



## Synthesis and Characterization of New Copoly(amide-imide)s Based on 1,3-bis[4,4'-(trimellitimido)phenoxy]propane and Fumaric acid

Khalil Faghihi<sup>\*</sup>, Akram Feyzi, Reza Mohammadi Pour

*Department of Chemistry, Faculty of Science, Arak University, Arak, 38156, Iran*

Received 25 December 2009; received in revised form 25 February 2010; accepted 26 February 2010

### Abstract

In this article six new copoly(amide-imide)s (**11a-c**) were synthesized through the direct polycondensation reaction of 1,3-bis[4,4'-(trimellitimido) phenoxy] propane (**6**) with 3,3'-diamino diphenyl sulfone (**7**), 4,4'-diaminodiphenyl ether (**8**) and 1,5-naphthalene (**9**) in the presence of fumaric acid (**10**) as a second diacid in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine. The resulted polymers were fully characterized by means of FT-IR spectroscopy, elemental analyses, inherent viscosity, and solubility tests. Thermal stabilities of a polymer (**11a-c**) were investigated by using TGA & DTG thermograms.

**Keywords:** High performance polymers; Copoly(amide-imide)s; Direct polycondensation.

### 1. Introduction

Aromatic polyimides (PIs) are well known for their excellent thermal stabilities, electric insulation properties, and chemical resistance. However, their applications are limited because of their high softening or melting temperatures and insoluble nature in most organic solvents [1-2]. To overcome these drawbacks, PI structures are often modified. One method uses copolymerization to synthesize copolymers to improve the processing ability, such as poly(amide-imide)s and copoly(amide-imide)s [3-7]. PAIs have the advantages of both PAs and PIs and possess thermal stability balanced with processability. These polymers can be synthesized from various aromatic monomers containing anhydrides, carboxylic acids, and aromatic diamines by condensation [8-10]. In this article six new copoly(amide-imide)s (**11a-c**) were synthesized. The characterizations of new copolymers such as thermal and physical properties are also investigated.

### 2. Experimental

#### 2.1. Monomer Synthesis

##### 1,4-bis[4,4'-nitrophenoxy] propane (3)

<sup>\*</sup>Corresponding author. Tel.: +98 861 2777400, fax: +98 861 4173406.  
E-mail address: k-faghihi@araku.ac.ir (Kh. Faghihi)

Into a 100 ml round-bottomed flask were added (6.00 g, 43.11 mmol) of 4-nitrophenol (**1**) and (2.97 g, 21.55 mmol) of dry K<sub>2</sub>CO<sub>3</sub> in 30 mL dimethyl formamide (DMF). Then a solution of (4.46g, 20.67 mmol) 1,3-dibromo propane (**2**) in 5 mL dry dimethyl formamide was added drop-wise to reaction mixture. The reaction mixture was heated for 6 hrs at 120°C, then was cooled and poured onto crushed ice. The precipitated white product was collected by filtration, dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed successively with NaOH (2M), HCl (1M) and water. The CH<sub>2</sub>Cl<sub>2</sub> solution was then dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum and product was recrystallized from ethanol, affording 2.89g (44%) of white solid (**3**), m.p: 133-135 °C, FTIR (KBr, cm<sup>-1</sup>): 3092 (w), 2962 (w), 1604 (s), 1504 (s), 1469 (m), 1340 (s), 1259 (s), 1172 (m), 1111 (s), 1053 (m), 966 (m), 841 (s). Elemental analysis: calculated for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>: C, 56.6; H, 4.4; N, 8.8; found: C, 56.2; H, 4.5; N, 8.3.

#### *1,4-bis[4,4'-aminophenoxy] propane (4)*

Into a 100 ml round-bottomed flask were added (1.00 g, 3.67 mmol) of 1,4-bis[4,4'-aminophenoxy] propane (**4**) and 0.1 g of 10% Pd-C, and 20 mL of ethanol were introduced into a 100-mL round-bottomed flask to which 7 mL of hydrazine monohydrate was added dropwise over a period of 1 h at 85 °C. After the complete addition, the reaction was continued at reflux temperature for another 5 h. Then, the mixture was filtered to remove the Pd-C and the filtrate was poured into water and dried to afford 0.31 g (37%). MP: 109-112 °C. FTIR (KBr, cm<sup>-1</sup>): 3391 (m), 2958 (m), 2885 (w), 1620 (w), 1512 (s), 1471 (m), 1381 (w), 1336 (w), 1296 (w), 1240 (s), 1170 (w), 1101 (w), 1062 (m), 997 (m), 825 (s) cm<sup>-1</sup>. <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>, TMS): δ; 6.78-6.74 (d, 4H), 6.66-6.62 (d, 4H), 4.09-4.05 (s, 4H), 3.41 (br, 2H), 2.20-2.15 (m, 2H) ppm. Elemental analysis: calculated for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.7; H, 6.9; N, 10.8; found: C, 69.3; H, 6.5; N, 10.3.

#### *1,4-Bis[4,4'-(trimellitimido)phenoxy]propane (6)*

Into a 100-mL, round-bottom flask, 0.204 g (0.75 mmol) of 1,4-bis[4,4'-aminophenoxy] propane (**4**), 0.29 g (1.5 mmol) of trimellitic anhydride (**5**), 20 mL of a mixture of acetic acid and pyridine (3:2) and a stirring bar were placed. The mixture was stirred at room temperature overnight and then was refluxed for 4 hrs. After this time the solvent was removed under reduced pressure, and the residue was dissolved in 100 mL of cold water; then, 5 mL of concentrated HCl was added. The solution was stirred until a brown precipitate was formed, and then the precipitate was filtered off and dried in vacuum to give 0.62g (88%) of dicarboxylic acid (**6**): mp>320°C, FTIR (KBr, cm<sup>-1</sup>): 2540-3113 (m, br), 1782 (w), 1720 (s, br), 1610 (w), 1514 (s), 1388 (s, br), 1300 (m), 1238 (m), 1172 (m), 1095 (m), 1053 (w), 935 (w), 864 (w), 729 (s), 526 (m) cm<sup>-1</sup>. <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>, TMS): δ; 13.5 (s, 2H), 8.39-8.37 (d, 2H), 8.26 (s, 2H), 8.04-8.02 (d, 2H), 7.38-7.34 (d, 4H), 7.13-7.07 (d, 4H), 4.22-4.20 (tr, 4H), 2.23 (m, 2H) ppm. Elemental analysis: calculated for C<sub>34</sub>H<sub>24</sub>N<sub>2</sub>O<sub>10</sub>: C, 65.3; H, 3.6; N, 4.6; found: C, 65.1; H, 3.2; N, 4.4.

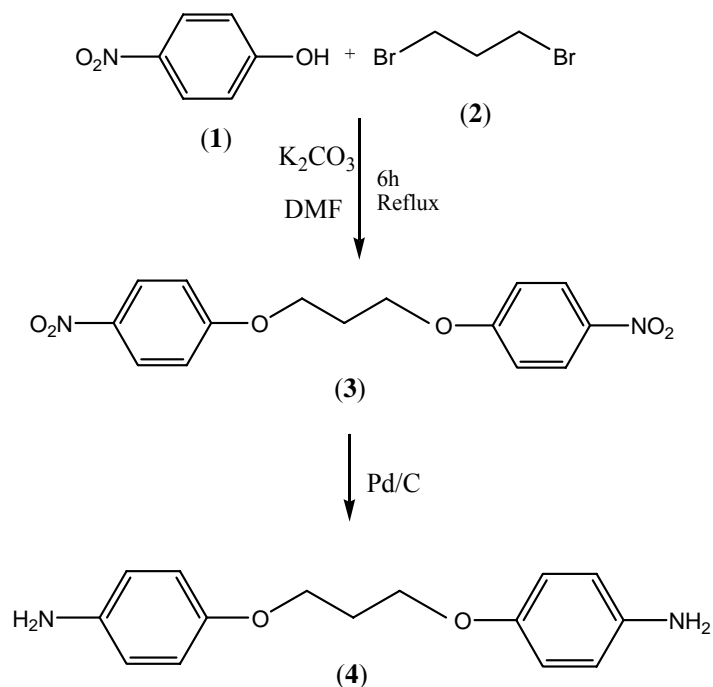
## *2.2. Polymer synthesis*

Into a 100 ml round bottomed flask were placed a mixture of diacid (**6**) (0.16 mmol), second diacid (**10**) (0.16 mmol), diamine (**7-9**) (0.32 mmol), 0.10 g of calcium chloride, 0.84 ml of triphenyl phosphite, 0.2 ml of pyridine and 3 ml NMP. The mixture was heated for 1 hr at 60 °C, 2 hrs at 90 °C and then refluxed at 130 °C for 8 hrs until a viscose solution was formed. Then it was cooled to room temperature and 30 ml of methanol was added to reaction mixture. The precipitate was formed, filtered off and washed with methanol. The resulting polymers (**11a-c**) were dried under vacuum.

### 3. Results and discussion

#### 3.1. Monomer Synthesis

1,4-bis[4,4'-aminophenoxy] propane (**4**) was synthesized by using a two-step reaction. At first 1,4-bis[4,4'-nitrophenoxy] propane (**3**) was prepared from the reaction of two equimolar 4-nitrophenol (**1**) and one equimolar 1,3-dibromo propane (**2**). Then dinitro compound (**3**) was reduced by using 10% Pd-C, ethanol and hydrazine monohydrate. (Scheme 1).



**Scheme 1** Synthetic route of monomer (**4**).

The chemical structure and purity of dinitro compound (**3**) was proved with elemental analysis,  $^1H$ -NMR and FTIR spectroscopy and diamine compound (**4**) was proved with elemental analysis, FTIR,  $^1H$ -NMR spectroscopy. The measured results in elemental analyses of these compounds were closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained. The FTIR spectrum of diamine (**4**) showed two peaks at 3321 and 3212  $cm^{-1}$ , which were assigned to the  $NH_2$  groups. Also, the absorptions found at 1062-1296  $cm^{-1}$  were assigned to the vibration of the C-O band.

$^1H$ -NMR spectrum of diamine (**4**) showed peaks as a doublet of doublet at 6.62-6.66 and 6.78-6.74 were related to aromatic protons. Also, a broad singlet peak at 3.41 ppm which was assigned to the proton of the  $NH_2$  group in this compound. The peak at 4.09-4.05 ppm was assigned to the proton of the two similar methylene groups ( $CH_2$ -O) The peak at 2.2-2.15 ppm, which was assigned to the proton of the methylene group (Fig. 1).

As shown in scheme 2, the dicarboxylic acid (**6**) was obtained by the condensation of the appropriate diamine (**4**) with two mole equivalents of trimellitic anhydride (**5**) in refluxing mixture of glacial acetic acid and pyridine. The condensation reaction between the amines and anhydride groups, as well as the subsequent cyclodehydration reaction was carried out in the heterogeneous solution. The chemical structure and purity of dicarboxylic acid (**6**) was proved with elemental analysis, FTIR,  $^1H$ -NMR spectroscopy. The FTIR spectrum of the dicarboxylic acid (**6**) showed absorption bands around 2500-3500  $cm^{-1}$  (acidic H's), 1782  $cm^{-1}$  (asymmetric imide C=O stretching), 1720 (symmetric imide C=O stretching and acid C=O stretching), and

1384  $\text{cm}^{-1}$  (imide ring vibration) confirming the presence of imide ring and carboxylic acid groups in the structure.

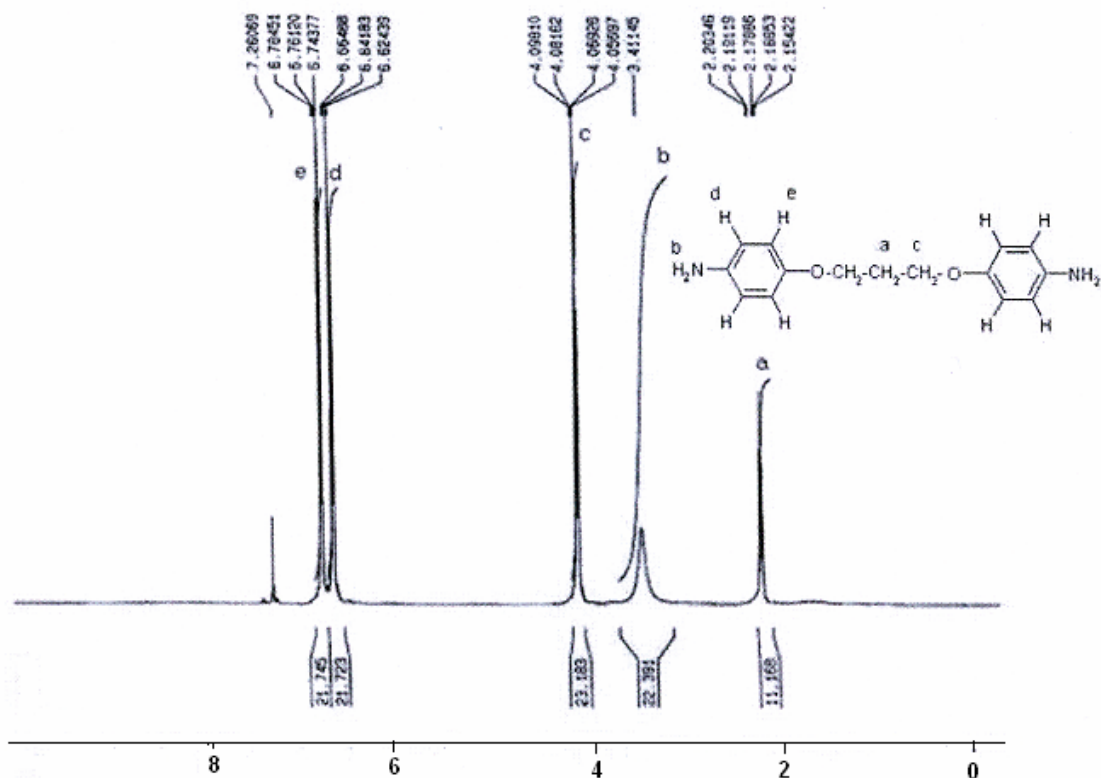
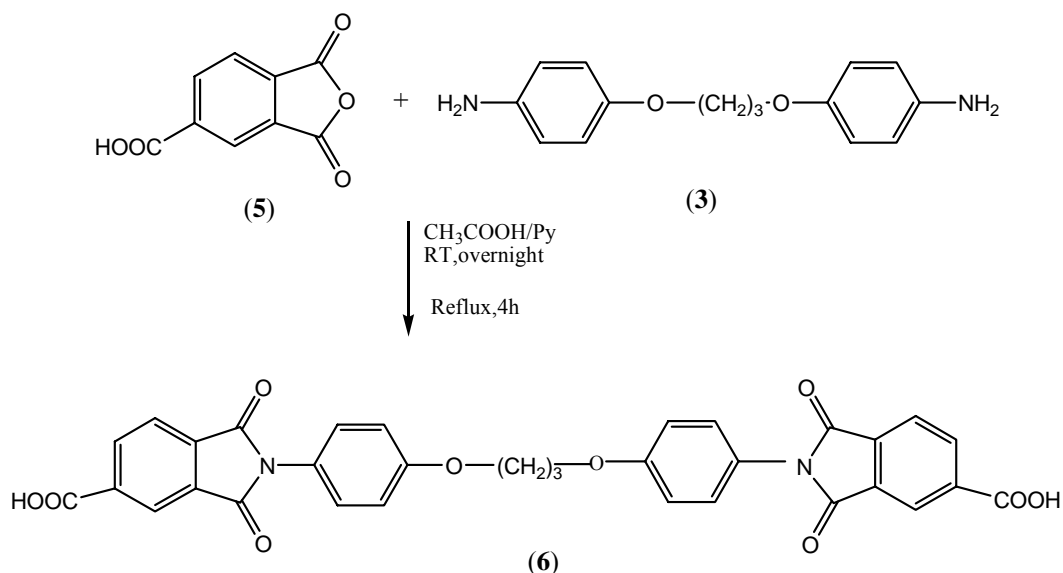


Fig. 1.  $^1\text{H-NMR}$  spectrum of diamine (4).



Scheme 2 Synthesis of diacid (6).

The  $^1\text{H-NMR}$  spectroscopic data of the dicarboxylic acid (6) are in the range of 8.02-8.39 ppm, which protons of the trimellitoyl groups create resonance signals around downfield regions (above 8 ppm). Peaks related to diamine moiety in the center of this compound were appeared in 7.07-7.38 ppm regions (below 8 ppm). Also a broad singlet peak at 13.5 ppm which was assigned to the proton of the acidic groups in this compound (Fig. 2).

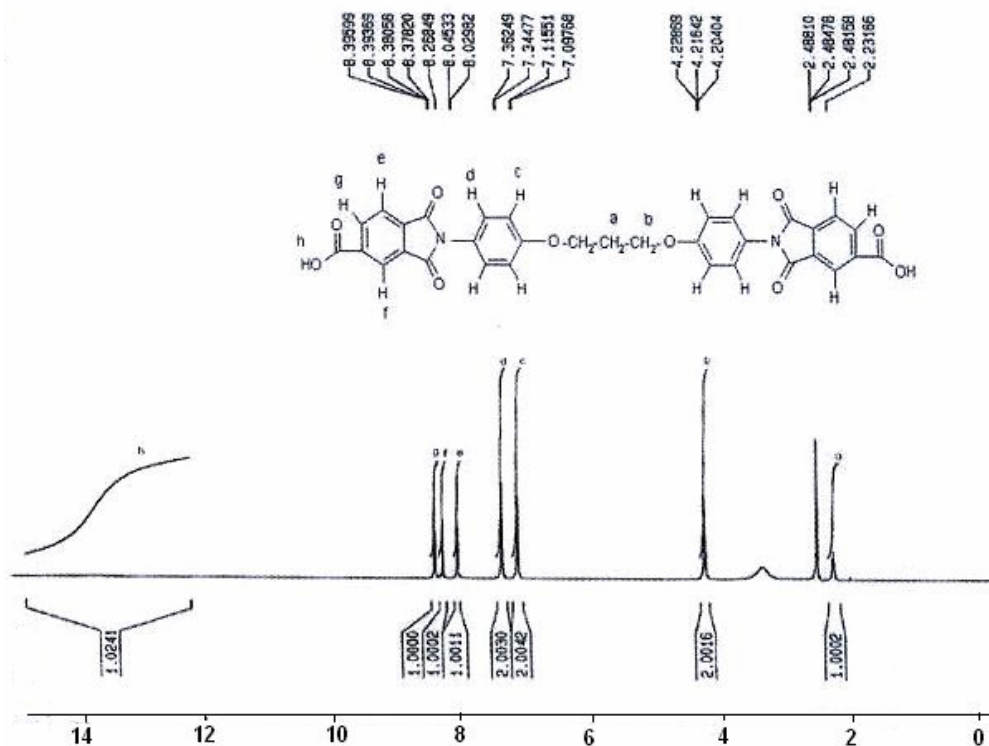
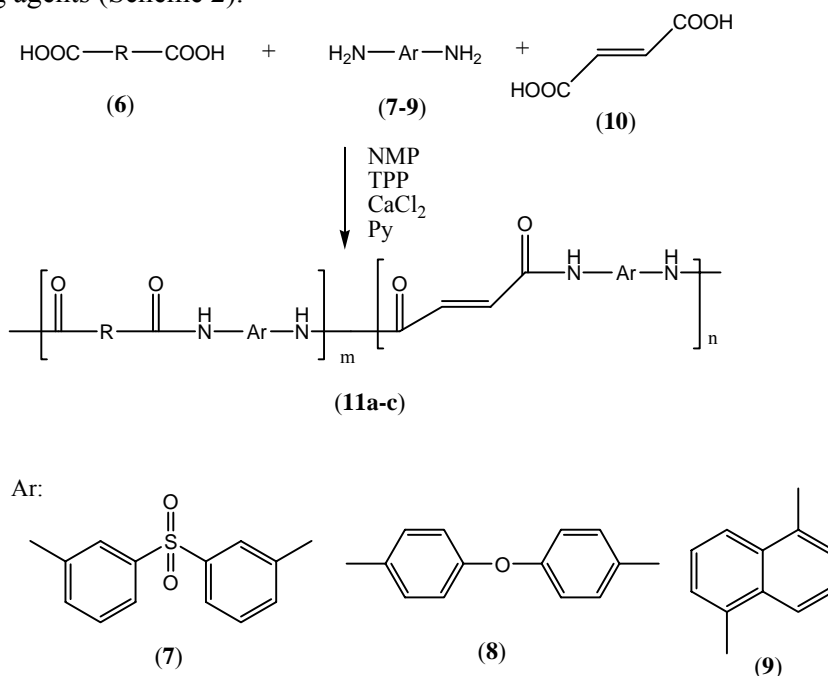


Fig. 2.  $^1\text{H-NMR}$  spectrum of diacid (6).

### 3.2. Polymer synthesis

Copoly(amide-imide)s (**11a-c**) were synthesized by the direct solution polycondensation reaction of an equimolar mixture of diacid (6), an equimolar mixture of diacid (10) with two equimolar mixture of aromatic diamines (7-9) by using triphenyl phosphate (TPP) and pyridine as condensing agents (Scheme 2).



Scheme 2 Synthetic route of copoly(amide-imide)s (**11a-c**).

The synthesis and some physical properties of these PAIs (**11a-c**) are given in Table 1. All the polymers were obtained in moderate to good yields and had inherent viscosities between 0.20-0.25 dLg<sup>-1</sup>.

**Table 1**  
Synthesis and Some Physical Properties of copoly(amide-imide)s (**11a-c**).

Copolymer	Diamne	Yield (%)	$\eta_{inh}(dL/g)^a$
<b>11a</b>	<b>7</b>	87.6	0.25
<b>11b</b>	<b>8</b>	92.4	0.20
<b>11c</b>	<b>9</b>	89.5	0.23

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMF at 25°C.

### 3.3. Polymer characterization

The synthesis and some physical properties of PAIs (**11a-c**) are summarized in Table 1. These polymers were confirmed to be CoPAIs by using FTIR spectroscopy and elemental analyses. FTIR spectroscopy data for all of (**11a-c**) are listed in Table 2.

**Table 2**  
FTIR data of (**11a-c**).

Copolymer	Spectra data
<b>11a</b>	<b>FT-IR Peaks (cm<sup>-1</sup>):</b> 3342(w), 3142 (w), 3049 (m), 1776 (m), 1712 (s), 1664 (m), 1498 (s), 1383 (s), 1282 (s), 1222 (s), 754(m).
<b>11b</b>	<b>FT-IR Peaks (cm<sup>-1</sup>):</b> 3350 (w), 3189(w), 2957 (w), 1778 (m), 1710 (s), 1591 (m), 1512 (s), 1383 (m), 1240 (s), 1220 (m), 939 (m), 692 (m).
<b>11c</b>	<b>FT-IR Peaks (cm<sup>-1</sup>):</b> 3348 (w), 3142 (w), 3057 (w), 1776 (m), 1712 (s), 1662 (m), 1498 (s), 1384 (s), 1282 (s), 1097 (s), 854 (s).

This polymer had absorption band between 1712 and 1660 cm<sup>-1</sup> due to imide and amide carbonyl groups. Absorption bands around 1380 cm<sup>-1</sup> and 730-710 cm<sup>-1</sup> demonstrated the presence of the imide heterocyclic absorption in this polymer. The other spectra showed similar patterns. The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures.

The solubility of CoPAIs (**11a-c**) was investigated with 0.01g polymeric samples in 2 ml of a solvent. All these PAIs were soluble in organic solvents such as N, N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC), DMSO, NMP and chloroform at room temperature and were insoluble in solvents such as ethanol, MeOH, acetone and water.

### 3.4. Thermal properties

The thermal properties of three samples of resulting polymers (**11a**) containing fumaric were investigated with TGA and DTG in nitrogen atmosphere at a rate of heating of 10 °C per minute, and thermal data are summarized in Table 3. The initial decomposition temperatures of 5 and 10% weight losses (T<sub>5</sub> and T<sub>10</sub>) and the char yields at 600 °C for them are summarized in Table 2. The polymer exhibited moderate resistance to thermal decomposition. T<sub>5</sub> for the polymer ranged from 102-105°C and T<sub>10</sub> for it ranged from 140-142°C, and residual weights for the polymer at 600 °C is 48% in nitrogen.

**Table 3**  
Thermal Behavior of (**11a**).

Polymer	T <sub>5</sub> (°C) <sup>a</sup>	T <sub>10</sub> (°C) <sup>b</sup>	Char Yield <sup>c</sup> (%)
<b>11a</b>	104-105	140-142	48

<sup>a,b</sup>Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10°C/min in N<sub>2</sub> respectively <sup>c</sup>Percentage weight of material left undecomposed after TGA analysis 600 °C.

#### 4. Conclusion

In this work, new thermally stable copoly(amide-imide)s (**11a-c**) were synthesized through the direct polycondensation reaction of 1,3-bis[4,4'-(trimellitimidido) phenoxy] propane (**6**) with 3,3'-diamino diphenyl sulfone (**7**) 4,4'-diaminodiphenyl ether (**8**) and 1,5-naphthalene (**9**) in the presence of fumaric acid (**10**) as a second diacid in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine. The presence of trimellitic rings, terphthalic and fumaric acid moieties into the backbone increased solubility of these polymers in common organic solvent in compare to aromatic polyimide. These properties could make these CoPAIs attractive for practical applications, such as processable high-performance engineering plastics.

#### References

- [1] D. Wilson, H.D. Stenzenberger, P.M. Hergenrother, Polyimides, Glasgow and London: Blackie, 1990.
- [2] M. K. Ghosh, K. L. Mittal, Polyimides: Fundamentals and Applications, Marcel Dekker: New York, 1996.
- [3] H. Deligoz, S. Vantansever, S. Naci Koc, F. Oksuzomer, S.M.A. Gurkaynak, J. Appl. Polym. Sci. 110 (2008) 1216-1224.
- [4] H. Behniafar, S. Haghghat, Polym. Advanced Technologies 19 (2008) 1040-1047.
- [5] S.S. Kothawade, M.P. Kulkarni, U.K. Kharul, A.S. Patil, S.P. Vernekar, J. Appl. Polym. Sci. 108 (2008) 3881-3189.
- [6] X. Zhao, Y.F. Li, Y. Shao, T. Ma, C.L. Gong, C.S. Huang, J. Appl. Polym. Sci. 107 (2008) 3119-3126.
- [7] D.J. Liaw, F.C. Chang, J.H. Liu, K.L. Wang, Kh. Faghihi, K.R. Lee, J.Y. Lai, J. Appl. Polym. Sci. 104 (2007) 3096-3102.
- [8] S. Mallakpour, M. Kolahdoozan, J. Appl. Polym. Sci. 104 (2007) 1248-1254.
- [9] Kh. Faghihi, Z. Mozaffari, J Appl. Polym. Sci. 108 (2008) 1152-1157.
- [10] Kh. Faghihi, H. Naghavi, J. Appl. Polym. Sci. 108 (2008) 1136-1145.