

Synthesis of Polyamides from Substituted Fluorene and Diamides in the Presence of a Copper(I) Catalyst

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Received 26 May 2008; accepted 30 July 2008

DOI 10.1002/app.29011

Published online 30 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: 2,7-Dibromo-9,9-dioctylfluorene was synthesized by a two-step reaction from fluorene and *n*-octylboronide. This was reacted with benzamide for the preparation of a model compound and with terephthalamide, isophthalamide, and adipamide for the preparation of polyamides in the presence of a mixture of 10 mol % CuI and 20 mol % *N,N'*-dimethylethylenediamine as a catalyst and K_2CO_3 as a base. The monomer and the model compound were characterized with Fourier transform infrared, proton nuclear magnetic resonance, and elemental analysis. The prepared polyamides were characterized with Fourier transform infrared, proton nuclear magnetic resonance, differential scanning calorimetry, thermogravimetric analysis, and solu-

bility and viscosity measurements. The obtained polyamides possessed excellent solubility in common organic solvents, and they exhibited inherent viscosities in the range of 0.93–1.19 dL/g. According to the differential scanning calorimetry analysis, the glass-transition temperatures of the polyamides were in the range of 84–154°C. Thermogravimetric analysis indicated that a 2% weight loss of the polyamides occurred in the temperature range of 218–253°C under a nitrogen atmosphere. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1588–1593, 2009

Key words: polyamides; thermal properties; polycondensation; solubility

INTRODUCTION

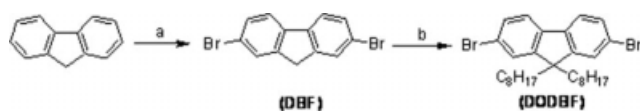
High-performance polyamides are an important class of polymers, and their applications are growing steadily. In the last few decades, thermally stable polymers have received extensive interest because of the increasing demands for high-temperature polymers as replacements for metals or ceramics in the automotive, aerospace, and microelectronics industries. Aromatic polyimides and polyamides (aramids) are certainly two of the most successful classes of high-temperature polymers. They possess thermal stability, chemical resistance, low flammability, and excellent mechanical properties.^{1–6} However, it is difficult for aramids to be used as thin films and coatings because of their low solubility and high melting temperature (T_m) and glass-transition temperature (T_g) values. To obtain different properties and for different applications, various structural changes have been introduced into the aramid backbone.^{7–15} The introduction of a flexible bond into the rigid polymer backbone is known to be an effective method for enhancing the solubility and also lowering T_g and T_m of these rigid polymers while minimizing the deterioration of their physical properties.^{16–18} Another conventional approach to

increasing the solubility is the introduction of bulky pendant groups into the polymer backbone.^{19–25} This modification lowers T_m and produces soluble and amorphous polymers.

Transition-metal-catalyzed C(aryl)–N bond forming processes play an important role in organic synthesis. Transition-metal-catalyzed cross-coupling of amides with aryl halides provides a straightforward route to *N*-arylamides. To date, catalysts based on several transition metals have been examined for the *N*-arylation of amides. One example is Pd, which often requires the use of expensive, unstable, and poisonous compounds, such as phosphine ligands. Removal of palladium residues from polar reaction products can also be challenging. In recent years, there have been many reports focused on the deliberate use of ligands to facilitate the copper-catalyzed aryl amidation reaction.^{26,27} Buchwald and coworkers^{27–29} developed a general, mild, and experimentally simple method for the amidation of aryl halides by using inexpensive and air-stable copper(I) iodide and *N,N'*-dimethylated 1,2-diamine ligands as precatalysts.

Polyamides are usually synthesized with common methods such as the polycondensation of dicarboxylic acids or diacid chlorides with diamines. For the first time, we have developed the aforementioned amidation method to prepare new polyamides by using the copper-catalyzed coupling of 9,9-dioctyl-2,7-dibromofluorene with different amides in the presence of K_2CO_3 as a base and CuI and *N,N'*-

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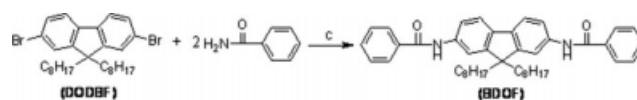
Scheme 1 Preparation of 9,9-dioctyl-2,7-dibromofluorene (a: Br₂, CH₃Cl, room temperature, 2 h; b: 1-bromohexane, triethylbenzylammonium chloride, DMSO, NaOH 50%, room temperature, 5 h).

dimethylethylenediamine (DMEDA) as catalysts. The polyamides have been fully characterized with Fourier transform infrared (FTIR), proton nuclear magnetic resonance (¹H-NMR), elemental analysis, and viscosity, solubility, and thermal stability measurements.

EXPERIMENTAL

Apparatus

IR spectra were recorded with a Bruker (USA) Vector 22 FTIR apparatus. ¹H-NMR and ¹³C-NMR spectra were obtained with a Bruker DRX 500 MHz Advance instrument and with CDCl₃ and deuterated dimethyl sulfoxide (DMSO-*d*₆) as solvents. Elemental analysis was carried out with a Leco (UK) CHN-600 elemental analyzer, and the melting point was measured with a Branstead Electrothermal Engineering (Germany) 9200 apparatus. Inherent viscosities (at a concentration of 0.5 g/dL) were measured in an Ubbelohde suspended-level viscometer at 25°C with *N,N*-dimethylformamide (DMF) as a solvent. Thermogravimetric analysis (TGA) in the temperature range of 50–600°C was carried out with a DuPont (USA) TGA 951 analyzer at a heating rate of 10°C/min under a nitrogen atmosphere (20 cm³/min). Differential scanning calorimetry (DSC) thermograms



Scheme 2 Preparation of model compound BDOF (c: CuI, DMEDA, K₂CO₃, toluene, under argon, at 110–115°C, 9 h).

were recorded with a PerkinElmer Pyris 6 differential scanning calorimeter under a nitrogen atmosphere (20 cm³/min) at a heating rate of 10°C/min.

Materials

All chemicals were purchased from either Merck or Fluka Co. (Germany). 2,7-Dibromo-9,9-dioctylfluorene was synthesized according to the procedure reported in the literature^{30,31} (Scheme 1). Terephthalamide, isophthalamide, and adipamide were prepared according to the procedure reported in the literature³² from relative diacid chlorides (terephthaloyl chloride, isophthaloyl chloride, and adipoyl chloride, respectively) and an ammonium solution at 0°C. DMF was purified by distillation over calcium hydride under reduced pressure. Toluene was purified by distillation over sodium. All other materials were used without further purification.

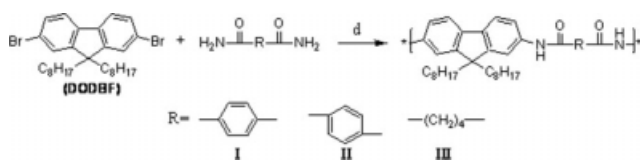
Synthesis

Preparation of model compound 2,7-bis(*N*-benzamido)-9,9-dioctylfluorene (BDOF)

A 25-mL two-necked flask equipped with a magnetic stirrer, a condenser, and an argon inlet/outlet tube was charged with CuI (0.0192 g, 0.1 mmol, 10 mol %), 9,9-dioctyl-2,7-dibromofluorene (0.274 g, 0.5 mmol), benzamide (0.151 g, 1.25 mmol), and K₂CO₃ (0.28 g, 2.03 mmol). The flask was briefly evacuated and

TABLE I
Yields, Spectroscopic Data, and Elemental Analysis

Polyamide code	Yield (%)	¹ H-NMR [δ (ppm)]	FTIR [ν (cm ⁻¹)]	Elemental analysis					
				Calcd (%)			Found (%)		
				C	H	N	C	H	N
BDOF	95.5	10.50 (s, 2H), 7.99 (s, 2H) 7.91 (d, 2H), 7.69 (t, 2H) 7.63–7.48 (m, 8H), 1.97 (t, 4H), 1.32–1.05 (m, 20H), 0.82 (t, 6H), 0.67 (b, 4H)	3288, 3064, 2929 and 2852, 1647, 1605, 1536, 1470, 705	82.12	8.33	4.45	82.02	8.35	4.25
I	94.5	10.37 (s, 2H), 8.05–7.49 (m, 10H), 1.95 (b, 4H), 1.05 (b, 20H), 0.75–0.63 (b, 10H)	3327, 3065, 2920 and 2856, 1657, 1600, 1537, 1473, 720	80.69	8.42	5.09	80.75	8.31	5.05
II	91.2	10.47 (s, 2H), 8.64–8.49 (d, 1H), 8.18–8.11 (d, 3H), 7.88–7.52 (m, 6H), 1.93 (b, 4H), 1.04 (b, 20H), 0.75 (b, 6H), 0.63 (b, 4H)	3327, 3065, 2928 and 2855, 1659, 1596, 1537, 1471, 721	80.69	8.42	5.09	80.59	8.48	5.15
III	93.5	9.91 (s, 2H), 7.69–7.53 (m, 6H), 2.36–2.31 (d, 4H), 1.85 (b, 4H), 1.56 (b, 4H), 1.14–0.99 (b, 20H), 0.76 (b, 6H), 0.53 (b, 4H)	3306, 2933 and 2860, 1663, 1597, 1546, 1469, 717	79.20	9.49	5.28	79.12	9.40	5.21



Scheme 3 Preparation of polyamides **I**, **II**, and **III** (d: CuI, DMEDA, K_2CO_3 , DMF, under argon, at 110–115°C, 24 h).

backfilled with argon. DMEDA (0.021 mL, 2 mmol) and toluene (5 mL) were added to the mixture under argon. The reaction mixture was stirred at 110–115°C for 9 h. The resulting bright yellow suspension was allowed to reach room temperature and then filtered through a $0.5 \times 1 \text{ cm}^2$ pad of silica gel eluting with 1 : 1 ethyl acetate/dichloromethane (10 mL). The filtrate was evaporated and then purified with column chromatography (SiO_2 , 1 : 4 ethyl acetate/dichloromethane). BDOF was a white, crystalline product with a yield of about 95.5% (0.30 g) and with a T_m value of 196–198°C. The reaction for the synthesis of the model compound is shown in Scheme 2.

General procedure for the preparation of the polyamides

A 50-mL, two-necked flask equipped with a magnetic stirrer, a condenser, and an argon inlet/outlet tube

was charged with CuI (0.076 g, 0.40 mmol, 10 mol %), 9,9-dioctyl-2,7-dibromofluorene (1.096 g, 2 mmol), diamide (terephthalamide, isophthalamide, and adipamide; 2.5 mmol), and K_2CO_3 (1.12 g, 8.12 mmol). The flask was briefly evacuated and backfilled with argon. DMEDA (0.086 mL, 0.80 mmol) and DMF (15 mL) were added to the mixture under argon. The reaction mixture was stirred at 110–115°C for 24 h. The resulting mixture was allowed to reach room temperature, diluted with 5 mL of DMF, and then filtered through a $0.5 \times 1 \text{ cm}^2$ pad of silica gel. The resulting solution was poured into 100 mL of water, and the product was filtered. This stringy polymer was purified with refluxing in methanol for 1 h and dried *in vacuo* at 100°C. The yields, elemental analysis data, and spectroscopy data of the polyamides are shown in Table I. The reaction for the synthesis of the polyamides is shown in Scheme 3.

RESULTS AND DISCUSSION

In this article, we report a new method for the synthesis of soluble and thermally stable polyamides from 9,9-dioctyl-2,7-dibromofluorene and diamides as monomers. In this catalytic amidation method, the polyamides were prepared with inexpensive and

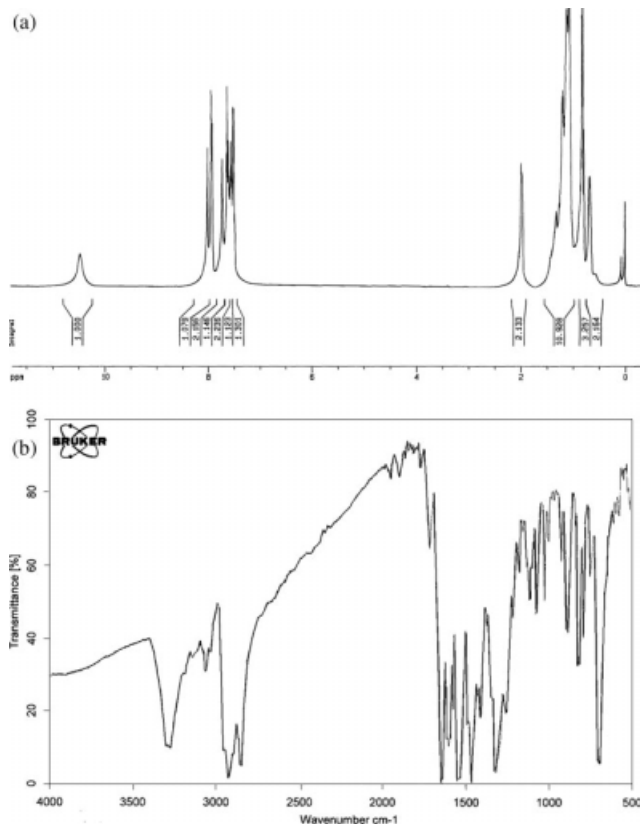


Figure 1 (a) 1H -NMR and (b) FTIR spectra of model compound BDOF.

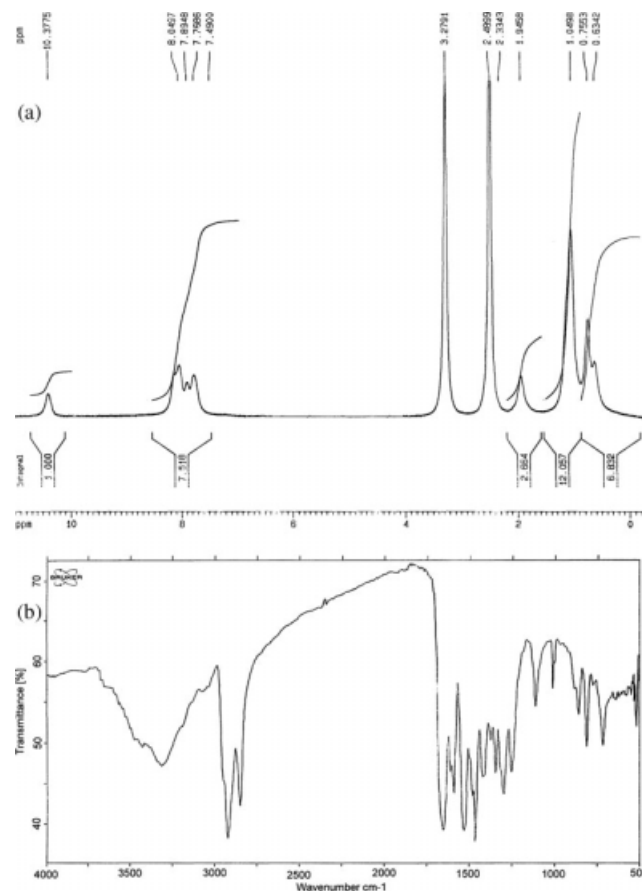


Figure 2 (a) 1H -NMR and (b) FTIR spectra of polyamide I.

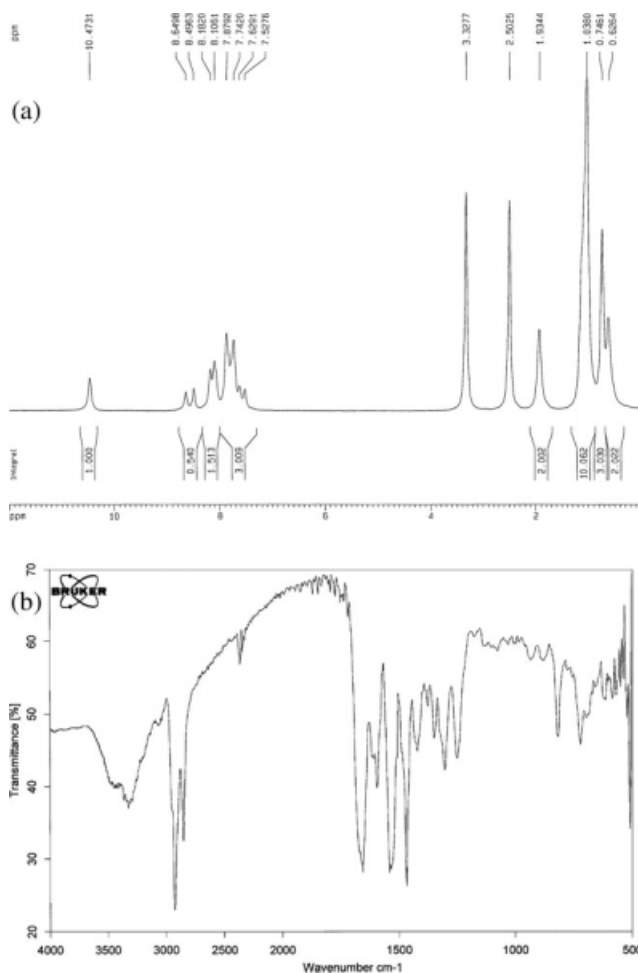


Figure 3 (a) $^1\text{H-NMR}$ and (b) FTIR spectra of polyamide II.

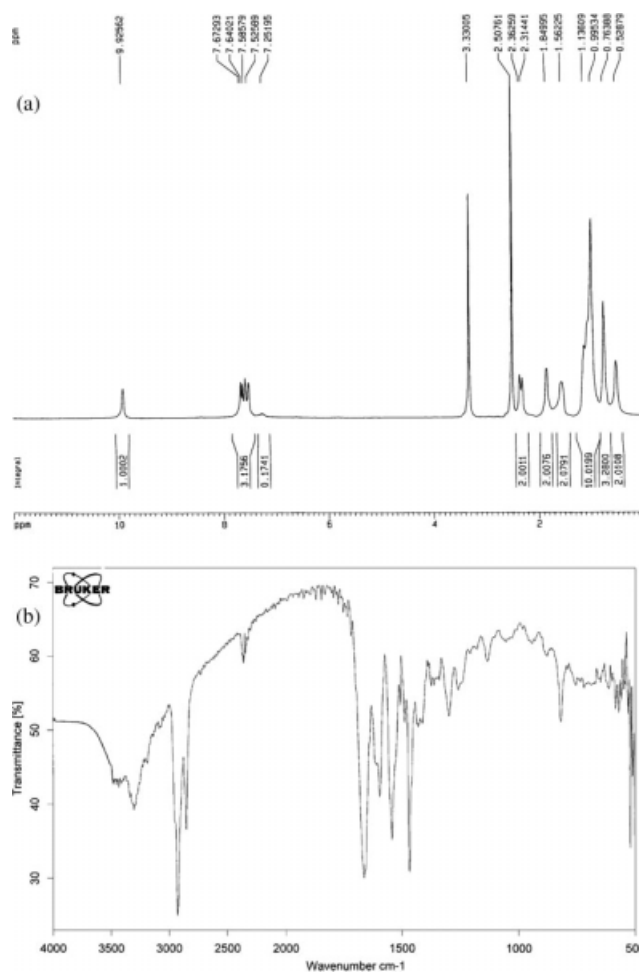


Figure 4 (a) $^1\text{H-NMR}$ and (b) FTIR spectra of polyamide III.

air-stable copper(I) iodide and DMEDA ligand as the precatalyst.

9,9-Dioctyl-2,7-dibromofluorene was synthesized in two steps according to a procedure described in the literature,^{30,31} and this is shown in Scheme 1. 9,9-Dioctyl-2,7-dibromofluorene was used as a starting material for the preparation of the model compound in a reaction with benzamide. The structure of the model compound was confirmed by common spectroscopic methods such as FTIR, $^1\text{H-NMR}$, and elemental analysis. The FTIR spectra of the model compound showed characteristic peaks at 3288

(related to NH stretching), 3064 (related to aromatic C—H stretching), 2929 and 2852 (related to aliphatic C—H stretching), 1647 (related to C=O), 1605 and 1470 (related to aromatic C=C), and 705 cm^{-1} (related to out-of-plane deformation of —C=O). The $^1\text{H-NMR}$ spectra showed the characteristic signal of amidic protons at 10.50 ppm. The elemental analysis results and the characteristic peaks of the spectroscopic methods are listed in Table I. FTIR and $^1\text{H-NMR}$ spectra are shown in Figure 1(a,b).

Polyamides were prepared in good yields by a reaction between 9,9-dioctyl-2,7-dibromofluorene

TABLE II
Inherent Viscosity and Solubility of the Polyamides

Polyamide code	Inherent viscosity (dL/g)	DMAC	DMF	NMP	DMSO	HMPA	DO	PY	THF	CCl_4
I	1.19	++	++	++	+h	++	++	++	++	±
II	0.96	++	++	++	++	++	++	++	++	+h
III	0.93	++	++	++	+h	++	++	++	++	+h

++ = soluble at room temperature; +h = soluble after heating (60°C); ± = partially soluble; DMAC = *N,N*-dimethylacetamide; DO = dioxane; HMPA = hexamethyl phosphor amide; NMP = *N*-methyl pyrrolidone; PY = pyridine; THF = tetrahydrofuran.

TABLE III
Thermal Data

Polyamide code	T_g (°C)	T_2 (°C)	T_5 (°C)	T_{10} (°C)	T_{max} (°C)	Char yield at 700°C (%) ^a
I	154.6	253	360	405	461	40.79
II	134.3	239	358	404	446	38.31
III	84.5	218	305	350	438	33.96

T_2 = temperature for 2% weight loss; T_5 = temperature for 5% weight loss; T_{10} = temperature for 10% weight loss; T_{max} = maximum decomposition temperature.

^a The weight of the polymer that remained at 700°C.

and diamides. The structure of the synthesized polyamides was confirmed by elemental analysis and spectroscopic methods. The presence of amidic bands at ≈ 3320 (related to N–H stretching), ≈ 1655 (related to C=O stretching), and ≈ 720 cm^{-1} (related to out-of-plane deformation of –C=O) in the FTIR spectra and also amidic protons at ≈ 10.50 ppm (for polyamides derived from aromatic amides) and at 9.91 ppm (for that derived from the aliphatic amide) in the $^1\text{H-NMR}$ spectra confirmed the amidic structure of the polyamides. The yields, the elemental analysis results, and the characteristic peaks of the spectroscopic methods are listed in Table I. FTIR and $^1\text{H-NMR}$ spectra are shown in Figures 2(a,b)–4(a,b).

One of the major objectives of this study was to produce modified polyamides with improved solubility. As shown in Table II, the polyamides were readily soluble in common polar aprotic solvents. This might be due to the presence of dioctyl groups at the 9-position. Among these polyamides, **III** (the polyamide derived from the aliphatic amide) was more soluble in common solvents, and a shorter time was needed for its complete dissolution. For this polyamide, the presence of methylene groups increased flexibility and also disturbed the planarity of aromatic units, which reduced the close packing and the

crystallinity. However, polyamides **I** and **II**, derived from aromatic amides, contained rigid phenylene groups that reduced the flexibility of the chain and increased close packing of the chains, and thus the solubility time increased. The inherent viscosity of the polymers, a suitable criterion for an evaluation of the molecular weight, was measured at a concentration of 0.5 g/dL in DMF at 25°C. The inherent viscosities were in the range of 0.93–1.19 dL/g, which indicated moderate molecular weights (Table II).

The thermal properties of the polyamides were evaluated with DSC and TGA. Polyamides **I**, **II**, and **III** showed T_g values of 154, 134, and 84°C, respectively. The decreasing trend of T_g was comparable to the decreasing order of stiffness and polarity of the polymer backbone. Lower T_g values of polymer **III** were mainly due to the incorporation of aliphatic groups into the polymer backbone. None of the polyamides showed clear melting endotherms in the DSC thermograms. This can be attributed to the amorphous nature of the polyamides. The obtained results are collected in Table III, and the representative DSC curves are shown in Figure 5.

The thermal stabilities of the polyamides were evaluated by TGA in a nitrogen atmosphere at the heating rate of 10°C/min. The 2% decomposition temperatures of the polyamides were about 218–253°C,

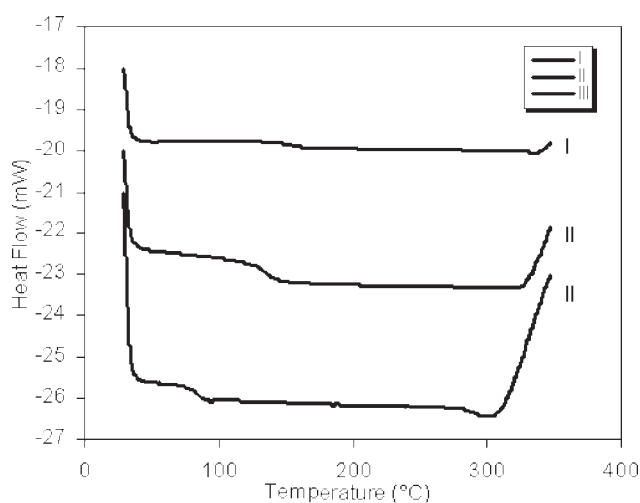


Figure 5 DSC curves of polyamides **I**, **II**, and **III**.

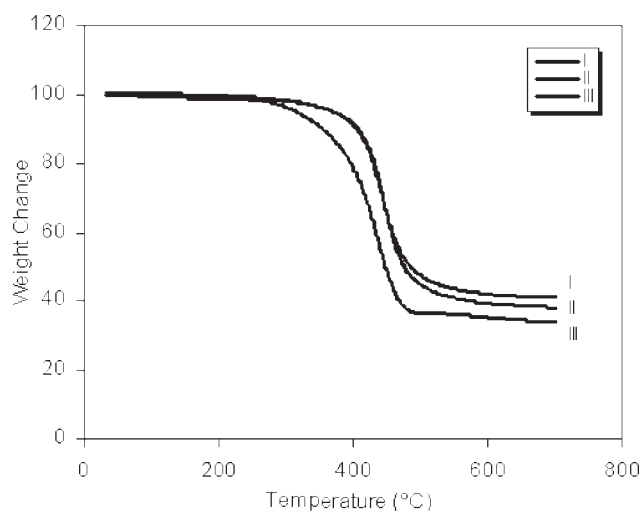


Figure 6 TGA curves of polyamides **I**, **II**, and **III**.

and the temperatures for 10% weight loss, important criteria for the evaluation of the thermal stability, were in the range of 350–405°C. The char yields of the polymers at 700°C were about 34–41%, which indicated good thermal stability. According to the obtained results, the polyamides showed suitable thermal stability, and those with a fully aromatic backbone were more stable than that with a semi-aromatic backbone; this confirmed that the incorporation of the thermostable phenylene group into the main chain of the aromatic backbone polyamides improved the thermal stability of these polymers. The obtained results are collected in Table III, and representative TGA curves are shown in Figure 6.

CONCLUSIONS

We have successfully developed a general, simple, and efficient method for the synthesis of polyamides from diamides and an aromatic dihalide. A noteworthy advantage of this reaction is that we can synthesize soluble thermostable polyamides without using diacid or diacid chloride, the synthesis and purification of which are usually difficult. The synthesized polyamides possessed T_g values in the range of 84–154°C, which depended on the stiffness of the polymer chain, and very good thermal stability with no significant weight loss up to 350–405°C. Also, the char yields of the polymers at 700°C (ca. 34–41%) indicated their good thermal stability. The resulting polyamides showed excellent solubility in various organic solvents because of the presence of dioctyl groups at the 9-position as side chains. The inherent viscosity of the polyamides was in the range 0.93–1.19 dL/g, which indicated moderate molecular weights.

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