

New Polyesters Derived from 4-Phenylenediacrylic Acid and Aromatic Diols: Synthesis and Properties

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Abstract

Introduction: Aromatic polyesters are certainly one of the most successful classes of high-temperature polymers. However these polymers encounter processing difficulty due to their infusibility and poor solubility in organic solvents. 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.

Aim: In this paper a series of novel polyesters were obtained by the solution polycondensation reaction of p-phenylene diacryloyl chloride (**4**) with six different of aromatic diols (**5a-f**) in DMAc solvent and in the presence of pyridine as a base. These polymers have a soft segment such as vinyl moiety in the main chain for improving the solubility in organic solvents in compare to aromatic polyesters. These polymers have been noticed because they can be used for preparing photosensitive liquid crystalline polymers. There are some reported papers about synthesis polyamides, polyimides, polyesters and poly(amid-co-imide)s containing p-phenylenediacrylic moiety in the main chain.

Materials and Methods: All chemicals were purchased from Fluka and Merck Chemical Company. The $^1\text{H-NMR}$ spectrum (300 MHz) was recorded on a Bruker Avance 300 spectrometer (Germany). Fourier transform infrared (FT-IR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (England).

Results: p-Phenylenediacrylic acid (**3**) was prepared by the reaction of terephthal aldehyde (**1**) and malonic acid (**2**) in the presence of pyridine. The diacid (**3**) was then converted to p-phenylenediacryloyl chloride (**4**) by the reaction with thionyl chloride. Solution polycondensation reactions of diacid chloride (**4**) with hydroquinone (**5a**), 2,7-dihydroxy naphthalene (**5b**), 4,4'-dihydroxy diphenyl sulfone (**5c**), bisphenol A (**5d**), 1,4-dihydroxy anthraquinone (**5e**) and phenol phethalein (**5f**) were carried out in DMAc solution and in the presence of pyridine as a base. The polycondensation reactions produce a series of new polyesters (**6a-f**) in high yields having inherent viscosity between 0.32-0.50 dL/g. The resulting polyesters were characterized by elemental analysis, viscosity measurements, thermal gravimetric analysis (TGA and DTG), differential scanning calorimetry (DSC), solubility test and FT-IR spectroscopy.

Conclusion: Several new polyesters (**6a-f**) have been synthesized by the solution polycondensation reaction of the monomer (**4**) with six different of aromatic diols (**5a-f**) in DMAc in the presence of pyridine as a base. These new polyesters are soluble in various

organic solvents and have good thermal stability. These properties can make these polyesters attractive for practical applications such as processable high-performance engineering plastics.

Key words: polyesters, 4-phenylenediacrylic acid, aromatic diol

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 polyesters are certainly one of the most successful classes of high-temperature polymers.^[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.^[10-24]

The conventional method for synthesis of polyesters begins from the reaction of diols with a diacid chloride by low temperature solution polycondensation.

In this paper a series of novel polyesters were obtained by the solution polycondensation reaction of p-phenylene diacryloyl chloride (**4**) with six different of aromatic diols (**5a-f**) in DMAc solvent and in the presence of pyridine as a base. These polymers have a soft segment such as vinyl moiety in the main chain for improving the solubility in organic solvents in compare to aromatic polyesters. These polymers have been noticed because they can be used for preparing photosensitive liquid crystalline polymers. There are some reported papers about synthesis polyamides, polyimides, polyesters and poly(amid-co-imide)s containing p-phenylenediacrylic moiety in the main chain.^[25-31]

Experimental

All chemicals were purchased from Merck Chemical Co. (Germany) and Aldrich (USA). 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 on DMF solutions 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. Differential scanning calorimetric analysis was performed on differential scanning calorimeter (Du Pont 910) at a heating 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. Into a 100 mL round-bottomed flask terephthal aldehyde (**1**) (3.48 g, 26 mmol), malonic acid (**2**) (8.27 g, 94 mmol) were added to 30 mL of pyridine containing small amount of pipyridine. 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, respectively and dried in a vacuum oven at room temperature to give 5.16 g (91 %) of white crystals 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} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS): δ 6.56 (d, 2H, J= 9.6 Hz), 7.58 (d, 2H, J= 9.6 Hz), 7.70 (s, 4H), 12.85 (b, 2H) ppm. Analysis: Calculated for $\text{C}_{12}\text{H}_{10}\text{O}_4$: C, 66.07, H, 4.58, found: C, 66.2, H, 4.4.

p-Phenylene diacryloyl chloride (4)

Into a 50 mL round-bottomed flask were placed p-phenylenediacrylic acid (**3**) (2.12 g, 10 mmol) and 15 mL of thionyl chloride and 0.1 mL DMF as a base. The mixture was heated on an oil bath up to 60°C, until the suspension mixture was converted to a clear solution. Then, the solution was stirred for overnight at room temperature. Unreacted thionyl chloride was removed under reduced pressure and the residue was washed with dry n-hexane two times, to leave 2.27 g (89%) of yellow crystals of compound (**4**): mp 170-172°C, FT-IR (KBr): 1738 (s, br), 1635 (w), 1597 (m), 1550 (w), 1460 (m), 1400 (m), 1304 (w), 1162 (m), 1091 (s), 1022 (w), 902 (w) cm^{-1} . Analysis: Calculated for $\text{C}_{12}\text{H}_8\text{O}_2\text{Cl}_2$: C, 56.49, H, 3.13, found: C, 56.6, H, 3.0.

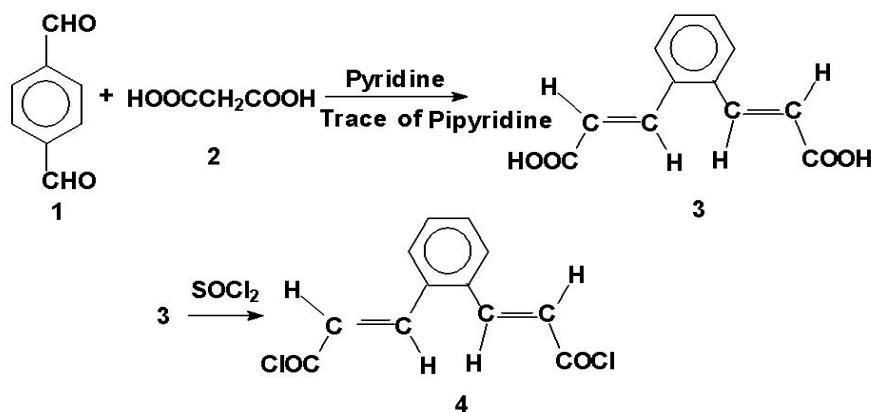
Polymer Synthesis

Into a 25 mL round-bottomed flask was fitted with a stirring bar were placed hydroquinone (**5a**) (0.22 g, 2 mmol) and 1.5 mL of DMAc. The mixture was cooled in an ice-water bath, and of pyridine (0.32 g, 4 mmol) was added to this solution. Then diacid chloride (**4**) (0.43 g, 2 mmol) was added all at once. The polymerization proceeded as the acid chloride was dissolved. The reaction mixture was stirred in an ice-water bath for 1 hr, the cooling bath was removed, the stirring continued at room temperature for overnight and then heated at 80°C for 12 h. The reaction mixture was poured into 50 mL of methanol. The precipitated polymer was collected by filtration, washed thoroughly with methanol and dried at 80°C for 12 hr under vacuum to leave 0.53 g (92 %) of polyester (**6a**).

Results and Discussion

Monomer Synthesis

p-Phenylenediacrylic acid (**3**) was synthesized by reaction of terephthal aldehyde (**1**) with malonic acid (**2**) in the presence of pyridine as a white solid in high yeild as shown in Scheme 1.



Scheme 1

The chemical structure and purity of compound (3) were proved by using elemental analysis, FT-IR and $^1\text{H-NMR}$ 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 (Fig. 1).

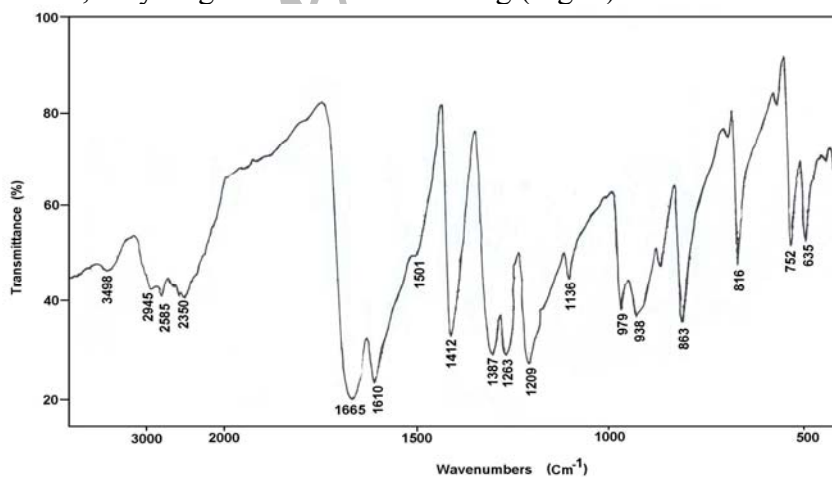


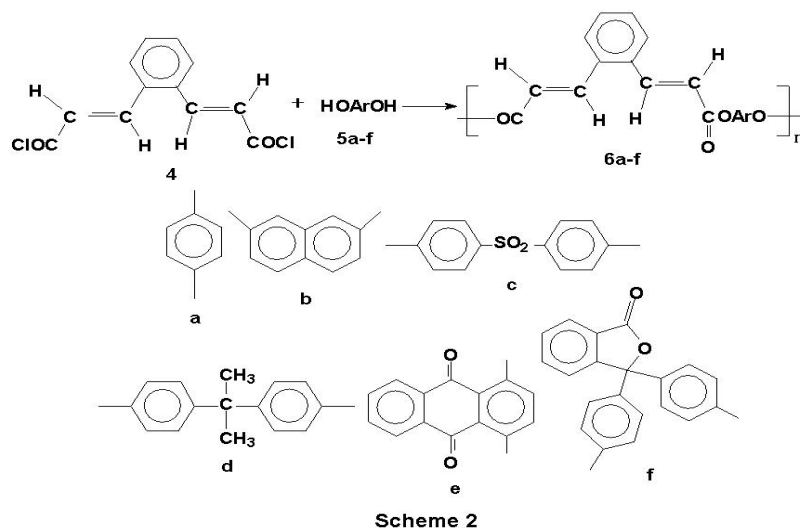
Fig. 1 FTIR Spectrum of Diacid 3

The $^1\text{H-NMR}$ spectrum of diacid (3) showed two doublet peaks at 6.56 and 7.58 ppm were assigned to the H_b and H_a protons of vinyl group. Peak at 7.70 ppm were assigned to the H_c protons of aromatic ring. Finally the broad peak between $12.80\text{--}13.00\text{ ppm}$ was assigned to H_d protons of COOH groups. The configurations of double bonds in diacid (3) were found as trans by measuring coupling constants of H_b and H_a protons of vinyl group.

The measured values of elemental analyses of compound (3) and (4) are close to the calculated values, demonstrating that the expected compound was obtained.

Polymer Syntheses

The polyesters (**6a-f**) were synthesized by solution polycondensation reactions of one equimolar diacid (**4**) with aromatic diols (**5a-f**) in DMAc in the presence of pyridine as a base (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. All of the polymers were obtained in quantitative yields with inherent viscosities between 0.32-0.50 dL/g.



Polymer characterization

Syntheses and some physical properties of polyesters (**6a-f**) are summarized in Table 1. These polymers have inherent viscosities in a range between 0.32-0.50 dL/g.

Table1- Synthesis and some physical properties of polyesters (6a-f)

Aromatic diols	Polyester	Yield (%)	$\eta_{inh}(\text{dL/g})^a$
5a	6a	92	0.50
5b	6b	87	0.45
5c	6c	90	0.43
5d	6d	83	0.40
5e	6e	91	0.37
5f	6f	90	0.32

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

The structures of the polymers were confirmed by means of FT-IR spectroscopy and elemental analysis. The found values of elemental analyses of the resulting polymers were in good agreement with the calculated values.

The representative FT-IR spectrum of polyester (**6a**) 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.

The UV-vis absorption spectrum of polyester (**6a**) in N,N-dimethyl formamide is shown in figure 2. The spectrum of diacid (**4**) exhibited two typical peaks at 269 nm ($\pi\rightarrow\pi^*$) and 328 nm ($n\rightarrow\pi^*$). Also the spectrum of polyester (**6a**) exhibited same two typical peaks at 268 nm ($\pi\rightarrow\pi^*$) and 330 nm ($n\rightarrow\pi^*$). By comparing two spectrums, a slightly blue shift was shown in polyester (**6a**).

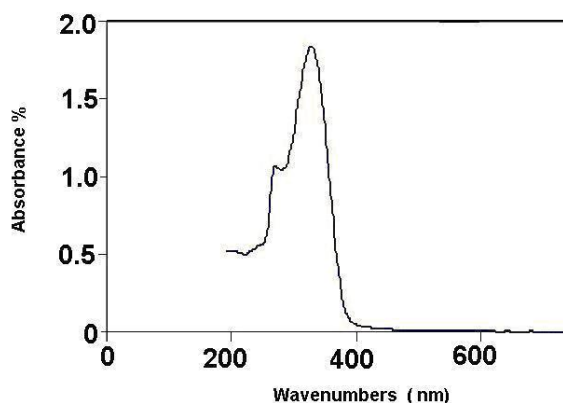


Fig. 2 Uv Spectrum of 6a

The solubility of polyesters (**6a-f**) was investigated as 0.01 g of polymeric sample in 2 ml of solvent. All of the polymers are soluble in polar organic solvents such as DMF, DMAc, DMSO, NMP and THF at room temperature, and are insoluble in solvents such as acetone, chloroform, methylene chloride, methanol, ethanol and water.

Table 2- Solubility of polyesters (6a-f)

Solvents	6a	6b	6c	6d	6e	6f
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
THF	+	+	+	+	+	+
Acetone	—	—	—	—	—	—
CHCl ₃	—	—	—	—	—	—
EtOH	—	—	—	—	—	—
MeOH	—	—	—	—	—	—
CH ₂ Cl ₂	—	—	—	—	—	—
H ₂ O	—	—	—	—	—	—

+: Soluble at room temperature, —: Insoluble at room temperature.

Thermal properties

The thermal properties of three samples of these polymers (**6a**, **e** and **f**) were investigated by means of thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analyses in a nitrogen atmosphere at a heating rate of 10°C/min and the results such as initial decomposition temperature, 5% and 10% weight loss (T_5 , T_{10}) and char yields at 600°C are summarized in Table 3 (Fig 3). These polymers exhibited good resistance to thermal decomposition up to 270-305°C in nitrogen and began to decompose gradually above that temperature. The residual weights for these polymers at 600°C were 20% to 59% in nitrogen. In the DSC experiments, there is no melting endotherm in the DSC thermograms. Glass transition temperatures of these polymers were found to be in the range of 140-155°C.

Table 3 -Thermal behavior of polyesters (6a, e & f)

Polymer	T _g (°C) ^a	T ₅ (°C) ^b	T ₁₀ (°C) ^c	Char Yield ^d (%)
6a	145	305-310	365-370	20
6e	155	295-300	345-350	59
6f	140	270-275	370-375	47

^aT_g data were measured by DSC technique ^{b,c}Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10°C/min in N₂ respectively ^dPercentage weight of material left undecomposed after TGA analysis 600 °C.

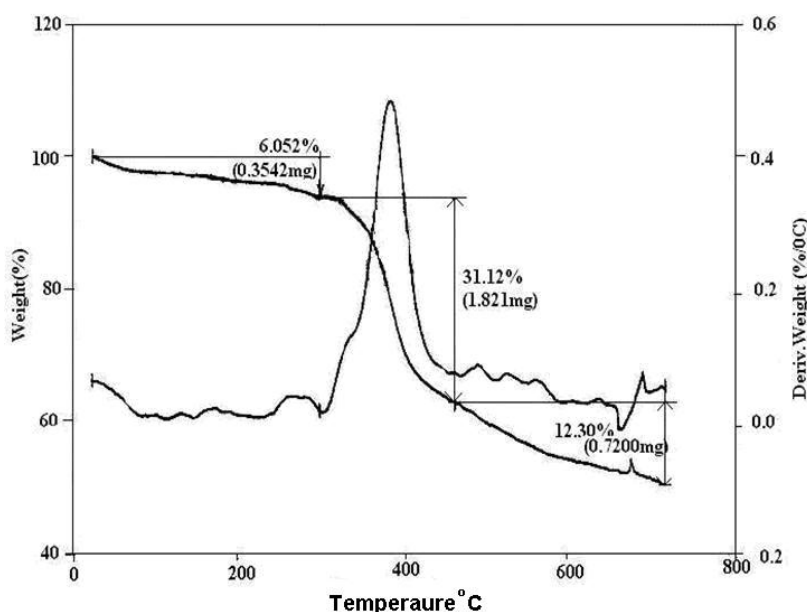


Fig. 3 TGA & DTG thermograms of Polyester 6f

Conclusion

In this work several new polyesters (**6a-f**) have been synthesized by the solution polycondensation reaction of the monomer (**4**) with six different of aromatic diols (**5a-f**) in DMAc in the presence of pyridine as a base. These new polyesters are soluble in various organic solvents and have good thermal stability. These properties can make these polyesters

attractive for practical applications such as processable high-performance engineering plastics.

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