppm for the toluene methyl group, a singlet at 3.05 ppm for the methyl groups of the dimethylaniline moiety, a broad peak at 3.5 ppm for the two N-H of the amide groups, a doublet at 6.9 ppm for the two aromatic protons which are in ortho position to the dimethylamino group, a multiplet at 7.2 ppm for the toluene aromatic protons and a multiplet at 7.9 ppm for other aromatic protons.

The UV-vis spectra of the azo dye model compound 2 and polyureas PU1, PU2 and PU3 were recorded in DMF and the data are shown in Table 1. It is apparent that the wavelengths of the maximum absorptions are related to the azo groups in the compounds and they are observed within 425–426 nm.

The polymers PU1, PU2 and PU3 are soluble in organic solvents such as DMF, dioxane, DMSO, DMAc and DMF, and are insoluble in solvents such as water, methanol, cyclohexane and chloroform.

### Thermal Properties

The thermal behaviour of polyureas PU1, PU2 and PU3 were measured by thermogravimetric analysis (TGA) at a rate of 10  $^{\circ}\text{C}/\text{min}$  in nitrogen atmosphere (Figures 1, 2 and 3). An examination of the data reveals that all of the above polyureas are thermally stable up to 140  $^{\circ}\text{C}$  in nitrogen atmosphere. The polymers PU1, PU2 and PU3 show 5% weight loss at 181, 140 and 200  $^{\circ}\text{C}$ , respectively.

### CONCLUSION

This investigation has shown that 4DPAPT 1 is an interesting monomer for the polycondensation reactions. This compound has two acidic N-H groups and it can be readily reacted with *n*-propylisocyanate to give 1,2-bis(*n*-propylamidocarbonyl)-4-[4'-(4-dimethylamino-1-phenylazo)phenyl]-1,2,4-triazolidine-3,5-dione 2 good yield and high purity.

Thus compound 1 can act as a bifunctional monomer and its polymerization reaction with aliphatic and aromatic diisocyanates gave novel polyureas with azo containing urazole linkages. Since these polyureas have azo functional group, they have potential to be used as photoresponsive materials.

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