

Chromophoric Poly(urea-urethane)s with Pendent 3-Hydroxynaphthalene Group: Synthesis and Characterization

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Received 9 March 2007; accepted 27 November 2007

DOI 10.1002/app.27841

Published online 23 January 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The reaction of 4-(3-hydroxynaphthalene)-1,2,4-triazolidine-3,5-dione (**3HNTD**) with *n*-propylisocyanate was performed at different molar ratios. The resulting monosubstituted urea and disubstituted urea-urethane derivatives were obtained in high yields and were used as model compounds for polymerization reactions. **3HNTD** as a monomer was used in the preparation of heterocyclic poly(urea-urethane)s to produce photoactive polymers, by polycondensation with different diisocyanates in *N,N*-dimethylacetamide (DMAc) solution. Chromophoric heterocyclic polymers containing naphthalene group, obtained in quantitative yields, possessed inherent viscosities in the range of 0.14–0.38 dL/g. The resulting

poly(urea-urethane)s is insoluble in most organic solvents, but easily soluble in polar solvents such as dimethyl sulfoxide (DMSO), DMAc, and *N*-methylpyrrolidone (NMP). The polymers were characterized by IR, ¹H-NMR, elemental analysis, and TGA. Fluorimetric and UV–vis studies of the monomer as well as polymers were performed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1323–1328, 2008

Key words: 4-(3-hydroxynaphthalene)-1,2,4-triazolidine-3,5-dione [4-(3-hydroxynaphthalene)urazole]; photoactive polymers; fluorescence; polycondensation; NMR; UV–vis spectroscopy; thermogravimetric analysis (TGA)

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.^{1–3} Little attention was given to polyurethanes and polyureas containing heterocyclic rings. We have already reported the synthesis of urazoles and the preparation of polyureas and polyamides from these monomers.^{4–6} Polyureas are polyamides of carbonic acid, they are very tough materials with high hardness, good chemical resistance, and suitable for elastomer and fiber applications.⁷ Polyureas generally have higher melting rate than polyamides with a similar amount of separation between functional groups. The greater extent of hydrogen bonding and higher polarity associated with the urea group are thought to account for the difference. Polyureas can be tailor-made to obtain properties that lead to versatile applications such as coating systems for water-

proofing and corrosion protection. Polyureas have been prepared by several methods such as reaction of diamines with phosgene,⁷ carbonate esters,⁸ carbonate alkali metals,⁹ carbon dioxides,¹⁰ and urea,¹¹ but the best and easiest method is to react diamine and diisocyanates.^{5,12–16} 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.¹⁷

Enhanced performance properties have driven the increased use of naphthalene polymers in a wide range of applications including films, fibers, bottles, additives, and engineering resins. Naphthalene structure as a chromophore gave special features such as rigid, bulky, moisture resistance, and low coefficient of thermal expansion to polymer. Incorporation of this double ring structure in the polymer chain increases thermal, chemical, mechanical, and barrier performance versus polymers based on single aromatic rings. The integration of naphthalene as a pendant group in a polymer chain has resulted in decreased crystallinity and enhanced solubility and thermal stability.¹⁸ On the other hand; the attachment of bulky lateral groups can increase the solubility because of decreasing packing and crystallinity.^{19–22}

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Contract grant sponsors: Research Affairs Division Isfahan University of Technology (IUT), Isfahan; Center of Excellency in Sensors and Green Chemistry Research (IUT).

Journal of Applied Polymer Science, Vol. 108, 1323–1328 (2008)
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Recently, we have reported the synthesis poly (urea-urethane)s (PUU)s from 4-(3-hydroxynaphthalene)-1,2,4-triazolidine-3,5-dione [4-(3-hydroxynaphthalene)urazole] (3HNTD) and various diisocyanates using room temperature ionic liquids (RTIL)s and molten tetrabutylammonium bromide under microwave irradiation as well as conventional heating.²³

In this article, we describe the synthesis and properties of PUUs containing naphthalene moiety in which the chromophore (naphthalene) is located in the side chain by conventional solvent. Thus polymerization of 3HNTD with different diisocyanates was performed in classical solution polycondensation using variety of catalysts and under no catalyst conditions. In an effort to investigate the influence of contemporaneous presence of naphthalene unit in combination with hydroxy link, we decided to incorporate 3-hydroxynaphthalene group along the backbone of PUUs by using an urazole 3HNTD aiming to enhance their solubility while maintaining their positive properties. The naphthalene moiety by allowing the attachment of pendent group also provides additional opportunities for generating polymers photoactive.

EXPERIMENTAL

Materials and equipments

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. Proton nuclear magnetic resonance ¹H-NMR (500 MHz) spectra were recorded on a Bruker (Germany), Avance 500 instrument. Multiplicities of proton resonance were designated as singlet (s) and multiplet (m). IR spectra were recorded on Shimadzu (Kyoto, Japan) 435 IR 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 Fenske Routine viscometer. Quantitative solubility was determined using 0.05 g of the polymer in 1 mL of solvent. 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. Thermal gravimetric analysis (TGA) data for polymers were taken on a TGA-PerkinElmer (Pyris 1) under N₂ atmosphere by the Research Institute of Polymer and Petrochemical of Iran (IPPI).

Synthesis of monomer

3HNTD (1) was prepared according to our previous work.²³

Preparation of model compounds

Model compounds were prepared to obtain information about the reactivity of active sites in the monomer 1. All model compounds were prepared by the same procedure with different molar ratios of 3HNTD (1) to isocyanate (1 : 1, 1 : 2, 1 : 3, and 1 : 12), in accordance with our previous work.²³

Polymer synthesis

All of the polymers were synthesized with two different methods.

Polymerization of 3HNTD (1) with hexamethylene diisocyanate (HMDI)

Method I

Into a 25-mL round-bottom flask 3HNTD (1) (0.1002 g, 4.12×10^{-4} mol) and pyridine (0.05 mL, 6.20×10^{-4} mol) were added to a solution of HMDI (2) (0.0693 g, 4.12×10^{-4} mol) in 0.5 mL of DMAc. The solution was stirred for 4 h at room temperature, 8 h at 60°C, and then 24 h at 95°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 0.134 g (79%) of PUU1A. The above polymerization was repeated, in the presence of triethylamine or dibutyltin dilaurate as a catalyst, respectively.

Method II

The above polymerization was repeated, but the reaction mixture was refluxed in DMAc for 1, 3, and 6 min, respectively, in the presence of different catalysts.

IR (KBr): 3320 (s), 3100 (w), 2905 (s), 1770 (s), 1730 (s), 1640 (s), 1530 (s), 1470 (m), 1410 (m), 1380 (m), 1360 (m), 1318 (m), 1220 (s), 1160 (m), 1110 (m), 1030 (m), 860 (m), 740 (m) cm⁻¹. ¹H-NMR (500 MHz, DMSO-*d*₆, ppm): δ 1.15–1.76 (m, br, 8H, CH₂), 3.25–3.85 (m, br, 4H, CH₂), 7.52–8.32 (m, br, 6H, Ar–H), 10.31 (s, 1H, N–H).

The other polymers (PUU2 and PUU3) were prepared with similar procedures using the other diisocyanates, isophorone diisocyanate (IPDI), and toluylene-2,4-diisocyanate (TDI), respectively.

PUU2A (IPDI)

IR(KBr): 3350 (m), 3100 (w), 2900 (s), 1770 (m), 1740 (m), 1630 (s), 1540 (s), 1460 (m), 1420 (m), 1380 (m),

1360 (m), 1300 (m), 1230 (m), 1150 (w), 1060 (w), 970 (w), 943 (m), 620 (m) cm^{-1} . $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, ppm): δ 0.83–1.30 (m, br, 11H, CH_3 , CH_2), 1.38–1.43 (m, br, 4H, CH_2), 2.79 (m, br, 2H, CH_2), 3.58 (m, br, 1H, CH), 7.56–8.25 (m, 8H, Ar—H, N—H), 10.63 (s, 1H, N—H).

PUU3A (TDI)

IR(KBr): 3300 (s), 2800 (s), 2700 (m), 1760 (m), 1650 (s), 1600 (s), 1520 (s), 1470 (s), 1440 (s), 1410 (s), 1300 (s), 1210 (s), 1120 (m), 1070 (w), 1030 (w), 980 (w), 940 (w), 870 (m), 800 (m), 740 (m) cm^{-1} . $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, ppm): δ 2.15 (m, br, 3H, CH_3), 7.51–8.32 (m, br, Ar—H), 7.62–8.22 (m, br, Ar—H, N—H), 10.23 (s, 1H, N—H).

RESULTS AND DISCUSSION

Monomer synthesis

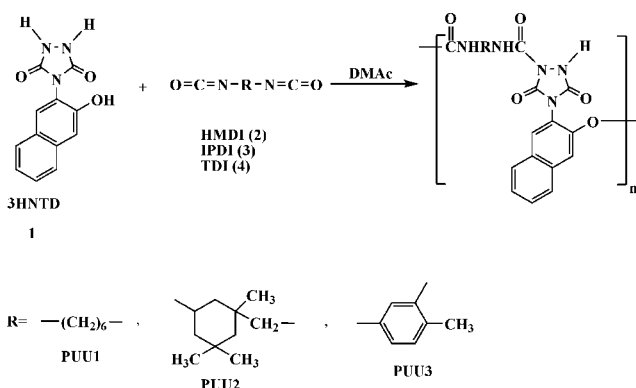
3HNTD (1) was prepared according to our previous work.²³

Model compounds studies

Because **3HNTD (1)** has two N—H and one O—H sites which can react with isocyanates, before the polymerization, we decided to examine the reactivity of these sites toward *n*-propylisocyanate. Thus, **3HNTD (1)** was allowed to react with different molar ratios of **3HNTD (1)** to *n*-propylisocyanate (1 : 1, 1 : 2, 1 : 3, and 1 : 12) in DMAc solution according to our previous work.²³

Polymerization reactions

Heterocyclic PUUs containing naphthalene side group were prepared from the reaction of **3HNTD (1)** with various diisocyanates using the optimized conditions (Scheme 1). **HMDI (2)**, **IPDI (3)**, and **TDI (4)**



Scheme 1 Polycondensation reactions of monomer **1** with different diisocyanates.

TABLE I
Reaction Conditions for the Polymerization of Monomer **3HNTD (1)** with **HMDI (2)** by Different Methods and Some Physical Properties for **PUU1A-PUU1J**

Polymer	Method ^a	Reaction Time (min)	Catalyst	Yield (%)	η_{inh} (dL/g) ^b
PUU1A	I	GH ^a	Py ^c	79	0.26
PUU1B	I	GH ^a	TEA ^d	81	0.28
PUU1C	I	GH ^a	DBTDL ^e	82	0.38
PUU1D	I	GH ^a	—	85	0.14
PUU1E	II	1 ^f	Py	79	0.28
PUU1F	II	1 ^f	TEA	81	0.32
PUU1G	II	1 ^f	DBTDL	83	0.33
PUU1H	II	1 ^f	—	88	0.13
PUU1I	II	3 ^f	DBTDL	82	0.28
PUU1J	II	6 ^f	DBTDL	83	0.28

^a Method I: Gradual heating (GH) at different temperatures.

^b Measured at a concentration of 0.5 g/dL in DMF and 2% LiCl at 25°C.

^c Pyridine.

^d Triethylamine.

^e Dibutyltin dilaurate.

^f Method II: Refluxing at 1, 3, and 6 min., respectively.

(**4**) were selected as diisocyanates. The reaction of monomer (**1**) with these diisocyanates was performed in a 1 : 1M ratio via solution polymerization. The polymerization reactions of **3HNTD (1)** with diisocyanates were performed with two different methods in the presence of different catalysts and without catalyst, respectively. The mechanism of the reaction of monomer **1** with the aforementioned diisocyanates is a step growth addition of N—H and O—H of the urazole group across the carbon-nitrogen double

TABLE II
Reaction Conditions for the Polymerization of Monomer **3HNTD (1)** with **IPDI (3)** by Different Methods and Some Physical Properties for **PUU2A-PUU2J**

Polymer	Method ^{a,b}	Reaction Time (min)	Catalyst	Yield (%)	η_{inh} (dL/g) ^c
PUU2A	I	GH ^a	Py ^d	85	0.14
PUU2B	I	GH ^a	TEA ^e	82	0.17
PUU2C	I	GH ^a	DBTDL ^f	81	0.19
PUU2D	I	GH ^a	—	81	0.11
PUU2E	II	1 ^b	Py	79	0.16
PUU2F	II	1 ^b	TEA	83	0.19
PUU2G	II	1 ^b	DBTDL	86	0.19
PUU2H	II	1 ^b	—	84	0.10
PUU2I	II	3 ^b	DBTDL	78	0.16
PUU2J	II	6 ^b	DBTDL	86	0.15

^a Method I: Gradual heating (GH) at different temperatures.

^b Method II: Refluxing at 1, 3, and 6 min., respectively.

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

^d Pyridine.

^e Triethylamine.

^f Dibutyltin dilaurate.

TABLE III
Reaction Conditions for the Polymerization of Monomer 3HNTD (1) with TDI (4) by Different Methods and Some Physical Properties for PUU3A-PUU3J

Polymer	Method ^{a,b}	Reaction Time (min)	Catalyst	Yield (%)	η_{inh} (dL/g) ^c
PUU3A	I	GH ^a	Py ^d	87	0.19
PUU3B	I	GH ^a	TEA ^e	81	0.23
PUU3C	I	GH ^a	DBTDL ^f	83	0.24
PUU3D	I	GH ^a	–	79	0.13
PUU3E	II	1 ^b	Py	85	0.22
PUU3F	II	1 ^b	TEA	78	0.25
PUU3G	II	1 ^b	DBTDL	87	0.29
PUU3H	II	1 ^b	–	82	0.12
PUU3I	II	3 ^b	DBTDL	80	0.18
PUU3J	II	6 ^b	DBTDL	82	0.18

^a Method I: Gradual heating (GH) at different temperatures.

^b Method II: Refluxing at 1, 3, and 6 min., respectively.

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

^d Pyridine.

^e Triethylamine.

^f Dibutyltin dilaurate.

bond, and there is no byproduct, this simplifies the polymerization process. The results of different reaction conditions are summarized in Tables I–III. In method I the reaction mixture was heated gradually from room temperature up to 95°C in the presence of pyridine, dibutyltin dilaurate, and triethylamine and without a catalyst, respectively. The resulting polymers PUU1-PUU3 were obtained in high yields and moderate inherent viscosities. In method II, the reaction mixture was refluxed for a period of 1, 3, and 6 min, respectively, in DMAc solution. It seems that DMAc was a suitable solvent for the fast reflux method because, during the reaction period (1, 3, and 6 min) under refluxing temperature, the reaction mixture was soluble and there was a possibility for polymer chains to grow well without any decomposition. The inherent viscosities and yields of the resulting polymers from method II were comparable with method I. According to Tables I–III, PUUs-based HMDI provided higher viscosities than the

TABLE IV
Elemental Analysis of PUUs^a

Polymer	Formula		C (%)	H (%)	N (%)
PUU1A (HMDI)	C ₂₀ H ₂₁ N ₅ O ₅ (411.418 g/mol)	Calcd.	58.39	5.14	17.02
		Found	57.51	5.58	16.46
PUU2A (IPDI)	C ₂₄ H ₂₇ N ₅ O ₅ (465.509 g/mol)	Calcd.	61.92	5.85	15.04
		Found	62.04	6.08	14.82
PUU3A (TDI)	C ₂₁ H ₁₅ N ₅ O ₅ (417.381 g/mol)	Calcd.	60.43	3.62	16.78
		Found	61.75	3.90	16.47

^a The polymer sample was dried in vacuum at 80°C for 8 h.

TABLE V
UV–Vis Spectra of 3HNTD (1) and PUUs in DMF

Code	Color	λ_{max} (A, ϵ M ⁻¹ cm ⁻¹)
Monomer	White	275 (0.834, 181326) 329 (0.214, 46630)
PUU1A	White	275 (0.9797, 171877) 331 (0.1473, 25842)
PUU2A	White	276 (0.519, 108229) 333 (0.147, 30688)
PUU3A	White	276 (0.909, 159474) 331 (0.279, 48947)

viscosities of PUUs-based TDI or IPDI. This could pertain to the better possibility of chain arrangement and chain growth, when was used from unsymmetric diisocyanates such as TDI and IPDI, compared to the symmetric HMDI. The resulting polymers were characterized by IR, ¹H-NMR, elemental analysis, UV–vis, and TGA.

The IR spectrum of PUUs showed characteristic bands at 3350–3300 for N–H stretching and three peaks in the region of 1770–1630 cm⁻¹ for the carbonyl groups. The ¹H-NMR spectrum of PUU1 showed a multiplet in the region of 1.15–1.76 ppm for the four central methylene groups and a multiplet in the region of 3.25–3.85 ppm for the other two methylene groups attached to the amide groups. Also shown peaks in the region of 7.52–8.32 ppm for aromatic protons, and N–H of the amide groups. A sharp peak showed at 10.31 ppm for N–H of the urazole group. The elemental analysis result is also in good agreement with the calculated percentages for carbon, hydrogen, and nitrogen contents in PUUs repeating unit (Table IV).

The UV–vis spectra of the 3HNTD (1) and PUUs were recorded in DMF and the data are shown in Table V. It is apparent that the wavelength of maximum absorption is related to the naphthalene group

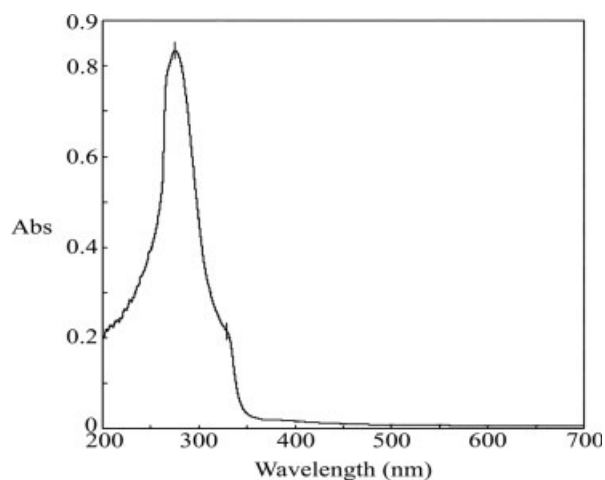


Figure 1 UV–vis absorption spectrum of monomer 1 in DMF solution.

TABLE VI
Fluorescence Spectra of 3HNTD (1) and PUUs in DMF

Code	C (M)	$\lambda_{\text{Ex.}}$ (nm)	$\lambda_{\text{Em.}}$ (nm)
Monomer	4.60×10^{-6}	269, 322 ^a	361, 427 ^b
		296, 350, 548, 610, 697 ^c	392, 403, 697 ^d
PUU1A	5.70×10^{-6}	266, 283 ^a	359, 429 ^b
		282, 341, 552, 611, 677 ^c	406, 426, 464 ^d
PUU2A	4.80×10^{-6}	278, 325, 362, 378, 405 ^a	356, 428 ^b
		278, 321, 359, 550, 605 ^c	366, 400, 658 ^d
PUU3A	5.80×10^{-6}	268, 316, 410 ^a	360, 398, 428, 454, 511, 580, 663 ^b
		273, 334, 481, 601 ^c	406, 427, 461 ^d

^a $\lambda_{\text{Em.}}$ for scanning excitation spectra = 260 nm.

^b $\lambda_{\text{Ex.}}$ for scanning emission spectra = 260 nm.

^c $\lambda_{\text{Em.}}$ for scanning excitation spectra = 348 nm.

^d $\lambda_{\text{Ex.}}$ for scanning emission spectra = 348 nm.

in the aforementioned compounds. All of these compounds show almost similar UV-vis spectra pattern. The UV-vis absorption spectrum of monomer 1 in DMF solution is shown in Figure 1.

The fluorescence spectra of the monomer, PUU1, PUU2, and PUU3 were recorded in DMF and the data are shown in Table VI. For example, in the case of the monomer, the compound was excited at 260 nm, and emission fluorescence wavelengths were observed at 361 and 427 nm, respectively. All of these compounds show almost similar fluorescence spectra pattern. Because these PUUs have naphthalene functional group, they have potential to be used as photolabing and photoresponsive materials. The fluorescent intensity of PUU3 is higher than of PUU1 and PUU2. This observation can be explained in terms of longer conjugate system exist in this polymer due to aromatic ring in comparison with other two polymers. The fluorescence spectrum of the monomer 1 in DMF solution, which was excited at 348 nm is shown in Figure 2.

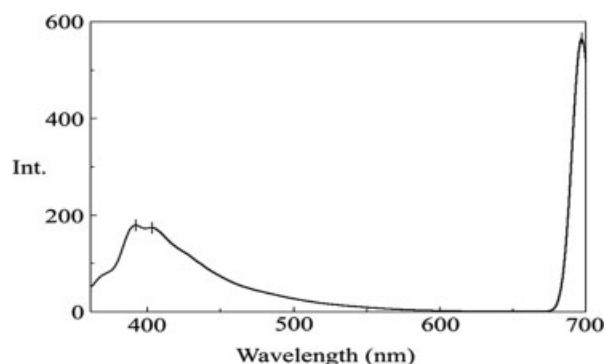


Figure 2 Fluorescence spectrum of monomer 1 in DMF solution which was excited at 348 nm.

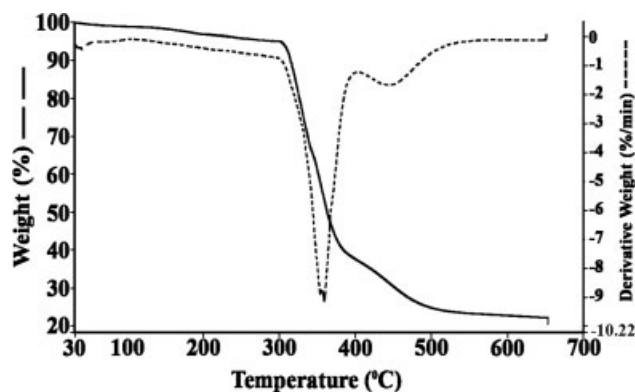


Figure 3 TGA/DTG of PUU1C with a heating rate of 10°C/min in a nitrogen atmosphere.

Solubility of polymers

The PUU2 and PUU3 are soluble in organic solvents such as *N*-methylpyrrolidone (NMP), DMF, DMAc, dimethyl sulfoxide (DMSO), and in H₂SO₄ and are insoluble in solvents such as water, methanol, acetone, cyclohexane, and chloroform. The PUU1 has lower solubility in DMF, DMSO, and DMAc, but it is readily soluble in DMF containing LiCl and concentrated H₂SO₄. On the other hand, it can be noted that PUUs prepared from symmetrical diisocyanate, HMDI, was less soluble compared with the other PUUs. This may have arisen from the fact that PUU1 possessed a higher structural regularity, which would facilitate a closer chain packing than the other polymers.

Thermal properties

The thermal stability of the PUU1C and PUU3G was investigated by thermogravimetric analysis (TGA) measurement. The 5 and 10% weight loss (T_5 , T_{10}) of the polymers and residue at 600°C (char yield) were used as criterions for their thermal stability. Typical TGA curves of representative polymers are shown in Figures 3 and 4. The temperatures of 5 and 10%

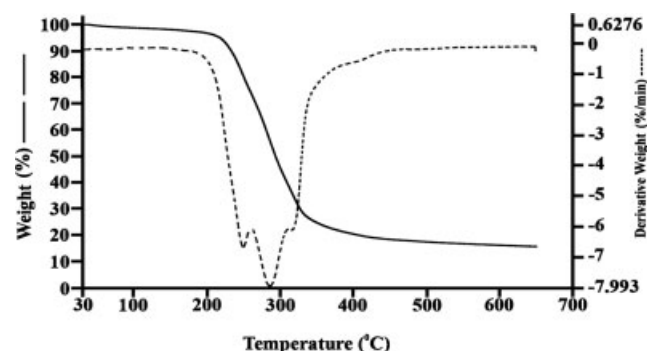


Figure 4 TGA/DTG of PUU3G with a heating rate of 10°C/min in a nitrogen atmosphere.

TABLE VII
Thermal Properties of PUU1C, PUU3G, PUU1, and PUU3

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char Yield (%) ^c
PUU1C	302	317	24
PUU3G	226	236	18
PUU1 ^d	317	331	10
PUU3 ^d	287	313	10

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of 10°C/min in a nitrogen atmosphere.

^b Temperature at which 10% weight loss was recorded by TGA at heating rate of 10°C/min in a nitrogen atmosphere.

^c Percentage weight of material left undecomposed after TGA analysis at a temperature of 600°C in a nitrogen atmosphere.

^d Polymers prepared using room temperature ionic liquid (RTIL) as a solvent and catalyst.²³

weight loss together with char yield at 600°C for PUU1C and PUU3G were calculated from their thermograms. The thermoanalyses data of PUU1C and PUU3G are summarized in Table VII. The thermal behavior of these polymers was also compared with PUUs, which was synthesized using RTIL as a solvent and catalyst (Table VII).²³ Polymers prepared by RTIL method show higher thermal stability.

CONCLUSIONS

Chromophoric polymers have been extensively explored in the last decade because of their potential technological application in electronic and optoelectronic devices. Naphthalene structure as a chromophore gave special features to polymer. In the present study, we successfully prepared an interesting heterocyclic monomer 3HNTD (**1**), containing naphthalene moiety. This compound can be used as a difunctional monomer with three acidic protons. 3HNTD (**1**) has two reactive sites for polymerization with diisocyanates. Heterocyclic PUUs containing naphthalene substitute with inherent viscosity values of 0.14–0.38 dL/g have been obtained from solution polycondensation of 3HNTD (**1**) with diisocyanates under two different methods. Because of the incor-

poration of naphthalene, the resulting PUUs are photoactive and exhibited good thermal stability and improved solubility in common organic solvents. Therefore, these polymers have potential to be used for high-temperature microelectronic devices and optical materials. Furthermore, because of the presence of NH groups in the polymer side chain it could readily be cured by reaction with excess diisocyanates or dianhydrides.

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