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# Synthesis of Photoactive Polyureas Derived from 4-(4-Dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione and Diisocyanates

**Shadpour Mallakpour (✉) and Zahra Rafiee**

Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, I.R. Iran
E-mail: MALLAK@CC.IUT.AC.IR, Fax: +98-311-3912350

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## Summary

4-(4-Dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (**DAPTD**) was prepared from 4-dimethylaminobenzoic acid in five steps. The reaction of monomer **DAPTD** with *n*-isopropylisocyanate was performed at room temperature in *N,N*-dimethylacetamide (DMAc) solution and the resulting bis-urea derivative was obtained in high yield and was finally used as a model compound for polymerization reaction. The step-growth polymerization reactions of monomer with hexamethylene diisocyanate (**HMDI**), isophorone diisocyanate (**IPDI**) and toluene-2,4-diisocyanate (**TDI**) were performed in DMAc solution in the presence of pyridine, triethylamine or dibutyltin dilurate as catalysts. Some physical properties and structural characterization of these novel polyureas are reported. Fluorimetric studies of the model compound as well as polymers were performed.

## Introduction

The synthesis of the polymers containing heterocyclic rings in the main chains has been the subject of considerable interest because of their relatively good thermal stability and some interesting novel properties [1-4]. Little attention was given to polyurethanes and polyureas containing heterocyclic rings. We reported the synthesis of urazoles and the preparation of polyureas from these monomers [5-6]. Polyureas are very tough materials with high hardness and good chemical resistance. They can be tailor-made to obtain properties which lead to versatile applications such as coating systems for waterproofing and corrosion protection [7]. A number of methods have been used to prepare polyureas, but the best method is to react diamine and diisocyanates. This reaction is a step-growth addition reaction of amine across the carbon-nitrogen double bond and there is no by product. Polyureas have been used for many applications including encapsulation of pharmaceutical, ink, dyes and the modification of wool fibers by interfacial grafting techniques [8].

Attempts to synthesize new types of thermally stable polyureas such as phosphorus-containing and heterocyclic polyureas to obtain different properties have been reported [9-10]. This article is concerned with the synthesis of 4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (**DAPTD**) as a new heterocyclic monomer and its polymerization reaction with commercially available diisocyanates.

## Experimental

### *Materials*

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany). DMAc (*N,N*-dimethylacetamide) was dried over BaO and then was distilled under reduced pressure.

### *Equipments*

Proton nuclear magnetic resonance $^1$H-NMR (500MHz) spectra were recorded on a Bruker (Germany), Avance 500 instrument. Multipilicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), and multiplet (m). FT-IR spectra were recorded on JASCO-680 (Japan) spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave number (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 Gallenham melting point apparatus. Inherent viscosities were measured by standard procedure using a Cannon Fensk Routine viscometer. Elemental analyses were performed by Research Institute of petroleum Industry, Tehran, I.R. Iran. Fluorescence and UV-Vis spectra were recorded on a spectrofluorometer, JASCO, FP-750 and UV/VIS/NIR spectrophotometer, JASCO, V-570, respectively. Mass spectra were recorded on a Fisons (Trio 1000) mass spectrometer. Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Stanton-650 TGA under $N_2$ atmosphere by the Iran Polymer and Petrochemical Institute (IPPI).

### *Preparation of 4-Dimethylaminobenzoyl azide (2)*

Into a 25-mL round bottom flask, the suspension of 4-dimethylaminobenzoic acid (1.00 g, $6.05 \times 10^{-3}$ mol) in acetone (10 mL) was cooled to 0 $^{o}$C and triethylamine (0.61 g, $6.05 \times 10^{-3}$ mol) was added over a period of 10 min. The reaction mixture was stirred for further 1 h and then a solution of ethylchloroformate (0.66 g, $6.05 \times 10^{-3}$ mol) in acetone (3 mL) was added at -10 $^{o}$C over a period of 10 min. The resulting reaction mixture was stirred for 3 h at the same temperature and then a solution of sodium azide (0.79 g, $1.21 \times 10^{-2}$ mol) in distilled water (5 mL) was added at -10 $^{o}$C dropwise. Finally, the reaction mixture was stirred for 2 h at the same temperature, 2 h at 0 $^{o}$C and finally 4 h at room temperature and then poured into 50 mL of ice-cold water. The white solid was filtered off, dried to give 0.84 g (76%) of compound **2**. Recrystallization from acetone-water mixture gave white crystals. m.p. = 90-92 $^{o}$C; IR (KBr): 3103 (m), 2913 (m), 2125 (s), 1666 (s), 1597 (s), 1529 (m), 1483 (w), 1446 (w), 1414 (w), 1375 (s), 1313 (w), 1265 (s), 1205 (s), 1174 (s), 1127 (m), 1066 (w), 1005 (m), 971 (m), 942 (m), 825 (w), 752 (m), 687 (w), 605 (w), 496 (w) cm$^{-1}$.

### *Preparation of 1-Ethoxycarbonyl-4-(4-dimethylaminophenyl) semicarbazide (4)*

Into a 100-mL round bottom flask compound **2** (3.00 g, $1.58 \times 10^{-2}$ mol) and 45 mL of dry toluene were added. The stirrer was started and the reaction mixture was refluxed under nitrogen atmosphere for 11 h. At the end of refluxing the reaction mixture was cooled, then filtered off immediately. The clear solution was transferred into a 100 mL two-necked round bottom flask. The solution was cooled in an ice bath and a solution of (1.64 g, $1.58 \times 10^{-2}$ mol) of ethyl carbazate in 20 mL of dry toluene was added dropwise in a period of 15 min. The suspension was stirred for 2 h in ice bath, then for 8 h at room temperature. The solid was filtered off, dried to give 4.12 g (98%) of white solid **4**. m.p. = 168-170 °C; IR (KBr): 3307 (m), 2988 (m), 1759 (s), 1655 (s), 1635 (m), 1606 (m), 1558 (m), 1520 (m), 1444 (w), 1384 (w), 1356 (w), 1302 (w), 1222 (s), 1204 (s), 1058 (w), 1033 (w), 946 (w), 899 (w), 818 (m), 697 (w), 582 (w), 527 (w) $cm^{-1}$.

### *Preparation of 4-(4-Dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (6)*

Into a 100-mL round-bottom flask, sodium metal (0.27 g, $1.17 \times 10^{-2}$ mol ) was dissolved in 25 mL of absolute ethanol. Nitrogen gas was bubbled through the solution and compound **4** (3.00 g, $1.13 \times 10^{-2}$ mol) was added at once. The solution was refluxed under nitrogen atmosphere for 7.5 h, then it was cooled in ice bath. The solution was neutralized with acetic acid to pH of 6. The product was isolated and dried to give 2.28 g (92%) of white solid **6**. Recrystallization from hot water gave white crystals. m.p. = 248-250°C. IR (KBr, $cm^{-1}$): 3195 (s, br), 3051 (s), 2988 (m), 1767 (w), 1676 (s), 1614 (s), 1568 (w), 1526 (s), 1450 (s), 1363 (s), 1229 (m), 1190 (m), 1173 (w), 1128 (w), 1103 (w), 1063 (w), 1034 (w), 998 (w), 945 (w), 790 (s), 681 (m), 664 (m), 587 (w), 523 (w), 493 (w), 430 (w) and $^1$H NMR (500 MHz, DMSO-$d_6$, δ, ppm): δ 2.91 (s, 6H), 6.75 (d, 2H, *J* = 8.3 Hz), 7.17 (d, 2H, *J* = 8.3 Hz), 10.63 (s, 2H). Anal. calcd for $C_{10}H_{12}N_4O_2$: 54.5% C; 5.5% H; 25.4% N. Found: 54.7% C; 5.3% H; 25.2% N. Mass (EI), m/z: 220 ([M$^+$], 100%), 219 (65%), 162 (46%), 161 (60%), 135 (40%).

### *Preparation of 1,2-Bis-(n-propylamidocarbonyl)-4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (model compound 7)*

Into a 25-mL round-bottom flask, *n*-propylisocyanate (1.0 mL, $1.09 \times 10^{-2}$ mol ) was added to a solution of **DAPTD (6)** (0.200 g, $9.08 \times 10^{-4}$ mol ) in 0.8 mL of dry DMAc. The solution was stirred for 24 h at room temperature. The excess *n*-propylisocyanate was removed by aspirator and the residue was percipitated in 30 mL of water. The resulting solid was filtered off, dried to give 0.305 g (86%) of white solid **7**. This solid was recrystallized from acetic acid, m.p. 183-184°C; IR(KBr, $cm^{-1}$): 3359 (m), 3100 (w), 2950 (w), 2927 (m), 2850 (w), 1773 (m), 1730 (s), 1699 (s), 1612 (s), 1523 (s), 1420 (s), 1371 (s), 1273 (m), 1231 (m), 1186 (s), 1142 (m), 1072 (w), 947 (w), 809 (m), 765 (m), 603 (m), 513 (m) and $^1$H NMR (500 MHz, DMSO-$d_6$, δ, ppm): δ 0.85 (t, 6H, *J* = 7.6 Hz), 1.46-1.53 (m, 4H), 2.98 (s, 6H), 3.16-3.20 (m, 4H), 6.74 (d, 2H, *J* = 8.3 Hz), 7.18 (d, 2H, *J* = 8.3 Hz), 7.72 (t, 2H, *J* = 8.75 Hz). Anal. calcd for $C_{18}H_{26}N_6O_4$: 55.3% C; 6.7% H; 21.5% N. Found: 55.2% C; 6.1% H; 21.7% N. Mass (EI), m/z: 331 (86%), 162 (100%), 161 (32%).

### *Polymerization of DAPTD with hexamethylene diisocyanate (HMDI)*

*Method I*: Into a 25-mL round-bottom flask **DAPTD** (0.1038 g, $4.71 \times 10^{-4}$ mol) and pyridine (0.04 mL, $4.71 \times 10^{-4}$ mol) were added to a solution of **HMDI (8)** (0.0793 g, $4.71 \times 10^{-4}$ mol) in 0.5 mL of DMAc. The solution was stirred for 6 h at room

temperature, 12 h at 60 °C and then 24 h at 85 °C. During of this period 0.6 mL of DMAc was added. The viscous solution was precipitated in 30 mL of methanol. The solid was filtered off, dried to give 0.148 g (81%) of polyurea **PU1A**. m.p. 198-206 °C. The above polymerization was repeated, in the presence of triethylamine and dibutyltin dilurate as a catalyst, respectively.
*Method II*: The above polymerization was repeated, but the reaction mixture was refluxed in DMAc for one min., 3 min. and 6 min. in the presence of different catalysts. IR(KBr, $cm^{-1}$): 3354 (m), 3100 (w), 2932 (m), 2856 (m), 1791 (m), 1745 (s), 1613 (m), 1524 (s), 1421 (m), 1357 (m), 1253 (m), 1187 (m), 1063 (m), 947 (m), 813 (m), 757 (m), 565 (m), 526 (m) and $^1H$ NMR (500 MHz, DMSO-$d_6$, δ, ppm): δ 1.25-1.46 (m, br, 8H, $CH_2$), 2.96 (s, 6H, $CH_3$), 3.15 (m, br, 4H, $CH_2$), 6.87 (s, br, 2H, Ar-H), 7.27 (s, br, 2H, Ar-H), 7.91 (s, br, N-H). ANAL. Calcd for $C_{18}H_{24}N_6O_4$: 55.6% C; 6.2% H; 21.6% N. Found: 53.9% C; 6.6% H; 21.0% N.

### *Polymerization of DAPTD with isophorone diisocyanate (IPDI)*

*Method I*: Into a 25-mL round-bottom flask **DAPTD** (0.0951 g, $4.32 \times 10^{-4}$ mol) and pyridine (0.04 mL, $4.95 \times 10^{-4}$ mol) was added to a solution of **IPDI (9)** (0.0990 g, $4.32 \times 10^{-4}$ mol) in 0.5 mL of DMAc. The solution was stirred for 6 h at room temperature, 12 h at 60 °C and then 24 h at 85 °C. During of this period 0.6 mL of DMAc was added. The viscous solution was precipitated in 30 mL of methanol. The solid was filtered off, dried to give 0.167 g (86%) of white polyurea **PU2A**. m.p. 212-224 °C. The above polymerization was repeated, in the presence of triethylamine and dibutyltin dilurate as a catalyst, respectively.
*Method II*: The above polymerization was repeated, but the reaction mixture was refluxed in DMAc for one min., 3 min. and 6 min. in the presence of different catalysts. IR(KBr, $cm^{-1}$): 3343 (m), 3100 (w), 2949 (m), 2916 (m), 1785 (m), 1736 (s), 1651 (m), 1526 (s), 1425 (m), 1356 (m), 1309 (w), 1238 (m), 1189 (m), 1062 (w), 945 (w), 813 (w), 756 (w), 589 (w) and $^1H$ NMR. (500 MHz, DMSO-$d_6$, δ, ppm): δ 0.83-1.11 (m, br, 11H, $CH_3$, $CH_2$), 1.19-1.48 (m, br, 4H, $CH_2$), 2.73 (m, br, 2H, $CH_2$), 2.95 (s, 6H, $CH_3$), 3.64 (m, br, 1H, CH), 5.60-5.81 (m, br, N-H, end group of amine), 7.02-7.68 (m, 6H, Ar-H, N-H).

### *Polymerization of DAPTD with tolylene-2,4-diisocyanate (TDI)*

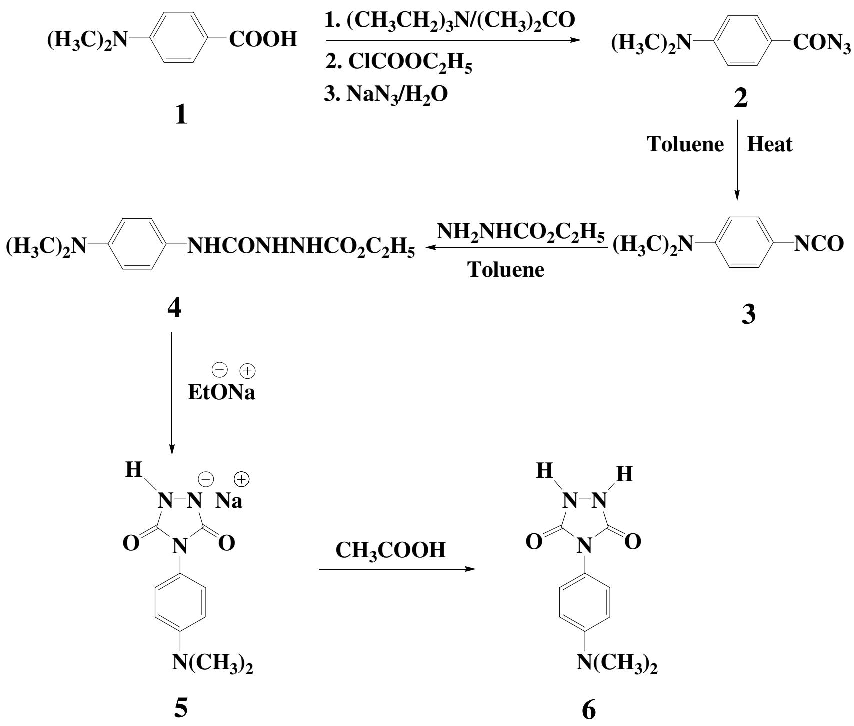
*Method I*: Into a 25-mL round bottom flask **DAPTD** (0.1094 g, $4.97 \times 10^{-4}$ mol) and pyridine (0.04 mL, $4.97 \times 10^{-4}$ mol ) was added to a solution of **TDI (10)** (0.0865 g, $4.97 \times 10^{-4}$ mol) in 0.5 mL of DMAc. The solution was stirred for 6 h at room temperature, 12 h at 60 °C and then 24 h at 85 °C. During of this period 0.6 mL of DMAc was added. The viscous solution was precipitated in 30 mL of methanol. The solid was filtered off, dried to give 0.178 g (91%) of white polyurea **PU3A**. m.p. 222 °C (dec.). The above polymerization was repeated, in the presence of triethylamine and dibutyltin dilurate as a catalyst, respectively.
*Method II*: The above polymerization was repeated, but the reaction mixture was refluxed in DMAc for one min., 3 min. and 6 min. in the presence of different catalysts. IR(KBr, $cm^{-1}$): 3287 (s, br), 3050 (w), 2926 (m), 1780 (w), 1706 (s), 1615 (s), 1529 (s), 1414 (m), 1303 (m), 1219 (s), 1010 (w), 940 (w), 879 (w), 813 (m), 756 (m), 596 (w), 529 (w), 456 (w) and $^1H$ NMR (500 MHz, DMSO-$d_6$, δ, ppm): δ 2.22 (m, br, 3H, $CH_3$), 2.97 (s, br, 6H, $CH_3$), 6.90-7.52 (m, br, 3H, Ar-H), 7.62-8.22 (m, br, 6H, Ar-H, N-H).

## Results and Discussion

### *Monomer synthesis*

The new heterocyclic monomer **DAPTD** was synthesized in five steps starting from 4-dimethylaminobenzoic acid. The synthesis of acyl azide was accomplished by "one-pot" Weinstock modification of the curtius reaction [11]. Here, the isolation of intermediate is not involved and the acyl azide is obtained in comparatively purer form and in good yield. The acyl azide was subjected to thermal decomposition in dry toluene at reflux temperature to yield isocyanate **3**. This isocyanate subsequently was reacted with ethyl carbazate and semicarbazide **4** was obtained in quantitative yield. Cyclization of compound **4** with sodium ethoxide gave new urazole **6** (Scheme 1).

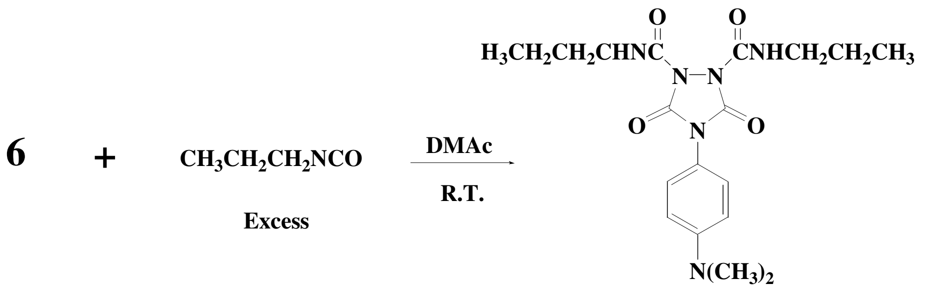
The purity of monomer **6** was checked by TLC. The $^1$H-NMR spectrum of **6** showed all peaks which are in agreement with the structure of compound **6**. The structure of urazole **6** was also confirmed by IR, UV-Vis, fluorimetric, mass spectra and elemental analysis.



**Scheme 1**. Synthesis of monomer **6**

### *Model Compound Studies*

**DAPTD (6)** was allowed to react with excess *n*-isopropylisocyanate in DMAc solution at room temperature for 24 h and gave compound **7** in high yield (Scheme 2). The compound **7** was characterized by IR, $^1$H-NMR, UV-Vis, fluorimetric, Mass spectra and elemental analysis. The IR spectrum of **7** show a medium peak at 3359 cm$^{-1}$ for the N-H bond. It also shows three peaks at 1773, 1730 and 1699 cm$^{-1}$ for the carbonyl groups. The first two peaks are characteristic pattern for the urazole moiety. The $^1$H-NMR spectrum of **7** showed all peaks which are in agreement with the structure of compound **7** (Figure 1). The purity of this model compound **7** was checked by TLC. The structure of model compound **7** was also confirmed by IR, UV-Vis, fluorimetric, Mass spectra and elemental analysis.



**7**

**Scheme 2**. Synthesis of model compound **7**

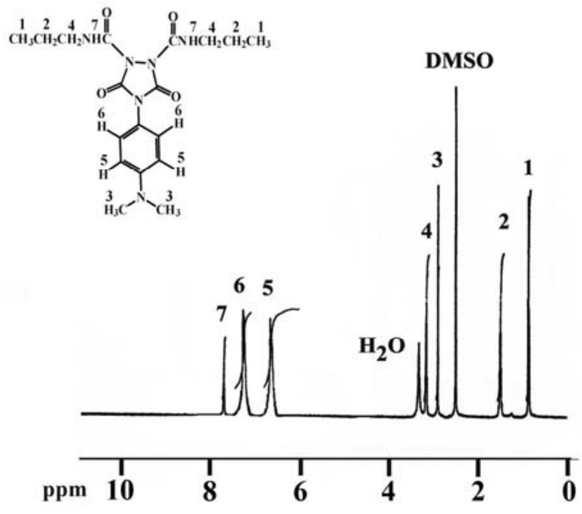
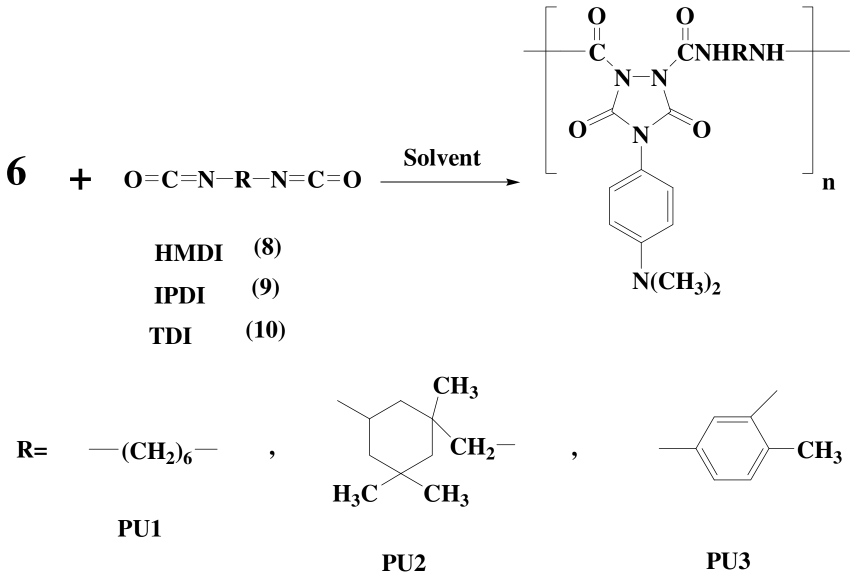


**Figure 1**. $^1$H-NMR (500 MHz) Spectrum of model compound **7** in DMSO-$d_6$ at rt

### *Polymerization Reactions*

Because compound **7** 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 photoactive polyureas. Thus HMDI **(8)**, IPDI **(9)** and TDI **(10)** were selected as diisocyanates. The polymerization reaction of monomer **6** with these diisocyanates were performed under conventional solution polymerization techniques as well as high temperture in the presence of different catalysts **PU1-PU3** (Scheme 3).

The polymerization reaction of monomer **6** with **HMDI** was carried out with two different methods. In method **I** the reaction mixture was heated gradually from room temperature to 85°C in the presence of pyridine, dibutyltin dilaurate and triethylamine, respectively. The resulting polyureas **PU1A-PU1C** have good inherent viscosity and high yield. In method **II** the reaction mixture was refluxed up for 1, 3 and 6 min. in DMAc.



**Scheme 3**. Polycondensation reactions of monomer **6** with diisocyanates

The resulting polyureas **PU1D-PU1H** have high yield and good inherent viscosity comparing with method **I**. Reaction conditions and some physical properties for **PU1A-PU1H** are summerized in Table 1. The resulting polymers were characterized by IR, $^1$H-NMR, elemental analysis, UV-Vis and fluorimetric spectrum.

The IR spectrum of polymer **PU1** showed two peaks at 1791 and 1745 cm$^{-1}$ for the carbonyl groups. The $^1$H-NMR spectrum (Figure 2) of polymer **PU1** showed all peaks for aliphatic and aromatic as well as end group N-H protons. The elemental analysis result is also in good agreement with calculated percentages for carbon, hydrogen and nitrogen contents in polymer repeating unit.

The polymerization reaction of monomer **6** with **IPDI** was also carried out with two different methods (Table 2). We obtained comparable results of two methods.

The IR spectrum of polymer **PU2** showed two strong peaks at 1785 and 1736 cm$^{-1}$ for the carbonyl groups which are related to the urazole moiety. The $^1$H-NMR spectrum of polymer **PU2** showed peaks that confirm its chemical structure.

The polymerization reaction of monomer **6** with **TDI** was also performed with two different methods (Table 3). Here also we obtained comparable results of two methods.

**Table 1**. Reaction conditions for the polymerization of monomer **DAPTD (6)** with **HMDI** (**8**) by different methods and some physical properties for **PU1A-PU1H**

| Polymer | Method[a] | Refluxing time (min.) | Catalyst | Yield (%) | $\eta_{inh}$ (dL/g)[e] |
|---|---|---|---|---|---|
| **PU1A** | I | - | Py[b] | 81 | 0.18 |
| **PU1B** | I | - | TEA[c] | 86 | 0.21 |
| **PU1C** | I | - | DBTDL[d] | 91 | 0.19 |
| **PU1D** | II | 1 | Py | 86 | 0.21 |
| **PU1E** | II | 1 | TEA | 85 | 0.23 |
| **PU1F** | II | 1 | DBTDL | 90 | 0.18 |
| **PU1G** | II | 3 | TEA | 75 | 0.17 |
| **PU1H** | II | 6 | TEA | 71 | 0.14 |

[a] Method I: gradual heating at different temperatures, Method II: Refluxing at 1, 3 and 6 minutes respectively.
[b] pyridine, [c] triethylamine, [d] dibutyltin dilaurate.
[e] Measured at a concentration of 0.5 g/dL in DMF and 6% LiCl at 25°C.

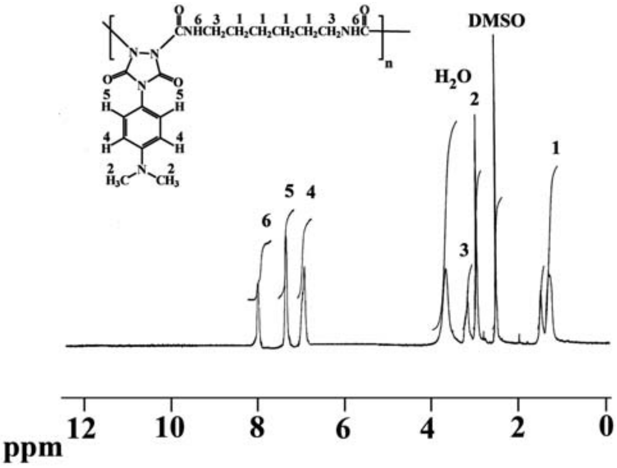


**Figure 2**. $^1$H-NMR (500 MHz) Spectrum of **PU1** in DMSO-$d_6$ at rt

The IR spectrum of polymer **PU3** showed two strong peaks at 1780 and 1706 cm$^{-1}$ for the carbonyl groups which are related to the urazole moiety. The UV-Vis spectra of the monomer **6**, model compound **7**, polyureas **PU1**, **PU2** and **PU3** were recorded in DMF and the data are shown in Table 4. It is apparent that the wavelength of maximum absorption are related to the dimethylaminophenyl group in the compounds. All of these compounds show almost similar UV-Vis spectra pattern.

Fluorescence spectra of the monomer **6,** model compound **7** and **PU1** were recorded in DMF and the data are presented in Table 5. All of these compounds show almost similar fluorescence spectra pattern. The absorption maxima of monomer shifted bathochromic than that of polymers. For example, the sample was excited at 260 nm and emision fluorescence wavelengths were observed at 361 nm and 427 nm. The fluorescent intensity of these compounds is almost medium. The fluorescent intensity **PU3** is higher that of **PU1** and **PU2**. It can be probably due to the rigidity enhancement of this polymer in compared with other two polymers. These fluorescent characteristic of monomer, model compound and polymers are due to *N,N*-dimethylaminophenyl chromophore [12].

**Table 2**. Reaction conditions for the polymerization of monomer **DAPTD** (**6**) with **IPDI** (**9**) by different methods and some physical properties for **PU2A-PU2H**

| Polymer | Method[a] | Refluxing time (min.) | Catalyst | Yield (%) | $\eta_{inh}$ (dL/g)[e] |
|---|---|---|---|---|---|
| **PU2A** | I | - | Py[b] | 86 | 0.18 |
| **PU2B** | I | - | TEA[c] | 85 | 0.18 |
| **PU2C** | I | - | DBTDL[d] | 87 | 0.15 |
| **PU2D** | II | 1 | Py | 82 | 0.13 |
| **PU2E** | II | 1 | TEA | 83 | 0.16 |
| **PU2F** | II | 1 | DBTDL | 91 | 0.11 |
| **PU2G** | II | 3 | TEA | 75 | 0.12 |
| **PU2H** | II | 6 | TEA | 68 | 0.11 |

[a] Method I: gradual heating at different temperatures, Method II: Refluxing at 1, 3 and 6 minutes respectively.

[b] pyridine, [c] triethylamine, [d] dibutyltin dilaurate.

[e] Measured at a concentration of 0.5 g/dL in DMF and 6% LiCl at 25°C.

**Table 3**. Reaction conditions for the polymerization of monomer **DAPTD** (**6**) with **TDI** (**10**) by different methods and some physical properties for **PU3A-PU3H**

| Polymer | Method[a] | Refluxing time (min.) | Catalyst | Yield (%) | $\eta_{inh}$ (dL/g)[e] |
|---|---|---|---|---|---|
| **PU3A** | I | - | Py[b] | 91 | 0.16 |
| **PU3B** | I | - | TEA[c] | 85 | 0.12 |
| **PU3C** | I | - | DBTDL[d] | 83 | 0.08 |
| **PU3D** | II | 1 | Py | 87 | 0.12 |
| **PU3E** | II | 1 | TEA | 82 | 0.11 |
| **PU3F** | II | 1 | DBTDL | 89 | 0.10 |
| **PU3G** | II | 3 | TEA | 82 | 0.16 |
| **PU3H** | II | 6 | TEA | 83 | 0.15 |

[a] Method I: gradual heating at different temperatures, Method II: Refluxing at 1, 3 and 6 minutes respectively.

[b] pyridine, [c] triethylamine, [d] dibutyltin dilaurate.

[e] Measured at a concentration of 0.5 g/dL in DMF and 6% LiCl at 25°C.

The polymers **PU1, PU2** and **PU3** are soluble in organic solvents such as NMP and $H_2SO_4$, partial soluble in DMF, DMSO, DMAc and are insoluble in solvents such as water, methanol, acetone, cyclohexane and chloroform.

**Table 4**. UV-Vis spectra of monomer **6,** model compound **7** and polymers **PU1-PU3** in DMF

| Code | Color | $\lambda_{max}$(A, ε $M^{-1}$ $cm^{-1}$) |
|---|---|---|
| **Compound 6** | White | 262 ( 0.729, 251551)<br>310 ( 0.100, 34565) |
| **Compound 7** | White | 268 ( 0.896, 203636)<br>307 ( 0.126, 28693) |
| **PU1** | White | 269 ( 0.125, 78006)<br>311 ( 0.055, 34262) |
| **PU2** | White | 264 (0.225, 46798)<br>308 (0.027, 5688) |
| **PU3** | White | 262 ( 0.433, 98486)<br>296 ( 0.058, 13105) |

**Table 5**. Fluorescence spectra of monomer **6,** model compound **7** and polymer **PU1** in DMF

| Code | C (M) | $\lambda_{Ex.}$ (nm) | $\lambda_{Em.}$ (nm) |
|---|---|---|---|
| **Compound 6** | $2.90 \times 10^{-6}$ | [a]269, 322 | [c]361, 427 |
| | | [b]299, 324, 360 | [d]467, 499, 547 |
| **Compound 7** | $4.40 \times 10^{-6}$ | [a]263, 281 | [c]357, 429 |
| | | [b]277, 318, 357 | [d]468, 500, 536 |
| **PU1** | $2.90 \times 10^{-6}$ | [a]266, 283 | [c]359, 429 |
| | | [b]279, 321, 359 | [d]463, 496, 530 |

[a] $\lambda_{Em.}$ for scanning emission spectra = 260 nm
[b] $\lambda_{Em.}$ for scanning emission spectra = 358 nm
[c] $\lambda_{Ex.}$ for scanning emission spectra = 260 nm
[d] $\lambda_{Ex.}$ for scanning emission spectra = 437 nm

## Thermal Properties

The thermal behavior of polyurea **PU2** was measured by thermaogravimetric analysis (TGA) at a rate of 10°C/min in nitrogen atmosphere. An examination of the data reveals that polyurea **PU2** is thermally stable up to 150 °C. Some weight loss below 150 °C are due to water or solvent loss. The temperatures of 5% and 10% weight loss together with char yield at 600 °C for this polyurea are 175 °C, 274 °C and 10%, respectively. Figure 3 show thermogram of **PU2**. The resulting polymers **PU1** and **PU2** are not thermally stable, this is due to the exisstance of the aliphatic chains. **PU3**, however, is expected to be more stable due to the presence of aromatic moiety [13].

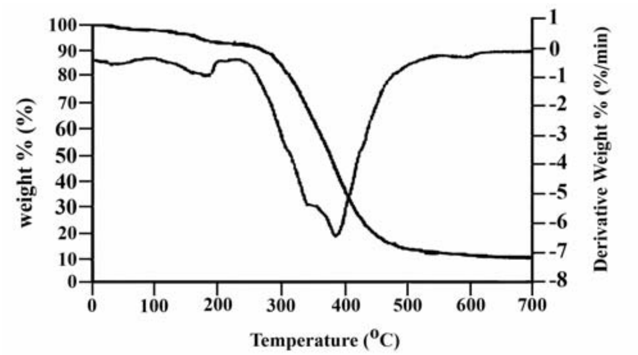


**Figure 3**. TGA/DTG of **PU2** with a heating rate of 10°C/min in nitrogen atmosphere

## Conclusion

A new urazole, 4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (**DAPTD**) was prepared from raw material 4-dimethylaminobenzoic acid. Polymerization of this novel monomer with three different commercial available aromatic diisocyanates gave novel polyureas with dimethylamino containing urazole linkages with inherent viscosities of 0.08-0.23 dL/g, which roughly correspond to molecular weight of 5000 to 10000 g/mol. Although all catalysts used in this polymerization reactions are usefull, but triethylamine seems to be more effective. We are currently using this method for the synthesis of novel polymers and modification of polymers. Since these polyureas have dimethylaminophenyl moieties, they have potential to be used as photoactive materials.

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