

Synthesis and Properties of New Polyamides Based on 4-Phenylene Diacrylic Acid and Aromatic Diamines

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Abstract

Six new polyamides **5a-f** were prepared by direct polycondensation reaction of 4-phenylenediacrylic acid **3** with six aromatic diamines **4a-f** by using thionyl chloride and pyridine as condensing agents in N-methyl-2-pyrrolidone (NMP) as solvent. These new polymers **5a-f** were obtained in high yield and inherent viscosity between 0.30-0.50 dL/g. The resulting polyamides were characterized by elemental analysis, viscosity measurements, thermal gravimetric analysis (TGA and DTG), solubility test, FT-IR and UV-vis spectroscopy. 4-Phenylenediacrylic acid **3** was prepared by the condensation reaction of terephthal aldehyde **1** with malonic acid **2** in the presence of pyridine.

Key words: Polyamides, 4-phenylenediacrylic acid, aromatic diamines

Introduction

Thermally stable polymers have been received extensive interest in recent decades because of increasing demands for high temperature polymers as the replacement for metals or ceramics in automotive, aerospace, and microelectronic industries.⁽¹⁻⁴⁾ Aromatic polyamides are certainly one of the most successful classes of high-temperature polymers, and have found extensive use in the aviation, automotive, and electronic industries.⁽⁵⁻⁷⁾ However these polymers encounter processing difficulty due to their infusibility and poor solubility in organic solvents.^(8,9) Therefore, more researches have been focused on maintaining considerable thermally stable and improving their solubility. These studies include:

- 1) Introducing rather soft segments on the main chain such as methylene and vinyl segments
- 2) Breaking its symmetry and regularity, thereby making crystallization impossible
- 3) Introducing the bulky side groups to be exempt from crystallization and 4) Destroying the hydrogen bonding by N-substitution with certain groups such as methyl.⁽¹⁰⁻¹⁹⁾

The conventional method for synthesis of polyamides begins with having diamine reaction with a diacid chloride monomer by low temperature solution polycondensation. In another method Yamazaki and co-workers reported a direct polycondensation reaction for synthesis of aromatic polyamides. According to their investigation, this procedure could obtain a high yield of polymers at a high molecular weight.⁽²⁰⁻²¹⁾

In this paper we used Yamazaki method for synthesis of a series of novel polyamides from the direct polycondensation reaction of 4-phenylenediacrylic acid **3** with six different aromatic diamines **4a-f** by using of thionyl chloride and pyridine as condensing agents in

NMP as solvent. These polymers have a soft segment such as vinyl moiety in main chain for improving solubility in organic solvents in compared to aromatic polyamides. On the other hand there is a considerable attention for synthesis polymers containing p-phenylenediacryloyl moiety in main chain, because they can be used for preparing photosensitive liquid crystalline polymers. There are some reported papers about synthesis polyester, polyimides, polyamides and poly(amid-co-imide)s containing p-phenylenediacryloyl moiety in main chain.⁽²²⁻²⁵⁾

Experimental

Materials

All chemicals were purchased from Merck Chemical Co. (Germany) and Aldrich Chemical Co. (USA).

Techniques

¹H-NMR spectra were recorded on a Bruker 500 MHz instrument. UV-vis absorption were recorded at 25 °C in the 200-700 nm spectral region with a Perkin-Elmer Lambda 19 spectrophotometer in DMF by using cell path lengths of 1 cm. Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were performed by using 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 using a Technico Regd Trad Merk Viscometer. Thermal Gravimetric Analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N₂ atmosphere at a rate of 10°C/min. Elemental analyses were performed by the Arak Petrochemical Company, Arak, Iran.

Monomer synthesis

4-Phenylenediacrylic acid 3

This compound was prepared according to a typical procedure that was shown in scheme 1.

p-Phenylenediacrylic acid 3

Into a 100 mL round-bottomed flask were added terephthal aldehyde 1 (3.48 g, 26 mmol), malonic acid 2 (8.27 g, 94 mmol) to 30 mL of pyridine containing small amount of piperidine. The reaction mixture was stirred for 2h at 45°C, 4h at 80°C and 3h at 110°C respectively. The solution was poured into large amount of distilled water and neutralized with 10% HCl to obtain white precipitate. The precipitate was filtered, washed with water, acetic acid and acetone and then dried in a vacuum oven at room temperature to give 5.16 g (91 %) of white crystal compound 3: mp >300°C, FT-IR (KBr): 3400-2500 (m, br), 1665 (s, br), 1610 (s), 1501 (w, sh), 1412(m), 1287 (s), 1262 (s), 1209 (s), 1135 (m), 979 (m), 938 (m), 862 (w) cm⁻¹. ¹H-NMR (DMSO-d₆, TMS): δ 6.54-6.57 (d, 2H, J=16 Hz); 7.56-7.59 (d, 2H, J=16 Hz); 7.70 (s, 4H); 12.85 (b, 2H) ppm. Analysis: Calculated for C₁₂H₁₀O₄: C, 66.07; H, 4.58; found: C, 66.2; H, 4.4.

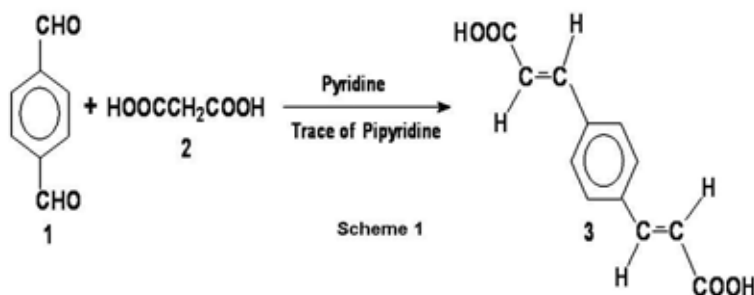
Polymer Synthesis

The Polyamides 5a-f were prepared by using the following general procedure: Taking polymer 5a as an example: The diacid 3 (0.218 g, 1 mmol) was dissolved in 10 ml of N-methyl pyrrolidone in a dry three necked flask. The solution was cooled down to -10°C and thionyl chloride (0.29 g, 2.5 mmol) was added and stirred for 5 min. 1,4-Phenylene diamine 4a (0.10 g, 1 mmol) and pyridine (0.19 g, 2.5 mmol) were added to the mixture and stirred for 15 h at 0°C . The mixture was warmed to room temperature and stirred for 2hrs. The viscous reaction mixture was poured into 25 ml of methanol. The precipitated polymer 5a was collected by filtration and dried at 80°C for 8 h under vacuum to leave 0.27 g (95 %) of product.

Results and Discussion

Monomer Synthesis

4-Phenylenediacyrylic acid 3 was synthesized from the reaction of terephthal aldehyde 1 with malonic acid 2 in pyridine as solvent and in the presence of pipyridine as catalyst (Scheme 1).



The chemical structure and purity of compound 3 was confirmed by elemental analysis, FT-IR and ¹H-NMR spectroscopic techniques. The FT-IR spectrum of compound 3 showed a broad peak between $2800\text{-}3500\text{ cm}^{-1}$ which was assigned to the COOH group. Several absorption bands at 1665 , 1610 , 1501 cm^{-1} were observed which were characteristic peaks for carbonyl bond, vinyl segment and aromatic ring, respectively (Fig. 1).

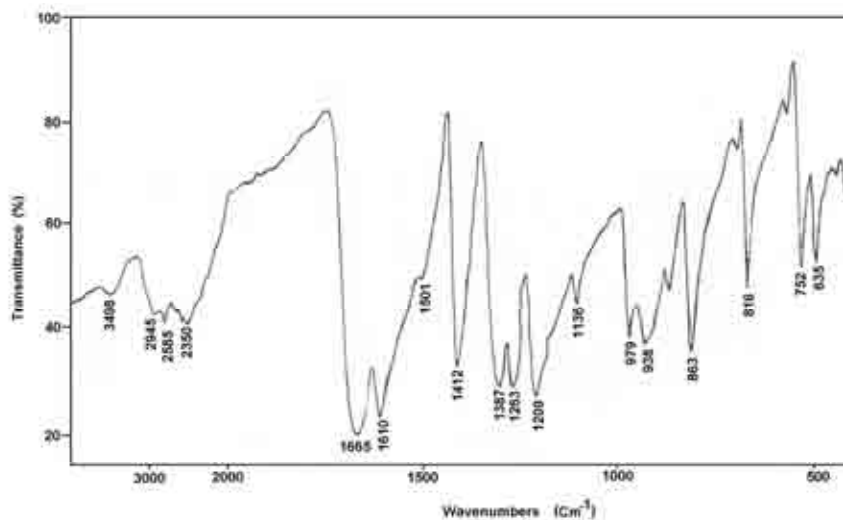


Fig. 1 FTIR Spectrum of Diacid 3

The $^1\text{H-NMR}$ spectrum of diacid 3 showed two doublet peaks at 6.54-6.57 and 7.56-7.59 ppm were assigned to the H_a and H_b protons of vinyl group. Peak at 7.70 ppm were assigned to the H_c protons of aromatic ring. Finally the broad peak between 12.80-13.00 ppm was assigned to H_d protons of COOH groups (Fig 2).

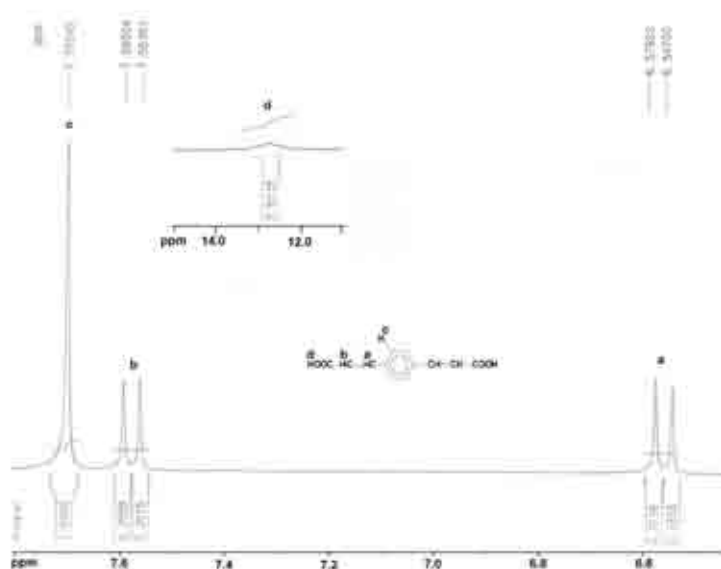


Fig. 2 $^1\text{H-NMR}$ (500 MHz) Spectrum of Diacid 3

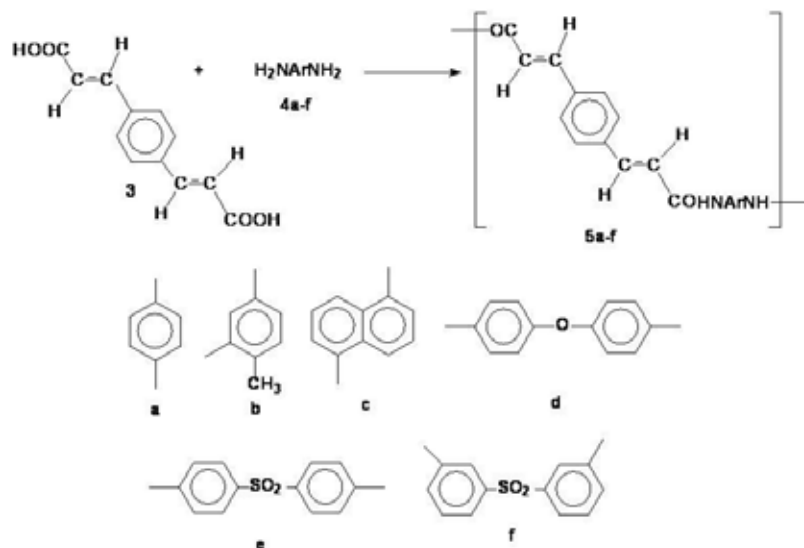
The measured results in elemental analyses of compound 3 are closely corresponded to the calculated values, demonstrating that the expected compound was obtained.

Polymer Synthesis

The polyamides 5a-f were synthesized by direct solution polycondensation reactions of an equimolar diacid 3 with six aromatic diamines 4a-f by using thionyl chloride and pyridine as condensing agents in NMP as solvent (Scheme 2). The entire polycondensation

readily proceeded to a homogeneous solution. Tough and stringy precipitates formed when the viscous polymers solutions were trickled into stirred methanol.

Polymer characterization



Scheme 2

Synthesis and some physical properties of polyamides 5a-f are summarized in Table 1. These polymers have inherent viscosities in a range between 0.30-0.50 dL/g.

Table 1. Synthesis and some physical properties of polyamide **5a-f**

Aromatic diamines	Polymer	Yield (%)	$\eta_{inh}(dL/g)^a$
4a	5a	95	0.50
4b	5b	91	0.40
4c	5c	88	0.42
4d	5d	87	0.40
4e	5e	90	0.31
4f	5f	92	0.30

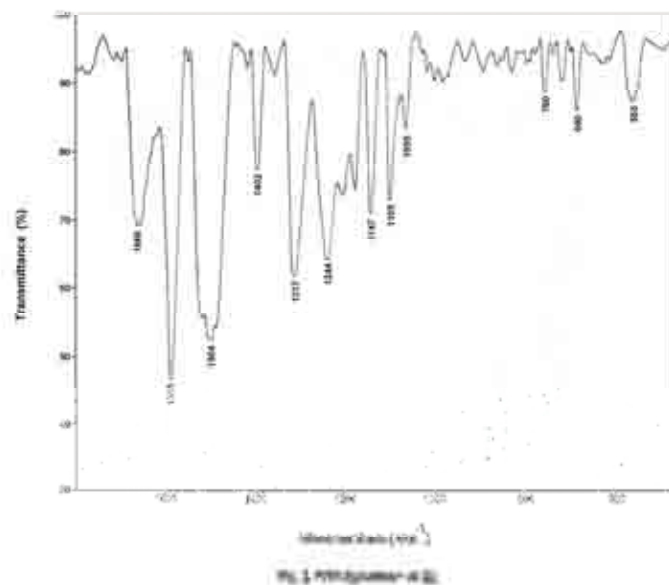
^a Measured at a concentration of 0.5g/dL in DMF at 25°C.

The structures of these polymers were confirmed as polyamides by means of FT-IR spectroscopy and elemental analyses. The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures (Table 2).

Table 2. Elemental Analysis of PAIs **5a-f**

Polymer	Formula		C%	H%	N%
5a	$C_{18}H_{14}N_2O_2$ (290.18) _n	Calc.	74.4	4.8	9.6
		Found	74.7	4.1	9.4
5b	$C_{19}H_{16}N_2O_2$ (304.19) _n	Calc.	75.0	5.2	9.2
		Found	74.6	4.9	8.8
5c	$C_{22}H_{16}N_2O_2$ (340.22) _n	Calc.	77.6	4.7	8.2
		Found	77.0	4.0	7.6
5d	$C_{24}H_{18}N_2O_3$ (382.24) _n	Calc.	75.4	4.7	7.3
		Found	74.9	4.4	6.9
5e	$C_{24}H_{18}N_2O_4S$ (430.24) _n	Calc.	66.9	4.1	6.5
		Found	66.0	3.8	6.0
5f	$C_{24}H_{18}N_2O_4S$ (430.24) _n	Calc.	66.9	4.1	6.5
		Found	66.2	3.9	6.1

The polymer shows absorption bands at 1668 cm^{-1} due to carbonyl of amide group. Also absorption bands around $1450\text{-}1600\text{ cm}^{-1}$ show the presence of the aromatic ring and vinyl moiety in this polymer. The other spectra show a similar pattern (Fig. 3).



The UV-vis absorption spectra of diacid **3** and polyamide **5a** in *N,N*-dimethyl formamide are shown in figures 4 and 5. The spectrum of diacid **3** exhibited two typical peaks at 269 nm ($\pi \rightarrow \pi^*$) and 328 nm ($n \rightarrow \pi^*$). Also the spectrum of polyamide **5a** exhibited same two typical peaks at 265 nm ($\pi \rightarrow \pi^*$) and 325 nm ($n \rightarrow \pi^*$). By comparing two spectra, a slightly blue shift was shown in polyamide **5a**.

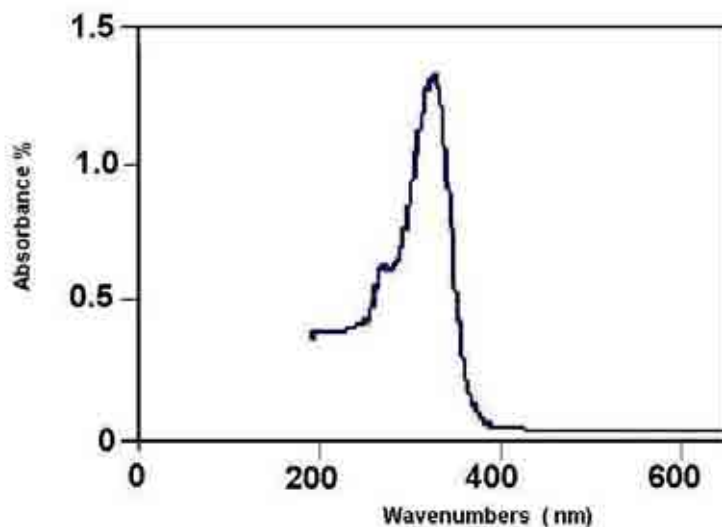


Fig. 4 Uv Spectrum of Diacid 3

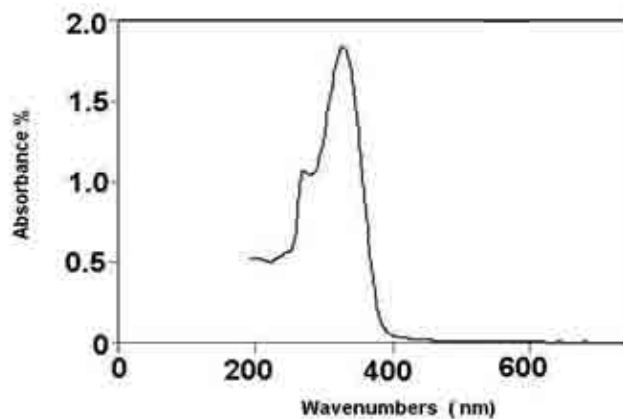


Fig. 5 Uv Spectrum of PA 5b

The solubility of polyamides 5a-f was investigated as 0.01 g of polymeric sample in 2 ml of solvent. All of the polyamides are soluble in polar aprotic solvents such as DMF, DMAc, DMSO and NMP at room temperature, and are insoluble in solvents such as THF, acetone, chloroform, methylene chloride, methanol, ethanol and water (Table 3).

Table 3. Solubility of polyamides **5a-f**
 +: Soluble at room temperature, -: Insoluble at room temperature

Solvents	5a	5b	5c	5d	5e	5f
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
THF	-	-	-	-	-	-
Acetone	-	-	-	-	-	-
CHCl ₃	-	-	-	-	-	-
EtOH	-	-	-	-	-	-
MeOH	-	-	-	-	-	-
CH ₂ Cl ₂	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-

Thermal properties

The thermal properties of two samples of these polymers (**5a** and **5e**) were investigated by means of thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis in a nitrogen atmosphere at a heating rate of 10^oC/min and the results such as initial decomposition temperature, 5% and 10% weight loss (T₅, T₁₀) and char yields at 600^oC are summarized in Table 4 (Fig. 6). These polymers exhibited good resistance to thermal decomposition up to 350-365^oC in nitrogen and began to decompose gradually above that temperature. The char yields of these polymers at 600^oC were 22 and 61 % in nitrogen.

Table 4. Thermal behavior of polyamides **5a & 5e**

Polymer	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char Yield ^c (%)
5a	350-355	365-370	22
5e	365-370	395-400	61

^{a,b}Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10^oC/min in N₂ respectively. ^cPercentage weight of material left undecomposed after TGA analysis 600^oC.

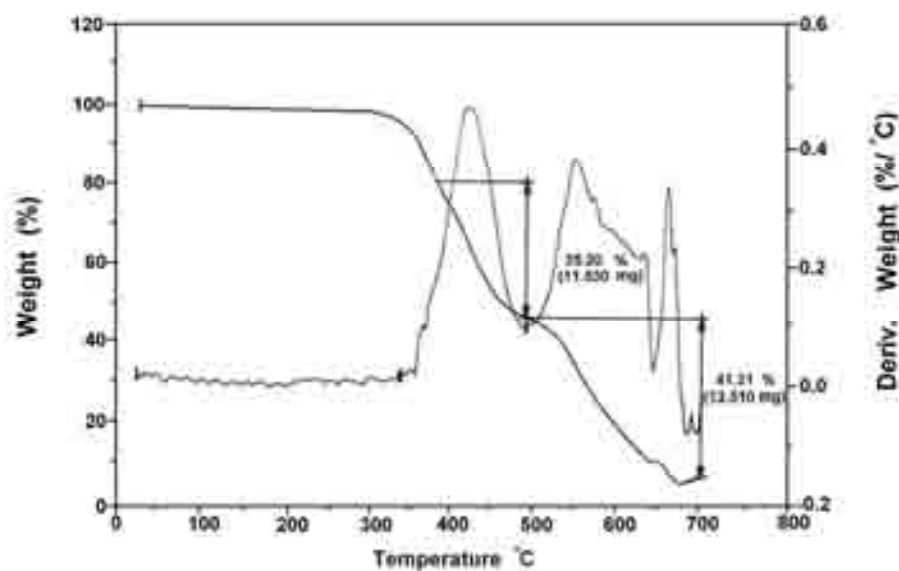


Fig. 5 TGA & DTG Thermogram of PA 5a

Conclusion

This work has synthesized several new polyamides 5a-f by direct polycondensation reaction of the monomer 3 with six diamines 4a-f by using thionyl chloride and pyridine as condensing agents in NMP as solvent. These new polyamides are soluble in various organic solvents and have good thermal stability. These properties can make these polyamides attractive for practical applications such as processable high-performance engineering plastics.

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