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An Alternative Method for Synthesis of Thermally Stable Aromatic Polyesters Containing Schiff Base Unites

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Abstract

In this paper, an efficient method for synthesis of aromatic polyesters containing schiff base units is described by preparation of two polyesters. These polyesters have been prepared by the reaction of terephthaloyl dichloride on Schiff bases derived from p-hydroxybenzyldehyde and 4,4-diamino diphenyl ether, 4,4-diamino diphenyl methane. The Polymers were characterized by IR, CHNS, thermal analyses (TGA) and viscosities. Inherent viscosities of polyesters were in the range of 0.28-0.31 dLg-1 and thermal stability determined by TGA in nitrogen atmosphere.

Keywords: *Aromatic polyesters, Schiff bases, Efficient method, Thermal stability.*

Introduction

Amongst polymers, polyesters have been the subject of numerous commercial applications. Wholly Aromatic polyesters have been well known for high thermal stability, chemical resistance, and outstanding mechanical properties and find applications in aviation and automobile industries [1, 2]. Polymers with a structure of conjugated aromatic and imine bonds in their main chain have been drawing the attention of scientists due to their importance in many aspects [3-8]. Schiff base type polymers, Generally, Schiff base bonds confers appropriate features such as; thermal stability, conductivity and chelating effects to polymers [9-11]. Aromatic structures in this class of polymers have a high thermal stability; they suffer from low solubility [12]. Schiff base type polymers, which have many special properties, such as thermal stability,

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liquid crystalline properties, conductivity, and chelating effect [13–15], has been drawing the attention of researchers for more than 50 years. A variety of Schiff base polymers have been synthesized and characterized [16].

More recently, it was found that aromatic heterocyclic polymers containing bithiazole rings are good ligands because the two nitrogen atoms in the bithiazole rings are able to chelate metal ions to form stable five-member rings [17]. Sun et al. [18, 19] synthesized bithiazole containing polymers and found their metal complexes have typically ferromagnetic properties. During recent years, interest has developed in the synthesis of Schiff base type polymers containing bithiazole in the main chain due to their interesting electrical and magnetic properties and excellent thermal resistance [20–23].

In this article, we investigate the synthesis by new method and characterization of polyesters containing Schiff base unit. The properties of polyesters were also measured by FTIR spectroscopy, thermogravimetric analysis (TGA). Also the inherent viscosity polymers were studied.

Experimental

Materials and Instruments

4,4–diaminodiphenyl ether, 4,4-diamino diphenyl methane, 4-hydroxybenzaldehyde, terephthaloyl dichloride and solvents were purchased from Fluka and used without further purification. ^{1}HNMR spectra were recorded on a 500 MHz Bruker Advance DRX instrument using DMSO-d_6 as solvent and tetramethylsilane as an internal standard. FT-IR spectra were recorded using a Bruker Vector 22 spectrometer on KBr pellets. The CHN-600 Leco analyzer was used for elemental analysis. Thermal gravimetric analysis (TGA) was performed using MetlerTolledo822e, respectively. Inherent viscosity ($[\eta]_{inh} = \ln_{\eta rel}/c$, at a concentration of 0.5 g/dL) was measured with an Ubbelhode suspended-level viscometer at 25°C in NMP solution.

Preparation of Monomers

In to a 250 mL round bottom flask were equipped with a magnetic stirring bar charged 4-hydroxybenzaldehyde (26 mmol) was dissolved in a mixture of 40 mL methanol, 1 mL of conc. HCl. A solution of 4,4–diaminodiphenyl ether or 4,4-diamino diphenyl methane (13 mmol) in 35 mL of methanol and few drops were added to the flask. The mixture was stirred for 2 h under reflux condition after cooling the reaction, the precipitated product, was collected by filtration, washed with ethanol and dried in a vacuum oven at 80 °C for 3 h. The melting points of compounds 4-4{oxy[1,4-phenylennitrilomethililiden]} diphenol (OPNDP) and 4,4- methylene[1,4-phenylennitrilomethililiden]}diphenol (MPNDP) were observed 249°C and 240°C as yellow products with 82% and 90% of theoretical yield respectively.

For OPNDP: IR (KBr) (υmax cm^{-1}): 3163 (OH),1604(C=N).^{1}HNMR (400, DMSO-d_6, TMS) δ ppm: 10.12(2H,OH), 6.59-7.78(16H, phenyl), 8.49(2H, imine).

For MPNDP: IR (KBr) (υmax cm^{-1}): 3215(OH),1578(C=C), 1607(C=N). ^{1}HNMR (400, DMSO-d_6, TMS) δ ppm: 10.10(2H, OH), 6.88-7.76(16H, phenyl), 3.96(2H, methylen), 8.45(2H, imine).

Preparation of polyesters

A solution of monomers (2mmol) and 2 mL DMAc in to a 50 mL round-bottomed flask was magnetically stirred at room temperature under nitrogen atmosphere. The mixture was cooled in an ice-water bath, and triethylamine (4 mmol) was added to this solution. Then was added 1,4-Benzenedicarbonyl dichloride (2mmol) in to flask. The mixture was stirred in an ice-water bath for one hours, then slowly stirring continued at 80 ◦C for overnight. The reaction mixture was poured into methanol; the precipitated polymer was filtered and washed several times with water. The crude polymer was thoroughly washed with deionized water and acetone. The light yellow solid was attained after dried under vacuum at 70°C for 24 h. yield (70-75% theoretical). The FT-IR absorption bands of OPNDP were found at 1737 cm^{-1} (C=O), 1649 cm^{-1}(C=N) and 1600 cm^{-1} (C=C$_{\text{Aromatic}}$). Analysis: calcd. for $C_{34}H_{22}N_2O_5$: C, 75.83%; H, 4.10%; N, 5.20%; found: C, 74.21%; H, 4.45%; N, 5.96%.

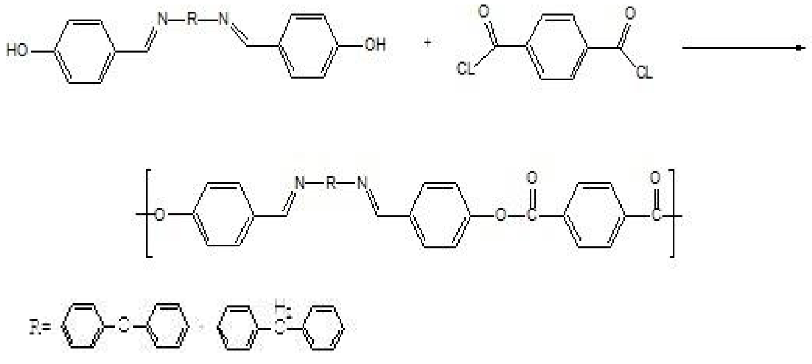

Figure 1. Synthesis of polyester.

Results and Discussion

Monomer synthesis and characterization

The Schiff base monomers were prepared by condensation of p-hydroxybenzyldehyde with 4,4–diaminodiphenyl ether and 4,4-diamino diphenyl methane in ethanolic solution containing 1 ml of hydrochloric acid. The characteristics data obtained from FT-IR and ^{1}H-NMR spectra are in good agreement with monomers structure. In the FT-IR spectrum of OPNDP, a band at 3163 cm-1was observed which corresponds to phenolic hydroxyl group and band at 1604 cm^{-1} showed of imine group, in the FT-IR spectrum of MPNDP, 3215 cm^{-1} showed band of phenolic hydroxyl group and the peak at 1607 cm^{-1} is characteristic of imine group. The ^{1}H-NMR spectra of Schiff base monomers indicated a peak within 10.12 ppm and 10.10 ppm due to hydroxyl group protons, the peaks at around 8.49 ppm and 8.45 ppm due to imine group protons, for OPNDP and MPNDP respectively. For two monomers, signals at 6-8 ppm related to the protons of aromatic groups. The methylene protons of MPNDP are observed in 3.96 ppm. Figure 2 shows ^{1}HNMR spectra, respectively of OPNDP along with the assignments.

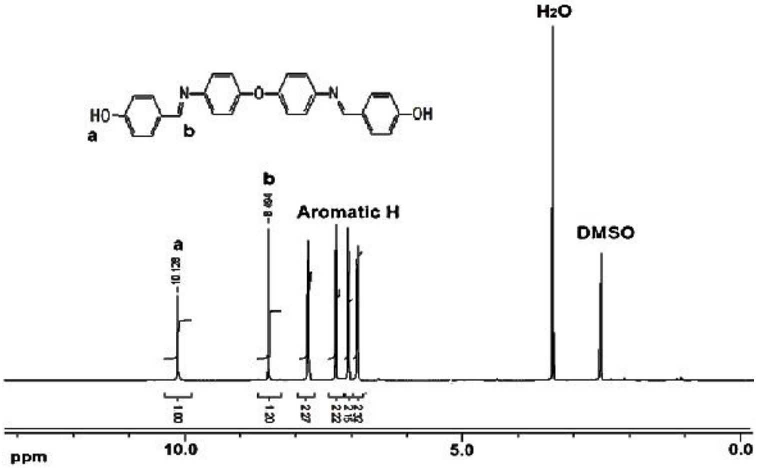

Figure 2. ^{1}HNMR OPNDP.

Polymer synthesis and characterization

The aromatic polyesters was synthesized by polycondensation new method of monomers containing Schiff base groups, OPNDP and MPNDP with 1,4-Benzenedicarbonyl dichloride in DMAc/Et$_3$ Nsolution, triethylamine was used to neutralize HCL produced during the reaction (Figure 1).Structure characterize of these polyesters were confirmed by elemental analysis and FT-IR. The results of the elemental analyses listed in Table 1.These two polyesters showed absorption bands within 1737cm^{-1} and 1740 cm^{-1} due to ester carbonyl groups, absorption at around 1600 cm-1 and 1596 cm^{-1} are due to aromatic groups, for the polyesters of OPNDP and MPNDP respectively. All of the polyesters stretching vibration of the C=N bond appears at about 1649 cm^{-1} and absorption bands around 1100-1300 cm^{-1} which correspond to C-O stretching of ester. In Figure 3, showed IR spectra the polyester of OPNDP.

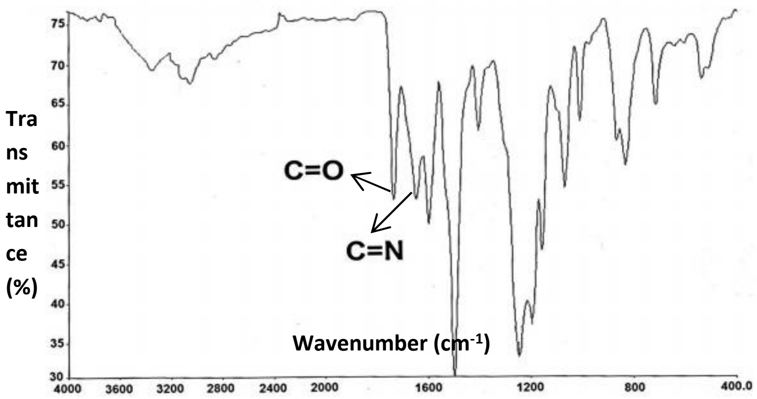

Figure 3. IR polyester OPNDP.

The elemental analysis of the resulted polymers is in good agreement with the calculated values for the polyesters structures. The results of the elemental analyses, FT-IR and yield listed in Table 1. Inherent viscosities of polyesters were in the range 0.28-0.31 dL g-1 in NMP at 25°C, indicating their moderate molecular weight.

Table 1.Spectra data and elemental analysis results of polyesters.

Substrate	Yield (%)	IR (KBr, cm^{-1})	Elemental analysis							
			Calc.				Found			
			C	H	N	S	C	H	N	S
Polyester OPNDP	70	1737(C=O), 1198,1248(C-O), 1600(C=C), 1649(C=N)	75.83	4.10	5.20	-	74.21	4.45	5.96	-
Polyester MPNDP	75	1740 (C=O), 1198, 1159 (C-O), 1596 (C=C), 1649 (C=N)	78.36	4.48	5.22	-	76.48	4.95	6.03	-

Thermal Properties of polyesters

Thermal properties of the organized polyesters were evaluated by means of thermogravimetric analysis (TGA) in a nitrogen atmosphere at a heating rate of 10◦C/min (Figure 4).

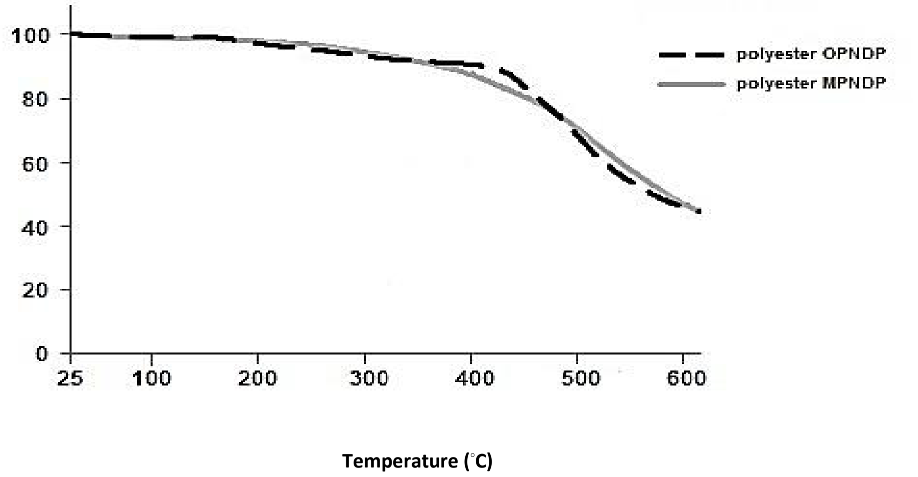

Figure 4.TGA of Polyester.

The thermal stability of polymers was studied by TGA. The first decomposition temperatures of 10 and 20% weight losses (T_{10} and T_{20}) and the char yield at 600 ◦C for these polyesters are abridged in Table 2. The T_{10} values of the polyesters stayed in the range of 382–422 ◦C, T_{20} for these polymers the ranged of 450-470 and the residual weight for these polyesters at 600 ◦C more than 45% in nitrogen. The thermal properties and Inherent viscosities of two polyesters are listed in Table 2.

Table 2. The Inherent viscosities and thermal properties of polyesters.

Substrate	η^{a}_{inh}(dl/g)	$T_{10\%}$^{b}(°C)	$T_{20\%}$^{c}(°C)	R_{w}(%)^{d}
Polyester OPNDP	0.28	422	470	46
Polyester MPNDP	0.31	382	450	47

[a] Detected in NMP with a concentration of 0.5 g/dL at 25 °C.

[b] 10% weight loss temperature. (Determined by TGA at a scan rate of 10 °C /min in N_2).

[c] 20% weight loss temperature. (Determined by TGA at a scan rate of 10 °C /min in N_2).

[d] Residual weight (%) when heated to 600 °C (Determined by TGA at a scan rate of 10 °C /min in N_2).

Conclusions

Two Schiff-base polyesters were prepared from the reaction of Schiff base diols monomers with the terephthaloyl dichloride by new method. Polyester was prepared, characterized and its thermal stability was investigated. This method has a good performance for Schiff-base polyesters Synthesis with high purity and yields. Thermal properties of these polyesters were investigated by TGA.

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