

A Novel Method for the Synthesis of Polyhydrazide and Polythiohydrazide from Urea and Thiourea

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Received 18 June 2009; accepted 31 October 2010

DOI 10.1002/app.33644

Published online 2 November 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A novel technique based on microwave irradiation was developed to synthesize polyhydrazide and polythiohydrazide. These polymers were readily synthesized by the reaction of aromatic and aliphatic dihydrazides with urea and thiourea. The effects of microwave irradiation time, power, solvent nature, and solid content of monomers on the inherent viscosity of

the polymers were investigated. The polymers were characterized by $^1\text{H-NMR}$ and IR spectroscopy and elemental analysis. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2508–2512, 2012

Key words: high performance polymers; polycondensation; thermal properties

INTRODUCTION

Polyhydrazides are interesting polymers with applications under extreme environmental conditions.¹ In fact, polyhydrazides can be transformed into heat-resistant polyoxadiazoles by simple heating.² They are also interesting for their high water absorption, high thermal stability, outstanding dyeability, and reducibility. This latter property has been used in the preparation of polymeric chelates and initiators of redox polymerization.³ Polyhydrazides are, in general, extremely hygroscopic, soluble in strongly polar organic or acidic solvents, and very elastic.^{4,5} In fact, the relative tractability of polyhydrazides, that is, solubility and sometimes moldability, renders them very attractive for incorporation by solution or melt-blending methods into polar thermoplastic matrixes, such as polyamides or polyesters, to improve properties such as moduli and thermal resistance. These properties originate in the nonarylated $-\text{NH}-$ group in the polyhydrazides. Polyhydrazides are generally prepared by two methods: (1) high-temperature solution polymerization and (2) low-temperature solution polymerization.

Each of these methods has its own merits and drawbacks. For example, the high-temperature method needs special (high-temperature), conditions and the obtained polymers are insoluble in a variety of solvents.⁵ The low-temperature method requires

certain precautions because chlorides are highly toxic and sensitive and their handling is difficult.⁶

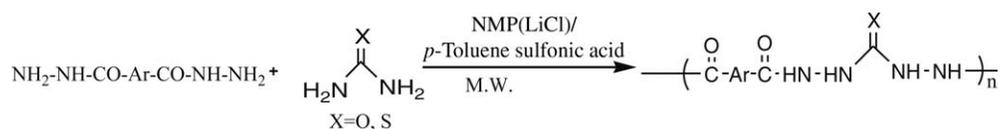
A literature survey has shown that microwave irradiation has brought a new perspective to synthetic organic chemistry, not only in terms of high yields and selectivity but also in terms of easy reaction conditions.^{7,8} The application of microwave energy in commercial domestic ovens to organic synthesis began in the mid 1980s. As an alternative to conventional heating techniques, the energy and molecular dipole moments of the starting materials are used. This *in situ* mode of energy conversion is quite attractive to chemists because its magnitude depends on the properties of the molecules. This allows some control of the properties of materials and may lead to selectivity of the reaction.^{9–11} Recently, we reported on an efficient and rapid synthesis of polyureas and polythioureas by the reaction of urea and thioureas with diamines under microwave irradiation.¹² Here, we report on a novel method for the synthesis of polyhydrazides and polythiohydrazides from aromatic and aliphatic dihydrazides with urea or thioureas under microwave irradiation. To the best of our knowledge, this report is the first of its kind on polymers.

EXPERIMENTAL

Materials and instruments

The solvent and reagents were purchased from Merck (Germany) and Fluka Co. (Switzerland). $^1\text{H-NMR}$ spectra were recorded on a Bruker Avance DPX-250 250-MHz spectrometer with tetramethylsilane as an internal standard. IR spectra were obtained on a Shimadzu FTIR 8000 spectrophotometer.

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Scheme 1 Synthesis of polyhydrazide and polythiohydrazide from urea and thiourea.

The inherent viscosities ($\eta_{inh} = \ln \eta_{rel}/C$, where η_{rel} is the relative viscosity and C is the concentration) of the polymers were determined in 0.5 g/dL solutions of dimethyl sulfoxide (DMSO) at 30°C with a Canon-Fenske viscometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were performed on a Stanton STA-G25 instrument at a heating rate of 10°C/min under N_2 . Elemental analyses were performed with a PerkinElmer 2400 CHN analyzer. The apparatus used for the polycondensation was a Butane domestic microwave oven (1000 W) without any modification, but for safety reasons, all of the reactions in the microwave oven were performed under an efficient hood to prevent contact with vapors.

Typical procedure for the preparation of the polyhydrazides and polythiohydrazides

A mixture of a terephthaloyl dihydrazide (DPH or **1a**; 1.94 g, 10 mmol), urea (0.6 g, 10 mmol) or thiourea (0.67 g, 10 mmol), and a catalytic amount of *p*-toluene sulfonic acid (0.17 g, 1 mmol) in *N*-methyl-2-pyrrolidone (NMP; 5 mL containing 5% LiCl) contained in a tall beaker was placed in the microwave oven. The beaker was covered with a watch glass and irradiated at 220 W for 7 min. It was again irradiated at 600 W for 10 min. To control the evolution of ammonia from the reaction mixture and to prevent splashing or frothing, we interrupted these two irradiation sequences at 1-min intervals. Then, the reaction mixture was allowed to cool to room temperature, and 5 mL of methanol was added. The precipitate was filtered off and washed with hot water and methanol.

After it was dried *in vacuo*, the pure product (**2a**): (from terephthaloyl dihydrazide + urea) was obtained (2.02 g, 92% yield).

Pure product: IR (KBr, ν , cm^{-1}): 3308, 1780, 1645, 1490, 1248, 906, 865. 1H -NMR [250 MHz, hexadeuterated dimethyl sulfoxide (DMSO- d_6), δ , ppm] 7.95 (t, 4H, Ar), 10.35 (s, 4H, NH). ANAL. Calcd: C, 49.09%; H, 3.66%; N, 25.44%. Found: C, 48.92%; H, 3.70%; N, 25.39%.

Other polyhydrazides and polythiohydrazides were synthesized in a similar manner. The following spectroscopic data were obtained:

2b: (from isophthaloyl dihydrazide + urea) IR (KBr, ν , cm^{-1}): 3259, 1780, 1665, 1500, 1240, 865. 1H -NMR (250 MHz, DMSO- d_6 , δ , ppm): 7.50–8.47 (m,

4H, Ar), 10.33 (s, 4H, NH). ANAL. Calcd: C, 49.09%; H, 3.66%; N, 25.44%. Found: C, 48.94%; H, 3.68%; N, 25.40%.

2c: (from 4,4'-biphenyl dicarbonyl dihydrazide + urea) IR (KBr, ν , cm^{-1}): 3280, 1779, 1670, 1491, 1249, 906, 865, 608. 1H -NMR (250 MHz, DMSO- d_6 , δ , ppm): 7.84 (d, 8H, Ar), 10.65 (s, 4H, NH). ANAL. Calcd: C, 60.80%; H, 4.08%; N, 18.90%. Found: C, 60.72%; H, 4.13%; N, 18.81%.

2d: (from oxalyl dihydrazide + urea) IR (KBr, ν , cm^{-1}): 3213, 1710, 1616, 1480. 1H -NMR (250 MHz, DMSO- d_6 , δ , ppm): 10.19 (s, 4H, NH). ANAL. Calcd: C, 25.00%; H, 2.79%; N, 38.88%. Found: C, 24.93%; H, 2.84%; N, 38.96%.

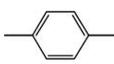
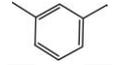
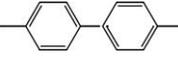
2e: (from succinyl dihydrazide + urea) IR (KBr, ν , cm^{-1}): 3195, 1710, 1604, 1339, 910. 1H -NMR (250 MHz, DMSO- d_6 , δ , ppm): 1.93 (s, 2H, CH_2), 10.17 (s, 2H, NH). ANAL. Calcd: C, 30.38%; H, 3.82%; N, 35.43%. Found: C, 30.25%; H, 3.88%; N, 35.37%.

2f: (from terephthaloyl dihydrazide + thiourea) IR (KBr, ν , cm^{-1}): 3201, 1660, 1596, 1465, 1279, 1110, 864, 632. 1H -NMR (250 MHz, DMSO- d_6 , δ , ppm): 8.07 (s, 4H, Ar), 10.76 (s, 4H, NH). ANAL. Calcd: C, 45.75%; H, 3.41%; N, 23.71%. Found: C, 45.67%; H, 3.45%; N, 23.64%.

2g: (from isophthaloyl dihydrazide + thiourea) IR (KBr, ν , cm^{-1}): 3205, 1660, 1458, 1279, 1110. 1H -NMR (250 MHz, DMSO- d_6 , δ , ppm): 7.59–8.60 (m, 4H, Ar), 10.75 (s, 4H, NH). ANAL. Calcd: C, 45.75%; H, 3.41%; N, 23.71%. Found: C, 45.63%; H, 3.46%; N, 23.65%.

2h: (from 4,4'-biphenyl dicarbonyl dihydrazide + thiourea) IR (KBr, ν , cm^{-1}): 3205, 1651, 1481, 1272,

TABLE I
Synthesis of the Polyhydrazides and Polythiohydrazides from the Reaction of the Aliphatic and Aromatic Dihydrazides with Urea and Thiourea

| Product | Ar | Yield (%) ^a | | η_{inh} (dL/g) ^b | |
|-------------------------|--|------------------------|-------|----------------------------------|-------|
| | | X = O | X = S | X = O | X = S |
| 2a and 2f |  | 92 | 88 | 0.52 | 0.50 |
| 2b and 2g |  | 91 | 86 | 0.34 | 0.32 |
| 2c and 2h |  | 89 | 86 | 0.42 | 0.41 |
| 2d and 2i | — | 88 | 85 | 0.28 | 0.26 |
| 2e and 2j | —(CH ₂)— | 85 | 82 | 0.20 | 0.19 |

^a Isolated yields on the basis of the dihydrazides.

^b Measured in DMSO at 30°C (0.5 g/dL).

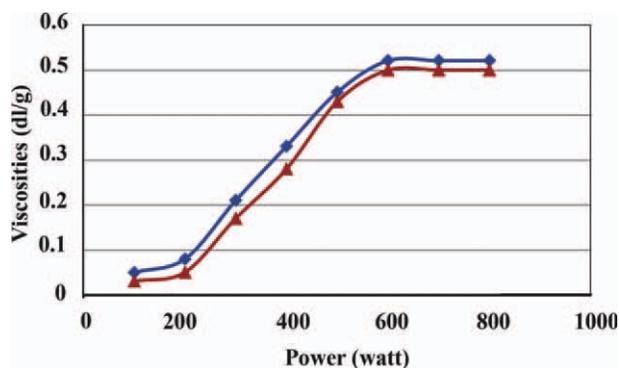


Figure 1 Dependence of the η_{inh} values on the microwave power: (blue) polyhydrazide and (red) polythiohydrazide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1110, 823, 748. $^1\text{H-NMR}$ (250 MHz, $\text{DMSO-}d_6$, δ , ppm): 7.93–8.08 (d, 8H, Ar), 10.66 (s, 4H, NH). ANAL. Calcd: C, 57.68%; H, 3.87%; N, 17.93%. Found: C, 57.62%; H, 3.91%; N, 17.85%.

2i: (from oxalyl dihydrazide + thiourea) IR (KBr, ν , cm^{-1}): 3209, 1700, 1612, 1458, 1180. $^1\text{H-NMR}$ (250 MHz, $\text{DMSO-}d_6$, δ , ppm): 10.79 (s, 4H, NH). ANAL. Calcd: C, 22.49%; H, 2.51%; N, 34.98%. Found: C, 22.43%; H, 2.54%; N, 34.93%.

2j: (from succinyl dihydrazide + thiourea) IR (KBr, ν , cm^{-1}): 3201, 1660, 1458, 1180. $^1\text{H-NMR}$ (250 MHz, $\text{DMSO-}d_6$, δ , ppm): 2.05 (s, 2H, CH_2), 10.67 (s, 2H, NH). ANAL. Calcd: C, 27.58%; H, 3.47%; N, 32.16%. Found: C, 27.52%; H, 3.52%; N, 32.13%.

RESULTS AND DISCUSSION

The polycondensation of aromatic and aliphatic dihydrazides with urea and thiourea in the presence of a catalytic amount of *p*-toluene sulfonic acid was studied under microwave conditions (Scheme 1, Table I).

The polymerization of DPH was investigated as a model substrate with urea in the presence of *p*-tolu-

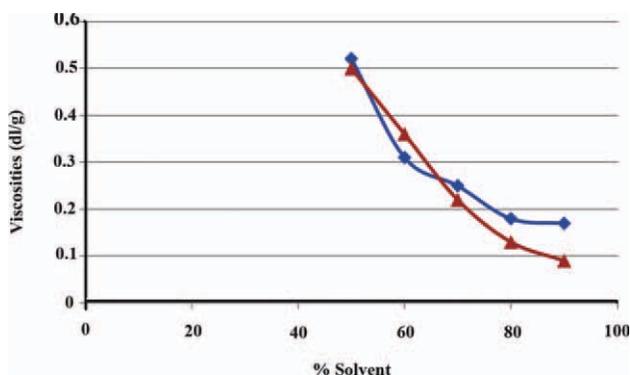


Figure 2 Dependence of the η_{inh} values on the amount of solvent: (blue) polyhydrazide and (red) polythiohydrazide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

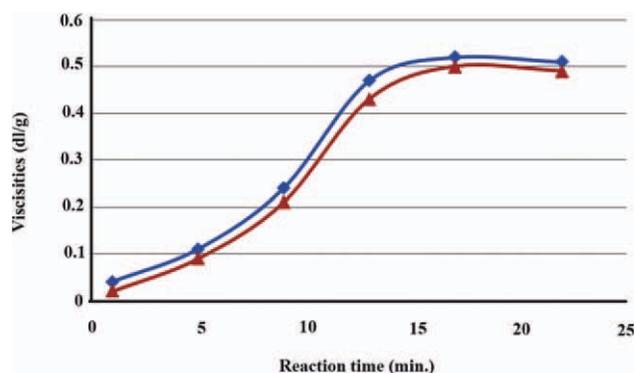
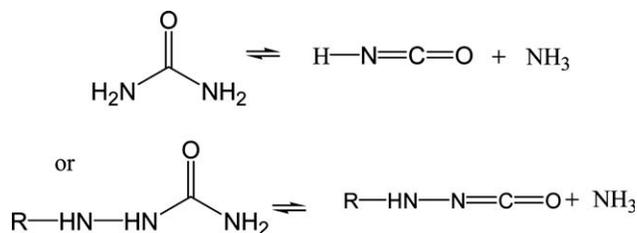


Figure 3 Dependence of the η_{inh} values on the reaction time: (blue) polyhydrazide and (red) polythiohydrazide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ene sulfonic acid in NMP as the solvent. A mixture of DPH and urea was irradiated at 220 W for 7 min and then at 600 W for 10 min. After it was washed with hot water and methanol, the pure polyhydrazide was obtained at a 92% yield (Table I). The reaction could have been performed with different organic solvents, such as DMSO, chlorobenzene, dioxane, toluene, *N,N*-dimethyl acetamides (DMac's), NMP, and NMP containing 5%LiCl. The latter was chosen as the most proper solvent because of the greater solubility of the substrates, the higher reaction rate, and its excellent energy-transfer properties.

To optimize the reaction conditions, a series of reactions were carried out in this solvent with DPH as the model compound. Figure 1 shows the dependence of the polyhydrazide and polythiohydrazide η_{inh} 's on the microwave power in the reaction of DPH with urea or thiourea with NMP containing 5%LiCl as the solvent.

The dependence of the monomer concentration on η_{inh} of the final polyurea or thiourea was also studied (Fig. 2). As shown, the viscosity values of the resulting polymers decreased gradually with increasing amounts of NMP containing 5%LiCl in the polymerization reaction. However, when the amount of solvent was less than 50%, a partially gelled polymer was obtained. The dependence of the reaction time on the η_{inh} values of the final polyhydrazide or thiohydrazide was also studied (Fig. 3) to find that



Scheme 2 Pyrolysis of urea and formation of an isocyanate.

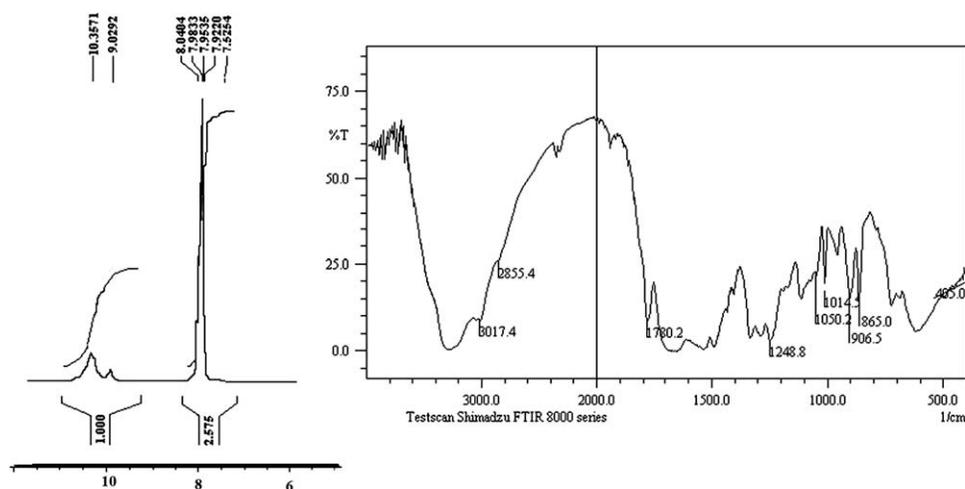


Figure 4 $^1\text{H-NMR}$ (in $\text{DMSO-}d_6$) and Fourier transform infrared (FTIR; KBr pellet) spectra of polyhydrazide **1a**.

increases in the irradiation time up to about 15 min increased the η_{inh} values; however, after this time (even up to 25 min), the viscosities remained almost constant. Increases in the reaction time up to 25 min in the case of aliphatic polymers resulted in the degradation of the polymers. Consequently, at lower viscosities, 600 W for 17 min in NMP containing 5%LiCl were, therefore, chosen as the optimized reaction conditions.

The polycondensation of aromatic dihydrazide with urea in the presence of a catalytic amount of *p*-toluene sulfonic acid in NMP containing 5%LiCl easily progressed under microwave conditions to afford polyhydrazide with the evolution of ammonia in high yields (Table I, entries **2a–2e**). Aliphatic dihydrazides were also rapidly and successfully converted to their corresponding polyhydrazides in good yields under similar reaction conditions. Furthermore, the usefulness of this method was also extended to the preparation of polythiohydrazides. The results show that interestingly, the reaction of thiourea with aromatic and aliphatic dihydrazides in the presence of a catalytic amount of *p*-toluene sulfonic acid in NMP containing 5%LiCl produced

polythiohydrazides in good yields (Table I, entries **2f–2j**). The viscosities of the polyhydrazides and polythiohydrazides showed that the polymerization in each case proceeded to an extent that yielded high-molecular-weight polymers.

As previously reported,^{13,14} this reaction might have proceeded by the pyrolysis of urea and the formation of an isocyanate and ammonia (Scheme 2).

This mechanism is true for thiocyanate formation, but the pyrolysis of thioureas needs more energy.

The new polymers (**2a–2j**) were prepared in excellent yields. Elemental analysis and IR spectroscopy were used for the structural characterization of the polyhydrazides and polythiohydrazides. Because the IR spectra had comparable structures, they displayed the same pattern with the characteristic absorption around $3195\text{--}3308\text{ cm}^{-1}$ with N–H bands and $1640\text{--}1670\text{ cm}^{-1}$ for the carbonyl groups. The C–N stretching frequency was absorbed at 1240 ± 10 for all of the polyhydrazides (Figs. 4 and 5).

These polymers were also characterized by $^1\text{H-NMR}$ spectroscopy in $\text{DMSO-}d_6$. All of the

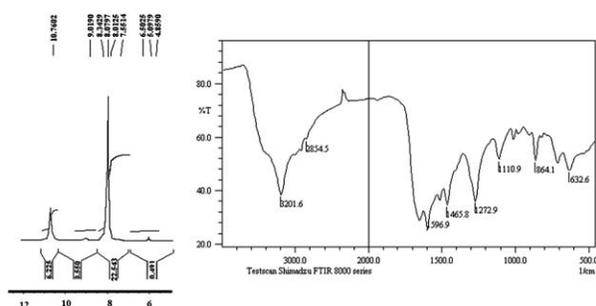


Figure 5 $^1\text{H-NMR}$ (in $\text{DMSO-}d_6$) and Fourier transform infrared (FTIR; KBr pellet) spectra of polythiohydrazide **1f**.

TABLE II
Solubility of the Polyhydrazides and Polythiohydrazides

| Polymer | <i>m</i> -Cresol | DMF | DMSO | DMAc | NMP | Pyridine |
|-----------|------------------|-----|------|------|-----|----------|
| 2a | ± | + | + | + | + | ± |
| 2b | + | + | + | + | + | + |
| 2c | ± | + | + | + | + | ± |
| 2d | + | + | + | + | + | + |
| 2e | + | + | + | + | + | + |
| 2f | ± | + | + | + | + | ± |
| 2g | + | + | + | + | + | + |
| 2h | ± | + | + | + | + | ± |
| 2i | + | + | + | + | + | + |
| 2j | + | + | + | + | + | + |

+, Soluble at room temperature; ±, soluble on heating; DMF, *N,N'*-dimethylformamide.

TABLE III
Thermal Behavior of the Polyhydrazides and Polythiohydrazides

| Polymer | DSC | TGA | | |
|---------|--|-------------------------|------------------------------|-----------------------------|
| | glass-transition temperature (°C) ^a | T_i (°C) ^b | $T_{10\%}$ (°C) ^c | Char yield (%) ^d |
| 2a | 198 | 288 | 339 | 21 |
| 2b | 190 | 280 | 325 | 21 |
| 2c | 195 | 285 | 333 | 18 |
| 2d | 172 | 247 | 300 | 13 |
| 2e | 165 | 240 | 293 | 13 |
| 2f | 202 | 284 | 347 | 23 |
| 2g | 193 | 278 | 333 | 21 |
| 2h | 198 | 285 | 344 | 19 |
| 2i | 175 | 255 | 306 | 15 |
| 2j | 168 | 244 | 298 | 14 |

^a From the second heating traces of the DSC measurements conducted with a heating rate of 10°C/min.

^b Initial decomposition temperature recorded at a heating rate of 10°C/min.

^c $T_{10\%}$ was recorded by TGA at a heating rate of 10°C/min under a nitrogen atmosphere.

^d Char yield in TGA at 800°C under a nitrogen atmosphere.

polyhydrazides showed two peaks in the region $\delta = 10.17\text{--}10.65$ ppm; these were assigned to the hydrogen of NH in the ¹H-NMR spectra of the polymers (Fig. 4). In the case of polythiohydrazide, these peaks were observed in the region 10.66–10.79 ppm (Fig. 5). The peak observed at 7.50–8.60 ppm was also ascribed to the aromatic protons.

It seemed that in this method, less crosslinking took place, and the linear polymers obtained possessed better solubility than the analogous polymers because of the low reactivity of the substance and the mechanism used. Table II lists the solubility behavior of the polymers. All of the polymers were readily soluble in a wide range of solvents, including DMAc, DMF, DMSO, and NMP. Most of the polymers were even soluble in *m*-cresol and pyridine. The polythiohydrazides were more soluble with a shorter time needed for their complete dissolution in the solvents.

The η_{inh} values of the polyhydrazides and polythiohydrazide were in the ranges 0.20–0.52 and 0.19–0.50 dL/g, respectively. Wholly aromatic polymers had a higher η_{inh} . Also, para-substituted polymers had a higher η_{inh} than the meta-substituted ones. The viscosities of the polymers showed that the polymerization proceeded completely to yield high-molecular-weight polymers.

The most important and yet the least reliable factor in the study of heat-stable polymers is the measurement or evaluation of their thermal stability. Numerous methods are used, and no two can be directly compared in all cases. TGA and DSC were

used to investigate the thermal properties of the polymers in this study. The results are summarized in Table III.

Differential thermograms of the polyhydrazides and polythiohydrazides were recorded in N₂. All of the polymers decomposed at temperatures between 240 and 288°C, as shown in Table III. Initial weight losses commenced only after 249°C. The temperature corresponding to the 10% weight loss ($T_{10\%}$) at a heating rate of 10°C/min fell between 293 and 347°C. A two-step degradation was observed in most cases; the first decomposition was due to the conversion of the polyhydrazide or polythiohydrazide to polyoxadiazole or polythiooxadiazole, and the second was due to the decomposition of the polymer chain. The 10% weight loss, which was taken as a measure of thermal stability, occurred above 293°C.

CONCLUSIONS

In summary, the proposed microwave-assisted procedure provided an efficient and very simple methodology for the preparation of soluble polyhydrazides and polythiohydrazides with urea and thioureas as very cheap and safe substances with good yields. Compared to the conventional thermal method, microwave irradiation decreased the reaction time and simplified the workup procedure. Because of the simplicity and generality of this method, we believe that the procedure will be a useful addition to the polycondensation reaction for the preparation of polyhydrazides and polythiohydrazides.

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