NEW COPOLYAMIDES CONTAINING AZOBENZENE GROUPS AND DIFFERENT DIACID AND DIAMINE IN THE MAIN CHAIN: SYNTHESIS AND CHARACTERIZATION

KHALIL FAGHIHI^{1*}, MEISAM SHABANIAN², LEILY GHADIRY¹

¹Polymer Research Laboratory, Department of Chemistry, Faculty of Science, Islamic Azad University, Arak Branch, Arak, Iran.

²Yang Researchers Club, Islamic Azad University, Arak Branch, Arak, Iran

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ABSTRACT

A new series of copolyamides CoPAs **7a-f** were synthesized through the direct polycondensation reaction of 4,4'-azobenzenedicarboxylic acid **1** with 1,5-naphthalenediamine **2**, 3,4-diaminobenzophenone **3** in the presence of adipic acid **4**, fumaric acid **5** and terephthalic acid **6** as a second diacid in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphate (TPP), calcium chloride and pyridine. The obtained polymers were characterized by means of FT-IR spectroscopy, elemental analyses and inherent viscosity. These CoPAs were highly soluble in polar aprotic solvents such as *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP) and other solvents such as sulfuric acid. Thermal properties of the CoPAs **7c**, **7d** and **7e** were investigated using thermal gravimetric analysis (TGA and DTG).

Key word: Copolymers; Azobenzene; Direct polycondensation, High-performance polymers

INTRODUCTION

Aromatic polyamides possess excellent mechanical properties and thermal stability; however, they are difficult to process because of their limited solubility and to high glass transition (T_g) or melt temperature due to chain stiffness and intermolecular hydrogen bonding between amide groups [1]. The processing of these thermoplastic polymers has been greatly hindered because they lack softening or melting behavior at usual processing temperature, and they tend to degrade before or at the softening temperature [2]. Several attempts have been made in order to diminish the T_g or melting temperature of aromatic polyamides to make them processable. One of the used methodologies has been the introduction of linked and flexible bridging units [3-6] into the polymers chain.

Also, synthesis and properties of polymeric materials containing deferent chromophores covalently attached to the polymer backbone have attracted increasing interest in the recent years, not only for their photophysical peculiarities but also for their applications [7-10]. Seeing the great versatility of polyurethanes and their special properties, various monomeric and polymeric materials carrying azoaromatic chromophores were prepared and their photo-behavior was studied considering the development of the new photochromic, nonlinear optical, liquid-crystal or biological systems [11-13].

In this article six new CoPAs **7a-f** were synthesized through the direct polycondensation reaction of 4,4'-azobenzenedicarboxylic acid **1** with 1,5-naphthalenediamine **2**, 3,4-diaminobenzophenone **3** in the presence of adipic acid **4**, fumaric acid **5** and terephthalic acid **6** as a second diacid in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine.

EXPERIMENTAL

Materials

1,5-Naphthalenediamine **2**, 3,4-diaminobenzophenone **3**, adipic acid **4**, fumaric acid **5**, terephthalic acid **6**, triphenyl phosphite, *N*-methyl-2-pyrrolidone and pyridine were purchased from Merck Chemical Company and used without previous purification. Also commercially available calcium chloride (CaCl_2) was purchased from Merck Chemical Company and dried under vacuum at 150 °C for 6 h. 4,4'-azobenzenedicarboxylic acid **1** was prepared from 4-nitrobenzoic acid.

Techniques

Fourier transform infrared (FT-IR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England) 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 Regd Trad 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 °C/min. Elemental analyses were measured in Arak Petrochemical

Company laboratories, Arak, Iran.

Monomer synthesis

Synthesis of 4,4'-azobenzenedicarboxylic acid **1**

This compound was prepared according to our previous works [14].

Polymer synthesis

Into a 100 mL round-bottomed flask were placed a mixture of 4,4'-azobenzenedicarboxylic acid **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 °C, 2 h at 90 °C and then refluxed at 130 °C 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

Polymer synthesis

Copolyamides **7a-f** were synthesized by the direct solution polycondensation reaction of an equivalent of diacid **1** as a first diacid, an equivalent of diacid **4**, **5** or **6** as second diacid, with two equivalents of aromatic diamines **2** or **3** using TPP, NMP and pyridine as condensation agents (Scheme 1). The polymerization yield and some physical properties of these CoPAs **7a-f** are given in Table 1. All of the polymers were obtained in good yields and had inherent viscosities between 0.31-0.58 dLg⁻¹.

Scheme 1. Synthesis of CoPAs **7a-f**

Table 1: Yield and some physical properties of CoPAs **7a-f**

Polymer	Second Diacid	Diamine	Yield (%)	η_{inh} (dl/g) ^a	Color ^b
7a	Adipic acid (4)	1,5-Naphthalenediamine (2)	91	0.31	R
7b	Fumaric acid (5)	1,5-Naphthalenediamine (2)	84	0.36	R
7c	Terephthalic acid (6)	1,5-Naphthalenediamine (2)	88	0.55	B
7d	Adipic acid (4)	3,4-Diaminobenzophenone (3)	87	0.30	C
7e	Fumaric acid (5)	3,4-Diaminobenzophenone (3)	89	0.44	R
7f	Terephthalic acid (6)	3,4-Diaminobenzophenone (3)	86	0.58	DR

^a Measured at a concentration of 0.5 g/dL in DMF at 25 °C.^b B= Brown, C= Cream, DR= Dark Red, R= Red**Polymer characterization**

These polymers were confirmed to be CoPAs by using FTIR spectroscopy and elemental analyses. These polymers had an absorption band around 1660 cm^{-1} due to amide and benzophenone (PA **7d-f**) carbonyl groups. It is possible to see a peak around 1425 cm^{-1} related to azo groups ($-\text{N}=\text{N}-$) in the polymer backbone. Also absorption band of amide group appeared around 3235 cm^{-1} (N-H stretching). All of the CoPAs showed similar patterns that summarized in Table 2. The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures (Table 3).

Table 2 FT-IR characterization of CoPAs **7a-f**

Polymer	Spectra data (n, cm^{-1})
7a	3230 (m), 2990 (m), 1662 (s), 1575 (w), 1428 (m), 1308 (m), 1230 (m), 1130 (m), 826 (w), 776 (w), 656 (m).
7b	3235 (m), 1664 (s), 1613 (w), 1582 (m), 1437 (m), 1256 (m), 1210 (m), 1145 (m), 1058 (m), 991 (w), 921 (m), 760 (w), 661 (w), 580 (w), 445 (w).
7c	3235 (w), 1664 (s), 1613(m), 1485 (m), 1447 (m), 1256 (m), 1135 (m), 1058 (m), 991 (w), 760 (m), 698 (w), 661 (w), 580 (w).
7d	3227 (m), 2970 (m), 1686 (s), 1654 (s), 1604 (m), 1425 (m), 1294 (w), 1212 (m), 1142 (m), 1030 (w), 923 (w), 774 (w), 698 (w), 501 (m).
7e	3232 (m), 2984 (m), 1660 (s), 1644 (s), 1610 (w), 1508 (m), 1432 (m), 1280 (m), 1202 (s), 1140 (m), 1051 (m), 856 (w), 794 (w), 625 (m).
7f	3238 (m), 2988 (m), 1655 (br), 1612 (s), 1430 (m), 1412 (m), 1260 (s), 1212 (w), 1134 (m), 1022 (m), 924 (w), 842 (w), 780 (w), 629 (w), 524(w).

Table 3 Elemental analyses results of CoPAs **7a-f**

Polymer	Formula		C%	H%	N%
7a	$\text{C}_{40}\text{H}_{28}\text{N}_6\text{O}_4$	Calcd.	73.16	4.30	12.80
	$(656.69)_n$	Found	72.06	4.01	11.96
7b	$\text{C}_{38}\text{H}_{22}\text{N}_6\text{O}_4$	Calcd.	72.84	3.54	13.41
	$(626.62)_n$	Found	72.12	3.42	13.06
7c	$\text{C}_{42}\text{H}_{24}\text{N}_6\text{O}_4$	Calcd.	74.55	3.57	12.42
	$(676.19)_n$	Found	74.04	3.63	12.24
7d	$\text{C}_{46}\text{H}_{32}\text{N}_6\text{O}_6$	Calcd.	72.24	4.22	10.99
	$(764.24)_n$	Found	72.21	3.94	10.11
7e	$\text{C}_{44}\text{H}_{26}\text{N}_6\text{O}_6$	Calcd.	71.39	3.57	11.44
	$(734.19)_n$	Found	70.41	3.34	11.01
7f	$\text{C}_{48}\text{H}_{28}\text{N}_6\text{O}_6$	Calcd.	73.46	3.60	10.71
	$(784.21)_n$	Found	72.73	3.18	10.01

The solubility of CoPAs **7a-f** was investigated with 0.01 g polymeric samples in 2 mL of a solvent (Table 4). All of these CoPAs were soluble in sulphuric acid and organic polar solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethyl sulfoxide and NMP at room temperature. Some CoPAs were soluble and partially soluble on heating in pyridine and *m*-cresol, and were insoluble in solvents such as ethanol, methanol, tetrahydrofuran (THF), chloroform and water.

Table 4 Solubility of CoPAs **7a-f**

Solvent	7a	7b	7c	7d	7e	7f
H_2SO_4	+	+	+	+	+	+
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
THF	β^-	β^-	β^-	β^-	β^-	β^-
MeOH	—	—	—	—	—	—
EtOH	—	—	—	—	—	—
CHCl_3	—	—	—	—	—	—
H_2O	—	—	—	—	—	—

Solubility: β , soluble at room temperature; —, insoluble at room temperature.

Thermal properties

The thermal properties of three samples (**7c**, **7d** and **7e**) containing three different of second diacids such as adipic, fumaric and terephthalic acid were

investigated with TGA and DTG in nitrogen atmosphere at a rate of heating of 10 °C per minute and the results are summarized in Table 5. The initial decomposition temperatures of 5% and 10% weight losses (T_5 and T_{10} respectively) and the char yields at 600 °C for them are summarized in Table 5. T_5 for these polymers ranged from 295-340 °C and T_{10} for them ranged from 335-370 °C, and residual weights for these polymers at 600 °C ranged from 36.03-48.02% under nitrogen atmosphere. According to the results the thermal stability of these polymers is related to the second diacid in the main chain. Thermal stability of polymer **7c** containing terephthalic acid was higher than two other polymers, because this polymer has a rigid aromatic structure in the main chain. Also polymer containing fumaric acid **7e** has higher thermal stability in compare to polymer **7d** with adipic acid as second diacid.

Fig.1. TGA and DTG thermogram of polymer **7c**

Fig. 1. TGA and DTG thermogram of CoPA **7c**

Table 5 Thermal behavior of CoPAs **7c**, **7d** and **7e**.

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c
7c	340	370	44.93
7d	300	335	36.03
7e	295	350	48.02

^{a,b} Temperature at which 5 or 10% weight loss was recorded in TGA analysis at a heating rate of 10°C/min in N_2 .

^c Weight percentage of material left after TGA analysis at maximum temperature 600 °C in N_2 .

CONCLUSION

In this work, six new thermally stable copolyamides **7a-f** were synthesized through the direct polycondensation reaction of 4,4'-azobenzenedicarboxylic acid **1** with 1,5-naphthalenediamine **2** or 3,4-diaminobenzophenone **3** in the presence of adipic acid **4**, fumaric acid **5** or terephthalic acid **6** as a second diacid in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine. By introducing azo group into the polymer backbone the rigid conformation of the chains is modified increasing the solubility in polar aprotic solvents. According to the thermal analyses, the stability of these polymers is related to the second diacid in the main chain. Thermal stability of polymer **7c** with terephthalic acid was higher than two other polymers, because this polymer has a rigid aromatic structure in the main chain. Thermal stability and solubility can make these polymers attractive for practical applications such as processable high-performance engineering plastics.

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