Bull. Chem. Soc. Ethiop. **2010**, 24(2), 289-294. ISSN 1011-3924
Printed in Ethiopia

SHORT COMMUNICATION

SYNTHESIS AND CHARACTERIZATION OF NEW COPOLY(AMIDE-IMIDE)S BASED ON N,N'-(4,4'-DIPHENYLSULFONE)BISTRIMELLITIMIDE WITH DIFFERENT DIACIDS AND DIAMINES

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(Received July 22, 2009; revised January 28, 2010)

ABSTRACT. In this paper six new copoly(amide-imide)s (**7a-f**) were synthesized through the direct polycondensation reaction of N,N'-(4,4'-diphenylsulfone)bistrimellitimide (**1**) with 4,4'-diamino diphenylsulfone (**2**), 4,4'-diamino diphenylether (**3**), in the presence of adipic acid (**4**), fumaric acid (**5**) or terephthalic acid (**6**) as the 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 FTIR spectroscopy, elemental analyses, inherent viscosity, solubility tests and UV-vis spectroscopy. Thermal stabilities of resulted polymers (**7a-c**) containing three different second diacids were compared by using TGA and DTG thermograms.

KEY WORDS: Highperformance polymers, Copoly(amide-imide)s, Direct polycondensation, Thermal properties

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 [8-11]. Among various methods for polyamidation reaction, direct polycondensation methods have been developed by several investigators and especially by Yamazaki and Higashi [12-15]. In these methods, preparation and isolation of acid chlorides are not required and the reactions proceed as one pot path-way using the free dicarboxylic acid, diamines in the presence of various activating agents.

In this article six new copoly(amide-imide)s (**7a-f**) were synthesized through the direct polycondensation reaction of N,N'-(4,4'-diphenylsulfone)bistrimellitimide (**1**) with 4,4'-diamino diphenylsulfone (**2**), 4,4'-diamino diphenylether (**3**), in the presence of adipic acid (**4**), fumaric acid (**5**) or terephthalic acid (**6**) as the second diacid in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine.

EXPERIMENTAL

Materials. 4,4'-diamino diphenylsulfone (**2**), 4,4'-diamino diphenylether (**3**), adipic acid (**4**), fumaric acid (**5**), terephthalic acid (**6**), triphenyl phosphite (TPP), N-methyl-2-pyrrolidone and pyridine were purchased from Merck Chemical Company and used without further purification.

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Also commercially available calcium chloride ($CaCl_2$) was purchased from Merck Chemical Company and dried under vacuum at 150 ºC for 6 h.

Measurements. Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (UK) as 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). Inherent viscosities were measured by a standard procedure by using a Technico® Merk Viscometer. Thermal gravimetric analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N_2 atmosphere at a rate of 10 ^{o}C/min. Elemental analyses were measured in Arak Petrochemical Company Laboratories, Arak, Iran. UV-vis absorptions were recorded at 25 ^{o}C in the 190-790 nm spectral regions with a Perkin-Elmer Lambda 15 spectrophotometer on DMF solution by using cell lengths of 1 cm.

Monomer synthesis. N,N'-(4,4'-diphenylsulfone)bistrimellitimide (**1**) was prepared according to our previous works [16].

Polymer synthesis. In a 100 mL round bottomed flask were placed a mixture of N,N'-(4,4'-diphenylsulfone)bistrimellitimide (**1**) (0.16 mmol), second diacid 4, 5 or 6 (0.16 mmol), diamine **2** or **3** (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 h at 60 ºC, 2 h at 90 ºC and then refluxed at 130 ºC for 8 h 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 (**7a-f**) were dried under vacuum.

RESULTS AND DISCUSSION

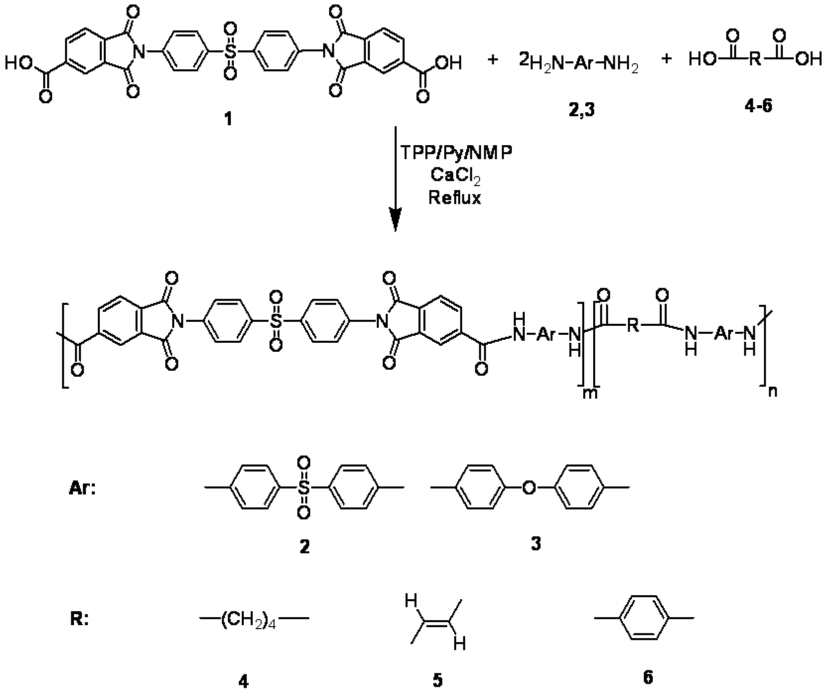
Monomer Synthesis. N,N'-(4,4'-diphenylsulfone)bistrimellitimide (**1**) was prepared in a one pot reaction sequence. Diacid (**1**) was synthesized through the condensation reaction of two equivalent trimellitic anhydride with one equivalent of 4,4'-diamino diphenylsulfone (**2**) in glacial acetic acid as solvent. After cooling the reaction mixture, the residue was dissolved in cold s water until a gummy solid was provided a white solid with the addition of excess water.

Polymer synthesis. Copoly(amide-imide)s (**7a-f**) were synthesized by the direct solution polycondensation reaction of an equimolar mixture of diacid (**1**) and diacids (**4-6**) with two moles of aromatic diamines (**2**, **3**) by using triphenyl phosphate (TPP) and pyridine as a condensing agents (Scheme 1). The synthesis and some physical properties of these CoPAIs (**7a-f**) are given in Table 1. All the polymers were obtained in moderate to good yields and had inherent viscosities between 0.42-0.60 dLg^{-1}.

Table 1. Synthesis and some physical properties of copoly(amide-imide)s (**7a-f**).

Polymer	Second diacid	Diamine	Yield (%)	η_{inh} (dL/g)^a	λ_{max}^{b}	Color^c
7a	Adipic acid (**4**)	4,4'-Diamino diphenylsulfone (**2**)	92	0.42	335	C
7b	Fumaric acid (**5**)	4,4'-Diamino diphenylsulfone (**2**)	89	0.55	325	B
7c	Terephthalic acid (**6**)	4,4'-Diamino diphenylsulfone (**2**)	91	0.60	322	DB
7d	Adipic acid (**4**)	4,4'-Diamino diphenylether (**3**)	88	0.59	324	Y
7e	Fumaric acid (**5**)	4,4'-Diamino diphenylether (**3**)	86	0.46	320	Y
7f	Terephthalic acid (**6**)	4,4'-Diamino diphenylether (**3**)	90	0.52	328	DY

^{a}Measured at a concentration of 0.5g/dL in DMF at 25˚C. ^{b}UV-vis absorptions were recorded at 25˚C in the DMF solution. ^{c}B = brown, C = cream, DB = dark brown, DY = dark yellow, Y = yellow.



Scheme 1. Synthetic route of copoly(amide-imide)s (**7a-f**).

Polymer characterization. The polymers were confirmed to be CoPAIs by using FTIR spectroscopy and elemental analyses. FTIR spectra for all CoPAIs showed similar patterns that summarized in Table 2. These polymers showed the C=O asymmetric stretching of imide around 1770 cm^{-1}, the C=O symmetric stretching of imide and amide groups around 1715 cm^{-1} and 1660 cm^{-1}, respectively, C-N stretching at 1380 cm^{-1}, C–O–C stretching at 1015-1240 cm^{-1}. All of these CoPAs exhibited strong absorption around 1380 and 725 cm^{-1}, which shows the presence of the heterocyclic imide groups. The elemental analysis values of the CoPAIs (**7d-f**) were in good agreement with the calculated values for the proposed structures (Table 3).

Table 2. FTIR Characterization of CoPAIs (**7a-f**).

Polymer	IR spectral data (cm^{-1})
7a	3402 (m, br), 2928 (w), 1783 (w), 1720 (s), 1668 (s), 1591 (w), 1531 (w), 1403 (m), 1380 (s), 1248 (m), 1210 (m), 1115 (m), 839 (w), 725 (w), 648 (m).
7b	3410 (m), 2990 (m), 1765 (w), 1715 (s), 1660 (s), 1607 (w), 1525 (w), 1428 (m), 1391 (m), 1310 (m), 1228 (m), 1191 (m), 1000 (w), 836 (w), 786 (w), 725 (w), 608 (w).
7c	3412 (m), 2984 (m), 1770 (w), 1712 (s), 1662 (s), 1602 (m), 1532 (m), 1421 (m), 1368 (m), 1340 (s), 1220 (m), 1121 (m), 794 (w), 756 (w), 725 (w), 658 (w).
7d	3370 (m), 2908 (w), 1785 (w), 1720 (s), 1692 (s), 1500 (m), 1377 (m), 1215 (m), 1142 (w), 905 (s), 727 (w), 608 (w).
7e	3340 (m, br), 3095 (w), 1765 (w), 1726 (s), 1660 (s), 1599 (w), 1510 (m), 1420 (m), 1369 (m), 1302 (s), 1255 (m), 1157 (m), 794 (w), 723 (m), 684 (w).
7f	3442 (m), 2988 (m), 1790 (w), 1715 (s), 1642 (s), 1565 (s), 1590 (m), 1510 (m), 1375 (s), 1312 (w), 1230 (m), 1122 (m), 770 (w), 729 (w), 512 (w).

Table 3. Elemental analyses of CoPAIs (**7d-f**).

Polymer	Formula		C %	H %	N %
7d	$C_{60}H_{42}N_6O_{12}S$	Calcd	67.28	3.95	7.85
	$(1071.07)_n$	Found	67.05	3.81	7.26
7e	$C_{58}H_{36}N_6O_{12}S$	Calcd	66.92	3.49	8.07
	$(1041.21)_n$	Found	66.08	3.42	7.92
7f	$C_{62}H_{38}N_6O_{12}S$	Calcd	68.25	3.51	7.70
	$(1091.06)_n$	Found	68.08	3.52	7.58

The solubility of CoPAIs **(7a-f)** was investigated with 0.05g polymeric samples in 1 mL of a solvent. All these CoPAIs 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, THF, methylene chloride and water.

Table 4. Solubility of CoPAIs (**7a-f**).

Solvent	**7a**	**7b**	**7c**	**7d**	**7e**	**7f**
H_2SO_4	+	+	+	+	+	+
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
MeOH	−	−	−	−	−	−
EtOH	−	−	−	−	−	−
$CHCl_3$	−	−	−	−	−	−
CH_2Cl_2	−	−	−	−	−	−
H_2O	−	−	−	−	−	−

+, Soluble at room temerature. ⁻, Insoluble at room temperature.

Thermal properties. The thermal properties of three resulted polymers (**7a-c**) containing three different second diacids such as adipic, fumaric and terephthalic acids were investigated with TGA and DTG in nitrogen atmosphere at a rate of heating of 10 ^{o}C/min, and thermal data are summarized in Table 5. The initial decomposition temperatures of 5 and 10% weight losses (T_5 and T_{10}) and the char yields at 600 ^{o}C for them are summarized in Table 5. These polymers exhibited moderate to good resistance to thermal decomposition, up to 282-355 °C in nitrogen, and began to decompose gradually that temperature. T_5 for these polymers ranged from 282-355 °C and T_{10} for theme ranged from 350-433 °C, and residual weights for these polymers at 600 ^{o}C ranged from 39.5, 14.5 and 10.0% in nitrogen, respectively. According to the results thermal stability of these polymers related to the second diacid in the main chain. According to the thermal stability results of these polymers related to the second diacid in the main chain. Thermal stability of polymer **7c** with terephthalic acid and sulfone moiety was higher than other polymers, because this polymer has a rigid aromatic structure in the main chain. Also polymer containing fumaric acid has higher thermal stability in compare to polymer with adipic acid as second diacid and CoPAs **7a-c** containing sulfone moiety have good thermal stability because these polymers have a rigid and polar moiety in the diamine structure such as sulfone moiety.

Table 5. Thermal behavior of CoPAIs (**7a**), (**7b**) and (**7c**).

Polymer	T_5 (ºC)[a]	T_{10} (ºC)[b]	Char yield (%)[c]
7a	282	350	14.5
7b	283	425	10.0
7c	355	433	39.5

[a,b]Temperature at which 5 or 10% weight loss was recorded TGA at a heating rate of 10 ºC/min in N_2. [c]Weight percentage of material left after TGA analysis at maximum temperature 600 ºC in N_2.

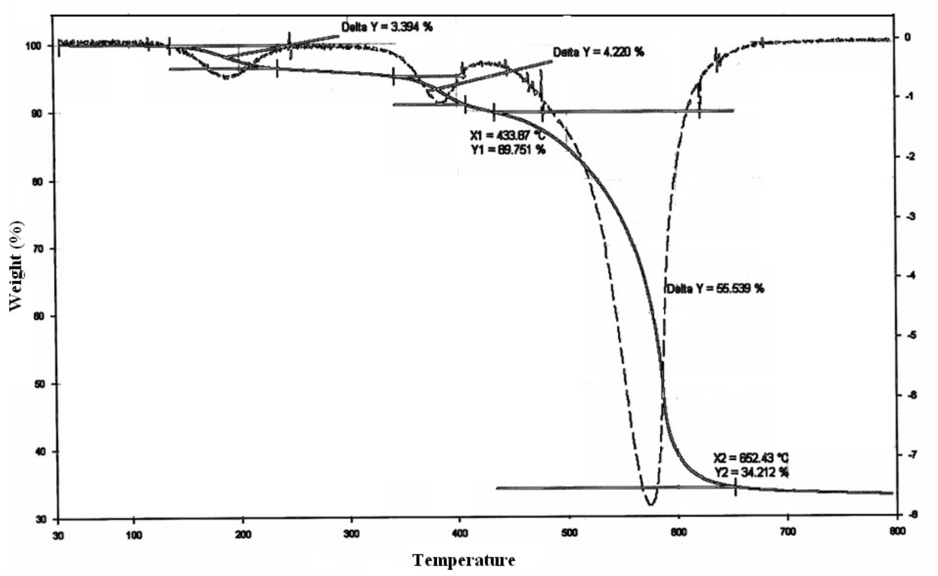


Figure 1. TGA and DTG thermograms of CoPAIs (**7c**).

CONCLUSIONS

In this work, six new thermally stable copoly(amide-imide)s (**7a-f**) were synthesized through the direct polycondensation reaction of N,N'-(4,4'-diphenylsulfone)bistrimellitimide (**1**) with 4,4'-diamino diphenylsulfone (**2**), 4,4'-diamino diphenylether (**3**), in the presence of adipic acid (**4**), fumaric acid (**5**) or terephthalic acid (**6**) as the second diacids in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine. The presence of sulfone groups, terephthalic, fumaric and adipic acids 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. Wilson, D.; Stenzenberger, H.D.; Hergenrother, P.M. *Polyimides*, Blackie: London; **1990**.
2. Ghosh, M.K.; Mittal, K.L. *Polyimides: Fundamentals and Applications*, Marcel Dekker: New York; **1996**.

3. Deligoz, H.; Vantansever, S.; Naci Koc, S.; Oksuzomer, F.; Gurkaynak, S.M.A. *J. Appl. Polym. Sci.* **2008**, 110, 1216.
4. Behniafar, H.; Haghighat, S. *Polym. Advanc. Technol.* **2008**, 19, 1040.
5. Kothawade, S.S.; Kulkarni, M.P.; Kharul, U.K.; Patil, A.S.; Vernekar, S.P. *J. Appl. Polym. Sci.* **2008**, 108, 3881.
6. Zhao, X.; Li, Y.F.; Shao, Y.; Ma, T.; Gong, C.L.; Huang, C.S. *J. Appl. Polym. Sci.* **2008**, 107, 3119.
7. Liaw, D.J.; Chang, F.C.; Liu, J.H.; Wang, K.L.; Faghihi, Kh.; Lee, K.R.; Lai, J.Y. *J. Appl. Polym. Sci.* **2008**, 104, 3096.
8. Faghihi, Kh.; Shabanian, M.; Hajibeygi, M. *Macromol. Res.* **2009**, 17, 912.
9. Faghihi, Kh.; Mozaffari, Z. *J. Appl. Polym. Sci.* **2008**, 108, 1152.
10. Faghihi, Kh.; Naghavi, H. *J. Appl. Polym. Sci.* **2008**, 108, 1136.
11. Faghihi, Kh.; Hajibeygi, M.; Shabanian, M. *Macromol. Res.* **2009**, 17, 739.
12. Higashi, F.; Yokote, S.; Murakawa, T.J. *Polym. Sci. Part A: Polym. Chem.* **2004**, 42, 4126.
13. Higashi, F. *New Method for Polymer Synthesis*, Plenum Press: New York; **1992**; chapter 7.
14. Higashi, F.; Nishi, T. *J. Polym. Sci. Part A: Polym. Chem.* 1**988**, 26, 3235.
15. Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci. Polym. Chem. Ed.* **1975**, 13, 1373.
16. Faghihi, Kh.; Naghavi, H. *J. Appl. Polym. Sci.* **2005**, 96, 1776.