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Synthesis and characterization of novel polyester containing Schiff-base unit

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Abstract

A new Schiff base type of polyester containing 2,2-dimethyl-1,3-diaminopropane was prepared by solution polycondensation of 1,4-benzenedicarbonyl dichloride with Bis(4-hydroxybenzilaldehid)-2,2-dimethyl-1,3-propildiimine (H_2HB_2P) which is derived from a 2,2-dimethyl-1,3-diaminopropane Schiff base reacted with a 4-hydroxybenzaldehyde monomer. The monomer and the polyester were characterized by FTIR, ^{1}HNMR, and elemental analysis. The prepared polyester showed inherent viscosity of 0.29 dl/g in NMP at 25 °C, indicating their moderate molecular weight. The Polyester was completely soluble in aprotic polar solvents such as *N*-methylpyrolidone (NMP), dimethylformamide (DMF), Dimethyl Acetamid (DMAC), dimthylsulfoxide (DMSO). TGA determined the 10% weight loss temperature (T_{10}) at 280 °C and residual weight at 600 °C ca. 41% under nitrogen atmosphere.

Keywords: *polyester, Schiff base, 2, 2-dimethyl-1, 3-diaminopropane, thermal stability.*

1. Introduction

Polymers have received significant attention due to their lightness and favorable physical and chemical properties. Amongst polymers, polyesters have been the subject of numerous commercial applications. This in turn, has attracted a plethora of researches and studies in the synthesis of polyesters from diols and diacid chlorides by condensation polymerizations[1,2]. Synthesis of polymers with conjugative bonds including –C=N– and–C=C– in the main chain has grabbed researcher's interests for many years[3-8]. Generally, Schiff base bonds confers appropriate features such as; thermal stability, conductivity, liquid crystal properties and chelating effects to polymers[9,10]. Nowadays, polyesters with Schiff base units have been an interesting area for researchers due to the particular properties. Aromatic structures in this class of polymers have a high thermal stability[11]. Aromatic polymers with Schiff base units have a high thermal stability, they suffer from low solubility. To solve this problem, many efforts were triggered toward increasing the solubility[12,13]. Substituting flexible groups along the main chain of polyesters with Schiff base units is of strategies to enhance the solubility in organic solvents[14]. In this paper for the first time we investigate the synthesis and characterization of polyester containing Schiff base unit with high solubility by solution polymerization of bis(4-hydroxybenzaldehyde)- 2,2 dimethyl-1,3-propyl diamin(H_2HB_2P) with terephthaloyl dichloride. Monomer and resultant polymer was characterized by FT-IR, ^{1}HNMR and CHNS. Also the inherent viscosity, solubility and thermal stability of the polymer were studied.

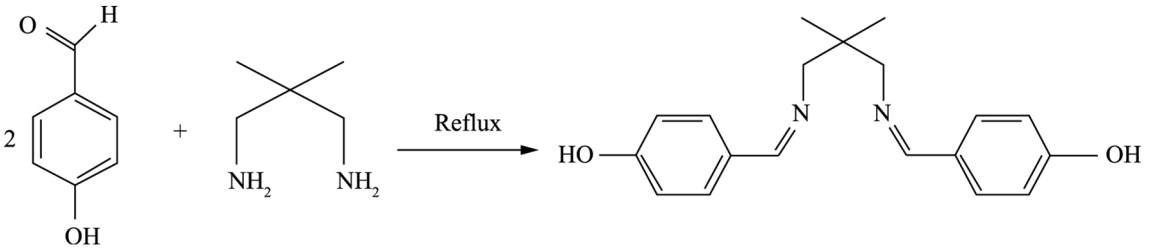
2. Experimental

2.1 Materials and instruments

2, 2-dimethyl-1, 3-diaminopropane, 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-d6 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) and differential scanning calorimetery (DSC) were performed using Perkin-Elmer Pyris and MetlerTolledo 822e, 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.

2.2 Pre-treatment of monomer

In a 250 mL round bottom flask equipped with a magnetic stirring, 4-hydroxybenzaldehyde (3.15 g, 26 mmol) dissolved in a mixture of 40 mL methanol, 1 mL of conc. HCl was added. A solution of 2, 2-dimethyl-1, 3-diaminopropane (1.32 g, 13 mmol) in 30 mL of methanol and few drops were added to the flask. The mixture was stirred for 5 h under reflux condition. After cooling the reaction, The precipitated product, Bis (4-hydroxybenzilaldehid)-2, 2-dimethyl-1,3-propildiimine (H_2HB_2P) (Scheme 1), was collected by filtration, washed with ethanol and dried in a vacuum oven at 70 °C for 3 h. A yellow product was obtained in 65% yield with a melting point of 186 °C. IR (KBr) (δ_{max} cm^{-1}): 3205 (OH), 1649 (CN), 1585 (C=C$_{Ar}$). ^{1}HNMR (400, DMSO, d_6, TMS) δ ppm: 9.86 (1H, S, OH),



Scheme 1. Synthesis of H_2HB_2P.

8.16 (1H, S, NH), 0.93-1.04 (6H, t, CH_{methyl}), 3.42-3.56 (4H, C, $CH_{methylene}$).

2.3 Preparation of polyester

In a two-necked flask 100 mL equipped with a dropping funnel and gas inlet tube was charged with a mixture of Bis(4-hydroxybenzilaldehid)-2,2-dimethyl-1,3-propildiimine (0.62 g, 2 mmol), 20 mL dimethylformamide (DMF) and triethylamine (0.8 mL). 1, 4-benzenedicarbonyl dichloride (0.40 g, 2 mmol) dissolved in 10 mL DMF was added drop wise to the stirred solution at 0 °C under N_2 atmosphere. The mixture was subsequently stirred at ambient temperature for 5 h under N_2 and then it was poured into cold water. The yellow solid product was separated by filtration and washed with $NaHCO_3$ solution. Then polymer washed with methanol, and dried under reduced pressure at 80 °C for 24 h.Yield 60%, IR (KBr) (δ_{max} cm^{-1}): 1736 (C=O), 1210 and 1270 (C-O), 1598 (C=C), 1660 (C=N). ^{1}HNMR (400, DMSO, d_6, TMS) δ ppm: 0.93-1.06 (6H, CH_{methyl}), 3.36-3.52 (4H, $CH_{methylene}$), 7.40-8.39 (12H, CH_{Ar}), 8.40 (2H, CH=N). Anal.Cald. for [$C_{27}H_{24}N_2O_4$]: C, 73.64; H, 5.45; N, 6.36. Found: C, 74.54; H, 5.22; N, 7.06.

3. Result and Discussion

Scheme 1 depicts route for synthesis of monomer (H_2HB_2P). The band at 3205 cm^{-1} is associated to OH, while the band at 1649 cm^{-1} can be attributed to the imine group(N=C). The absorption peak at 1585 cm^{-1} is characteristic of double bond group (C=C). The Figure 1, ^{1}HNMR spectra showed the OH protons in 9.86 ppm, the peak at around 8.16 ppm is assigned to NH, and methyl peak is observed in 1.04-0.93 ppm and the peak from 3.42-3.47 ppm is characteristic of methylene. Polyester is synthesized by polymerization of H_2HB_2P with terephthaloyl dichloride in the presence of triethylamine. Reaction was carried out in DMF as H_2HB_2P solvent and terephthaloyl dichloride in nitrogen atmosphere at room temperature. The result of elemental analysis is closely similar to calculated percentages. Elemental percentages are obtained as follows: C, 74.54% (73.64% calculated); H, 5.22% (5.45%); N, 7.06% (6.36%). Polyester was also characterized with ^{1}HNMR and IR Spectroscopy. In Figure 2, showed IR spectra peaks; the peak at 1736 cm^{-1} is associated to (stretch C=O), and the peak at 1660 cm^{-1} is characteristic of (N=C) and the peak at 1598 cm^{-1} is related to (stretch C=C). ^{1}HNMR spectra of the representative polyester, in Figure 3, showed signals at 8.40 ppm due to the proton of azomethine, at 7.40-8.39 ppm related to the protons of aromatic groups, the protons of methyl at 0.93-1.06 ppm and in the regions

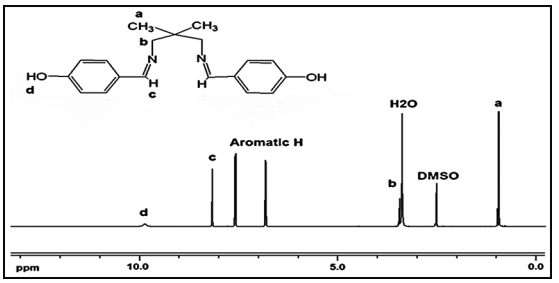


Figure 1. ^{1}HNMR of H_2HB_2P.

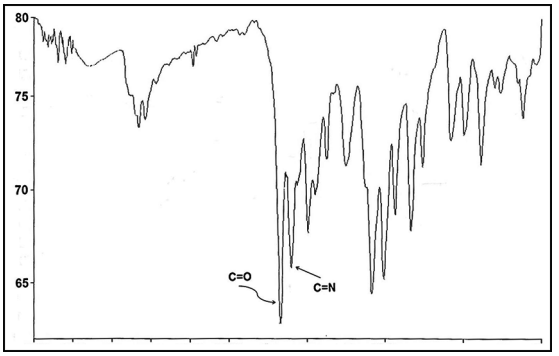


Figure 2. IR of polyester.

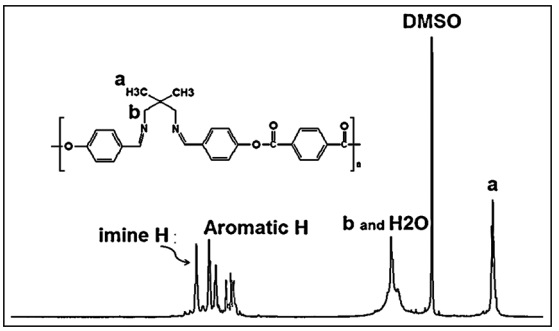


Figure 3. ^{1}HNMR of polyester.

of 3.36-3.52 ppm corresponding to aromatic protons and water proton. The inherent viscosity [η] of polymer was measured in NMP, equal to 0.29 dl/g. It is well established that viscosity has direct relation with molecular weight therefore polyester possess a reasonable molecular weight. Polyester was dissolved easily in NMP, DMF, DMAC and

Table 1. The physical and thermal properties of polyester.

Yield (%)	η^{a}_{inh}(dl/g)	T_g [b] (°C)	$T_{10\%}$ [c](°C)	$T_{20\%}$ [d](°C)	R_w(%)[e]
60	0.29	174	268	341	41.4

[a]Detected in NMP with a concentration of 0.5 g/dl at 25 °C. [b]Detected by DSC at a heating rate of 10 °C /min in N2. [c]10% weight loss temperature (Determined by TGA at a scan rate of 10 °C /min in N2). [d]20% weight loss temperature (Determined by TGA at a scan rate of 10 °C /min in N2). [e]Residual weight (%) when heated to 600 °C (Determined by TGA at a scan rate of 10 °C /min in N2).

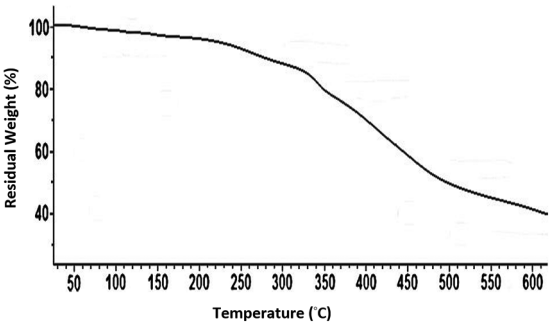


Figure 4. TGA of polyester.

DMSO at room temperature. It is hypothesized that this is because aliphatic structure of H_2HB_2P monomer enhance the flexibility of polymer. The polyester was insoluble in acetone and methanol. Thermal stability of polyester was investigated with TGA and DSC instruments. Differential scanning calorimeter (DSC) analysis was performed at a heating rate of 10 °C/ min. The scanning of polymer was carried out over 300 °C. The glass transition temperature was recorded about 170 °C. As anticipated, the T_g value of this polyester depended on the structure of the diol aliphatic part employed. Thermal stability was carried out in nitrogen atmosphere. Polymer showed 10 percent weight loss over 270 °C and 50 percent weight loss over 400 °C. 41.4% of the polymer remained unchanged around 600 °C (Figure 4). Physical and thermal properties were shown in Table 1.

4. Conclusion

Polyester was prepared from H_2HB_2P diol and terephthaloyl dichloride. With molar ratio of diol to diacid chloride 2:2 the polymerization was performed at room temperature under N_2 atmosphere within 5 hours. Polyester was prepared, characterized and its thermal stability was investigated. The presence of aliphatic group increased the flexibility of diol and as a result enhanced the solubility of polyester. The poyester has a 10 percent weight loss at 268 and 20% weight loss at 341 °C and a residual weight (41.4%) at 600 °C. The polyester has a glass transition temperature at 174 °C and it showed that the polyester is a thermally stable material. The inherent viscosity of polyester is 0.29 dl/g and showed a high molecular weight for polymer.

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