



Synthesis and Characterization of New Optically Active Copolyamides Based on *N*-Phthaloyl-L-Glutamic Acid, Terephthalic, Fumaric and Adipic Acids

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Six new copolyamides (**9a-f**) were synthesized by direct polycondensation reaction of *N*-phthaloyl-L-glutamic acid (**3**) with 4,4'-diamino diphenylether (**4**), 4,4'-diamino diphenylsulfone **5** in the presence of adipic acid (**6**), fumaric acid (**7**) and terephthalic acid (**8**) as a second diacid in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine. *N*-phthaloyl-L-glutamic acid (**3**) was synthesized by reaction of phthalic anhydride (**1**) with L-glutamic acid (**2**) in acetic acid solution. The resulting polymers were characterized by means of FTIR spectroscopy, elemental analyses, inherent viscosity and specific rotation. Phthalimide rings as a bulky pendent group in the polymer chains disturb interchain and intrachain interactions and make these PAs readily soluble in polar aprotic solvents such as *N,N*-dimethyl acetamide, *N,N*-dimethyl formamide, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone and solvents such as sulfuric acid. Thermal properties of these polymers were investigated using thermal gravimetric analysis and differential thermal gravimetry.

Key Words: High performance polymers, Copolyamides, Direct polycondensation, L-glutamic acid, Chiral polymers, Thermal analysis.

INTRODUCTION

The development of heat-resistant and high-performance polymers in the past decades has been quite dramatic and has drawn the attention of many polymer scientists all over the world. The aromatic polymers such as polyimides and polyamides have already been noted for their high temperature resistance and excellent physico mechanical properties¹⁻⁴. However the application of polyamides is limited due to their high softening or melting temperatures and their insoluble nature in most organic solvents. To overcome these drawbacks, modifications of the polyamide structure have often been applied, such as the introduction of flexible linkages, non-symmetrical structure, or bulky constituents into the polymer backbone^{5,6}. It is well known that polyamides containing heterocyclic units in the main chain have excellent thermal stabilities^{7,8}. Among various methods for polyamide synthesis, direct polycondensation methods have been developed by several investigators and especially by Yamazaki and Higashi⁹. In these methods, preparation and isolation of acid chlorides are not required and the reactions proceed as one pot pathway by using the free dicarboxylic acid and diamines in the presence of various activating agents. Also optically active polymers have found interesting applications because of their specific properties such as the ability of molecular recognition,

which caused to use them as a chiral stationary phase in chromatography methods for enantiomeric separations¹⁰. They can also be used as chiral media for asymmetric synthesis and chiral liquid crystals in ferroelectric and nonlinear optical devices¹¹. Recently the optically active polymers have been synthesized by reaction of an optically active monomer with several diamines by using usual polymerization techniques¹². In this article six new copolyamides (**9a-f**) were synthesized through the direct polycondensation reaction of *N*-phthaloyl-L-glutamic acid (**3**) with 4,4'-diamino diphenylether (**4**), 4,4'-diamino diphenylsulfone **5** in the presence of adipic acid (**6**), fumaric acid (**7**) and terephthalic acid (**8**) as a second diacid in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine.

EXPERIMENTAL

Phthalic anhydride (**1**), L-glutamic acid (**2**), 4,4'-diamino diphenylether (**4**), 4,4'-diamino diphenylsulfone (**5**), adipic acid (**6**), fumaric acid (**7**), terephthalic acid (**8**), triphenyl phosphite (TPP), *N*-methyl-2-pyrrolidone and pyridine were purchased from Merck Chemical Company and used without previous purification. Also commercially available calcium chloride (CaCl₂) was purchased from Merck Chemical Company and dried under vacuum at 150 °C for 6 h. ¹H NMR and ¹³C NMR

TABLE-1
 SYNTHESIS AND SOME PHYSICAL PROPERTIES OF COPOLYAMIDES **9a-f**

Polymer	Second diacid	Diamine	Yield (%)	η_{inh} (dl/g) ^a	$[\alpha]_D^{25a}$
9a	Adipic acid (6)	4,4'-diamino diphenyl ether (4)	95	0.34	+58
9b	Fumaric acid (7)	4,4'-diamino diphenyl ether (4)	88	0.40	+45
9c	Terephthalic acid (8)	4,4'-diamino diphenyl ether (4)	93	0.48	+81
9d	Adipic acid (6)	4,4'-diamino diphenyl sulfone (5)	94	0.39	+92
9e	Fumaric acid (7)	4,4'-diamino diphenyl sulfone (5)	91	0.40	+69
9f	Terephthalic acid (8)	4,4'-diamino diphenyl sulfone (5)	89	0.45	+77

^aMeasured at a concentration of 0.5 g/dL in DMF at 25 °C

spectra were recorded on a Bruker 300-MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England) as solid by using KBr pellets. Inherent viscosities were measured by a standard procedure using a Technico Regd Trad Mark Viscometer and Specific Rotations were measured by an A-Kruss polarimeter. The eluents were monitored with a UV detector (JMST Systems, USA, VUV-24) at 254 nm and Polystyrene was used as the standard. Thermal gravimetric analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 system under N₂ atmosphere at rate of 10 °C/min and Elemental analyses were measured by various EL equipment in Arak University.

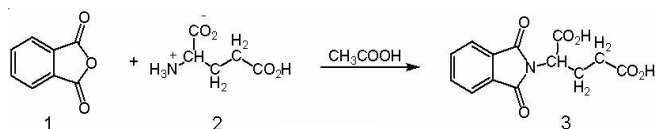
Monomer synthesis

N-Phthaloyl-L-glutamic acid (3): This compound was prepared according to a typical procedure was shown in **Scheme-I**¹³.

Polymer synthesis: In a 100 mL round bottomed flask were placed a mixture of *N*-phthaloyl-L-glutamic acid **3** (0.16 mmol), second diacid (**6-8**) (0.16 mmol), diamine (**4-5**) (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 (**9a-f**) was dried under vacuum.

RESULTS AND DISCUSSION

Monomer synthesis: *N*-Phthaloyl-L-glutamic acid **3** was synthesized by the condensation reaction of one equimolar of phthalic anhydride (**1**) with one equimolar of L-glutamic acid (**2**) in an acetic acid solution (**Scheme-I**).

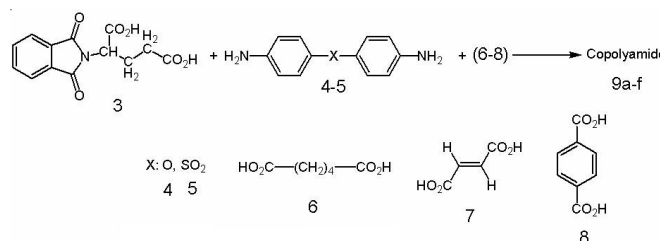


Scheme-I Synthetic route of *N*-Phthaloyl-L-glutamic acid **3**

The chemical structure and purity of diacid **3** were proved by using elemental analysis, ¹H NMR, ¹³C NMR and FTIR spectroscopy¹³.

Polymer synthesis: Copolyamides (**9a-f**) were synthesized by the direct solution polycondensation reaction of an equimolar mixture of diacid (**3**), an equimolar mixture of diacid

(**6-8**) with two equimolar mixture of aromatic diamines (**4-5**) by using triphenyl phosphite (TPP) and pyridine as condensing agents (**Scheme-II**). The synthesis and some physical properties of these polyamides (**9a-f**) are given in Table-1. All the polymers were obtained in moderate to good yields and had inherent viscosities between 0.34-0.48 dL g⁻¹. The incorporation of chiral unit into the polymer structure was confirmed by measuring their specific rotations based on of optically active nature of these polymers (Table-1).



Scheme-II Synthetic route of copolyamides **9a-f**

Polymer characterization: These polymers were confirmed to be copolyamides by using FTIR spectroscopy and elemental analyses. The representative FTIR spectrum of copolyamides (**9b**) was shown in Fig. 1. The polymer showed the C=O asymmetric stretching of imide and ester at 1774 cm⁻¹, the C=O symmetric stretching of imide and ester groups at 1707 cm⁻¹, C-N stretching at 1377 cm⁻¹, C-O-C stretching at 1201-1068 cm⁻¹. All of these copolyamides exhibited strong absorption around 1383 and 729 cm⁻¹, which shows the presence of the heterocyclic imide groups (Table-2). Table-2 shows elemental analysis of polyamides (**9a-f**).

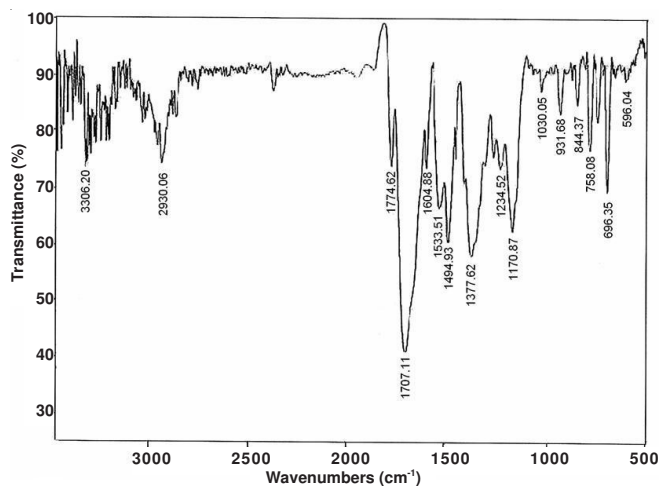


Fig. 1. FTIR spectrum of copolyamide **9b**

TABLE-2
 FTIR CHARACTERIZATION OF COPOLYAMIDES **9a-f**

Polymer	Spectra data
9a	FT-IR peaks (cm⁻¹): 3296 (w), 2970 (m), 1774 (m), 1710 (s), 1598 (w), 1491 (m), 1383 (s), 1201 (m), 1155 (m), 1107 (w), 976(w), 725 (w), 684 (w). C ₄₃ H ₃₇ N ₅ O ₈ (751.43) _n . Calc. C % 68.72; H % 4.92; N % 9.31. Found C % 67.60; H % 4.50; N % 8.90.
9b	FT-IR peaks (cm⁻¹): 3306 (m), 2930 (m), 1774 (m), 1707 (s), 164 (w), 1533 (m), 1494 (m), 1377 (s), 1234 (w), 1170 (m), 1030 (w), 844 (w), 727 (w), 596 (w). C ₄₁ H ₃₁ N ₅ O ₈ (721.22) _n . Calc. C % 68.23; H % 4.33; N % 9.70. Found C % 67.90; H % 4.30; N % 9.60.
9c	FT-IR peaks (cm⁻¹): 3308 (m), 2968 (w), 1776 (m), 1710 (s), 1603 (w), 1514 (w), 1462 (w), 1386 (s), 1199 (s), 1068 (w), 839 (m), 725 (w), 688 (w). C ₄₅ H ₃₃ N ₅ O ₈ (771.45) _n . Calc. C % 70.052; H % 4.27; N % 9.07. Found C % 70.00; H % 4.00; N % 8.10.
9d	FT-IR peaks (cm⁻¹): 3301 (w), 2968 (m), 1776 (w), 1712 (s), 1678 (m), 1609 (w), 1541 (m), 1464 (m), 1383 (s), 1321 (w), 1201 (m), 1113 (w), 723 (w). C ₄₃ H ₃₇ N ₅ O ₁₀ S ₂ (847.91) _n . Calc. C % 60.91; H % 4.40; N % 8.26. Found C % 60.20; H % 4.30; N % 8.10.
9e	FT-IR peaks (cm⁻¹): 3309 (w), 2958 (w), 1774 (m), 1707 (s), 1632 (m), 1591 (m), 1481 (m), 1383 (m), 1246 (w), 1109 (m), 729 (w), 698 (m), 501 (w). C ₄₁ H ₃₁ N ₅ O ₁₀ S ₂ (817.41) _n . Calc. C % 60.24; H % 3.79; N % 8.56. Found C % 60.00; H % 3.50; N % 8.00.
9f	FT-IR peaks (cm⁻¹): 3315 (w), 2972 (w), 1774 (m), 1710 (s), 1589 (m), 1494 (w), 1384 (s), 1300 (w), 1140 (m), 1103 (w), 848 (m), 729 (m), 611 (w). C ₄₅ H ₃₃ N ₅ O ₁₀ S ₂ (867.17) _n . Calc. C % 62.27; H % 3.83; N % 8.07. Found C % 62.00; H % 3.70; N % 7.90.

The solubility of copolyamides (**9a-f**) was investigated with 0.01 g polymeric samples in 2 mL of a solvent. All these PAs were soluble in organic solvents such as *N,N*-dimethyl formamide (DMF), *N,N*-dimethylacetamide (DMAc), DMSO, NMP at room temperature and were insoluble in solvents such as ethanol, methanol, methylene chloride and water.

Thermal properties: The thermal properties of three samples of resulting polymers **9d-f** (Fig. 2) containing three different of second diacids such as adipic acid, fumaric acid and terephthalic acid were investigated with TGA and DTG in nitrogen atmosphere at a rate of heating of 10 °C per min and thermal data are summarized in Table-3. The initial decomposition temperatures of 5 and 10 % weight losses (T_5 and T_{10}) and the char yields at 600 °C for them are summarized in Table-3. These polymers exhibited moderate to good resistance to thermal decomposition, up to 270-330 °C in nitrogen and began to decompose gradually that temperature. T_5 for these polymers ranged from 375-335° and T_{10} for them ranged from 315-365 °C and residual weights for these polymers at 600 °C ranged from 51.85-60.40 % in nitrogen. According to the results thermal stability of these polymers related to the second diacid in the main chain. Thermal stability of polymer **9f** with 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 **9e** has higher thermal stability in compare to polymer **9d** with adipic acid as second diacid.

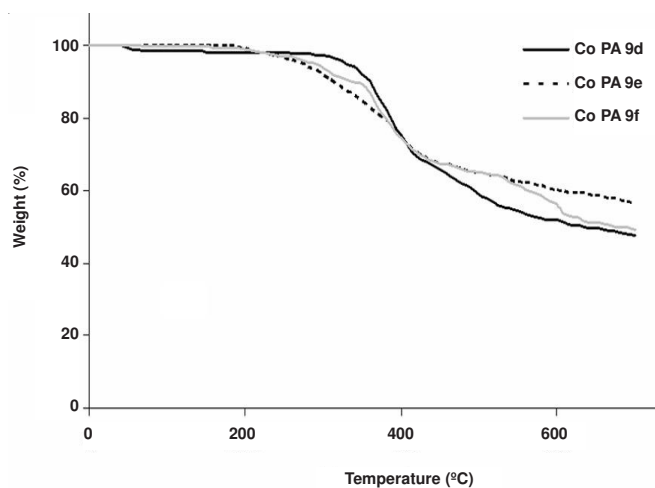

 Fig. 2. TGA Thermograms of copolyamides **9d-f**

 TABLE-3
 THERMAL BEHAVIOUR OF COPOLYAMIDES **9d-f**

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c
9d	330-335	360-365	51.85
9e	270-275	310-315	60.40
9f	290-295	340-345	56.41

^{a,b}Temperature at which 5 or 10 % weight loss was recorded TGA at a heating rate of 10 °C/min in N₂; ^cWeight percentage of material left after TGA analysis at maximum temperature 600°C in N₂

Conclusion

In this work, six new thermally stable copolyamides (**9a-f**) were synthesized through the direct polycondensation reaction of *N*-phthaloyl-L-glutamic acid (**3**) with 4,4'-diamino diphenylether (**4**), 4,4'-diamino diphenylsulfone (**5**) in the presence of adipic acid (**6**), fumaric acid (**7**) and terephthalic acid (**8**) as a second diacid in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine. On the other hand by introducing pendent units into the polymer side chain can disturb interchanging hydrogen bond, inherent macromolecular rigidity and diminishing packing efficiency and crystallinity that increases solubility in polar aprotic solvents. Since, these optically active polymers have chiral center in the polymer architecture and also have optical activity. Thermal stability and optically active properties can make these polymers attractive for practical applications such as processable high-performance engineering plastics used as chiral stationary phase and chiral media for asymmetric synthesis.

REFERENCES

- P.E. Cassidy, *Thermally Stable Polymers: Synthesis and Properties*, New York, Marcel Dekker (1980).
- Kh. Faghihi and M. Hagibeygi, *Eur. Polym. J.*, **39**, 2307 (2003).
- J.P. Critchley, G.J. Knight and W.W. Wright, *Heat Resistant Polymers*, New York: Plenum Press (1983).
- S. Bhuvana, M. Madhumathi and M. Sarojadevi, *Polym. Bull.*, **57**, 61 (2006).
- S.H. Hsiao, C.W. Chen and G.S. Liou, *J. Polym. Sci. Part A: Polym. Chem.*, **42**, 3302 (2004).
- S. Mallakpour and M. Kolahdozan, *J. Appl. Polym. Sci.*, **104**, 1248 (2007).
- M. Onciu, *J. Appl. Polym. Sci.*, **103**, 2013 (2007).
- S. Mallakpour and Z. Rafiee, *J. Appl. Polym. Sci.*, **103**, 947 (2007).
- N. Yamazaki, M. Matsumoto and F. Higashi, *J. Polym. Sci. Part A: Polym. Chem.*, **13**, 1373 (1975).
- L. Cianga, *Eur. Polym. J.*, **39**, 2271 (2003).
- Y. Okamoto and T. Nakano, *Chem. Rev.*, **94**, 349 (1994).
- Kh. Faghihi, M. Hagibeygi and M. Shabaniyan, *Macromol. Res.*, **17**, 739 (2009).
- Kh. Faghihi, M. Shabaniyan and A. Izadkhan, *Chin. J. Polym. Sci.*, **28**, 589 (2010).