

Synthesis and Characterization of New Polyureas Based on 4-(4'-Aminophenyl)urazole and Various Diisocyanates

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ABSTRACT: 4-(4'-Aminophenyl)urazole (AmPU) was prepared from 4-nitrobenzoic acid in six steps. The reaction of monomer AmPU with *n*-isopropylisocyanate was performed in *N,N*-dimethylacetamide solutions at different ratios, and the resulting disubstituted and trisubstituted urea derivatives were obtained in high yields and were finally used as models for polymerization reactions. The step-growth polymerization reactions of AmPU with hexamethylene diisocyanate, isophorone diisocyanate, and toluene-2,4-diisocyanate were performed in *N*-methylpyrrolidone solutions in the presence of pyridine as a catalyst. The re-

sulting novel polyureas had inherent viscosities of 0.11–0.18 dL/g in dimethylformamide at 25°C. These polyureas were characterized with IR, ¹H-NMR, elemental analysis, and thermogravimetric analysis. Some physical properties and structural characterization of these novel polyureas are reported. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2692–2700, 2003

Key words: viscosity; step-growth polymerization; thermogravimetric analysis (TGA)

INTRODUCTION

Although much research has been performed on the synthesis, characterization, and applications of polyesters, polyamides, polyurethanes, and polyimides, little work has been reported on the synthesis of polyureas. This could be due to their low solubility and high melting points. Because polyureas have —NH—CO—NH— functional groups, they can form hydrogen bonds from different sides. Polyureas are polyamides of carbonic acid and are tough, high-melting, and suitable for fiber applications.¹ A number of methods have been used to prepare polyureas, but the best method is to react diamine with diisocyanates. This reaction is a step-growth addition reaction of amine across the carbon–nitrogen double bond, and there is no byproduct. Polyureas have been used for many applications, including the encapsulation of pharmaceuticals, inks, dyes, and the modification of wool fibers by interfacial grafting techniques.²

4-Substituted urazoles are five-member heterocyclic compounds that have two N—H protons. These protons are rather acidic. The urazole derived from the

ene reaction of triazolinediones with alkenes and polydienes has one N—H proton, which seems to be very acidic. The acidity of this proton has been measured, and it is quite acidic with a pK_a value of 4.71, which is almost the same as that of acetic acid.³ The urazole compounds have the potential to undergo N-acylation. 4-Substituted urazole was converted into 1-acyl derivatives by an acylation reaction with a series of carboxylic acid anhydrides.⁴ A simplified procedure for the N-acylation of oxazolidin-2-one chiral auxiliaries has also been reported.⁵

Recently, we have been able to take advantage of this acidic N—H in a compound, 1-methyl-2,5-bis(4-phenylurazoily) pyrrole, and synthesize novel polymers via N-alkylation and N-acylation reactions.^{6,7} The polymerization of 4-phenylurazole (PHU) with phosgene, terephthaloyl chloride, and epichlorohydrin has been reported to give insoluble polymers.⁸ The polymerization of PHU with aliphatic diacid chlorides gave soluble polyamides with an inherent viscosity (η_{inh}) of 0.39 dL/g.⁹ The copolymerization of 4-cyclohexylurazole (CHU) with aliphatic diacid chlorides gave soluble polyamides.¹⁰

In a previous article, we reported the reaction of PHU and CHU with diisocyanates.^{11,12} The resulting novel polyureas had η_{inh} values of 0.04–0.23 and 0.044–0.206 dL/g, respectively. Here we report successful step-growth polymerization reactions in which 4-(4'-aminophenyl)urazole (AmPU or 7) as a novel monomer is used for the synthesis of soluble polyureas.

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EXPERIMENTAL

Materials and equipment

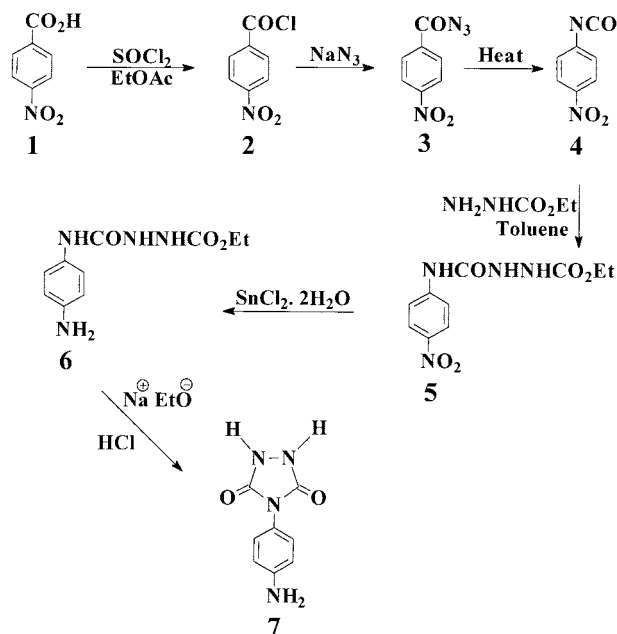
Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), and Riedel-deHaen AG (Seelze, Germany). AmPU was prepared in six steps according to our previous work.¹³ *N,N*-Dimethylacetamide (DMAc) was dried over BaO and then was distilled under reduced pressure. ¹H-NMR (90 MHz) spectra were recorded on a Varian EM-390 instrument (Palo Alto, CA). Tetramethylsilane (TMS) was used as an internal reference. IR spectra were recorded on a Shimadzu 435 IR spectrophotometer (Shimadzu, Japan). The spectra of the solids were carried out with KBr pellets.

All melting points were taken with a Gallenham melting-point apparatus (Germany). The η_{inh} values were measured by a standard procedure with a Cannon-Fensk routine viscometer (Hofheim, Germany). Thermogravimetric analysis (TGA) data for the polymers were taken on a Mettler TGA-50 (England). Elemental analyses were performed at Malek Ashter University (Tehran, Iran).

Reaction of AmPU with *n*-propylisocyanate (1:1 molar ratio)

Into a 25-mL, round-bottom flask, AmPU (0.250 g, 1.30×10^{-3} mol) was dissolved in 0.5 mL of DMAc, and then *n*-propylisocyanate (0.121 mL, 1.30×10^{-3} mol) and one of drop triethyl amine were added; the solution was stirred for 40 h at room temperature and then for 9 h at 60°C. The reaction mixture was precipitated in 25 mL of distilled water. The resulting solid was filtered off and dried to give 0.253 g of a crude, white solid. This solid was washed with dilute HCl (pH 2) and was extracted with 20 mL of ethyl acetate to give 0.18 g (76.3%) of a white solid, 1-(*n*-propylamidocarbonyl)-4-[(*n*-propylamidocarbonyl)phenyl]-1,3,4-triazolidine-3,5-dione (8).

mp: 186–188°C. IR (KBr): 3350 (m), 3250 (w), 3100 (m), 2950 (w), 2860 (w), 1790 (s), 1735 (s), 1645 (m, sh), 1600 (m), 1550 (s), 1515 (s), 1460 (w), 1430 (s), 1410 (w), 1385 (w), 1350 (w), 1295 (m), 1260 (w), 1230 (w), 1190 (w), 1170 (w), 1140 (m), 1100 (w), 1010 (w), 885 (w), 845 (w), 825 (w), 800 (w), 760 (m), 725 (m), 675 (w), 635 (m), 540 (w), 500 cm^{-1} (w). ¹H-NMR [90 MHz, dimethyl sulfoxide-*d*6 (DMSO-*d*6), TMS, δ]: 0.78–1.20 (t, 6H, $J = 6.25$ Hz), 1.30–1.70 (m, 4H), 3.00–3.50 (m, 4H), 6.08–6.32 (t, 1H, $J = 6.00$ Hz), 7.30–7.55 (d, 2H, $J = 9.00$ Hz), 7.55–7.80 (d, 2H, $J = 9.00$ Hz), 7.82–8.04 (t, 2H, $J = 6.00$ Hz), 8.58–8.72 (s, 1H), 10.50 (s, br, 1H). ELEM. ANAL. Calcd. for C₁₆H₂₂N₆O₅: C, 53.03%; H, 6.12%; N, 23.19%. Found: C, 53.09%; H, 6.35%; N, 23.55%.



Scheme 1 Synthesis of monomer 7.

Reaction of AmPU with *n*-propylisocyanate (1:2 molar ratio)

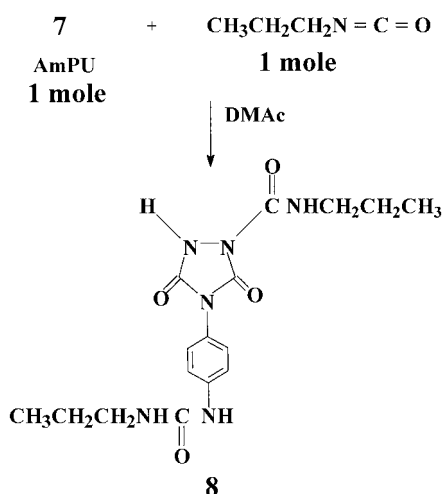
The aforementioned experiment was repeated with twice the amount of *n*-propylisocyanate. The resulting solid was filtered off and dried to give 0.38 g of a crude, white solid. Thin-layer chromatography (TLC) showed two spots and the formation of two products. This solid was chromatographed over silica gel with ethylacetate/cyclohexane (85:15) as an eluent. Fraction one, 0.21 g (52.6%) of a white solid, 1,2-bis(*n*-propylamidocarbonyl)-4-[(*n*-propylamidocarbonyl)phenyl]-1,3,4-triazolidine-3,5-dione (9; $R_f = 0.74$), was collected.

mp: 180–182°C. IR (KBr): 3340 (m), 3100 (m), 2950 (m), 2860 (w), 1780 (m), 1730 (s), 1680 (w), 1645 (s), 1600 (m), 1550 (s), 1510 (s), 1455 (w), 1415 (s), 1385 (w), 1345 (w), 1310 (m), 1255 (s), 1170 (w), 1145 (w), 1070 (w), 1050 (w), 1015 (w), 950 (w), 8405 (w), 810 (w), 740 (m), 680 (w), 620 (w), 510 cm^{-1} (w). ¹H-NMR (90 MHz, DMSO-*d*6, TMS, δ): 0.78–1.08 (t, 9H, $J = 6.25$ Hz), 1.22–1.74 (m, 6H), 3.00–3.40 (m, 6H), 6.10–6.38 (t, 1H, $J = 6.00$ Hz), 7.35–7.55 (d, 2H, $J = 9.00$ Hz), 7.55–7.80 (d, 2H, $J = 9.00$ Hz), 7.88–8.10 (t, 2H, $J = 6.00$ Hz), 8.60–8.78 (s, 1H). ELEM. ANAL. Calcd. for C₂₀H₂₉N₇O₅: C, 53.68%; H, 6.53%; N, 21.91%. Found: C, 53.12%; H, 6.86%; N, 21.71%.

Fraction two, 0.17 g (35.2%) of the white solid 8 ($R_f = 0.17$, mp = 186–187°C, was collected. Its IR and ¹H-NMR spectra were similar to those of compound 8.

Reaction of AmPU with *n*-propylisocyanate (1:3 molar ratio)

The aforementioned experiment was repeated with AmPU (1 mol) and *n*-propylisocyanate (3 mol). The



Scheme 2 Preparation of model compound 8.

resulting solid was filtered off and dried to give 0.46 g of a crude, white solid. TLC showed two spots and the formation of two products. This solid was chromatographed over silica gel with ethyl acetate/cyclohexane (85:15) as an eluent. Fraction one, 0.37 g (65.0%) of the white solid **9** ($R_f = 0.74$, mp = 180–182°C), was collected. Fraction two, 0.08 g (17.0%) of the white solid **8** ($R_f = 0.17$, mp = 186–187°C), was also collected.

Reaction of AmPU with *n*-propylisocyanate (1:12 molar ratio)

The aforementioned experiment was repeated with AmPU (1 mol) and *n*-propylisocyanate (12 mol). The

resulting solid was filtered off and dried to give 0.46 g of a crude, white solid. TLC showed two spots and the formation of two products. This solid was chromatographed over silica gel with ethyl acetate/cyclohexane (85:15) as an eluent. Fraction one, 0.45 g (77.0%) of the white solid **9** ($R_f = 0.74$, mp = 180–182°C), was collected. Fraction two, 0.04 g (8.0%) of the white solid **8** ($R_f = 0.17$, mp = 186–187°C), was also collected.

Polycondensation of AmPU with hexamethylene diisocyanate (HMDI or 10)

HMDI (0.093 g, 5.53×10^{-4} mol) was placed into a 25-mL, round-bottom flask. Then, 0.089 mL (1.10×10^{-3} mol) of pyridine and 0.35 mL of *N*-methylpyrrolidone (NMP) were added. To this solution, AmPU (0.1062 g, 5.53×10^{-4} mol) was added. The mixture was stirred for 4 h at room temperature, for 48 h at 60°C, and for 72 h at 75°C; during this period, 0.15 mL of NMP was added. The viscous reaction mixture was precipitated in 40 mL of distilled water. The white solid PU1 was filtered and dried to give 0.169 g (85%).

mp: 206°C (dec). η_{inh} [0.5 g/dL of dimethylformamide (DMF), 25°C]: 0.18 dL/g. IR (KBr): 3370 (m, br), 2940 (w), 2880 (w), 1780 (m, sh), 1730 (s, br), 1700 (s, sh), 1600 (m), 1545 (s, sh), 1515 (s), 1415 (s), 1320 (m), 1240 (m), 1180 (w), 1150 (w), 1020 (w), 845 (m), 770 (w), 620 cm⁻¹ (m, br). ¹H-NMR (90 MHz, DMSO-*d*₆, TMS, δ): 1.05–1.70 (m, br), 2.80–3.50 (m, br), 5.60–5.85 (s, br), 6.08–6.35 (distorted t, br), 7.22–7.56 (d, $J = 9.00$ Hz), 7.56–7.78 (d, $J = 9.00$ Hz), 7.78–7.96 (distorted t,

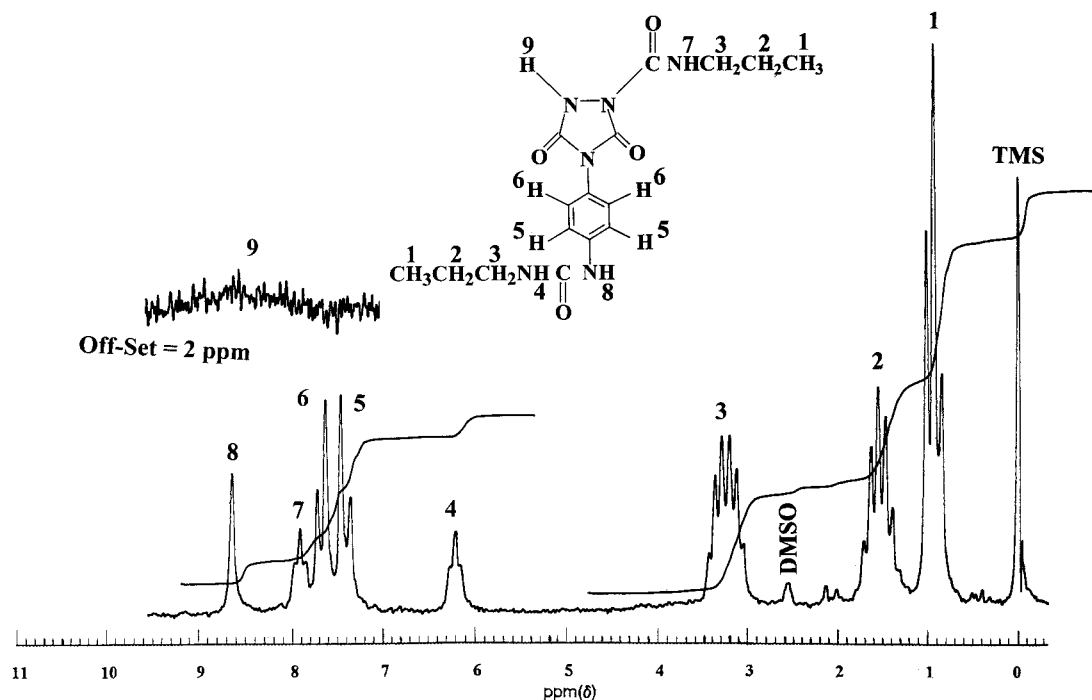


Figure 1 ¹H-NMR (90 MHz) spectrum of model compound **8** in DMSO-*d*₆ at room temperature. An N—H peak appears at 10.50 ppm.

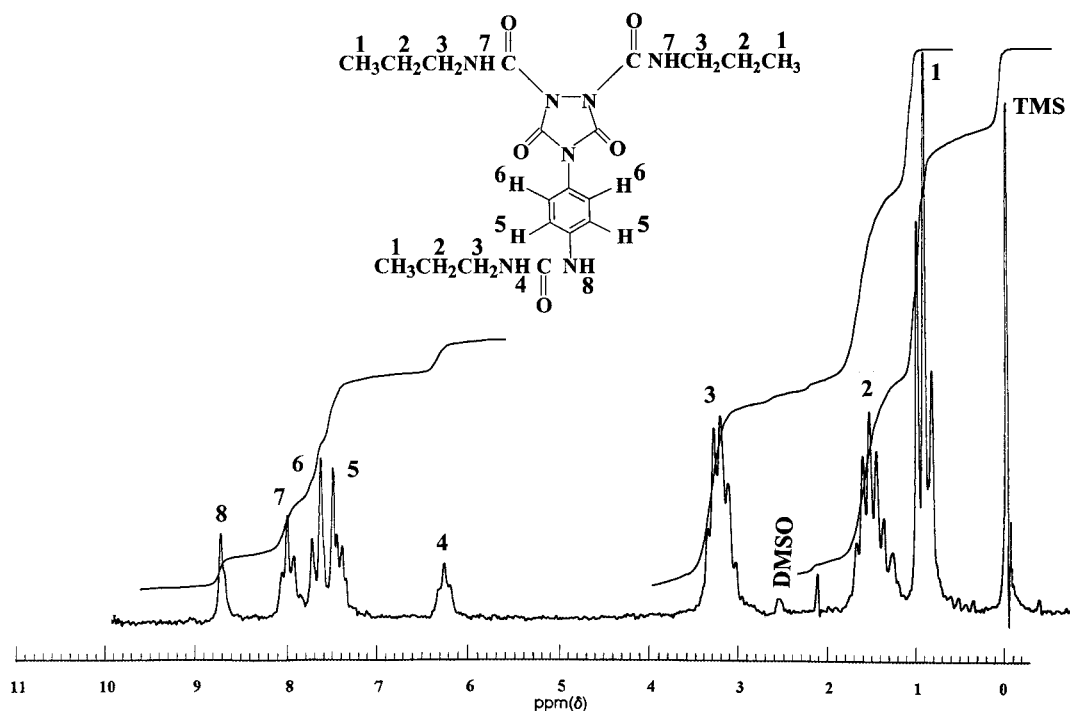


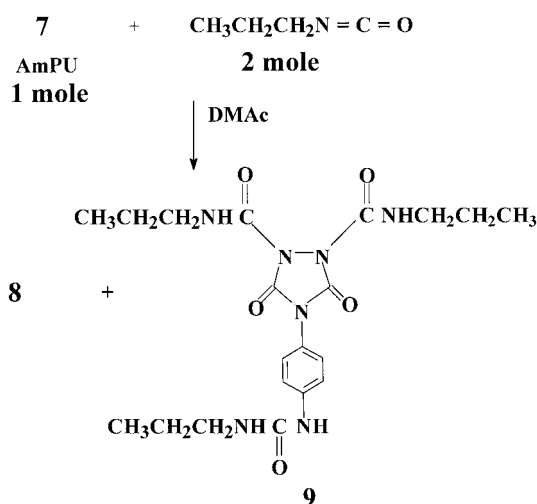
Figure 2 $^1\text{H-NMR}$ (90 MHz) spectrum of model compound 9 in $\text{DMSO-}d_6$ at room temperature.

br), 10.10–10.90 (s, br). ELEM. ANAL. Calcd. for $[(\text{C}_{16}\text{H}_{20}\text{N}_6\text{O}_4)_{0.34}, (\text{C}_{20}\text{H}_{26}\text{N}_7\text{O}_5)_{0.66}]$: C, 53.08%; H, 5.75%; N, 22.50%. Found: C, 53.24%; H, 6.23%; N, 23.09%.

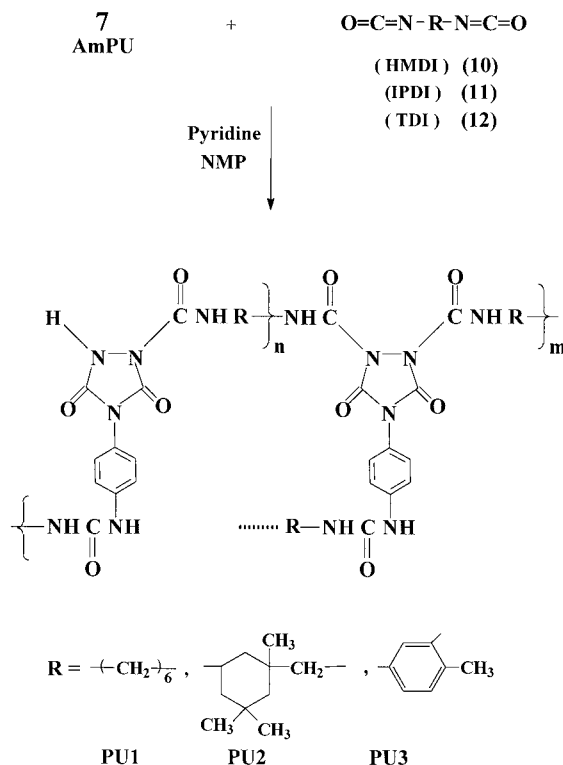
precipitated in 40 mL of distilled water. The white solid PU2 was filtered off and dried to give 0.29 g (92%).

Polycondensation of AmPU with isophorone diisocyanate (IPDI or 11)

This polycondensation was performed by a method similar to the aforementioned procedure. The mixture was stirred for 10 h at room temperature, for 24 h at 70°C , and for 90 h at 85°C ; during this period, 0.6 mL of NMP was added. The viscous reaction mixture was



Scheme 3 Preparation of model compounds 8 and 9.



Scheme 4 Polycondensation reactions of monomer 7 with the diisocyanates.

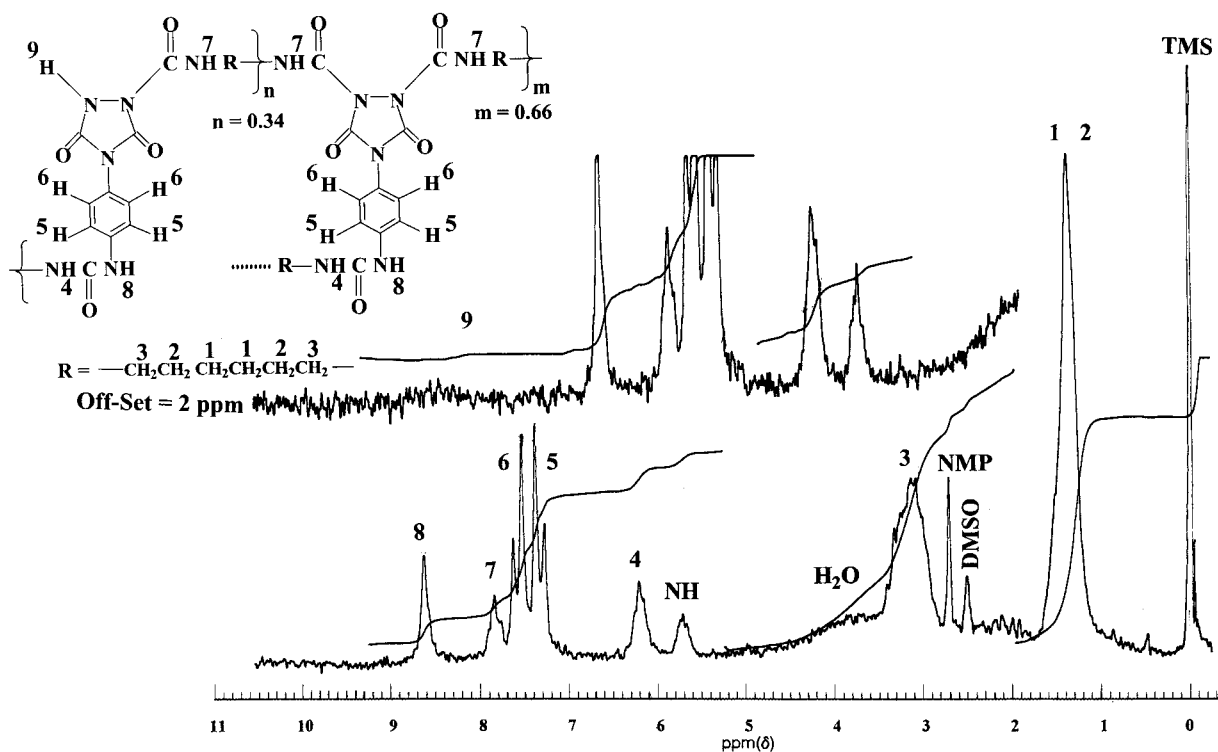


Figure 3 $^1\text{H-NMR}$ (90 MHz) spectrum of polymer PU1 in $\text{DMSO-}d_6$ at room temperature.

mp: 265°C (dec). η_{inh} (0.5 g/dL of DMF, 25°C): 0.12 dL/g. IR (KBr): 3350 (s, br), 2900 (s), 2880 (w), 1770 (m, sh), 1730 (s, br), 1700 (s, sh), 1670 (s, br), 1600 (w), 1540

(s, br), 1510 (s), 1460 (w), 1410 (s), 1365 (w, sh), 1310 (s), 1225 (s), 1140 (w), 1110 (m, sh), 1045 (w), 1020 (w), 830 (m), 760 (m), 630 cm^{-1} (m, br). $^1\text{H-NMR}$ (90 MHz,

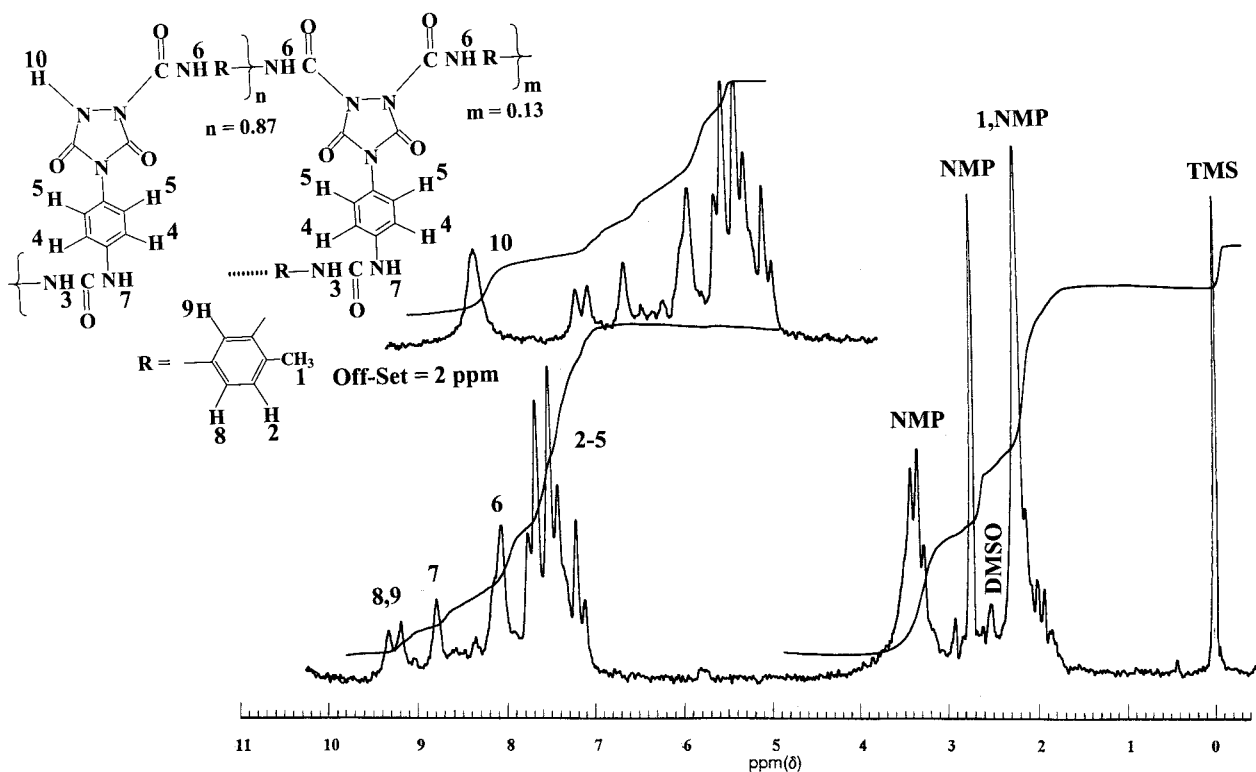


Figure 4 $^1\text{H-NMR}$ (90 MHz) spectrum of polymer PU3 in $\text{DMSO-}d_6$ at room temperature.

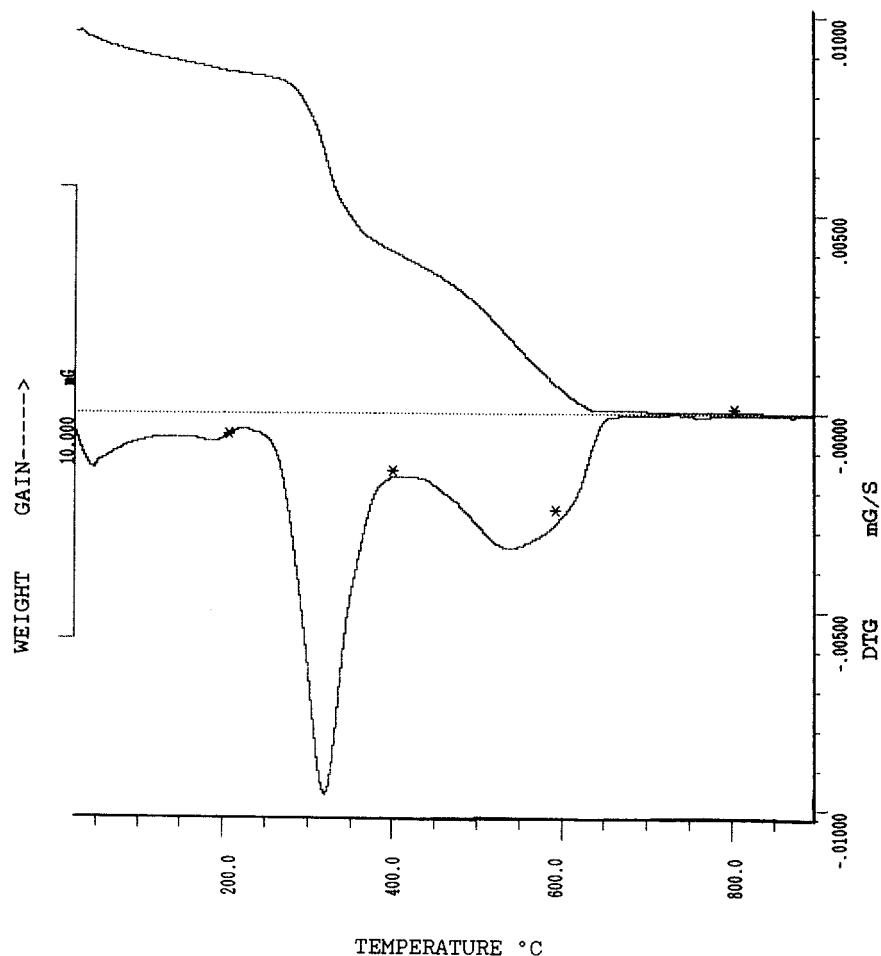


Figure 5 TGA and DTG thermograms of polymer PU1 under a nitrogen atmosphere.

DMSO-*d*₆, TMS, δ): 0.70–1.40 (m, br), 1.40–1.80 (m, br), 2.60–4.35 (m, br), 5.40–6.50 (s, br), 7.30–7.52 (d, $J = 9.00$ Hz), 7.52–7.74 (d, $J = 9.00$ Hz), 7.74–8.10 (m, br), 8.47–8.87 (s, br), 9.60–10.40 (s, br). ELEM. ANAL. Calcd. for [(C₂₀H₂₆N₆O₄)_{0.55}, (C₂₆H₃₅N₇O₅)_{0.45}]: C, 58.63%; H, 6.46%; N, 19.56%. Found: C, 56.99%; 7.21%, H; N, 19.38%.

(90 Mz, DMSO-*d*₆, TMS, δ): 0.70–1.40 (m, br), 1.40–1.80 (m, br), 2.60–4.35 (m, br), 5.40–6.50 (s, br), 7.30–7.52 (d, $J = 9.00$ Hz), 7.52–7.74 (d, $J = 9.00$ Hz), 7.74–8.10 (m, br), 8.47–8.87 (s, br), 9.60–10.40 (s, br). ELEM. ANAL. Calcd. for [(C₁₇H₁₄N₆O₄)_{0.87}, (C_{21.5}H₁₇N₇O₅)_{0.13}]: C, 55.90%; H, 3.81%; N, 22.78%. Found: C, 55.63%; 5.05%, H; N, 22.91%.

Polycondensation of AmPU with toluene-2,4-diisocyanate (TDI or 12)

This polycondensation was performed by a method similar to the aforementioned procedure. The reaction mixture was stirred for 24 h at room temperature, for 24 h at 60°C, and for 72 h at 75°C; during this period, 0.15 mL of NMP was added. The viscous reaction mixture was precipitated in 40 mL of distilled water. The white solid PU3 was filtered off and dried to give 0.169 g (80%).

mp: 262°C (dec). η_{inh} (0.5 g/dL of DMF, 25°C): 0.13 dL/g. IR (KBr): 3260 (m, br), 3100 (m, br), 1780 (m, sh), 1720 (s, br), 1680 (s, br), 1600 (s), 1530 (s, br), 1510 (s), 1440 (m), 1410 (s), 1310 (s), 1215 (s), 1115 (m), 1000 (m, sh), 860 (m, sh), 755 (m), 640 cm⁻¹ (m, br). ¹H-NMR

RESULTS AND DISCUSSION

Monomer synthesis

AmPU (7) was prepared in six steps starting from 4-nitrobenzoic acid (Scheme 1).¹³ The structures of all the compounds were confirmed by IR and ¹H-NMR spectra. The purity of monomer 7 was checked by TLC, which showed one spot in a chloroform/methanol mixture (70:30) with $R_f = 0.48$.

Model compound studies

Because monomer AmPU has three N—H sites that can react with isocyanates, we thought it would be interesting to examine the reactivity of these sites to-

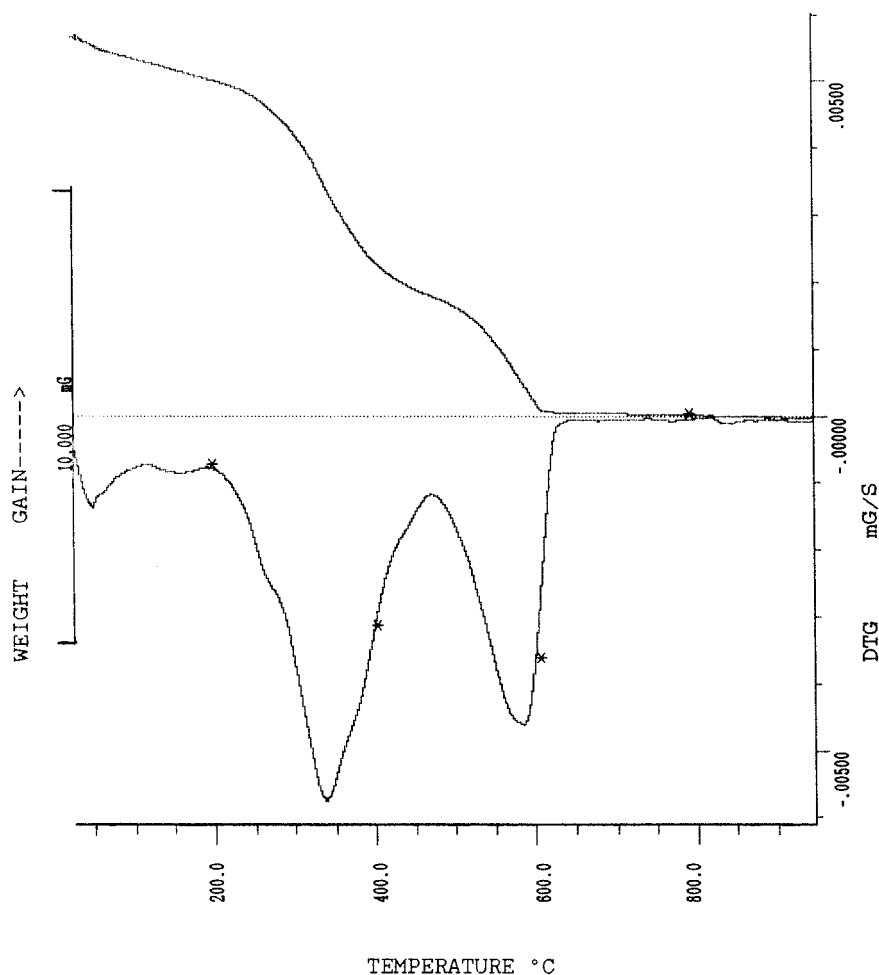


Figure 6 TGA and DTG thermograms of polymer PU2 under a nitrogen atmosphere.

ward isocyanates. Therefore, AmPU was allowed to react with *n*-propylisocyanate (1:1) in a DMAc solution, and it gave **8** in a high yield (Scheme 2). The model compound **8** was characterized by IR, $^1\text{H-NMR}$, and elemental analysis. The IR spectrum of **8** showed a strong peak at 3350 cm^{-1} for the N—H bond and three peaks at 1790 , 1735 , and 1645 cm^{-1} for the carbonyl groups. The first two peaks were characteristic patterns for the urazole moiety. The $^1\text{H-NMR}$ spectrum (Fig. 1) of **8** showed all the peaks that agreed with the structure of compound **8**. The elemental analysis results were in good agreement with the structure of **8**. The purity of **8** was checked by TLC, which showed one spot in an ethyl acetate/cyclohexane mixture (85:15) with $R_f = 0.17$. This result shows that NH2 is as reactive as NH and is even more reactive than the second NH.

The aforementioned reaction was performed with 2 mol of *n*-propylisocyanate. A TLC examination of the reaction mixture showed the formation of two adducts. Two products were isolated via chromatography. Fraction one was isolated and characterized with elemental analysis, IR, and $^1\text{H-NMR}$ spectroscopy. The

$^1\text{H-NMR}$ spectrum (Fig. 2) of this compound showed all the peaks that agreed with the structure of compound **9**. Fraction two was similar to compound **8** (Scheme 3).

The aforementioned experiment was repeated with 3 and 12 mol of *n*-propylisocyanate. In each case, two products, **8** and **9**, were formed and isolated. As the number of moles of *n*-propylisocyanate increased, the formation of product **9** increased. These compounds were used as model compounds for the study of polymerization reactions.

Polymerization reactions and characterization

Because **8** and **9** as model compounds were synthesized in good yields and purity, we became interested in performing this type of reaction for the formation of novel polyureas. Therefore, HMDI, IPDI, and TDI were selected as diisocyanates. The reaction of monomer **7** with these diisocyanates was performed in a 1:1 molar ratio via solution polymerization. The reactions were carried out in NMP solutions in the presence of pyridine as a catalyst, and the resulting polyureas

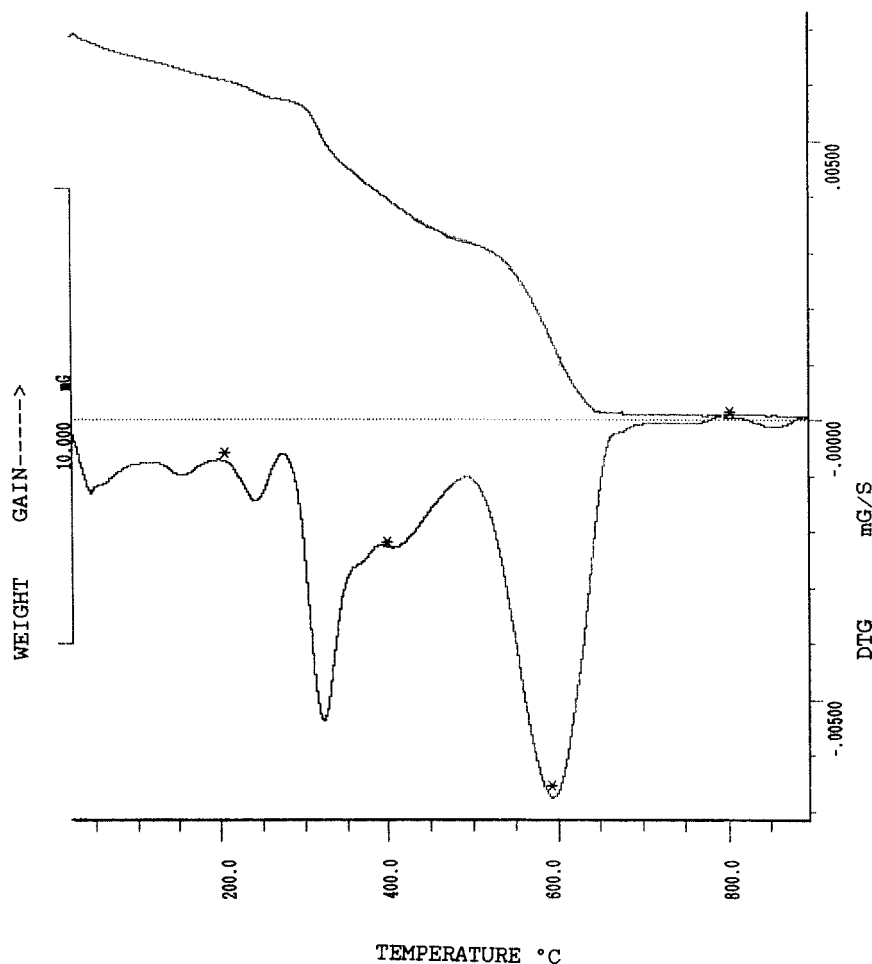


Figure 7 TGA and DTG thermograms of polymer PU3 under a nitrogen atmosphere.

PU1–PU3 were obtained as white solids in good yields (Scheme 4). The mechanism of the reaction of monomer 7 with the aforementioned diisocyanates is a step-growth addition of N—H of the urazole group across the carbon–nitrogen double bond, and there is no byproduct (this simplifies the polymerization process).

The resulting polymers were characterized by IR, $^1\text{H-NMR}$, elemental analysis, and TGA. The IR spectrum of polymer PU1 showed a medium peak at 3370 cm^{-1} for the N—H bond, peaks at 2940 and 2880 cm^{-1} for the aliphatic C—H bounds, and three strong peaks at 1780 , 1730 , and 1700 cm^{-1} for the carbonyl groups. These peaks were characteristic patterns for the urazole moiety. The $^1\text{H-NMR}$ spectrum of PU1 (Fig. 3) showed a multiplet at 1.40 ppm for the four central methylene groups and a multiplet at 3.20 ppm for the other two methylene groups attached to the amide groups. Also shown were a broad peak at 5.70 ppm for N—H of the amine end groups, a doublet at 7.30 ppm for the two aromatic protons in the ortho position to the NH group and another doublet at 7.55 ppm for two other aromatic protons, a broad and

distorted triplet peak at 7.85 , a broad peak at 8.60 ppm , and a broad peak at 10.5 ppm for N—H of the amide group and N—H of the urazole group. From the integral calculation of the area of N—H peaks, it was possible to determine the ratios of 1:2 and 1:3 for the structural formation of PU1. These data show that the amount of the 1:2 structure in PU1 was equal to 34%, and the amount of the 1:3 structure was equal to 66%. The elemental analysis results were also in good agreement with the structure of PU1.

The IR and $^1\text{H-NMR}$ spectra of PU2 showed peaks that confirmed its chemical structure. In this case, two chemical structures, 1:2 and 1:3, were also formed. From the integral calculation, it was found that the amount of the 1:2 structure in PU2 was equal to 55%, and that of the 1:3 structure was equal to 45%. The elemental analysis results were also in good agreement with the calculated percentages for carbon, hydrogen, and nitrogen in the polymer repeating unit of PU2.

The IR and $^1\text{H-NMR}$ spectra (Fig. 4) of PU3 showed peaks that confirmed its chemical structure. In this case, two chemical structures, 1:2 and 1:3, were also

formed. From the integral calculation, it was found that the amount of the 1:2 structure in PU3 was equal to 87%, and that of the 1:3 structure was equal to 13%. The elemental analysis results were also in good agreement with the calculated percentages for carbon, hydrogen, and nitrogen in the polymer repeating unit of PU3.

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

Thermal properties

The thermal behavior of polyureas PU1, PU2, and PU3 were measured by TGA and derivative thermogravimetry (DTG) analysis at a rate of 10°C/min in a nitrogen atmosphere (Figs. 5–7). An examination of the data reveals that all of the aforementioned polyureas were thermally stable up to 200°C in a nitrogen atmosphere. All of these polymers showed some weight loss below 100°C, which could be due to water or solvent loss. The polymers PU1, PU2, and PU3 showed 10% weight losses at 200, 182, and 192°C, respectively.

CONCLUSIONS

This investigation has shown that AmPU is an interesting monomer for polycondensation reactions. This compound has three acidic N—H groups, and it can

readily be reacted with *n*-propylisocyanate to give 1:2 and 1:3 adducts in good yields and high purity. Therefore, AmPU can act as both bifunctional and trifunctional monomers, and its polymerization reaction with aliphatic and aromatic diisocyanates can give novel polyureas containing urazole linkages in two and three dimensions.

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