

SYNTHESIS AND CHARACTERIZATION OF NEW HEAT RESISTANCE AND ORGANOSOLUBLE POLY(ETHER-AMIDE)

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(Received September 25, 2012; revised March 16, 2013)

ABSTRACT. New series of olefinic poly(ether-amide)s (OPEA)s **6a-f** was synthesized from 4,4'-bis(1,4-diphenoxybutane)diacrylic acid **4** and aromatic diamine **5a-f** via a direct polycondensation reaction. The resulting polymers were characterized by Fourier transform infrared spectra (FTIR), nuclear magnetic resonance (¹H-NMR), solubility test and inherent viscosity. The thermal properties of the polymers **6a-c** were investigated by thermogravimetric analysis (TGA). Polymer **6c** due to presence of SO₂ group as a polar group shows better thermal properties compare with polymer **6a** and **6b**.

KEY WORDS: Polycondensation, Polyamide, Ether group, Thermal properties

INTRODUCTION

Aromatic polyamides are noted for high transparency, excellent mechanical properties, heat resistance, good char yield, low flammability, good barrier properties, and outstanding strength-to-weight ratios and solvent resistance [1-4]; however, they are difficult to process because of limited solubility and high glass transition (T_g) [5-7]. The processing of these polymers has been greatly hindered because they lack softening or melting property at usual processing temperature, and they tend to decompose at the softening temperature. Many efforts have been made to create structurally modified aromatic polyamides having better solubility and processability. It is known that the solubility of polyamides is often increased when flexible bonds such as [-CH₂-, -O-, -SO₂-, -C(CF₃)₂], bulky pendent groups, polar components or large pendent groups are incorporated into the polymer backbone due to the altering crystallinity and intermolecular interactions [8-13], synthesis of polyamides with noncoplaner unit in the polymer chains [14], preparation of copolymers such as poly(amide-imide)s [15-18], poly(ester-imide)s [19], poly(amide-ester-imide)s [20] and the introduction of bulky side groups into the polymer chains [21-23] resulted a series of modified polyamides.

It has been recognized that the incorporation of aryl-ether linkages generally imparts an enhanced solubility, processability, and toughness of aromatic polyamides without substantial diminution of thermal properties [24]. Aromatic polymers that contain aryl ether linkages generally have lower glass transition temperatures, greater chain flexibility, and tractability in compared to their corresponding polymers without these groups in the chain [25-27]. The lower glass transition temperatures and also improved solubility are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation [28].

In this article, new series of olefinic poly(ether-amide)s **6a-f** were synthesized by reacting 4,4'-bis(1,4-diphenoxybutane) diacrylic acid **4** and various diamine **5a-f** via a direct polycondensation reaction in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, USA), Merck Chemical Co. (Germany) and Acros Organics NV/SA (Belgium).

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Techniques

The Fourier transform infrared spectra (FTIR) were measured using the Bruker Vertex 80 V spectrometer over the wavenumber range of 600–4000 cm^{-1} . NMR measurements were performed with a Bruker 300 MHz and Bruker 500 MHz spectrometer. DMSO- d_6 was used as the solvent and the solvent signal was used for internal calibration (DMSO- d_6 : δ (^{13}C) = 39.6 ppm, δ (^1H) = 2.5 ppm). Inherent viscosities were measured by a standard procedure by using a Technico Regd Trad Mark Viscometer. Thermal gravimetric analysis (TGA) data for the polymers were taken on a Mettler TA4000 System in the range between room temperature and 800 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

Monomer synthesis

Synthesis of 4,4'-bis(1,4-diphenoxybutane) diacrylic acid 4. At first 4,4'-bis(1,4-diphenoxybutane) dialdehyde **3** was synthesized from the reaction of 4-hydroxybenzaldehyde (34 mmol) **1** and 17 mmol of dry K_2CO_3 in 30 mL dimethyl formamide (DMF) with 17 mmol of 1,4-dibromo butane **2** in 5 mL dry dimethyl formamide. The reaction mixture was heated for 6 h at 120 $^\circ\text{C}$, then was cooled and poured onto crushed ice. The solid was precipitated, washed with the cold water and filtered at room temperature until product was obtained. $^1\text{H-NMR}$ (DMSO- d_6 , TMS) δ : 1.9 (s, 4H), 4.11–5.15 (d, 4H), 7.10–7.13 (d, 4H), 7.84–7.87 (d, 4H), 9.86 (s, 2H) ppm. Then 5 mmol of 4,4'-bis(1,4-diphenoxybutane) dialdehyde **3** were placed in a 100 mL beaker with 11 mmol malonic acid using 1 mL morpholine under solvent-free conditions. The mixture compounds were heated until completely melted. Then the heating was removed and 20 mL of 5% HCl was added in the reaction mixture slowly with stirring and the stirring continued at room temperature for 2 h. After that the white precipitate was filtered and washed with 20 mL H_2O and filtered until white product was obtained. M.p. 323–325 $^\circ\text{C}$, FTIR (KBr): 2400–3500 (s, br), 1688 (s), 1627 (s), 1602 (s), 1510 (s), 1429 (s), 1310 (s), 1219 (s), 1171 (m), 1018 (s, br), 827 (m), 680 (m), 510 (w) cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS) δ : 1.87 (s, 4H), 4.08 (s, 4H), 6.34–6.40 (d, 2H), 6.98–7.11 (d, 4H), 7.51–7.57 (d, 2H), 7.62–7.86 (d, 4H), 12.36 (s, br, 2H) ppm. $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 168.32, 160.77, 144.23, 130.42, 127.19, 115.87, 115.25, 67.73, 25.73 ppm.

Synthesis of olefinic poly(ether-amide)s

Polyamides **6a–f** were synthesized by direct polycondensation reaction. As an example the preparation of OPEA **6e** is described below. OPEA **6e** was prepared from the reaction of 4,4'-bis(1,4-diphenoxybutane) diacrylic acid **4** with 4,4'-diaminodiphenyl-ether **5e**. In a 25 mL round-bottomed flask which was fitted with a stirring bar were placed diacid **4** (0.64 mmol), 4,4'-diaminodiphenylether **5e** (0.64 mmol), calcium chloride (0.20 g, 1.80 mmol), triphenyl phosphite (1.68 mL, 6.00 mmol), pyridine (0.36 mL) and N-methyl-2-pyrrolidone (2 mL). The reaction mixture was heated under reflux on an oil bath at 60 $^\circ\text{C}$ for 1 h, then 90 $^\circ\text{C}$ for 2 h, and 120 $^\circ\text{C}$ for 6 h. The OPEA **6e** formed was viscous, then the reaction mixture was poured into 50 mL of methanol and the precipitated polymer was collected by filtration and washed thoroughly with hot methanol and dried at 60 $^\circ\text{C}$ for 12 h under vacuum to leave solid OPEA **6e**.

Polymer 6a. FTIR (KBr): 3320 (m), 2947 (m), 1689 (s), 1589 (m), 1541 (m), 1481 (m), 1384 (m), 1186 (m), 690 (w), 501 (w) cm^{-1} .

Polymer 6b. FTIR (KBr): 3310 (w), 3075 (m), 2957 (m), 1685 (s), 1622 (s), 1578 (m), 1539 (m), 1480 (m), 1424 (m), 1380 (m), 1278 (m), 1170 (m), 1079 (m), 950 (w), 729 (m), 699 (m) cm^{-1} .

Polymer 6c. FTIR (KBr): 3328 (w), 3032 (m), 2960 (m), 1688 (s), 1615(s), 1522 (m), 1540 (m), 1483 (m), 1427 (m), 1380 (m), 1308 (m), 1180 (m), 1071 (m), 962 (w), 727 (m), 650 (m) cm^{-1} .

Polymer 6d. FTIR (KBr): 3287 (w), 3025 (m), 2955 (m), 1670(s), 1550 (m), 1481 (m), 1435 (m), 1385 (m), 1310 (m), 1165 (m), 1064 (m), 952 (w), 730 (m), 652 (m) cm^{-1} .

Polymer 6e. FTIR (KBr): 3267 (w), 3020 (m), 2945 (m), 1669 (s), 1549 (m), 1479 (m), 1435 (m), 1388 (m), 1268 (m), 1165 (m), 1062 (m), 952 (w), 731 (m), 655 (m) cm^{-1} .

Polymer 6f. FTIR (KBr): 3332 (w), 3018 (m), 2975 (m), 1684 (s), 1549 (m), 1479 (m), 1435 (m), 1388 (m), 1259 (m), 1165 (m), 1068 (m), 952 (w), 726 (m), 651 (m) cm^{-1} .

RESULTS AND DISCUSSION

Monomer synthesis

Dicarboxylic acid **4** containing aryl ether and methylene group was synthesized by using two step reactions. At first 4,4'-bis(1,4-diphenoxybutane)dialdehyde **3** was prepared from the reaction of one equimolar 1,4-dibromobutane **2** and two equimolars 4-hydroxybenzaldehyde **1**. Then dialdehyde compound **3** was reacted with malonic acid at presence of catalytic amount of morpholine under a solvent free condition. The chemical structure and purity of dicarboxylic acid compound **4** were confirmed by FTIR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopy.

Polymer synthesis

Olefinic poly(ether-amide)s **6a-f** were synthesized via direct polycondensation reaction of diacid **4** with aromatic diamine **5a-f** via direct polycondensation reaction in a medium consisting of N-methyl-2-pyrrolidone (NMP), triphenyl phosphite (TPP), calcium chloride and pyridine (Scheme 1). The OPEAs **6a-f** were obtained in good yields (Table 1).

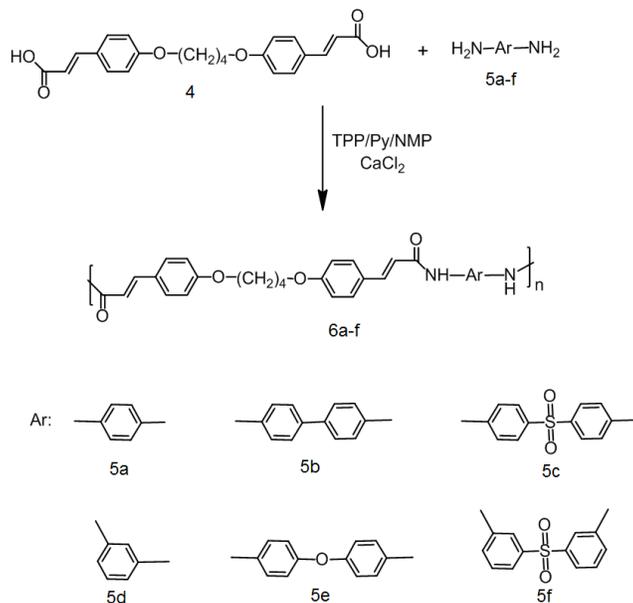
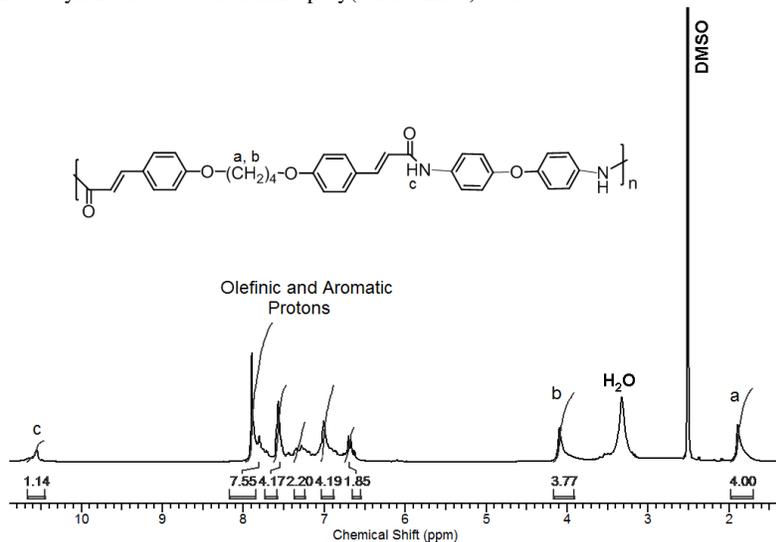
Table 1. Some physical properties of OPEAs **6a-f**.

Polymer	Yield (%)	η_{inh} (dL/g) ^a	Color ^b
6a	93	0.72	Y
6b	96	0.66	Y
6c	95	0.67	C
6d	91	0.61	C
6e	94	0.58	Y
6f	89	0.57	B

^aMeasured at a concentration of 0.5g/dL in DMF at 25°C. ^bB = Brown, C = Cream, Y= Yellow.

Polymer characterization

The structure of polymer was confirmed by $^1\text{H-NMR}$ and FTIR spectroscopies. FTIR data of OPEAs **6a-f** exhibited characteristic absorption bands around 1670 cm^{-1} for the amide group (C=O stretching vibration) and the N-H stretching absorption bands of amide groups around 3280 cm^{-1} (N-H stretching). The $^1\text{H-NMR}$ spectrum of polymer **6e** showed peaks that confirm its chemical structure (Figure 1). The aromatic and olefinic protons related to polymer backbone appeared in the region of 6.6-7.8 ppm. The protons related to methylene group appeared at 1.9 and 4.1 ppm and the peak in the region of 10.5 ppm is assigned for NH of the amide groups in the polymer chain.

Scheme 1. Synthesis route of olefinic poly(ether-amide) **6a-f**.Figure 1. ¹H-NMR spectrum of OPEA **6e**.*Solubility test*

One of the main objectives of this study was producing modified polyamides with improved solubility. The incorporation of monomers with flexible group such as ether moieties in the polymer backbone, led to these polymers have good solubility in various solvents, especially organic aprotic solvents. The solubility of OPEAs **6a-f** was investigated as 0.01 g of polymeric

sample in 2 mL of solvent. Remarkably, all of OPEAs were easily soluble at room temperature in aprotic polar solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF) and insoluble in solvents such as acetone, chloroform, ethanol and methanol (Table 2).

Table 2. Solubility of OPEAs **6a-f**.

Solvent	6a	6b	6c	6d	6e	6f
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
Cyclohexanone	-	-	-	-	-	-
CHCl ₃	-	-	-	-	-	-
Acetone	-	-	-	-	-	-
EtOH	-	-	-	-	-	-
MeOH	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-

Solubility: + : soluble; -: insoluble.

Thermal properties

Thermal stability of the OPEA **6a-c** determined under inert atmosphere is shown in Figure 2. The initial decomposition temperatures of 5% and 10% weight losses (T_5 and T_{10}) and the char yield at 800 °C are summarized in Table 3. Thermal decomposition temperatures of the polymers were found in the range 237-241 °C. Compared with the thermal decomposition behavior of OPEA **6a**, OPEA **6b** and **6c** with two benzene rings show higher 5 wt% and 10 wt% and delay the decomposition. The weight retained at 800 °C shows higher char residue at high temperature and improves significantly with percent of SO₂ group.

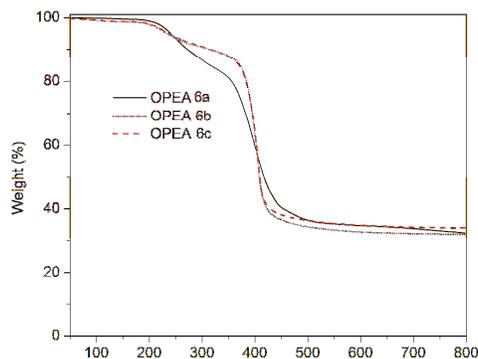


Figure 2. TGA curves of OPEAs **6a-c**.

Table 3. Thermal and fire measurements of OPEAs **6a-c**.

Polymer	T_5 (°C) ^a	T_{10} (°C) ^a	Char yield ^b
OPEA 6a	241	273	33.34
OPEA 6b	234	315	33.10
OPEA 6c	237	316	34.96

^aTemperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10 °C/min under N₂.

^bWeight percentage of material left after TGA analysis at a maximum temperature of 800 °C.

CONCLUSIONS

In this article, an efficient method for the synthesis of 4,4'-bis(1,4-diphenoxybutane) diacrylic acid **4**, containing ether and olefinic groups, has been developed under solvent free condition in presence of morpholine as a catalyst. New poly(ether-amide)s with good inherent viscosity were prepared by the direct polycondensation reaction of the synthesized diacid and aromatic diamine **5a-f**. The results presented herein also clearly demonstrate that incorporating the ether group into the polymer main chain as well as combination of the wholly aromatic backbone and several functional groups remarkably enhanced the solubility in organic solvents of the new polymers. The thermal stability and char residue of the OPEA **6c** due to presence SO₂ have been increased as compared with the OPEA **6a**. These properties could make these OPEAs attractive for practical applications such as processable high-performance engineering plastics.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the support of this work by the research council of Farahan branch, Islamic Azad University, Farahan, Iran.

REFERENCES

1. Hsiao, S.H.; Chang, Y.H. *Eur. Polym. J.* **2004**, *40*, 1749.
2. Chatfield, D.A.; Einhorn, I.N.; Mickelson, R.W.; Futrell, J.H. *J. Polym. Sci. Part A: Polym. Chem.* **1979**, *17*, 1353.
3. Faghihi, K.; Shabani, M. *Macromol. Res.* **2010**, *18*, 1148.
4. Zulfiqar, S.; Ahmad, Z.; Ishaq, M.; Sarwar, M. I. *Mat. Sci. Eng. A.* **2009**, *525*, 30.
5. Sarwar, M.I.; Zulfiqar, S.; Ahmad Z. *Polym. Int.* **2008**, *57*, 292.
6. Shabani, M.; Faghihi, K.; Shabani, F. *Polym. Bull.* **2012**, *68*, 375.
7. Liou, G.S.; Lin, H.Y.; Yen, H.J. *J. Mater. Chem.* **2009**, *19*, 7666.
8. Faghihi, K.; Hajibeygi, M.; Shabani, M. *J. Macromol. Sci. Part A: Pure Appl. Chem.* **2010**, *47*, 44.
9. Diakoumakos, C.D.; Mikroyannidis, J.A. *Polymer.* **1994**, *35*, 1986.
10. Faghihi, K.; Shabani, M. *J. Thermoplast. Compos. Mater.* **2012**, *25*, 89.
11. Faghihi, K.; Shabani, M.; Emamdadi, N. *Macromol. Res.* **2010**, *18*, 753.
12. Faghihi, K.; Shabani, M.; Izadkhah, A. *Chinese J. Polym. Sci.* **2010**, *28*, 589.
13. Mllakpour, S.; Kowsari, E. *Polym. Adv. Technol.* **2005**, *16*, 732.
14. Liaw, D.J.; Hsu, P.N.; Liaw, B.Y. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 63.
15. Hajibeygi, M.; Shabani M.; Khodaei-Tehrani, M. *Des. Monomers Polym.* **2011**, *14*, 617.
16. Ghaemy, M.; Khajeh, S. *Chinese J. Polym. Sci.* **2012**, *30*, 82.
17. Mansoori, Y.; Shah Sanaei, S.; V. Atghia, S.; Zamanloo M.R.; Gh. Imanzadeh. *Chinese J. Polym. Sci.* **2011**, *29*, 699.
18. Hajibeygi, M.; Faghihi, K.; Shabani, M. *J. Appl. Polym. Sci.* **2011**, *121*, 2877.
19. Patel, H.S.; Patel, B.P.; Patel, D.B. *Int. J. Polym. Mater.* **2009**, *58*, 625.
20. Liaw, D.J.; Liaw, B.Y. ; Yang, C.M. *Macromol. Chem. Phys.* **2001**, *202*, 1866.
21. Ayala, V.; Maya, E.M.; Garcia, J.M.; de la Campa, J.G.; Lozano, A.E.; Abajo, J. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 112.
22. Hsiao, S.H.; Yang, C.P.; Chen, C.W.; Liou, G.S. *Eur. Polym. J.* **2005**, *41*, 511.
23. Sava, I.; Bruma, M. *Macromol. Symp.* **2006**, *239*, 36.
24. Hajibeygi, M.; Shabani, M. *J. Appl. Polym. Sci.* **2012**, *126*, 280.

25. Hale, W.F.; Farnham, A.G.; Johnson, R.N.; Clendinning, R.A. *J. Polym. Sci. Part A: Polym. Chem.* **1976**, *5*, 2399.
26. Johnson, R.N.; Farnham, A.G.; Clendinning, R.A.; Hale, W.F.; Merriman, C.N. *J. Polym. Sci. Part A: Polym. Chem.* **1967**, *5*, 2375.
27. Faghihi, K.; Hajibeygi, M. *Chinese J. Polym. Sci.* **2010**, *28*, 517.
28. Gutch, P.K.; Banerjee, S.; Jaiswal, D.K. *J. Appl. Polym. Sci.* **2003**, *89*, 691.