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Synthesis and characterization of novel aromatic polyesters from 5-[3-phenyl-2-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)propanoyl amino] isophthalic acid and various diols

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Abstract: Soluble novel aromatic polyesters containing pendent L-phenylalanine-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido units in the side chain have been prepared via direct polycondensation of 5-[3-phenyl-2-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)propanoylamino]isophthalic acid with different aromatic diols using tosyl chloride (TsCl), pyridine (Py) and *N*,*N*-dimethylformamide (DMF) system as condensing agent. The polycondensation reaction was successfully applied to the preparation of thermally stable polyesters with good yields and inherent viscosities in the range of 0.40-0.58 dL/g. All polymers derived were readily soluble in the aprotic polar solvents such as *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylacetamide, DMF, Py, dimethyl sulfoxide. Thermogravimetric analysis (TGA) data showed that these polyesters are thermal stable, with 10% weight loss being recorded above 410 °C.

Keywords: Polyester, TsCl/Py/DMF condensing agent, Direct polycondensation, Thermal properties.

Introduction

Aromatic polyesters (PE)s are materials exhibiting an excellent pattern of physical properties. They are significant class of high performance and engineering materials, which show good thermal stability, solvent resistance and good mechanical properties and therefore, used widely in the aviation, automobile, and electronic industries [1-3]. Aromatic PEs are also well known as rigid-rod liquid-crystalline polymers [4,5]. PEs are generally prepared by solution or an interfacial reaction between aromatic dicarboxylic acids and diols under severe conditions [6]. But, the direct polycondensation reaction involves the use of free carboxylic acid and diols under mild conditions using activating reagents. Several condensing agents suitable for the direct polycondensation reaction such as diphenyl chlorophosphate and arylsulfonyl chlorides have been developed in the past decades [7]. It was found that Vilsmeier adduct derived from arylsulfonyl chlorides and *N*,*N*-dimethylformamide (DMF) in pyridine (Py) was successfully applied as a suitable condensing agent for the synthesis of aromatic polyesters by the direct polycondensation of aromatic dicarboxylic acids and bisphenols [8,9]. Recently, the reaction with thionyl chloride as a condensing agent was applied with limited success to the preparation of polyamides and polyesters, giving polymers of low molecular weights [10,11]. These polymers are generally difficult to process, because of their high glass transition or melting temperatures coupled with insolubility in common organic solvents by virtue of their rigid structures. One of the approaches for improving solubility of aromatic PEs without extreme loss of their high thermal stability is introduction of

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*Corresponding author. Tel: (+98) 7432223048, Fax: (+98) 7432223048, E-mail: z.rafiee@mail.yu.ac.ir flexible units in the main chain [12,13]. Incorporation of bulky, packing-disruptive groups into the polymer backbone is also of particular attention because this approach produces a separation of chains and lowering the chain packing with a gain of free volumes [14-17]. Bulky side groups also decrease the molecular mobility, so that the overall observable effect is an increase of the glass transition temperature and an improvement of solubility at the same time.

One of the methods of improving the thermal properties of PEs is to introduce some thermally stable groups, such as amide groups into their main chains. Improvements of the mechanical and thermal properties and crystallinity of polymers by the incorporation of a certain amount of amide groups into the main chains of PEs have been reported [18,19].

Synthesis of optically active polymers is an important field in polymer science as they find wide variety of potential uses based on the chiral structure. An important application of these macromolecules is chiral recognition. This ability of chiral polymers has been utilized in various forms of catalytic and separation chemistry [20,21]. Optically active polyamides are promising materials where chiro-optical effects can be combined with good mechanical and thermal properties [22]. On the other hand, incorporation of α-amino acid moieties along the polyamide chain could be an effective strategy for enhancing the biodegradability [23].

In this study, we wish to describe the successful synthesis and characterization of new PEs containing L-phenylalanine-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido units moiety using tosyl chloride (TsCl)/DMF/pyridine (Py) as condensing agent. The incorporation of the bulky L-phenylalanine-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido pendent group into the polymer backbone may disrupt the molecular packing, reducing the intermolecular interactions and enhancing the solubility and thermal stability of the polymers.

Results and discussion

Monomer synthesis:

As shown in Scheme **1**, monomer diacid 8 was synthesized in four steps according to our previous work [24].

Polymer synthesis:

Polyesterification is an important polycondensation reaction from both the scientific and the technological point of view. Novel aromatic PEs with pendent L-phenylalanine-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido groups were synthesized with the aim of achieving better solubility and thermal stability. These polymers 10a-10j were prepared by direct polycondensation of a diacid monomer 8 with several different aromatic diols 9a-9j in a system of TsCl/Py/DMF (Scheme **2**). In this investigation for the polycondensation reaction of diacid 8 with aromatic diols, a Vilsmeier adduct was prepared by dissolving TsCl in a mixed solvent of Py and DMF. The polycondensation was carried out in the following way: TsCl was dissolved in Py and after a certain period of time (aging time) the solution was treated with DMF for 30 min. The reaction mixture was added to a solution of diacid in Py. After a period of time a solution of diol in Py was added and the whole solution was maintained at elevated temperature for several hours.

All of the reaction parameters such as aging times, reaction time, temperature and molar ratio of chemical additives to diacid have the considerable effect on the reaction progress, were optimized in previous work [25] and applied for direct polyestrification of diacid 8. The reaction yields and some physical data of these PEs are listed in Table **1**.

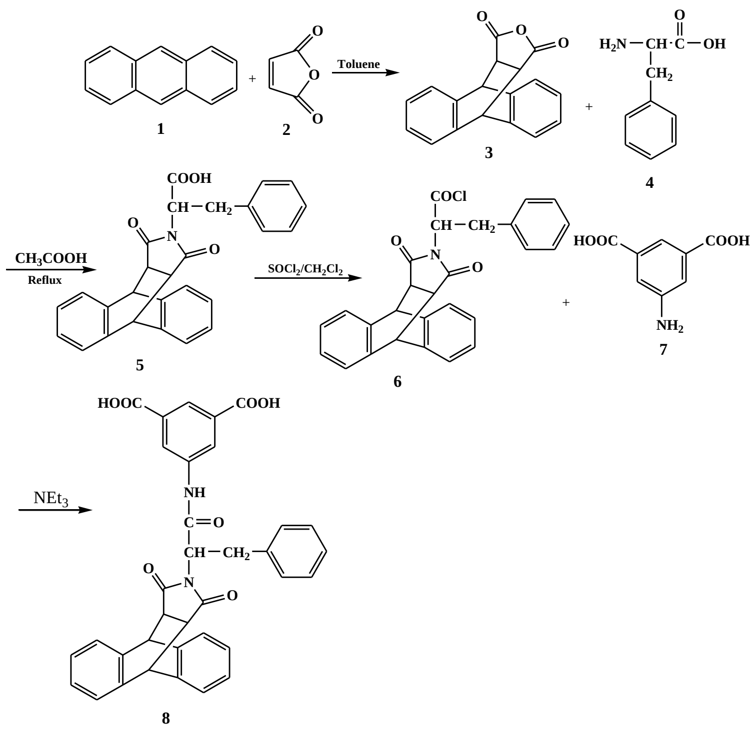
The inherent viscosities of the resulting polymers under optimized conditions were in the range of 0.40-0.58 dL/g and the yields were 74-98%.

Polymer characterization:

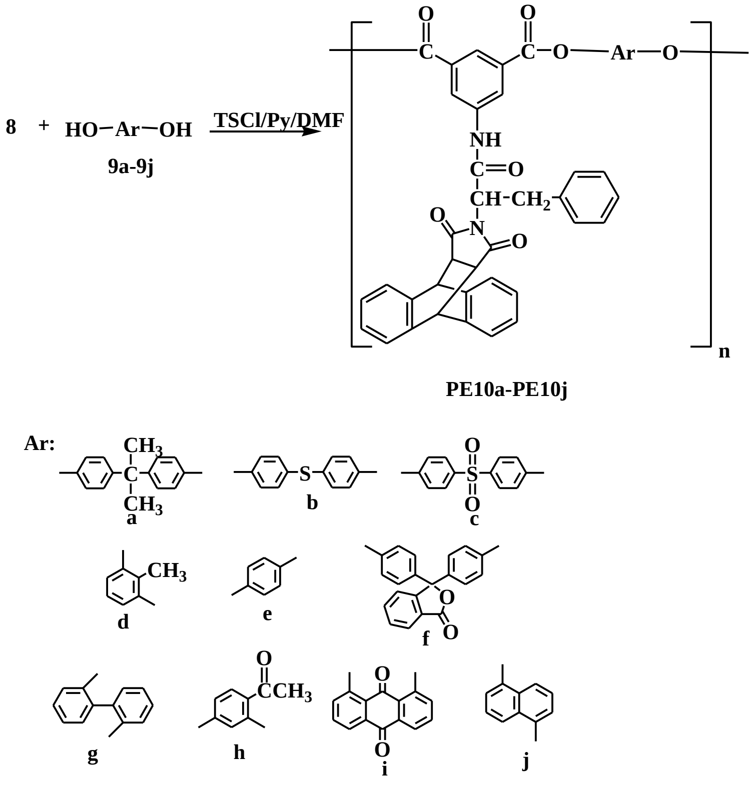
The formation of PEs was confirmed by FTIR spectroscopy analysis. FT-IR spectra of all polymers show the characteristic absorption peaks for characteristic absorption peaks at 1742, 1674 and 1628 cm^{-1}, due to the symmetrical and asymmetrical carbonyl stretching vibrations. Band of amide N-H group appeared around 3423 cm^{-1}. A strong band corresponding to C-O stretching can also be observed at 1201 cm^{-1}.

Solubility of PEs:

The solubility of PEs was tested quantitatively in various solvents are listed in Table **2**. All of the PEs are soluble in organic solvents such as DMF, DMAC, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone, Py and in H_2SO_4 at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water. The incorporation of the pendent L-phenylalanine-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido in the side chain PEs enhanced their solubility in polar solvents.



Scheme 1: Synthesis of 5-[4-(2-phthalimidiylpropanoyl amino)benzoylamino]-isophthalic acid (8).



Scheme 2: Polyesterification reactions of monomer 8 with aromatic diols.

Thermal properties:

The thermal stability of polymers was studied by TGA/DTG under a nitrogen atmosphere. The 5 and 10% weight loss (T_5 and T_{10}) of the polymers and residue at 600 °C (char yield) for these polymers are summarized in Table **3**. The polymers are thermally stable up to above 370 °C.

Table 1: Synthesis and some physical properties of PE10a-PE10j**.**

Entry	Diol	Polymer			
		Polymer	Yield (%)	$\eta_{inh}{}^{a}$ (dL/g)	Color
1	9a	10a	98	0.58	Off-white
2	9b	10b	84	0.48	Off-white
3	9c	10c	83	0.42	Light-brown
4	9d	10d	85	0.40	Light-brown
5	9e	10e	87	0.43	Off-white
6	9f	10f	91	0.41	Light-brown
7	9g	10g	81	0.44	Off-White
8	9h	10h	74	0.46	Light-brown
9	9i	10i	79	0.40	Light-brown
10	9j	10j	88	0.43	Light-brown

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

Table 2: Solubility of PE10a-PE10j[a].

Solvent	10a	10b	10c	10d	10e	10f	10g	10h	10i	10j
DMAc	+	+	+	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+	+	+	+
Py	+	+	+	+	+	+	+	+	+	+

H_2SO_4	+	+	+	+	+	+	+	+	+	+
MeOH	–	–	–	–	–	–	–	–	–	–
EtOH	–	–	–	–	–	–	–	–	–	–
$CHCl_3$	–	–	–	–	–	–	–	–	–	–
CH_2Cl_2	–	–	–	–	–	–	–	–	–	–
H_2O	–	–	–	–	–	–	–	–	–	–

[a] Concentration: 5 mg mL^{-1}; (+) Soluble at room temperature, (–) Insoluble at room temperature.

Table 3: Thermal properties of PE10a and PE10e.

3	Decomposition Temperature (°C)		Char Yield (%)[c]
	T_5 [a]	T_{10} [b]	
PE10a	384	421	57
PE10e	375	410	48

[a] Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10 °C/min under nitrogen atmosphere.
[b] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C/min under nitrogen atmosphere.
[c] Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600 °C under nitrogen atmosphere.

Conclusion

In this research work, direct polycondensation was carried out by the reaction of diacid monomer 8 with several aromatic diols using TsCl/DMF/Py as a condensing agent to prepare novel aromatic PEs. The polycondenstation leads to the formation of polymers having inherent viscosity ranging from 0.40-0.58 dL/g. By introducing L-phenylalanine-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido pendent group to the aromatic PEs side chain, polymers with substantially increased solubility and good thermal stability were obtained. Since these PEs are readily soluble in many organic solvents, they can be used for film forming and coating materials.

Experimental

Materials:

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. Bisphenol A (9a) was purified by recrystallization from acetic acid-water. The other diols were used as obtained without further purification. DMF was dried over BaO and then was distilled under reduced pressure.

Techniques:

FT-IR spectra were recorded on (Jasco-680, Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fenske routine viscometer. Thermal gravimetric analysis (TGA) data for polymers were taken on TGA-PerkinElmer (Pyris 1) under nitrogen atmosphere at a heating rate of 10^{o}C/min.

Monomer synthesis:

5-[3-Phenyl-2-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)propanoylamino]isophthalic acid (8) as a optically active diacid was prepared according to our pervious published paper [24].

Polymer synthesis:

The PEs were prepared by the following general procedure: as an example for the preparation of PE10a,

A Py (0.40 mL, 5.0 × 10^{-3} mol) solution of TsCl (0.162 g, 8.52 × 10^{-4} mol) after 30 min. stirring at room temperature, was treated with DMF (0.10 mL, 1.3 × 10^{-3} mol) for 30 min. and was added dropwise to a solution of diacid 8 (0.100 g, 1.7 × 10^{-4} mol) in Py (0.15 mL). The mixture was maintained at room temperature for 30 min. and then to this mixture, a solution of bisphenol A (9a) (0.039 g, 1.7 × 10^{-4} mol) in Py (0.15 mL) was added dropwise at room temperature and the whole solution was stirred at room temperature for 30 min. and at 120 ^{o}C for 2.5 h. As the reaction ensued, the solution became viscous. Then the viscous liquid was precipitated in 30 mL of methanol to yield 0.136 g (98%) of the PE10a.

FTIR (KBr): 3423 (m), 3043 (w), 2971 (m), 1742 (s), 1674 (s), 1628 (s), 1592 (s), 1534 (m), 1514 (s), 1459 (s), 1411 (m), 1344 (s), 1201 (s), 1164 (s), 1068 (m), 1013 (m), 911 (m), 841 (m), 806 (m), 744 (s), 684 (m), 562 (m), 481 (m) cm^{-1}.

The PE10b-PE10j were prepared with similar procedures.

References

[1] Barashkove, N. N.; Gander, O. A. Fluorescent Polymers, Ellis Harwood, Chichester, UK, **1994**.

[2] Seymour, R. B.; Kirshenbaum, G. S. editors. *High performance polymers: their origin and development*, New York: Elsevier; **1986**.

[3] Han, H.; Bhowmik, P. K. *Prog. Polym. Sci*. **1997**, *22,* 1431.

[4] Jadhav, J. Y.; Kantor, S. W. In: Kroschwitz, J. I. editor. *High performance polymers and composites*, New York: Wiley; **1991**.

[5] Wang, Y. Z.; Chen, X. T.; Tang, X. D. *J. Appl. Polym. Sci*. **2002**, *86,* 1278.

[6] Morgan, P. W. *Condensation polymers by interfacial and solution methods*; Interscience: New York, **1965**.

[7] Higashi, F.; Mashimo, T. *J. Polym. Sci., Polym. Chem. Ed*. **1985**, *23,* 2999.

[8] Higashi, F.; Akiyama, N.; Takashi, I.; Koyama, T. *J. Polym. Sci., Polym. Chem. Ed*. **1984**, *2*, 1653.

[9] Higashi, F.; Ng, C.; Kada, Y. *J. Polym. Sci., Part A: Polym. Chem*. **1999**, *37*, 3625.

[10] Mallakpour, S.; Moghaddam, E. *Iranian Polym. J.* 2006, *15*, 547.

[11] Mallakpour, S.; Kolahdoozan, M. *Eur. Polym. J.* **2007**, *43*, 3344.

[12] Liaw, D. J.; Chen, P. S. *J. Polym. Sci. Polym. Chem*. **1996**, *34*, 885.

[13] Bucio, E.; Fitch, J. W.; Venumbaka, S. R.; Cassidy, P. E. *Polymer* **2005**, 46, 3971.

[14] Loria-Bastarrachea, M. I.; Vazquez-Torres, H.; Aguilar-Vega, M. J. *J. Appl. Polym. Sci.* **2002**, *86*, 2515.

[15] Tamami, B.; Yeganeh, H.; Kohmereh, G. A. *Eur. Polym. J.* **2004**, *40*, 1651.

[16] Mallakpour, S.; Rafiee, Z. *Polym. J.* **2007**, *39*, 1185.

[17] Honkhambe, P. N.; Avadhani, C. V.; Wadgaonkar, P. P.; Salunkhe, M. M. *J. Appl. Polym. Sci.* **2007**, *106*, 3105.

[18] Van der Shuur, M.; Gaymans, R. J. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 4769.

[19] Deep, P.; Sona, C.; Jayakannan, M. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 5557.

[20] Dobashi, A.; Nishida, S.; Kurata, K.; Hamada, M. *Anal. Sci*. **2002**, *18*, 35.

[21] Nakano, T. *J. Chrom. A* **2001**, *906*, 205.

[22] Iribarren, J. I.; Martynez de Ilarduya, A.; Aleman, C.; Oraison, J. M.; Rodryguez-Galan, A.; Munoz-Guerra, S. *Polymer* **2000**, *41*, 4869.

[23] Naira, L. S.; Laurencin, C. T. *Prog. Polym. Sci*. **2007**, *32*, 762.

[24] Mallakpour, S.; Rafiee, Z. *Polymer* **2008**, *49*, 3007.

[25] Mallakpour, S.; Kolahdoozan, M. *Iranian Polym. J.* **2006**, *15*, 307.