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Synthesis and Characterization of Polyamide Containing Maleimide Pendant Group

Amir Abdolmaleki[*1,2], **Parvin Pashaie**[1]

[1]*Department of Chemistry, Isfahan University of Technology, Isfahan, Iran.*
[2]*Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, Isfahan, Iran.*

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Abstract

A series of new polyamides containing maleimide pendant group were prepared by low temperature polycondensation of 5-(4-(2,5-dioxo-2H-pyrrol-1(5H)-yl)benzamido)isophthaloyl chloride as a new monomer with various aromatic diamines in NMP. Monomer and polymers structures were identified through FT-IR, 1H-NMR and elemental analysis. Obtained polymers were soluble in polar solvents and non soluble in aprotic solvents. The inherent viscosities of the polymers have been determined in NMP and had values from 0.35 to 0.39 dL/g. Thermal stability of polymers was investigated with thermal gravimetry analysis (TGA) and diffraction scanning calorimetry (DSC). Also thermal behavior of monomer was studied with DSC analysis. X-ray diffraction measurement was used to indicate amorphous structure of polyamide.

Key words: *Maleimide pendant group, Polyamide, Thermal properties, High performance polymer.*

Introduction

Aromatic polymers are well known as high performance materials with outstanding thermal stability, good chemical resistance and excellent mechanical properties. Aromatic polyamides are a very important class of high performance polymers in various applications requiring high thermal, mechanical and electrical characteristics because of their unique mechanical properties, and thermal stability [1-3]. There are many different modifications for enhance polymer's processing, solubility, flexibility and thermal stability with bulky substituent as pendant group in polymer back bone [4]. The positive proceed for modifying the properties of polyamides is the introduction of aromatic or heterocyclic rings into the polymer backbone.

Bismaleimides (BMI) is one of the most

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[*] ***Corresponding author:*** *Amir Abdolmaleki, Department of Chemistry, Isfahan University of Technology, P. O. Box: 84156-83111, Isfahan, Iran. E-mail: abdolmaleki@cc.iut.ac.ir, Tel.: +98 3113912351; fax: +98 3113912350.*

interesting compounds, which can be self-polymerized through double bond of maleimides that makes high crosslinked, dense and brittle polymers with poor solubility and processability [2, 3]. Hence, modification of BMI has an active research field [4-7] to improve processing characteristic [8,9] and thermomechanical properties [10] by reduction of crosslinking and brittleness in polymer's structure. One of the most important pathway; is Michael addition reaction of BMI [13, 14] with different nucleophilic compounds such as amines [8, 12, 15-19] to produce polyaspartimides, and also thiols [20-23] to obtain polymer with biochemistry applications.

The peculiar polymerization characteristics of electron-deficient maleimide group make it an attractive monomer for designing special polymers and so many other compounds [27-30]. Also it is known to form alternating copolymers with electron rich monomers. Polymers containing maleimide group in polymeric backbone and as pendant group, are an important type of thermoset polymeric materials that have found wide applications ranging from microelectronics to aerospace due to their good processability, high glass transition temperature and interesting optical properties [31-33].

Maleimide group in polymer and other materials such as pendant group, have many applications like being useful electrophile to attacked by thiols in thiol-maleimide conjugation strategy [34, 35], Au nano particle [36] having a useful reaction in drug delivery and successful utilization of maleimide as a reagent for the chemical modification of protein [37]. Also, maleimide containing compounds are a widely utilized class of substrates employed in chemical and biological applications due to their reactivity in Michael-addition reactions and their dienophilic nature [38]. In contrast to ionic and coordination polymerization, maleimide is tolerant for many functionalities they have been incorporated into monomers and building polymer chains by the groups that used for orthogonal and robust chemistry such as "click", epoxy transformation, thiol-ene reaction, reversible multiple hydrogen bonding and many others [39].

Thermal stability is affected by the chemical structure of the polymer backbone as well as the pendent groups. The maleimide structure has been introduced into many polymeric systems aiming to improve thermal stability and Tg. There is some report [40-42] on cross-linkable polyamides having reactive maleimide and phthalimide groups. Curable polyamides possessing pendent enaminonitrile groups were reported by Kim et al [43-45]. Cross-linked polyamides showed an improving thermal stability. However, cross-linked polyamides lost fabrication ability and showed high brittleness and rigidity. In this study some new polyamide are synthesized in which polymer backbones have a maleimide pendant group and are able to be crosslinkable polyamides, which can be processed into thin films and other forms and then thermally or photochemically cross- linked.

Experimental

Materials

5-Aminoisophthalic acid and maleic anhydride were purchased from Fluka. *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP) and Triethylamine (TEA) were purchased from Merck and distilled under reduced pressure after dehydration with BaO. Other chemical reagents were used as received.

Characterization

FT-IR spectra were recorded on JASCO-680 spectrophotometer through using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). All melting points were taken with a Gallenham melting point apparatus. ^1H-NMR and ^{13}C-NMR spectra were recorded with a Bruker, Avance 400 and 500 MHz instrument in DMSO-d_6. Multiplicities of proton resonance were designed as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), and multiplet (m). Inherent viscosities were measured by a standard procedure using a routine Cannon–Fensk viscometer. Thermal gravimetric analysis (TGA) data for polymers was taken on a Perkin-Elmer thermal gravimetry analyzer (STA503 win Ta) using a heating rate of 10 °C /min in N_2 within the temperature range of 50-800 °C. Elemental analysis was performed with CHNS-932, Leco instrument. Differential scanning calorimetry (Perkin-Elmer DSC-7) was made at a scan rate of 10 °C/min under nitrogen atmosphere. Also, the X-ray diffraction patterns were recorded by using a Philips Xpert MPD diffractometer equipped with a Cu Kα anode ($\lambda = 1.51418$ Å).

Synthesis of 4-maleimidobenzoic acid

2.740 g (0.02 mol) of 4-amino benzoic acid was dissolved completely in (12 mL) acetone and then a solution of 1.60 g (0.021 mol) maleic anhydride in (8 mL) acetone was gradually added to the mixture. The yellow precipitate was obtained immediately. Suspension was stirred for 4 hours at room temperature and then filtered off and washed with acetone. Obtained amic acid was recrystalized from DMF/ Ethanol (1/1, wt/wt) solution and dried in vaccum. Yield: 86%, m.p. : 242-244 ºC , Lit; m.p. : 244-246 °C [46].

For cyclodehydration, the amic acid with 0.54 g of sodium acetate and acetic anhydride (6 mL) in DMF (3 mL) was heated for 4 hours at 65 °C. The resulting solution was poured into the water and yellow precipitate was collected, washed with water and dried in vacuum. Yield: 85%, m.p. : 232-234 ºC, Lit; m.p. : 234-236 °C [24]; FT-IR (KBr, cm^{-1}): υ= 3476-2961 (COOH), 1775 and 1710 (C=O imide group), 1398-1381 (C–N–C), 760-700 cm^{-1} (N–C=O), and 667 cm^{-1} (=C–H, OOP).

Synthesis of 4-maleimidobenzoyl chloride

In 50 mL round bottom flask, 5 mmol of 4-maleimidobenzoic acid was dissolved in 2 mL of toluene with 2 drops of dry DMF, and then 5 mL of thionyl chloride was added. The mixture was refluxed for 4 hours. Excess thionyl chloride was removed by distillation after reaction completion. The yellow powder was dried under N2 atmosphere. Yield: 100%, m.p.: 164-168 oC. Lit; m.p. : 166-169 ^{o}C [46]; FT-IR (KBr, cm^{-1}): υ= 1775 and 1710 (C=O imide ring), 1395 (C=C) and 667 (=C–H, OOP).

Synthesis of 5-(4-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)benzamido)isophthalic acid

1.5 mmol (0.271 g) of 5-aminoisophthalic acid was added into a 25 mL round bottom flask and completely dissolved in NMP and then 1.5 mmol (0.352 g) of 4-maleimidobenzoyl chloride was added gradually with constant stirring. The mixture was stirred for 2 hours at 0^{o}C and 2 hours at room temperature. The viscose solution was poured into methanol to precipitate yellowish powder. The product was filtered, washed with methanol and dried under reduced pressure at 60 oC. Yield: 80%; m.p. >300 ^{o}C (decomposed at 305 ^{o}C).

FT-IR (KBr, cm^{-1}): υ= 3381 (COOH), 3361(N–H amide group), 3100 (=C–H), 1775 and 1719 (C=O imide groups), 1667 (C=O amide groups), 1380 (C–N), 676 (=C–H, OOP). ^{1}H-NMR(500 MHz, DMSO-d_6): δ = 13.23 (1H, s, H-1); 10.62 (1H, s); 8.64 (2H, s); 8.18 (1H, s); 8.08-8.06 (2H, d, *J*=8.35 Hz); 7.51-7.50 (2H, d, H-6, *J*=8.35 Hz); 7.20 (2H, s) ppm; ^{13}C-NMR (400MHz, DMSO-d_6): δ = 170.09 (C=O, acid); 166.96 (C=O, amid); 165.64 (C=O, maleimide ring); 140.25 (CH aromatic); 135.33 (C=C, vinyl group); 135.11 (CH aromatic); 133.73 (CH aromatic); 132.14 (CH aromatic); 128.88 (CH aromatic); 126.68 (CH aromatic); 125.50 (CH aromatic); 125.16 (CH aromatic) ppm; Elemental analysis, Calculated: C, 60.00%; H, 3.18%; N, 7.37%. Found: C, 59.92%; H, 3.27%; N, 7.22%.

Synthesis of 5-(4-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)benzamido)isophthaloyl chloride

In order to prepare the acyl chloride of synthetic monomer, 0.55 mmol (0.210 g) of diacid monomer, 1.5 mL dichloromethane, 1.5 mL $SOCl_2$ and 2 drops of dry DMF were charged into a 25 mL round bottom flask. The temperature of the reaction mixture was raised to 60 ^{o}C and stirred for 10 hours. Then excess of thionyl chloride was removed with distillation and residual powder was dried under N2 atmosphere. Yield: 92%. FT-IR (KBr, cm^{-1}): υ= 1779 (C=O imide groups), 1727 (C=O amide groups), 1392 (C–N), 668 (=C–H, OOP).

Synthesis of polyamides

Into a 25 mL round-bottom flask, 2.1 mmol (0.09 g) of diacid chloride monomer was gradually added to the solution of 2 drops of dry TEA and 2 mmol (0.049 g) of 4,4’-diaminodiphenyl sulfone that was dissolved in NMP (1 mL) and mixture was stirred at 0 °C for 3 hours. Then solution was poured into methanol (50 mL) to precipitate yellow powder that was filtered and dried under reduced pressure at 60 °C. Yield: 97%, decomposed at >300 °C. The inherent viscosity of the PA1 was 0.39 dL/g measured in NMP at a concentration of 0.5 g/dL at 25 °C. FT-IR (KBr, cm^{-1}): υ = 3434 (N–H), 1734 and 1653 (C=O), 1399 (C–N–C stretching), 691cm^{-1} (C=C stretching). 1H-NMR (DMSO-d_6) δ = 11-10.78 (2H, m, NH amide), 8.57 (2H, CH aromatic), 8.42 (1H, CH aromatic), 8.29-7.81 (8H, CH aromatic), 7.56-7.50 (4H, m, CH aromatic), 6.64-6.42 (2H, d, =C–H) ppm; Elemental analysis $(C_{31}H_{20}N_4O_7S)_n$ (592.58 $g/mol)_n$, Calculated: C, 62.83%; H, 3.40%; N, 9.45%; S, 5.41%. Found: C, 62.25%; H, 3.85%; N, 9.01%; S, 5.13%. Other polyamides were prepared by an analogous procedure.

PA2: Yield: 90%, η_{inh}= 0.35 dL/g; FT-IR (KBr, cm^{-1}): υ = 3420 (m, NH), 1734 and 1653 (C=O), 681 (=C–H, OOP); ^{1}H-NMR (DMSO-d_6) δ = 11.00-10.83 (3H, NH amid), 8.58 (2H, CH aromatic), 8.14-8.06 (4H, CH aromatic), 7.99 (1H, CH aromatic), 6.59 (2H, =C–H vinyl group) ppm; Elemental analysis $(C_{31}H_{20}N_4O_6)_n$ (544.51 g/mol)n; calculated: C, 68.38%; H, 3.70%; N, 10.29%. Found: C, 68.08%; H, 3.84%; N, 9.98%.

PA3: Yield: 83%, η_{inh}= 0.35 dL/g; FT-IR (KBr, cm^{-1}): υ = 3420 (NH amid), 1734 and 1653 (C=O), 681 (=C–H, OOP). ^{1}H-NMR (DMSO-d_6) δ = 11.16-10.73 (m, 3H, NH), 8.53-7.36 (15H, CH aromatic), 6.57 (w, 2H, HC=CH, vinylic) ppm; Elemental analysis $(C_{32}H_{20}N_4O_6)_n$ (556.52 g/mol)n; calculated: C, 69.02%; H, 3.62%; N, 10.07%. Found: C, 68.65%; H, 3.86%; N, 9.69%.

PA4: Yield: 90%, η_{inh}= 0.32 dL/g; FT-IR (KBr, cm^{-1}): υ= 3435 (m, NH amid), 1735 (m) and 1663 (s)(C=O), 671 (w, =C–H, OOP); Elemental analysis $(C_{33}H_{24}N_4O_5)_n$ (556.57 g/mol)n; calculated: C, 71.21%; H, 4.35%; N, 10.07%. Found: C, 71.08%; H, 4.49%; N, 9.93%.

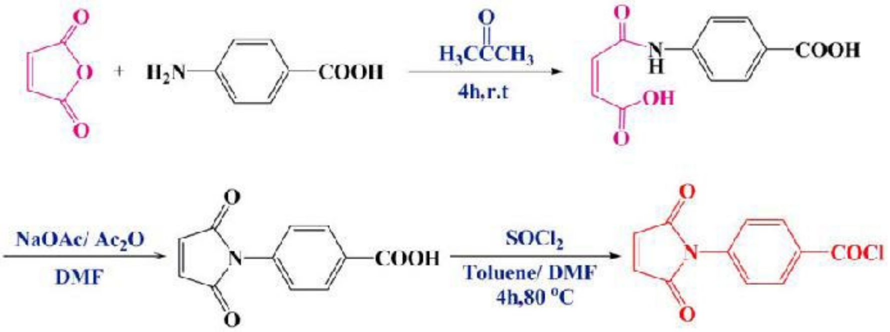
Results and discussion

Preparation of 4-maleimidobenzoic acid

To prepare 4-maleimidobenzoic acid, the amic acid synthesized from maleic anhydride and 4-aminobenzoic acid, was dehydrated. FT-IR analysis exhibits a broad peak in a range of 3476-2961 cm^{-1} due to acidic OH and peaks in 1775 cm^{-1} is due to stretching in plane and 1710 cm^{-1} out of plane of C=O groups. Stretching vibration of C–N–C band has absorption at 1398-1381 cm^{-1} and absorption at 760-700 cm^{-1} that is due to carbonyl group in imide ring and 667 cm^{-1} that is due to out of plane of =C–H vibration that confirms the formation of maleimide ring.

Preparation of 4-maleimidobenzoyl chloride

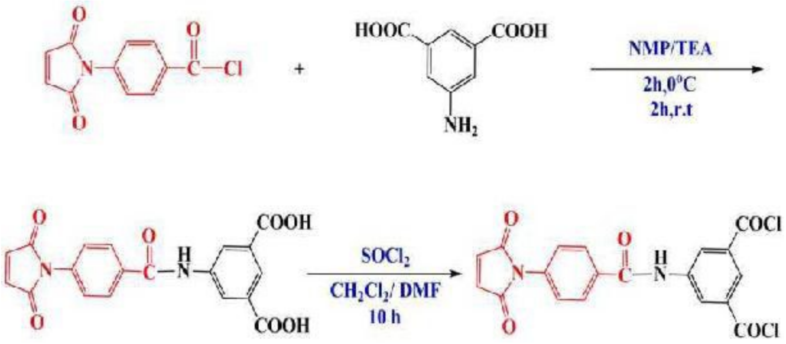
4-maleimidobenzoyl chloride was prepared from reaction between 4-maleimidobenzoic acid, thionyl chloride and DMF in toluene at 67 ºC (Scheme 1). In FT-IR, shift of C=O peak to 1778 cm^{-1} due to stretching of carbonyl from imide group in acyl chloride and disappearance of the peak in 2900-3400 cm^{-1}, confirms acyl chloride formation.



Scheme 1. Preparation of 4-maleimidobenzoyl chloride.

Characterization 5-(4-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)benzamido)isophthalic acid

Scheme 2 outlines the method to construct monomer synthesis. Characterization of monomer by FT-IR exhibits a broad peak at 2900-3400 cm^{-1} due to OH band and vibration stretching at 3413 cm^{-1} due to NH band in amid group. Symmetric and asymmetric vibrations of carbonyl groups have absorption peaks at 1719 and 1775 cm^{-1} respectively. Short and strong peak at 688 cm^{-1} is due to out of plane stretching of two cis hydrogen in maleimid ring. In ^{1}H-NMR spectrum of this monomer, a signal at 13.26 ppm is due to carboxylic hydrogens and 10.62 ppm is due to N–H group. Aromatic CHs introduced in monomer's structure from 4-maleimidobenzoyl chloride were appeared at 8.08-8.06 and 7.51-7.50 ppm. Also, vinylic hydrogens in maleimide ring were signaled at 7.20 ppm. The ^{13}C-NMR of monomer exhibited 11 peaks of various absorptions for aromatic carbons. Absorption peak at 170.09 ppm is assigned to carboxylic carbons and signals at 166.96 and 165.64 ppm were related to carbonyl groups of maleimide and amide groups, respectively. The vinylic carbons of maleimide ring were assigned at 140.25 ppm. The chemical structures of polymers were also verified from the elemental analysis result, and the data corresponded well with the calculated values (Table I).



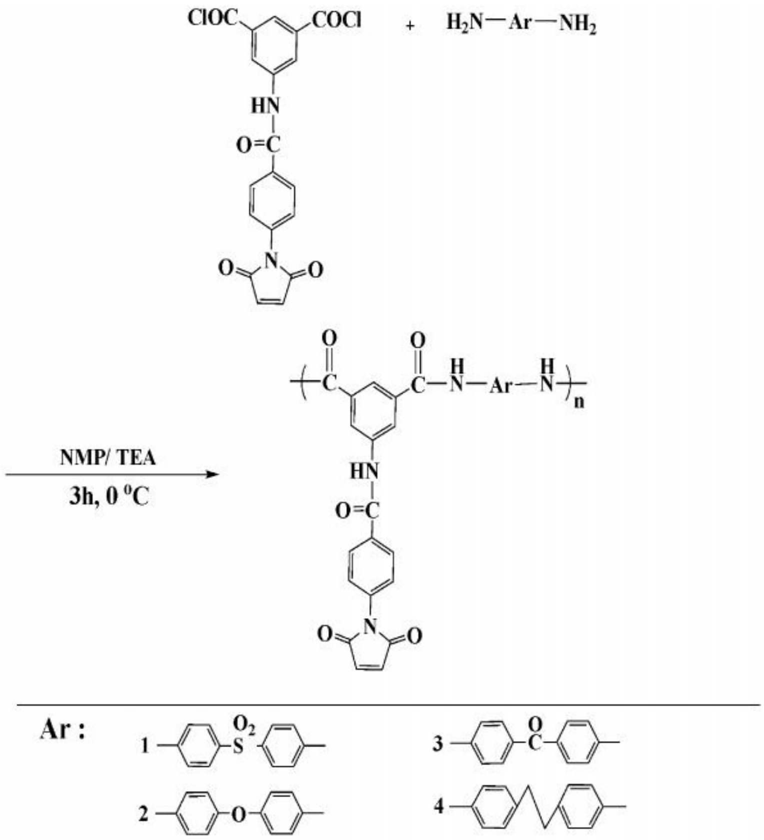
Scheme 2. Synthesis of monomer and acyl chloride of monomer.

Characterization of 5-(4-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)benzamido) isophthaloyl chloride

The acyl chloride of monomer was synthesized by thionyl chloride in dichloromethane. In FT-IR of acyl chloride, disappearing of broad peak at 2900-3400 cm^{-1} is due to elimination of OH and shift of carbonyl vibrational stretching to higher frequency indicates that acyl chloride was formed.

Preparation and characterization of polyamides with maleimide pendant group

Polyamides possessing maleimide pendent groups were obtained by conventional method starting from reaction of acyl chloride and various diamines as schematically presented in scheme 3. The structure of polyamides was confirmed by FT-IR, 1H-NMR and elemental analysis. The reaction yields and the inherent viscosities for all polyamides are listed in Table 2. FT-IR spectrum of PA1 shown absorption at 3400 cm^{-1} due to NH in amide group and asymmetric and symmetric stretching vibrations of the amide and imid carbonyl groups are represented at 1653 and 1734 cm^{-1} In 1H-NMR spectrum of **PA1** (Figure 1), protons of amide groups were assigned at 11.16-10.78 ppm that shaped short broad peak. Various aromatic hydrogens were assigned in the range of 8.57-7.50 ppm and two hydrogens of vinyl group in maleimide ring were assigned as doublet at 6.64-6.42 ppm. Also, elemental analysis data for the **PA1** and **PA2** agree with the calculated values (Table 1).



Scheme 3. Preparation of polyamides (PA1-4).

Table 1. Elemental analysis data of polyamides (**PA1-4**).

		C (%)	H (%)	N (%)	S (%)
Monomer	Calculated	60.00	3.18	7.37	–
	Found	59.92	3.27	7.22	
PA1	Calculated	62.83	3.40	9.45	5.41
	Found	62.25	3.85	9.01	5.13
PA2	Calculated	69.02	3.62	10.07	–
	Found	68.65	3.86	9.69	

Table 2. Characterization data of polyamides (**PA1-4**).

Polymer	Inherent viscosity η* (dL/g)	Yield (%)	Color
PA1	0.39	97.0	Pale yellow
PA2	0.35	90.0	Pale green
PA3	0.35	83.3	Pale green
PA4	0.32	89.9	Pale green

*. 0.5 g/dL polymers in DMAc at 25 ºC.

Solubility of polyamides

Solubility of polyamides was tested in aprotic solvents such as NMP, DMF, DMAc (*N,N*-dimethylacetamide), DMSO (Dimethylsulfoxide), tetrahydrofuran (THF) and trichloromethane ($CHCl_3$). All polymers, require heating to be soluble in aprotic solvents, and they are not soluble in THF and $CHCl_3$ (Table 3). Resulted polyamides exhibit moderate viscosity in a range of 0.32-0.39 (dL/g).

Table 3. Solubility behavior of polymides **(PA1-4).**

	NMP	DMF	DMSO	DMAc	THF	$CHCl_3$
PA1	++	++	++	++	_	_
PA2	++	++	++	++	_	_
PA3	++	++	++	++	_	_
PA4	++	++	++	++	_	_

+ Soluble at room temperature, ++ Soluble on heating, – Insoluble.

Also, in order to study the crystallinity of polyamides, X-ray diffraction measurement was carried out in the region of 2θ= 10-80^o for **PA1** (Figure 1). Amorphous diffraction pattern that was detected in the diffractograms is reasonable because the presence of the bulky pendant groups attached to the macromolecular backbone causes a weak chain packing and decreases crystallinity and intermolecular forces between the polymer chains [47].

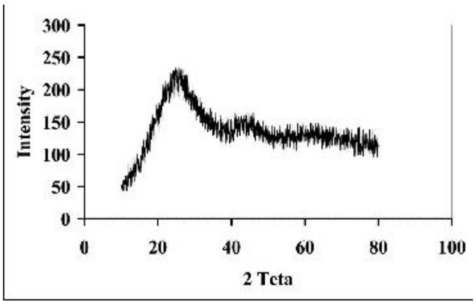


Figure 1. XRD analysis of **PA1**.

Thermal stability of polyamides and curing behavior of diacid monomer and polyamides

Thermal analysis of diacid monomer, **PA1** and **PA2** were investigated through differential scanning calorimetry (DSC) under N_2 atmosphere with the rate of 10 ^{o}C/min. DSC of monomer determined the temperature region of homopolymerization of maleimide ring presence in monomer's structure in temperature range between 120 ^{o}C and 200 ^{o}C (Figure 2).

Figure 3 shows the changes in DSC thermograms for two polyamides subjected to thermal behaviours in nitrogen. No Tg`s were observed for either polymers. Such data reveals that the resulting polymers do not show glass transition points clearly. This is due to the presence of relative big pendant group in polymer chains that decrease the freedom in rotation for Tg measurements and ability to form polymer networks that were raised from maleimide cross-linking potential. The data shows that maleimide groups in polymers are able to undergo a self-addition reaction upon heating and cross-linked polymers were obtained.

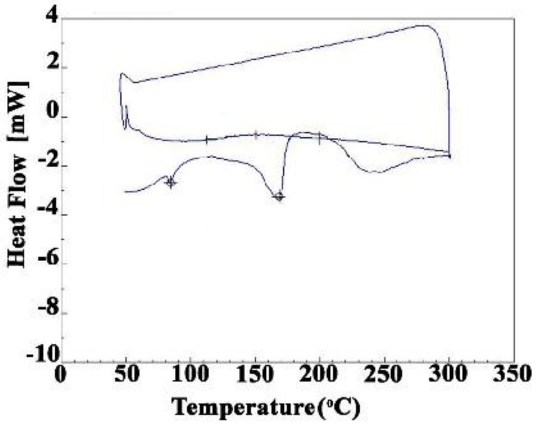


Figure 2. DSC analysis of monomer.

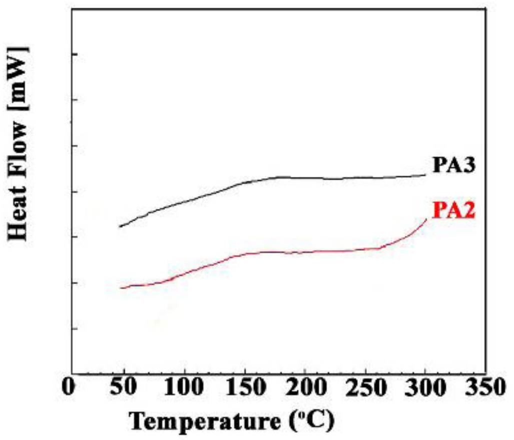


Figure 3. DSC analyses of **PA2** and **PA3**.

The thermal behavior data of all polymers is summarized in Table 4. The representative TGA of polyamides **PA1-4** exhibits that all polyamides have a similar pattern of decomposition and do not show significant weight loss below 300 °C in nitrogen (Figure 4). Thermograms of **PA2** and **PA3** show a broad single stage weight loss and other polymers have two-stage decomposition. Char yield of PA1 that has sulfoxide linkage in its structure, is higher than other polymers that may emanate from higher crosslinking in polymer backbone. Others have close values of char yields. The T10% values of these polyamides are in the range of 340–468 °C.

Table 4. Thermal properties of polyamides.

	$^{a}T_{5\%}$(°C)	$^{b}T_{10\%}$(°C)	^{c}Char yield (%)
PA1	246	352	48
PA2	381	465	39
PA3	422	468	37
PA4	256	340	34

[a]. Temparature at 5% weight loss of polymer.
[b]. Temparature at 10% weight loss of polymer.
[c]. Char yield at 800 °C.

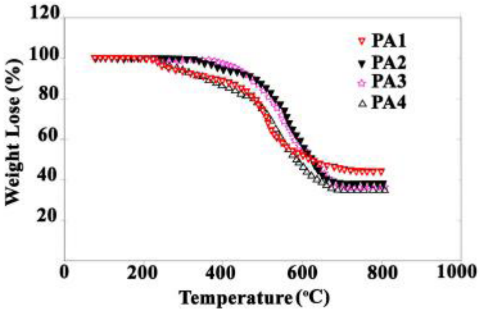


Figure 4. Thermograms analyses of polyamides.

Conclusion

In summary, in this paper a new monomer with maleimide pendant group has been synthesized and copolymerized with various diamines. For this aim, at first a new diacyl chloride was fabricated through condensation of 4-maleimidobenzoyl chloride and 5-aminosiophthalic acid in DMF. Then polyamides were fabricated through step-growth polycondensation of diacid chloride and various diamines. DSC of monomer confirms that the homopolymerization rose from maleimide structure. Also, thermal behavior of polyamides indicates presence of homopolymerization of maleimide group in polymers backbone.

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