

New thermally stable polyesters based on 2,5-pyridinedicarbonyl dichloride and aromatic diols: Synthesis and characterization

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Abstract

Six new thermally stable polyesters (**4a–f**) were synthesized through the solution polycondensation reaction of 2,5-pyridine dicarbonyldichloride (**2**) with six aromatic diols in *N,N'*-dimethyl acetamide (DMAc) solution and in the presence of pyridine as a base. The polycondensation reactions produce a series of new polyesters (**4a–f**) in high yields, and inherent viscosity between 0.30 and 0.55 dL/g. The resulting polyesters were characterized by elemental analysis, viscosity measurements, thermal gravimetric analysis (TGA and DTG), solubility test, Fourier transform infrared (FT-IR) spectroscopy and gel permeation chromatography (GPC).

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High-performance-heat resistance polymers such as aromatic polyimides, poly(amide-imide)s, polyamides and polyesters are characterized by their excellent balance of thermal and mechanical properties which makes them useful materials for engineering applications. However, these polymers particularly those with para-substituted rings exhibit poor processability and limited solubility in organic solvents. Therefore, many efforts have been made to create structurally modified aromatic polymers having increased solubility and processability with retention of their high thermal stability [1–9]. In this paper the synthesis of a new series of polyesters (**4a–f**) containing pyridyl moieties in the main chain was reported by polycondensation reaction of 2,5-pyridinedicarbonyl dichloride (**2**) with six different aromatic diols (**3a–f**) in *N,N'*-dimethyl acetamide (DMAc) solution and in the presence of pyridine as a base. These polymers have a heterocyclic aromatic ring such as pyridyl moiety in the main chain that cases better solubility in organic solvents in compared to aromatic polyesters.

1. Experimental

All chemicals were purchased from Merck Chemical Co. (Germany) and Aldrich (USA). Fourier transform infrared (FT-IR) spectra were recorded on Galaxy series FT-IR 5000 spectrophotometer (England) as KBr pellets.

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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 by using a Technico Regd Trad Merk Viscometer. Thermal Gravimetric Analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N_2 atmosphere at a rate of $10^\circ\text{C}/\text{min}$. Elemental analyses were measured in Arak Petrochemical Company laboratories, Arak, Iran. Weight-average molecular weights (M_w) and number-average molecular weights (M_n) were determined by gel permeation chromatography (GPC). The eluents were monitored with a UV detector (JMST Systems, USA, VUV-24) at 254 nm. Polystyrene was used as the standard.

Into a 100 mL round-bottomed flask were placed 2.0 g (11.9 mmol) of 2,5-pyridinedicarboxylic acid (**1**), 20 mL of thionyl chloride and 0.1 mL pyridine as a base. Reaction mixture was heated on an oil bath at 70°C , until the suspension mixture was converted into a clear solution. Then unreacted thionyl chloride was removed by distillation and the residue was placed under vacuum leaving 2.0 g (83%) of 2,5-pyridine dicarbonyl dichloride (**2**). FT-IR (KBr): 1726 cm^{-1} (s), 1602 cm^{-1} (w, sh), 1402 cm^{-1} (s), 1234 cm^{-1} (s, sh), 1128 cm^{-1} (s), 748 cm^{-1} (s), 491 cm^{-1} (m), 277 cm^{-1} (m). Analysis: calcd. for $\text{C}_7\text{H}_3\text{NO}_2\text{Cl}_2$: C, 41.19; H, 1.47; N, 6.86; found: C, 41.00; H, 1.37; N, 6.70.

The polyesters (**4a–f**) were prepared by the following general procedure (using polymer (**4a**) as an example). Into a 25 mL round-bottomed flask, which was fitted with a stirring bar was placed (0.22 g, 2 mmol) hydroquinone (**3a**) and 1.5 mL of DMAc. The mixture was cooled in an ice-water bath, and (0.32 g, 4 mmol) of pyridine was added to this solution. Then (0.40 g, 2 mmol) of 2,5-pyridinedicarbonyl dichloride (**2**) was added all at once. The polymerization proceeds as the acid chloride was dissolved. The reaction mixture was stirred in an ice-water bath for 1 h, 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 a flask containing 50 mL of methanol. The precipitated polymer was collected by filtration, washed thoroughly with methanol and dried at 80°C for 12 h under vacuum to leave 0.44 g (92%) of polymer (**4a**). The polyesters (**4a–f**) were analyzed by using FT-IR spectroscopy.

2. Results and discussion

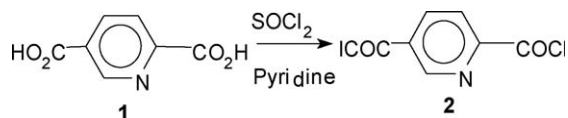
2,5-Pyridinedicarbonyl dichloride (**2**) was prepared by reaction of 2,5-pyridinedicarboxylic acid (**1**) with thionyl chloride in the presence of a small amount of pyridine (Scheme 1).

The chemical structure and purity of 2,5-pyridinedicarbonyl dichloride (**2**) were proved with elemental analysis and FT-IR spectroscopy. The measured results in elemental analyses of compound (**2**) closely corresponded to the calculated ones, demonstrating that the expected compound was obtained. In the FT-IR spectrum of compound (**2**) disappearing a broad peak at $2500\text{--}3100\text{ cm}^{-1}$ confirmed a complete conversion of diacid (**1**) to diacid chloride (**2**). On the other hand, because of the electron withdrawing character of the Cl groups, carbonyl peaks of the diacid chloride (**2**) in comparison with diacid (**1**), were shifted to a higher frequency.

Polyesters (**4a–f**) were synthesized by the direct polycondensation reaction of an equimolar mixture of 2,5-pyridinedicarbonyl dichloride (**2**) with six aromatic diols (**3a–f**) in DMAc solution and in the presence of pyridine as a base (Scheme 2).

The synthesis and some physical properties of these new polyesters (**4a–f**) are given in Table 1. The entire polycondensation reactions readily proceeded in a homogeneous solution while tough and stringy precipitates formed as the viscous polyester solution was obtained in moderate to good yields. These polymers exhibited M_n and M_w in the range of $1.4\text{--}2.2 \times 10^4$ and $4.8\text{--}5.9 \times 10^4\text{ g/mol}$ respectively, as measured by GPC, relative to polystyrene standards.

Also these polymers have inherent viscosities around $0.35\text{--}0.55\text{ dL/g}$ and show white to yellow crystal. These polymers confirmed as polyester with FT-IR spectroscopy and elemental analyses (Table 2). FT-IR spectra shows that the carbonyl peak of polymer shift to lower frequency in comparison with diacid chloride (**2**) and stretching OH peak at $2500\text{--}3100\text{ cm}^{-1}$ of diol disappeared. The elemental analysis of the resulted polymers is in good agreement with the calculated values for the proposed structures. The solubility of these polymers was investigated with 0.01 g polymeric samples in 2 mL of solvent. All polymers were dissolved in organic solvents such as N,N' -dimethyl formamide



Scheme 1. Synthetic route of 2,5-pyridinedicarbonyl dichloride (**2**).

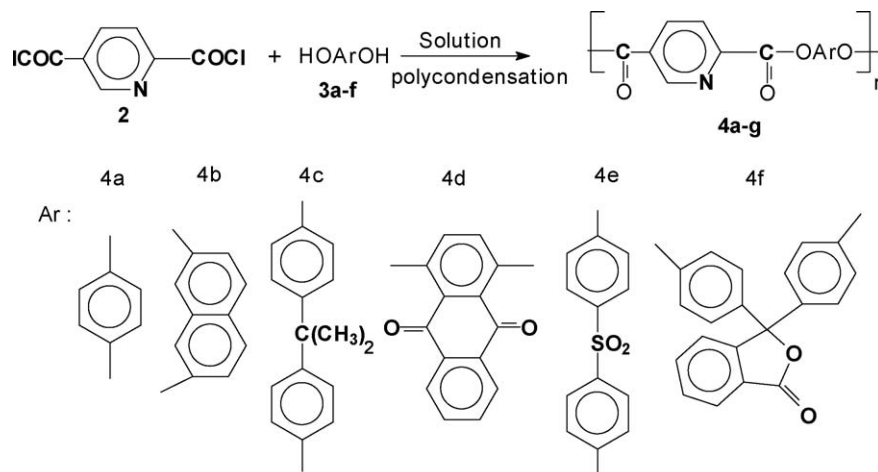


Table 1
Synthesis and some physical properties of polyesters (4a–f).

Diols	Polymer	Yield (%)	η_{inh} (dL/g) ^a	\bar{M}_n (10^4) ^b	\bar{M}_w (10^4) ^b	PDI
3a	4a	92	0.35	1.9	5.8	3.05
3b	4b	85	0.55	1.8	5.6	3.11
3c	4c	81	0.42	1.4	4.9	3.50
3d	4d	80	0.50	1.9	5.9	3.10
3e	4e	92	0.50	2.1	4.8	2.28
3f	4f	88	0.37	2.2	5.5	2.50

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

^b Measured by GPC in DMF, polystyrene was used as standard.

(DMF), DMAc, dimethyl sulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP) at room temperature and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water.

2.1. Thermal properties

The thermal properties of polyesters (4a–f) were investigated with TGA and DTG in a nitrogen atmosphere at a heating rate of 10 °C/min and the thermal data are summarized in Table 2. The initial decomposition temperatures of 5 and 10% weight losses (T_5 and T_{10}) and the char yield at 600 °C for these polymers are summarized in Table 2. These polymers exhibit good resistance to thermal decomposition, up to 305–385 °C in nitrogen, and began to decompose

Table 2
Thermal behavior of polyester (4a–f).

Polyester	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield ^c (%)
4a	310–315	330–335	42
4b	385–390	395–400	22
4c	350–355	375–380	20
4d	305–310	335–340	22
4e	315–320	340–345	23
4f	340–345	360–365	24

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of 10 °C/min in N₂, respectively.

^b Temperature at which 10% weight loss was recorded by TGA at heating rate of 10 °C/min in N₂, respectively.

^c Percentage weight of material left undecomposed after TGA analysis 600 °C.

gradually above that temperature. T_5 for these polymers ranged from 305 to 385 °C and T_{10} for all polymers ranged from 330 to 395 °C, and the residual weight for these polymers at 600 °C ranged from 20 to 42% in nitrogen. These results show polyesters (**4a–f**) have thermal resistance and they can be used as engineering plastic in many applications.

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