

Synthesis and Characterization of New Polyamides Derived from 4-(4'-Aminophenyl)urazole and Aliphatic Diacid Chlorides

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ABSTRACT: 4-(4'-Aminophenyl)urazole (AmPU) was prepared from 4-nitrobenzoic acid in six steps. The reaction of AmPU with acetyl chloride was performed in *N,N*-dimethylacetamide solutions at different ratios, and the resulting disubstituted and trisubstituted amide derivatives were obtained in high yields and were used as models for polymerization reactions. Polycondensation reactions of AmPU with succinyl chloride, suberoyl chloride, and sebacoyl chloride were performed with conventional solution polymerization techniques in the presence of different catalysts, such as pyridine, triethylamine, and dibutyltin dilaurate, and led

to the formation of novel aliphatic polyamides. The resulting novel polyamides had inherent viscosities of 0.11–0.22 dL/g in dimethylformamide or H₂SO₄ at 25°C. These polyamides were characterized with IR, ¹H-NMR, elemental analysis, and thermogravimetric analysis. Some physical properties and structural characterization of these novel polyamides are reported. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3173–3185, 2004

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

INTRODUCTION

4-Substituted urazoles are five-membered 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 p*K_a* value of 4.71, which is almost the same as that of acetic acid.¹ Urazole compounds have the potential to undergo N-acylation. 4-Substituted urazoles have been converted into 1-acyl derivatives by an acylation reaction with a series of carboxylic acid anhydrides.² A simplified procedure for the N-acylation of oxazolidin-2-one chiral auxiliaries has also been reported.³

Recently, we have been able to take advantage of these acidic N—H protons in 1-methyl-2,5-bis(4-phenylurazoyl) pyrrole and synthesize novel polymers via N-alkylation and N-acylation reactions.^{4,5} The polymerization of 4-phenylurazole (PHU) with phosgene, terephthaloyl chloride, and epichlorohydrin has been reported to produce insoluble polymers.⁶ The polymerization of PHU with aliphatic diacid chlorides

yields soluble polyamides with an inherent viscosity of 0.39 dL/g.⁷ The copolymerization of 4-cyclohexylurazole (CHU) with aliphatic diacid chlorides produces soluble polyamides.⁸

In a previous article, we reported the reaction of PHU and CHU with diisocyanates.^{9,10} The resulting novel polyureas had inherent viscosities of 0.04–0.23 and 0.044–0.206 dL/g, respectively.

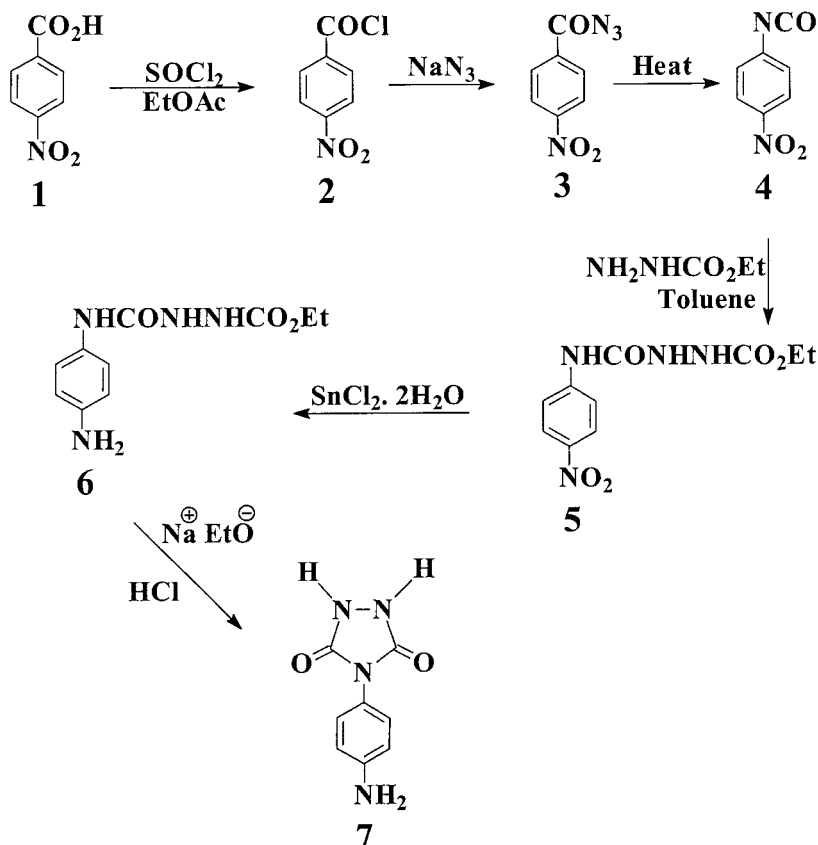
4-(4'-Aminophenyl)urazole (AmPU or 7) is an interesting trifunctional monomer that can be prepared in several steps from readily available starting materials. AmPU, reacted with *n*-propylisocyanate, produces different products. The polymerization of this monomer with diisocyanates yields novel polyureas.¹¹ Here we report successful step-growth polymerization reactions in which AmPU, as a novel monomer, is used for the synthesis of soluble polyamides.

EXPERIMENTAL

Materials and equipment

The reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), and Riedel-de Haën AG (Seelze, Germany). AmPU was prepared in six steps according to our previous work.¹² *N,N*-Dimethylacetamide (DMAc) was dried over BaO and then was distilled under reduced pressure. ¹H-NMR spectra (90 and 500 MHz) were recorded on a Varian EM-390 instrument (Varian Associates, Palo Alto, CA) and a Bruker Avance 500 instrument (Rheinstetten, Germany), respectively. Tetramethylsilane

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Scheme 1 Synthesis of monomer 7.

(TMS) was used as an internal reference. Proton resonances were designated as singlet (s), doublet (d), doublet of doublet (dd), and multiplet (m). IR spectra were recorded on a Shimadzu model 435 IR spectrophotometer (Shimadzu, Kyoto, Japan) and a Unicomm Mattson model 1000 Fourier transform spectrophotometer (Unicom Mattson, London, UK). The spectra of the solids were obtained with KBr pellets. The vibrational transition frequencies are reported as wave numbers (cm^{-1}). The band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br).

All the melting points were taken with a Gallenham melting-point apparatus (Loughborough, UK). The inherent viscosities were measured by a standard procedure with a Cannon-Fenske routine viscometer (Mainz, Germany). Thermogravimetric analysis (TGA) data for the polymers were obtained on a Mettler TGA-50 (London, UK). Elemental analyses were performed at Malek Ashter University (Tehran, Iran).

Reaction of AmPU with acetyl chloride (1:2 molar ratio)

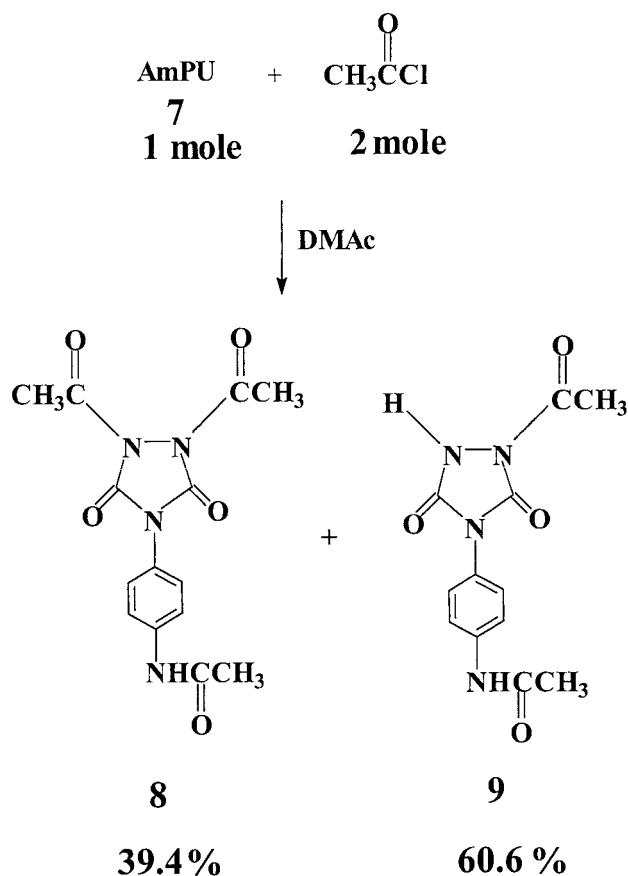
In a 25-mL, round-bottom flask, AmPU (0.200 g, 1.04×10^{-3} mol) was dissolved in 1 mL of DMAc, and acetyl chloride (0.1634 g, 2.08×10^{-3} mol) was added; the solution was stirred for 24 h at room temperature

and then for 24 h at 50°C . The reaction mixture was precipitated in 25 mL of distilled water. The resulting solid was filtered and dried; 0.300 g of a crude, white solid was obtained. This solid was chromatographed over silica gel with ethyl acetate/cyclohexane (80:20) as an eluent. Fraction one was 0.114 g (39.4%) of a white solid, 1,2-bisacetyl-4-[4'-acetamidophenyl]-1,2,4-triazolidine-3,5-dione (**8**; $R_f = 0.62$, where R_f is the ratio of the distance moved by the substance to the distance moved by the solvent front).

mp: $194\text{--}195^\circ\text{C}$. IR (KBr): 3330 (s), 1810 (m, sh), 1750 (s), 1725 (s), 1690 (s), 1680 (s), 1600 (s), 1530 (s), 1600 (m), 1515 (s), 1470 (w), 1407 (s), 1370 (s), 1310 (s), 1245 (s), 1225 (s), 1167 (s), 1040 (s), 1010 (s), 965 (s), 875 (m), 840 (s), 800 (s), 750 (s), 720 (m, sh), 700 (m), 670 (w), 650 (w), 610 (m), 580 (s), 520 cm^{-1} (w). $^1\text{H-NMR}$ [500 MHz, dimethyl sulfoxide- d_6 (DMSO- d_6), δ]: 2.08 (s, 3H), 2.48 (s, 6H), 7.41–7.43 (d, 2H, $J = 8.75$ Hz), 7.71–7.73 (d, 2H, $J = 8.75$ Hz), 10.17 (s, 1H). ANAL. Calcd for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_5$: C, 52.83%; H, 4.43%; N, 17.60%. Found: C, 52.72%; H, 4.59%; N, 17.72%.

Fraction two was 0.176 g (60.6%) of a white solid, 1-(acetyl)-4-[4'-acetamidophenyl]-1,2,4-triazolidine-3,5-dione (**9**; $R_f = 0.14$).

mp: $256\text{--}258^\circ\text{C}$. IR (KBr): 3320 (s), 3050 (m), 1790 (m), 1715 (s), 1667 (s), 1640 (m, sh), 1607 (s), 1525 (s),



Scheme 2 Reaction of monomer 7 with acetyl chloride in a ratio of 1:2.

1440 (s), 1407 (s), 1370 (s, sh), 1320 (s, sh), 1280 (s), 1250 (s, sh), 1160 (m), 1000 (m), 840 (m), 820 (m), 670 (m), 615 cm^{-1} (m). $^1\text{H-NMR}$ (90 MHz, $\text{DMSO-}d_6$, TMS, δ): 2.00–2.15 (s, 3H), 2.50–2.60 (s, 3H), 7.40–7.65 (d, 2H, $J = 6.00$ Hz), 7.80–8.00 (d, 2H, $J = 6.00$ Hz), 10.20–10.40 (s, 1H), 10.50–10.75 (s, 1H). ANAL. Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_4$: C, 52.17%; H, 4.38%; N, 20.28%. Found: C, 52.19%; H, 4.27%; N, 20.29%.

Reaction of AmPU with acetyl chloride (1:3 molar ratio)

The aforementioned experiment was repeated with acetyl chloride in a ratio of 1:3. The resulting solid was filtered and dried to give 0.275 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 ethyl acetate/cyclohexane (80:20) as an eluent. Fraction one was 0.163 g (64.10%) of the white solid 8 ($R_f = 0.62$, mp = 194–196°C). Fraction two was 0.091 g (35.9%) of the white solid 9 ($R_f = 0.14$, mp = 254–256°C). Its IR and $^1\text{H-NMR}$ spectra were similar to those of 8.

Reaction of AmPU with acetyl chloride (1:10 molar ratio)

The aforementioned experiment was repeated with acetyl chloride in a ratio of 1:10. The resulting solid was filtered and dried to give 0.268 g (81.0%) of a white solid. TLC showed only one spot and the formation of 8.

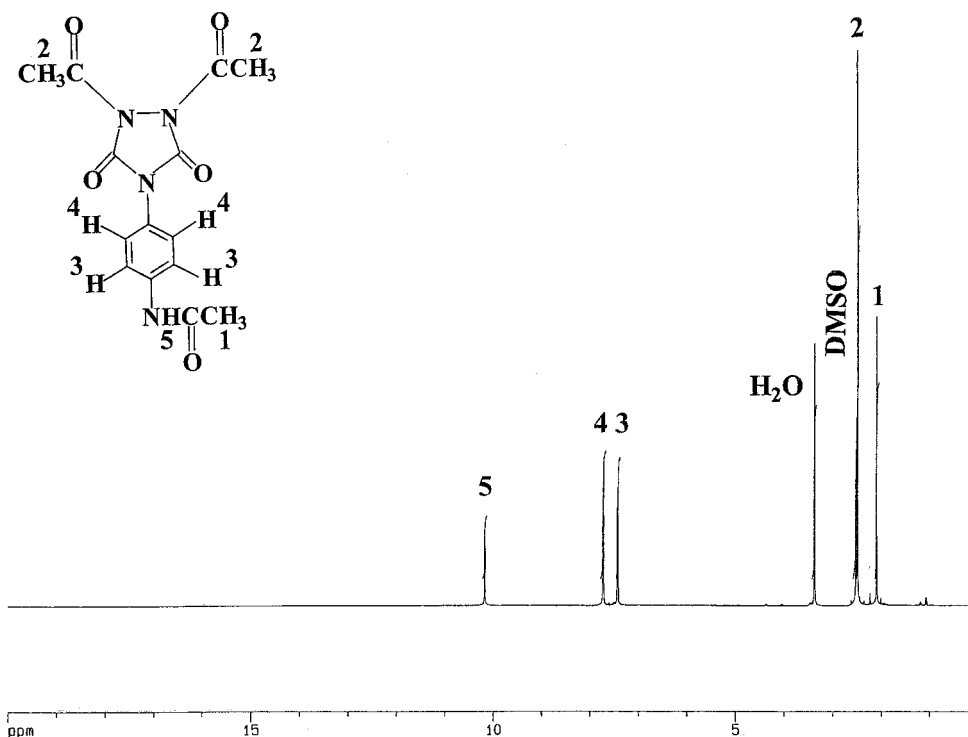


Figure 1 $^1\text{H-NMR}$ (500 MHz) spectrum of model compound 8 in $\text{DMSO-}d_6$ at room temperature.

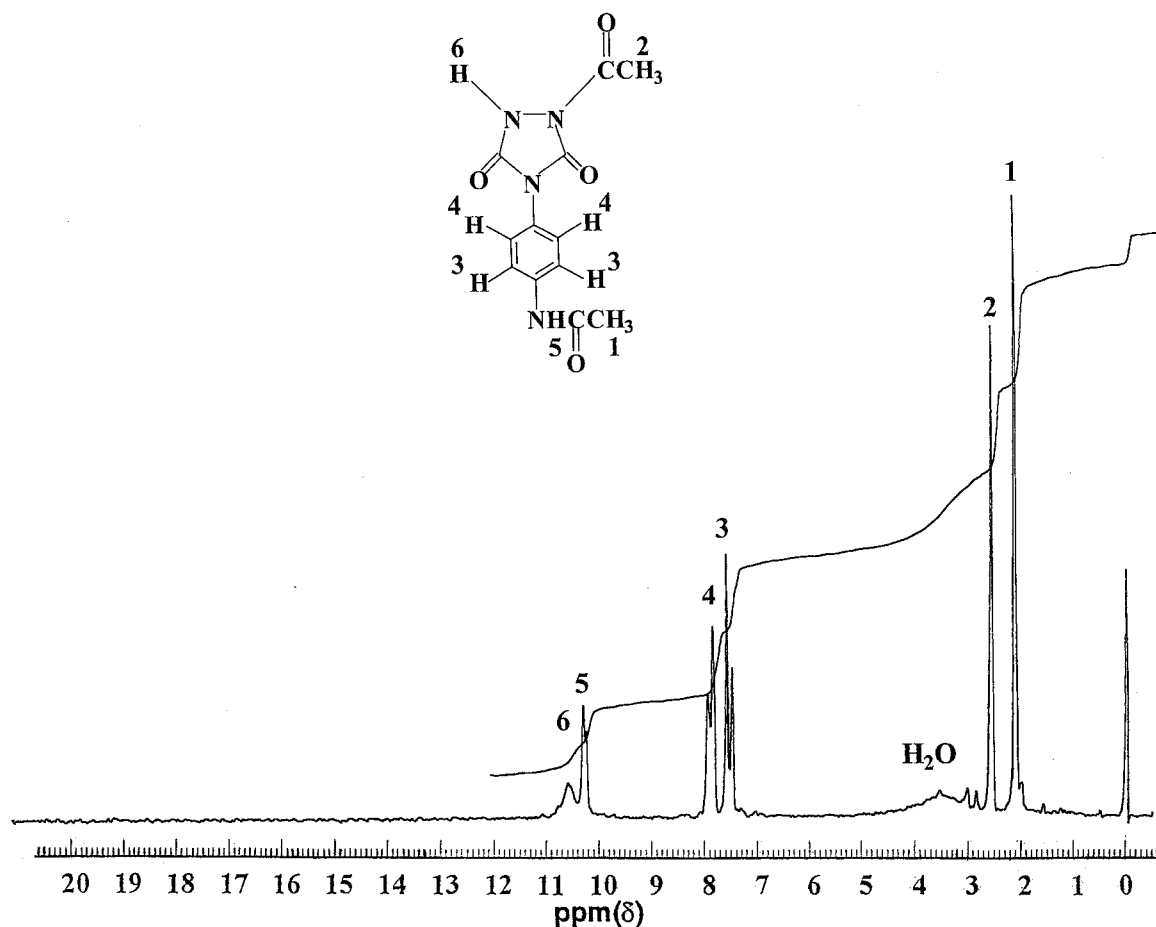


Figure 2 $^1\text{H-NMR}$ (90 MHz) spectrum of model compound **9** in $\text{DMSO-}d_6$ at room temperature.

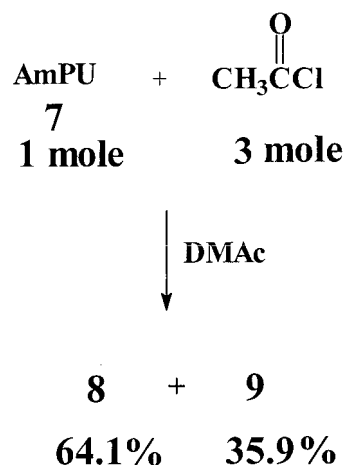
Polymerization of AmPU with succinyl chloride (**10**)

In a 25-mL, round-bottom flask, AmPU (0.1862 g, 9.69×10^{-4} mol) and pyridine (0.156 mL, 1.94×10^{-3} mol) were added to a solution of **10** (0.1501 g, 9.69×10^{-4} mol) in 0.5 mL of DMAc. The solution was stirred for 3 h at -5°C , then for 8 h at room temperature, and finally for 12 h at 85°C . During this period, 0.7 mL of DMAc was added. The viscous solution was precipitated in 25 mL of methanol. The solid was filtered and dried to give 0.289 g (86%) of polyamide PA1A (mp = $274\text{--}278^\circ\text{C}$). This polymerization was repeated in the presence of triethylamine and dibutyltin dilaurate as catalysts.

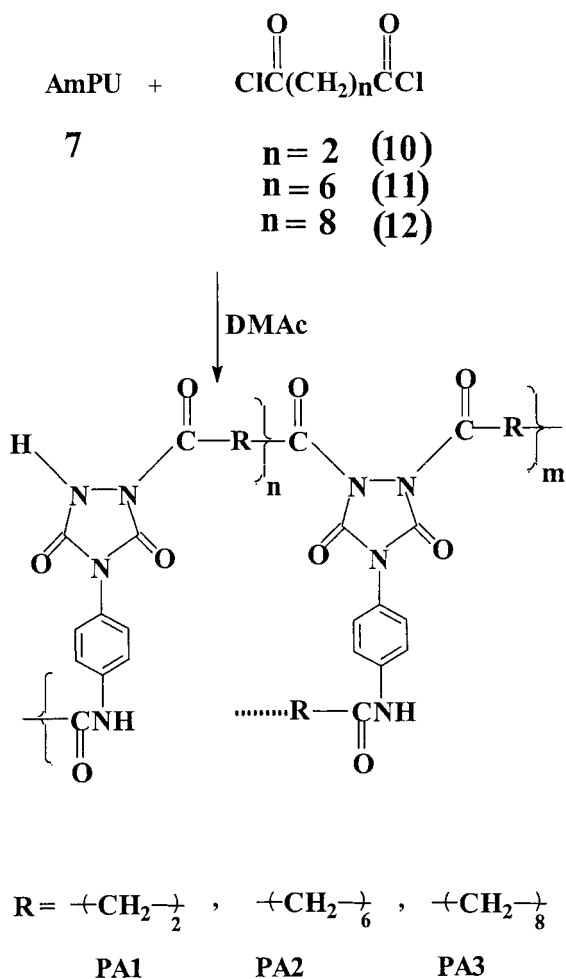
IR (KBr): 3328 (m), 3203 (m), 3072 (m), 2958 (w), 2058 (w), 1750 (m), 1712 (s), 1655 (s), 1604 (m), 1518 (s), 1411 (s), 1338 (m), 1248 (m), 1176 (m), 958 (w), 835 (w) 663 cm^{-1} (w). $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ): 2.70 (s, br, CH_2), 2.78–2.81 (s, br, CH_2), 7.34–7.36 (d, 2H, $J = 8.4$ Hz), 7.39–7.40 (d, 2H, $J = 8.0$ Hz), 7.68–7.70 (d, 2H, $J = 8.4$ Hz), 7.72–7.73 (d, 2H, $J = 8.0$ Hz), 10.21 (s, 1H), 10.26 (s, 1H), 10.44 (s, 1H). ANAL. Calcd for $(\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_4)_{0.66}(\text{C}_{14}\text{H}_{11}\text{N}_4\text{O}_5)_{0.34}$: C, 52.84%; H, 3.62%; N, 19.44%. Found: C, 52.34%; H, 3.90%; N, 20.18%.

Polymerization of AmPU with suberoyl chloride (**11**)

In a 25-mL, round-bottom flask, AmPU (0.0954 g, 4.96×10^{-4} mol) and pyridine (0.08 mL, 9.93×10^{-4} mol) were added to a solution of **11** (0.1048 g, 4.96×10^{-4} mol) in 0.5 mL of DMAc. The solution was stirred for



Scheme 3 Reaction of monomer **7** with acetyl chloride in a ratio of 1:3.



Scheme 4 Polycondensation reactions of monomer 7 with diacid chlorides.

3 h at -5°C , then for 8 h at room temperature, and finally for 12 h at 85°C . During this period, 0.7 mL of DMAc was added. The viscous solution was precipitated in 30 mL of methanol. The solid was filtered and dried to give 0.165 g (82.5%) of polyamide PA2A (mp

= $184\text{--}192^\circ\text{C}$). This polymerization was repeated in the presence of triethylamine and dibutyltin dilaurate as catalysts.

IR (KBr): 3441 (m), 3340 (m), 2928 (w), 1758 (m), 1718 (s), 1690 (s), 1604 (m), 1518 (s), 1411 (s), 1305 (m), 1249 (m), 1176 (m), 912 (w), 837 (w), 758 (w), 630 (w), 524 cm^{-1} (w). $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ): 1.23–1.35 (m, br, CH_2), 1.62 (s, br, CH_2), 2.34 (s, br, CH_2), 2.82–2.88 (m, br, CH_2), 7.33–7.41 (m, br, 4H), 7.65–7.71 (m, br, 4H), 10.06 (s, 1H), 10.10 (s, 1H), 10.44 (s, 1H). ANAL. Calcd for $(\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_4)_{0.68}(\text{C}_{20}\text{H}_{17}\text{N}_4\text{O}_5)_{0.32}$: C, 58.89%; H, 5.60%; N, 15.90%. Found: C, 57.84%; H, 5.92%; N, 16.43%.

Polymerization of AmPU with sebacoyl chloride (12)

In a 25-mL, round-bottom flask, AmPU (0.1522 g, 7.92×10^{-4} mol) and pyridine (0.125 mL, 1.58×10^{-3} mol) were added to a solution of 12 (0.1894 g, 7.92×10^{-4} mol) in 0.7 mL of DMAc. The solution was stirred for 3 h at -5°C , then for 8 h at room temperature, and finally for 20 h at 85°C . During this period, 0.7 mL of DMAc was added. The viscous solution was precipitated in 30 mL of methanol. The solid was filtered and dried to give 0.280 g (82%) of polyamide PA3A (mp = $198\text{--}208^\circ\text{C}$). This polymerization was repeated in the presence of triethylamine and dibutyltin dilaurate as catalysts.

IR (KBr): 3319 (m), 3194 (w), 2928 (m), 2854 (w), 1790 (w), 1724 (s), 1680 (s), 1604 (m), 1518 (s), 1411 (s), 1313 (m), 1248 (m), 1176 (w), 837 cm^{-1} (w). $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ): 1.26–1.31 (m, br, CH_2), 1.60 (s, br, CH_2), 2.32 (m, br, CH_2), 2.73–2.90 (m, br, CH_2), 7.33–7.41 (m, br, 4H), 7.67–7.71 (m, br, 4H), 10.05 (s, 1H), 10.09 (s, 1H), 10.44 (s, 1H). ANAL. Calcd for $(\text{C}_{18}\text{H}_{22}\text{N}_4\text{O}_4)_{0.71}(\text{C}_{23}\text{H}_{29}\text{N}_4\text{O}_5)_{0.29}$: C, 61.07%; H, 6.33%; N, 14.65%. Found: C, 59.83%; H, 6.32%; N, 15.40%.

TABLE I
Reaction Conditions for the Polymerization of AmPU with 10 and Some Physical Properties of PA1A–PA1C

Polymer	Solvent	Catalyst	Reaction time	Nonsolvent	Yield (%)	Inherent viscosity (dL/g) ^a	mp ($^\circ\text{C}$)
PA1A	DMAc	Py ^b	3 h, -5°C ; 8 h, RT; 12 h, 85°C	MeOH	86.0	0.18	274–278
PA1B	DMAc	TEA ^c	3 h, -5°C ; 8 h, RT; 12 h, 85°C	MeOH	91.0	0.22	268–274
PA1C	DMAc	DBTDL	3 h, -5°C ; 8 h, RT; 12 h, 85°C	MeOH	82.0	0.12	258–264

Py = pyridine; TEA = triethylamine; DBTDL = dibutyltin dilaurate; RT = room temperature.

^a Measured at a concentration of 0.5 g/dL in H_2SO_4 at 25°C .

TABLE II
Reaction Conditions for the Polymerization of AmPU with 11 and Some Physical Properties of PA2A–PA2C

Polymer	Solvent	Catalyst	Reaction time	Nonsolvent	Yield (%)	Inherent viscosity (dL/g)	mp (°C)
PA2A	DMAc	Py	3 h, -5°C; 8 h, RT; 12 h, 85°C	MeOH	82.5	0.14 ^a	184–192
PA2B	DMAc	TEA	3 h, -5°C; 8 h, RT; 12 h, 85°C	MeOH	75.0	0.12 ^a	178–186
PA2C	DMAc	DBTDL	3 h, -5°C; 8 h, RT; 12 h, 85°C	MeOH	74.0	0.11 ^b	180–192

Py = pyridine; TEA = triethylamine; DBTDL = dibutyltin dilaurate; RT = room temperature.

^a Measured at a concentration of 0.5 g/dL in H₂SO₄ at 25°C.

^b Measured at a concentration of 0.5 g/dL in DMF at 25°C.

RESULTS AND DISCUSSION

Monomer synthesis

AmPU was prepared in six steps starting from 4-nitrobenzoic acid¹² (Scheme 1). The structures of all the compounds were confirmed with IR and ¹H-NMR spectra. The purity of the monomer was checked with TLC, which showed one spot in a chloroform/methanol mixture (70:30) with *R_f* = 0.48, with ¹H-NMR spectroscopy, and with elemental analysis.

Model compound studies

Because AmPU has three N—H sites that can react with acetyl chloride, we decided to examine the reactivity of these N—H sites toward acetyl chloride. Thus, AmPU was allowed to react with acetyl chloride (1:2) in a DMAc solution, and this produced **8** and **9** in a ratio of 1:1.54 (Scheme 2). Model compound **8** was characterized with IR, ¹H-NMR, and elemental analysis. The IR spectrum of **8** showed a strong peak at 3330

cm⁻¹ for the N—H bond and four peaks at 1810, 1750, 1725, and 1690 cm⁻¹ for the carbonyl groups. The first two peaks are characteristic of the urazole moiety. The ¹H-NMR spectra (Fig. 1) of **8** showed all the peaks, and this agreed with the structure of **8**. The elemental analysis results were in good agreement with the structure of **8**. The purity of **8** was checked with TLC, which showed one spot in an ethyl acetate/cyclohexane mixture (80:20) with *R_f* = 0.62.

The other model compound, **9**, was also characterized with IR, ¹H-NMR, and elemental analysis. The IR spectrum of **9** showed a strong peak at 3320 cm⁻¹ for the N—H bond and three peaks at 1790, 1715, and 1667 cm⁻¹ for the carbonyl groups. The first two peaks are characteristic of the urazole moiety. The ¹H-NMR spectrum (Fig. 2) of **9** showed all the peaks, and this agreed with the structure of **9**. The elemental analysis results were in good agreement with the structure of **9**. The purity of **9** was checked with TLC, which showed one spot in an ethyl acetate/cyclohexane mixture (80:20) with *R_f* = 0.14.

TABLE III
Reaction Conditions for the Polymerization of AmPU with 12 and Some Physical Properties of PA3A–PA3C

Polymer	Solvent	Catalyst	Reaction time	Nonsolvent	Yield (%)	Inherent viscosity (dL/g) ^a	mp (°C)
PA3A	DMAc	Py	3 h, -5°C; 8 h, RT; 20 h, 85°C	MeOH	82.0	0.12	198–208
PA3B	DMAc	TEA	3 h, -5°C; 8 h, RT; 20 h, 85°C	MeOH	86.0	0.11	186–194
PA3C	DMAc	DBTDL	3 h, -5°C; 8 h, RT; 20 h, 85°C	MeOH	85.5	0.11	188–200

Py = pyridine; TEA = triethylamine; DBTDL = dibutyltin dilaurate; RT = room temperature.

^a Measured at a concentration of 0.5 g/dL in DMF at 25°C.

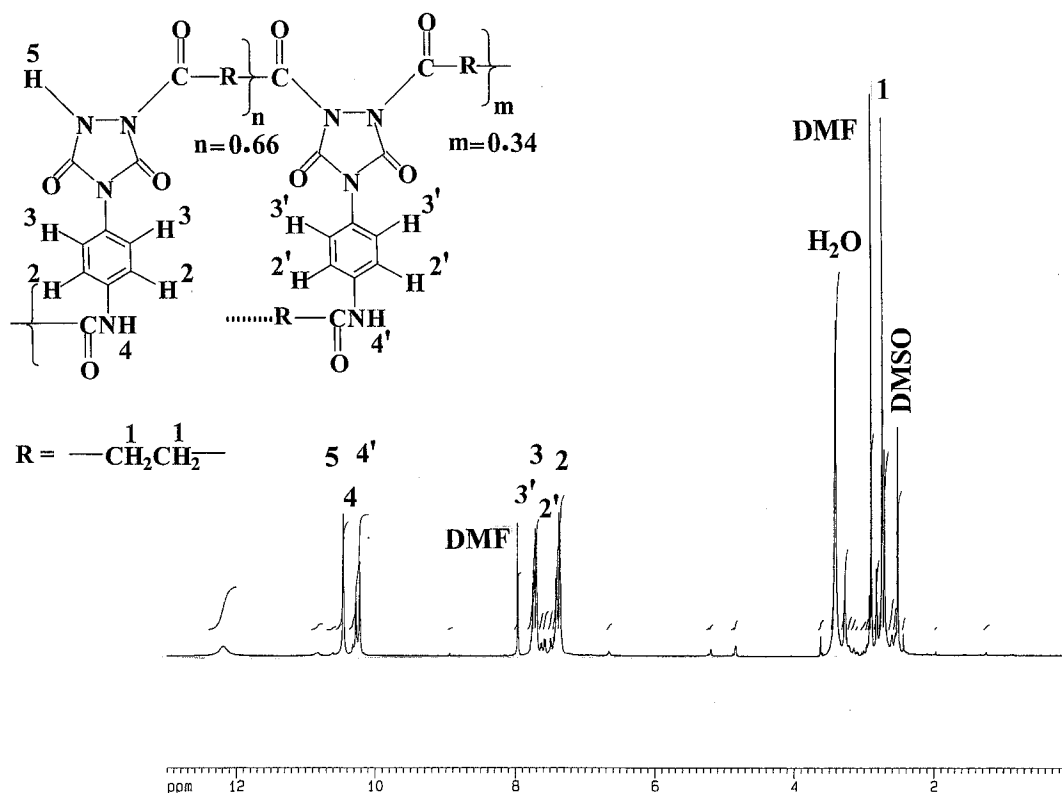


Figure 3 $^1\text{H-NMR}$ (500 MHz) spectrum of polymer PA1 in $\text{DMSO-}d_6$ at room temperature.

The aforementioned reaction was performed with 3 mol of acetyl chloride. A TLC examination of the reaction mixture showed the formation of two ad-

ducts. Two products were isolated via chromatography. Compounds 8 and 9 were formed in a ratio of 1.8:1 (Scheme 3).

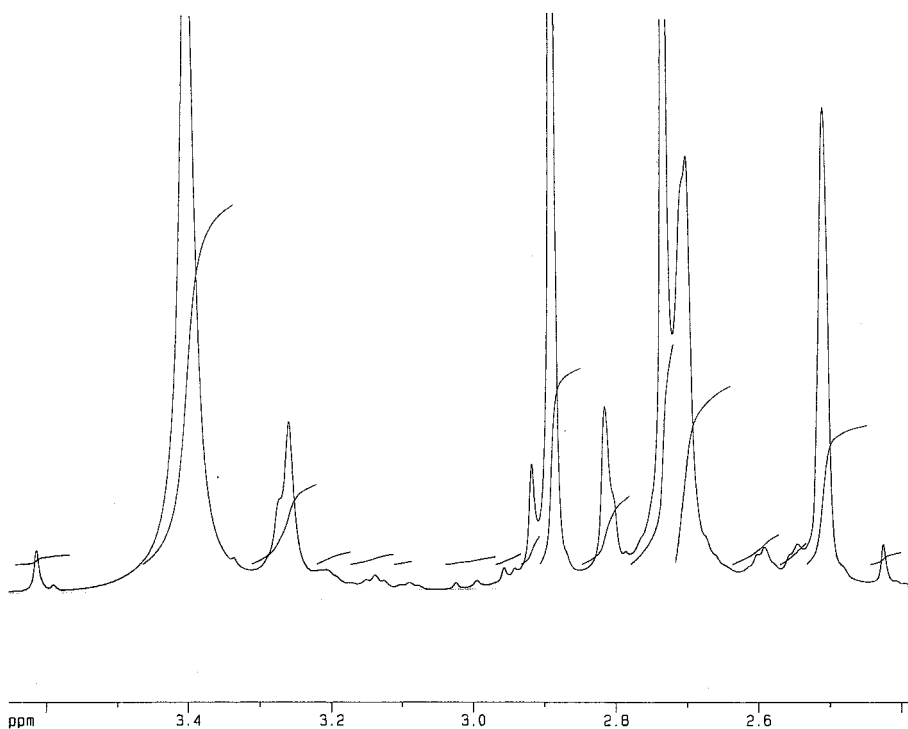


Figure 4 $^1\text{H-NMR}$ (500 MHz) spectrum of polymer PA1 in $\text{DMSO-}d_6$ at room temperature. An expanded region is shown for the aliphatic protons ($\delta = 2.4\text{--}3.6$ ppm).

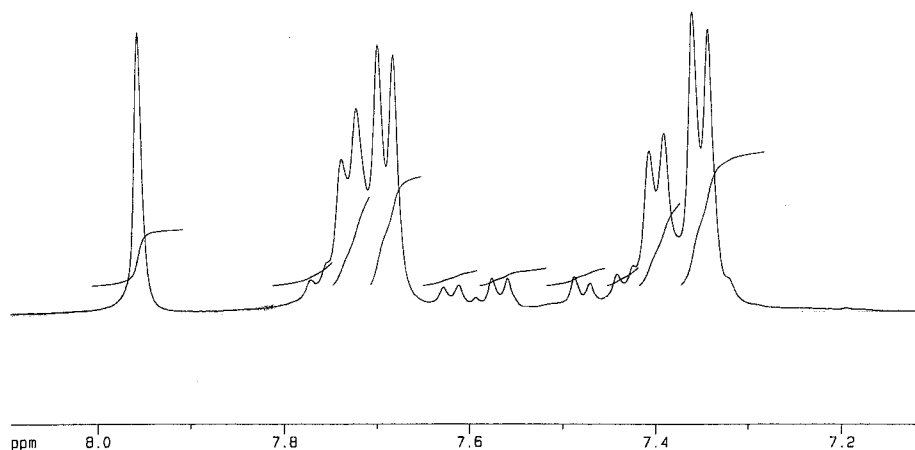


Figure 5 $^1\text{H-NMR}$ (500 MHz) spectrum of polymer PA1 in $\text{DMSO-}d_6$ at room temperature. An expanded region is shown for the aromatic protons ($\delta = 7.2\text{--}8.0$ ppm).

The aforementioned experiment was repeated with 10 mol of acetyl chloride. In this case, only **8** was formed and isolated. As the number of moles of acetyl chloride increased, the formation of **8** increased. These compounds were used as model compounds for the study of the polymerization reactions.

Polymerization reactions and characterization

Because model compounds **8** and **9** were synthesized in good yields and purities, we became interested in

performing this type of reaction for the formation of novel polyamides. Thus, **10**, **11**, and **12** were selected as diacid chlorides. The reaction of monomer **7** with these diacid chlorides was performed in a 1:1 molar ratio via solution polymerization. The reactions were carried out in DMAc solutions in the presence of pyridine, triethylamine, and dibutyltin dilaurate as catalysts, and the resulting polyamides (PA1–PA3) were obtained in good yields and with moderate inherent viscosities (Scheme 4 and Tables I–III).

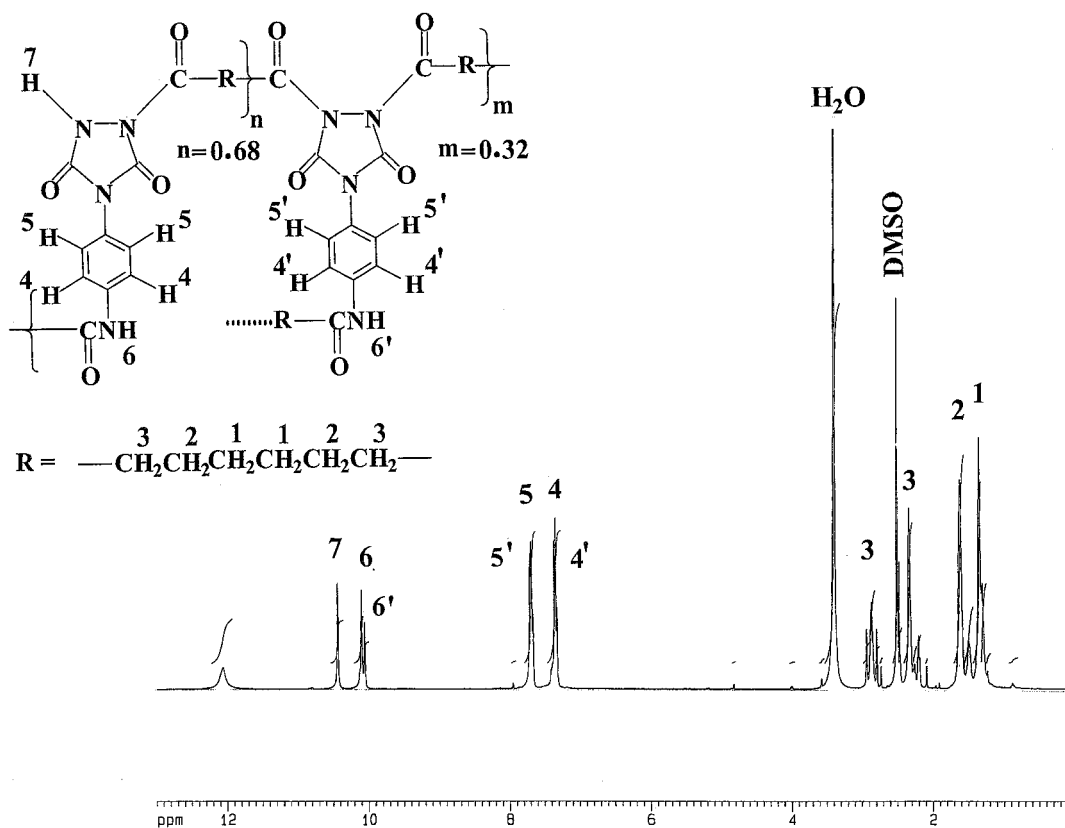


Figure 6 $^1\text{H-NMR}$ (500 MHz) spectrum of polymer PA2 in $\text{DMSO-}d_6$ at room temperature.

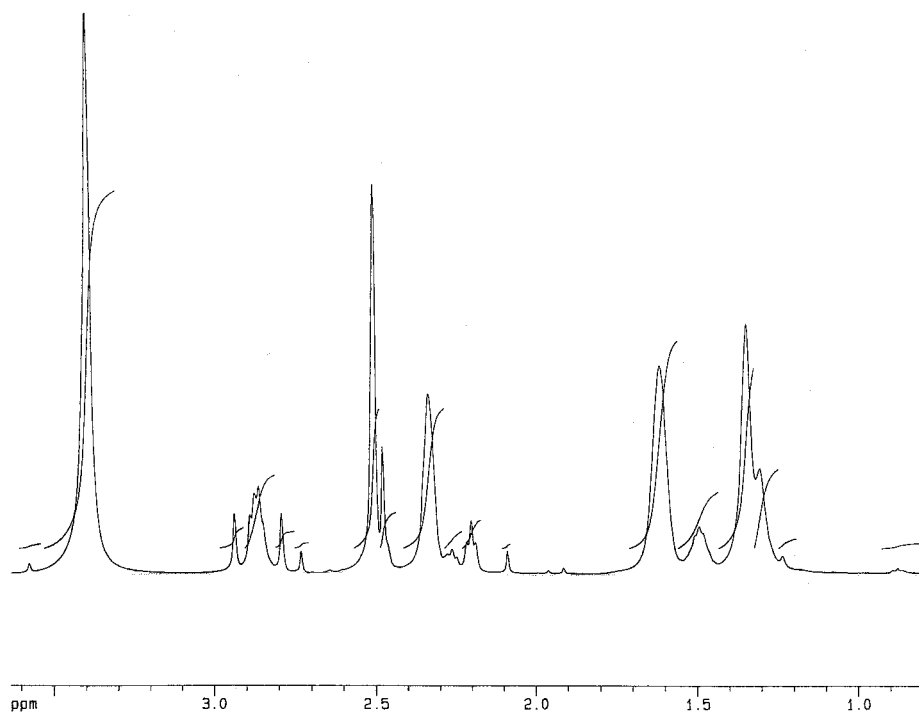


Figure 7 $^1\text{H-NMR}$ (500 MHz) spectrum of polymer PA2 in $\text{DMSO-}d_6$ at room temperature. An expanded region is shown for the aliphatic protons ($\delta = 0.8\text{--}3.6$ ppm).

The resulting polymers were characterized with IR, $^1\text{H-NMR}$, elemental analysis, and TGA. The IR spectrum of polymer PA1 showed medium peaks at 3328 and 3203 cm^{-1} for the N-H bond, peaks at 2958 cm^{-1}

for the aliphatic C-H bonds, and three strong peaks at 1750 , 1712 , and 1655 cm^{-1} for the carbonyl groups. The first two peaks are characteristic of the urazole moiety. The $^1\text{H-NMR}$ spectra of PA1 are shown in

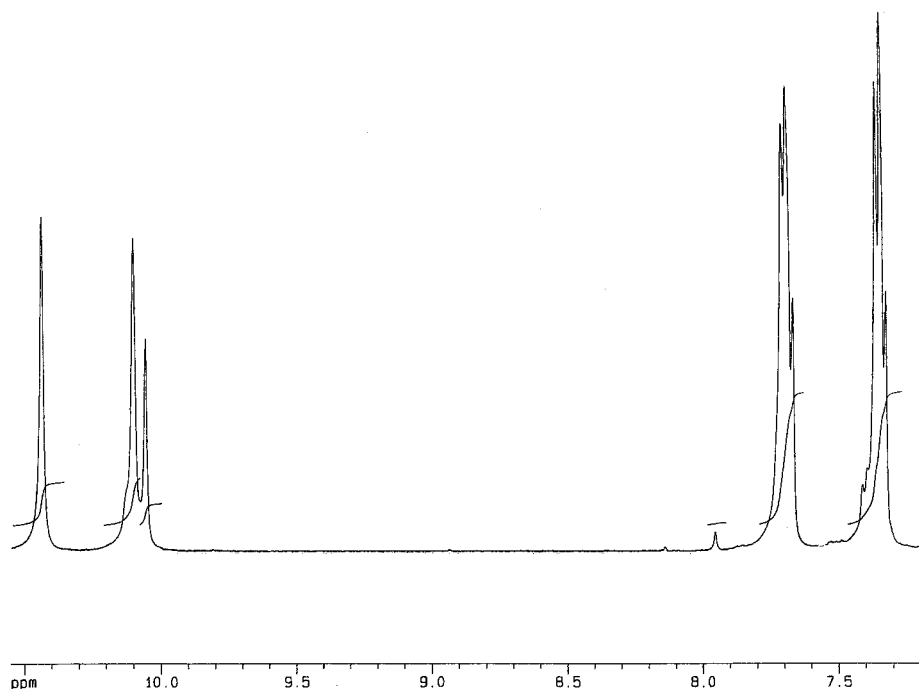


Figure 8 $^1\text{H-NMR}$ (500 MHz) spectrum of polymer PA2 in $\text{DMSO-}d_6$ at room temperature. An expanded region is shown for the aromatic and N-H protons ($\delta = 7.2\text{--}10.5$ ppm).

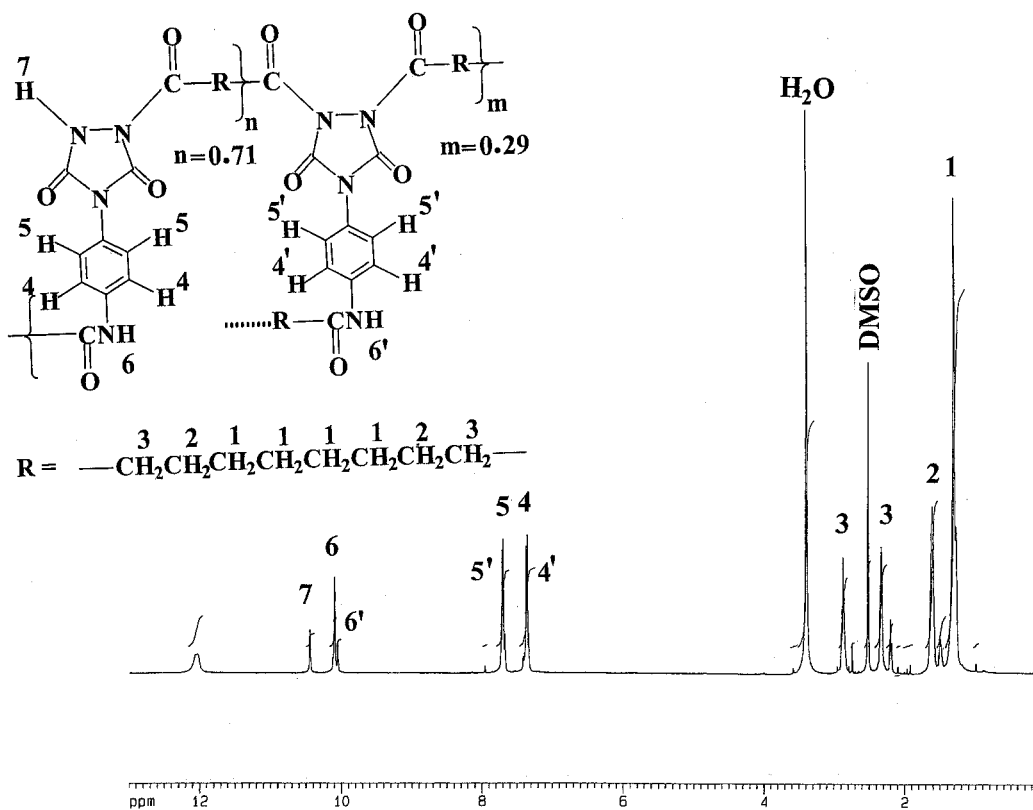


Figure 9 $^1\text{H-NMR}$ (500 MHz) spectrum of polymer PA3 in $\text{DMSO-}d_6$ at room temperature.

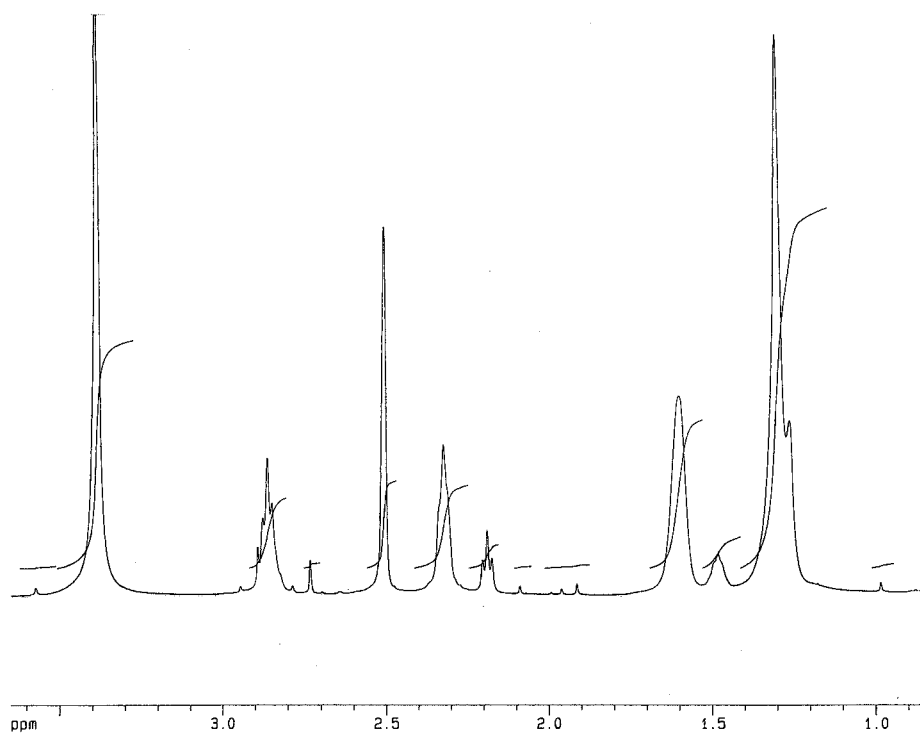


Figure 10 $^1\text{H-NMR}$ (500 MHz) spectrum of polymer PA3 in $\text{DMSO-}d_6$ at room temperature. An expanded region is shown for the aliphatic protons ($\delta = 0.9\text{--}3.6$ ppm).

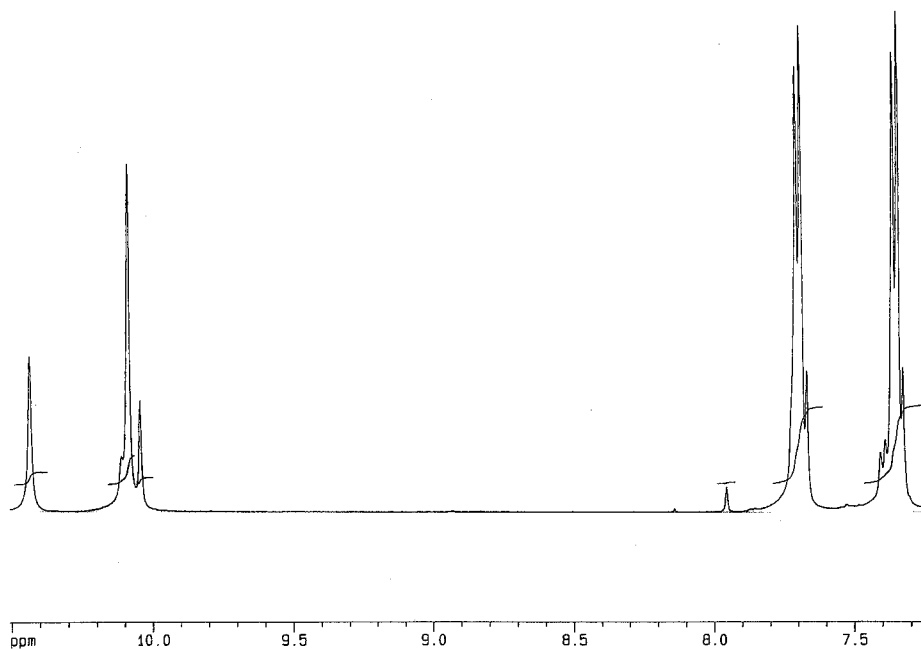


Figure 11 $^1\text{H-NMR}$ (500 MHz) spectrum of polymer PA3 in $\text{DMSO-}d_6$ at room temperature. An expanded region is shown for the aromatic and N—H protons ($\delta = 7.3\text{--}10.5$ ppm).

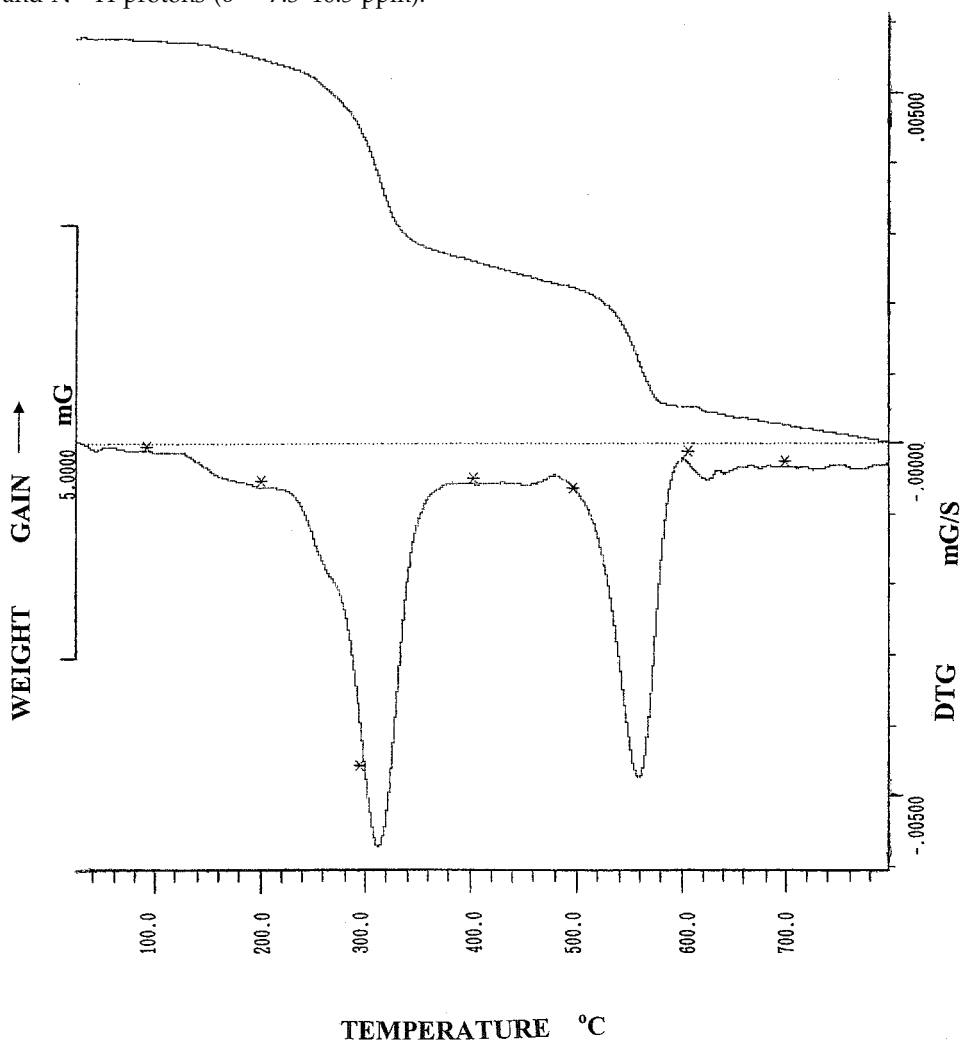


Figure 12 TGA and DTG thermograms of polymer PA1 under a nitrogen atmosphere.

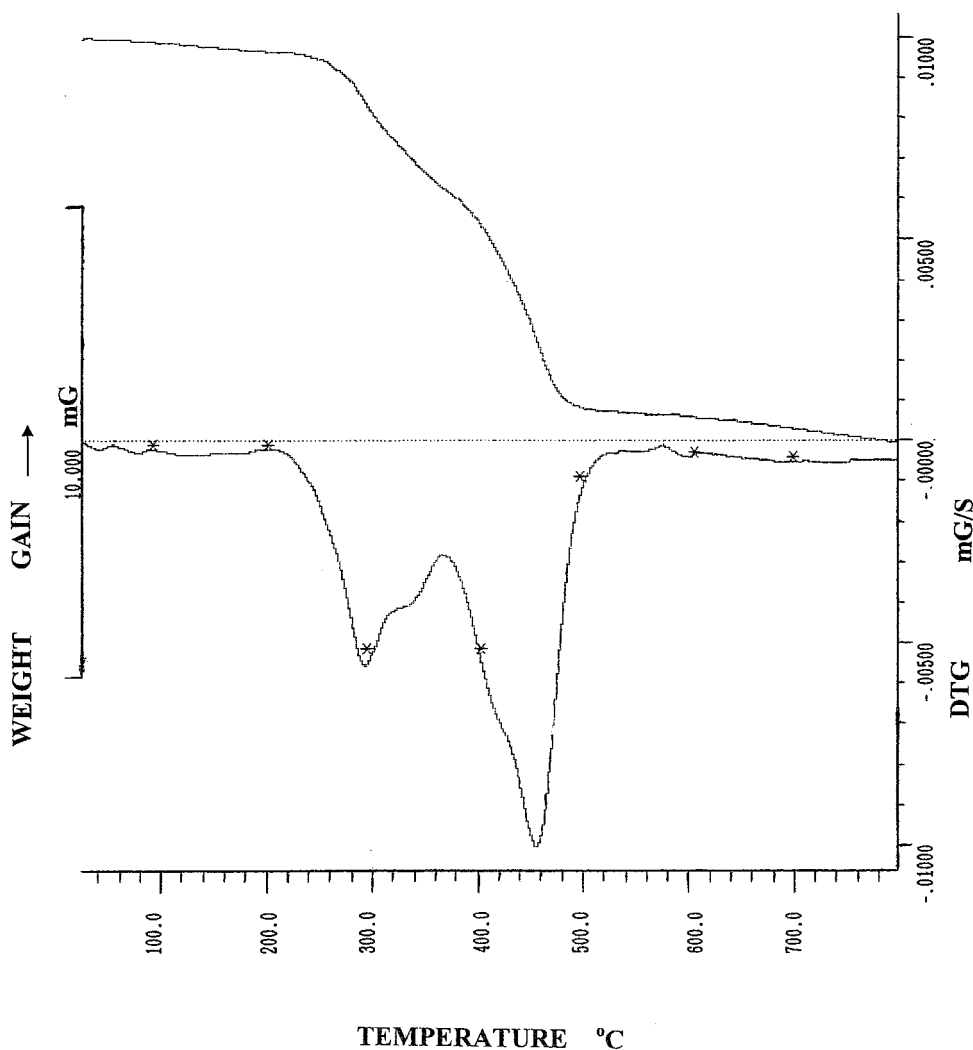


Figure 13 TGA and DTG thermograms of polymer PA2 under a nitrogen atmosphere.

Figures 3–5. Figure 4 shows an expanded region for the aliphatic protons, and Figure 5 shows an expanded region for the aromatic protons and N—H proton. The patterns of the spectra are similar to those of model compounds **8** and **9**. From the integral calculation of the area of the N—H peaks, we determined the ratios of 1:3 and 1:2 for the structural formation of PA1. These data show that the amount of the 1:3 structure in PA1 was equal to 34%, and that of the 1:2 structure was equal to 66%. The elemental analysis results were also in good agreement with the structure of PA1.

The IR and $^1\text{H-NMR}$ spectra (Figs. 6–8) of PA2 showed peaks, which confirmed its chemical structure. In this case, two chemical structures, 1:3 and 1:2, were also formed. From the integral calculations, we found that the amount of the 1:3 structure in PA2 was equal to 32%, and that of the 1:2 structure was equal to 68%. The elemental analysis results were also in good agreement with the calculated percentages for the carbon, hydrogen, and nitrogen contents in the polymer repeating unit of PA2.

The IR and $^1\text{H-NMR}$ spectra (Figs. 9–11) of PA3 showed peaks, which confirmed its chemical structure. In this case, two chemical structures, 1:3 and 1:2, were also formed. From the integral calculations, we found that the amount of the 1:3 structure in PA3 was equal to 29%, and that of the 1:2 structure was equal to 71%. The elemental analysis results were also in good agreement with the calculated percentages for carbon, hydrogen, and nitrogen contents in the polymer repeating unit of PA3.

PA1, PA2, and PA3 were soluble in organic solvents such as dimethylformamide (DMF), DMSO, DMAc, and 1-methyl-2-pyrrolidinone, *N*-methylpyrrolidone (NMP) and were insoluble in solvents such as water, methanol, cyclohexane, and chloroform.

Thermal properties

The thermal behavior of polyamides PA1, PA2, and PA3 was determined with TGA and derivative thermogravimetry (DTG) at a rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere (Figs. 12–14). An examination of

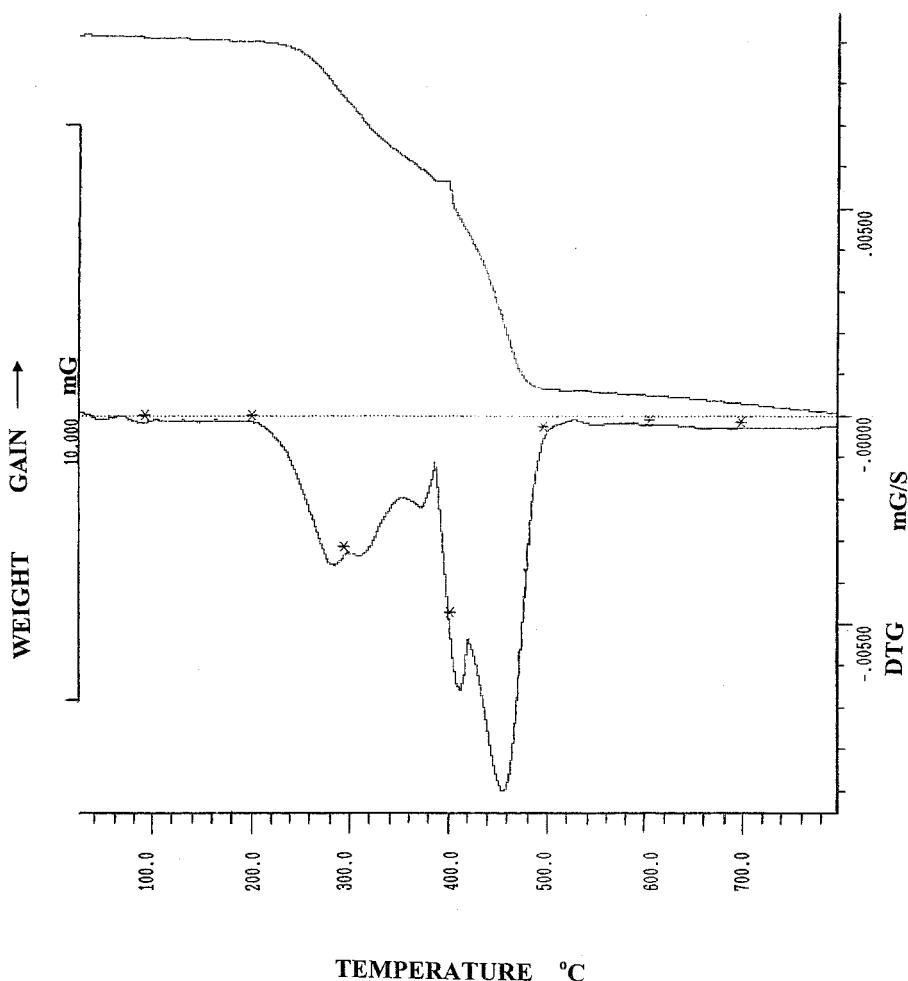


Figure 14 TGA and DTG thermograms of polymer PA3 under a nitrogen atmosphere.

the data revealed that all of the polyamides were thermally stable up to 200°C under a nitrogen atmosphere. The 5 and 10% weight-loss temperatures and the char yield at 600°C for PA1, PA2, and PA3 were 240°C, 280°C, and 39.6%, 265°C, 283°C, and 12.4%, and 270°C, 291°C, and 16.2%, respectively. From this information, we can note that the resulting polymers were rather thermally stable. All of these thermograms show two-step decomposition. This could be due to the presence of disubstituted and trisubstituted structures in the polymer backbone (linear and branch structures).

CONCLUSIONS

AmPU is an interesting trifunctional monomer for polycondensation reactions. This compound has three acidic N—H groups and can be readily reacted with acetyl chloride to give 1:2 and 1:3 adducts in good yields and high purities. Thus, AmPU can act as a bifunctional monomer and as a trifunctional monomer, and its polymerization reaction with aliphatic diacid chlorides produces novel polyamides contain-

ing urazole linkages in two and three dimensions. Three different catalysts have been used in these polymerization reactions. All of these catalysts are suitable for polycondensation reactions.

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