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Synthesis and characterization of Schiff-base polymer derived from 2,5-dichloroaniline and 2-hydroxybenzaldehyde

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Abstract

Schiff base sal-2,5-Clan = 2-(2,5-dichlorobenzylideneamino)phenol was used as a new precursor for preparation of poly-2-(2,5-dichlorobenzylideneamino)phenol (PDCBAP). In anaqueous alkaline medium, NaOCl oxidant is capable of oxidative poly-condensation reaction (OP). Both sal-2,5-Clan and PDCBAP were characterized by solubility tests, FT-IR, ^{1}H-NMR spectroscopy and TG-DTA studies. FT-IR and ^{1}H-NMR spectrum of PDCBAP indicates the formation of Ar-O-Ar bond. According to TG/DTA curves, PDCBAP demonstrated higher resistance against temperature than sal-2,5-Clan. At optimum reaction conditions, *viz*. time = 14h, $[NaOCl]_0$= 0.12 M, $[KOH]_0$ = 0.1 M and T = 90°C, the yield of PDCBAP is52.17%. Thermal studies indicated that PDCBAP is more stable than sal-2,5-Clan.

Keywords: Oxidative poly-condensation; spectroscopy; thermal studies.

Introduction

Compounds containing imine group (-CH=N-) known as Schiff bases are usually prepared by condensing primary amines with active carbonyl compounds [1]. In recent years, considerable attention has been focused on the synthesis of new poly Schiff base compounds containing bulky aromatic groups [2]. Moreover, oxidative polycondensation method is cheaper as it involves simple oxidants [3]. These compounds have also been widely studied for their high thermal stability [4], versatile use in electronics [5], optoelectronics and photonics [6] and antimicrobial activity [7]. Additionally, poly Schiff base compounds have high mechanical strength [8], good conductivity and environmental stability [9], and are widely used to prepare various composites [10] and materials [11]. Preparation and characterization of poly Schiff base compounds by oxidative poly-condensation method have been widely studied by Kaya and co-workers [2-4,10].

Herein, we report the synthesis and characterization of Schiff base compound 2-(2,5-dichlorobenzylideneamino)phenol (sal-2,5-Clan) and its polymer PDCBAP (Scheme 1).

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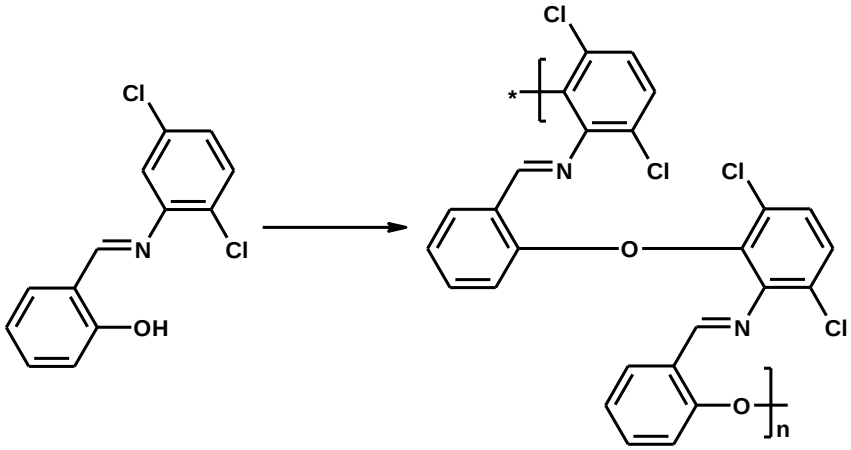

Scheme 1. Structures of sal-2,5-Clan and its polymer PDCBAP

Experimental

Materials and Instruments

All solvents and reagents were purchased from Merck Co. and used as received. Infrared spectra were recorded using KBr disk on a FT-IR (Perkin–Elmer) spectrometer. The ^{1}H-NMR spectra were recorded in DMSO-d_6 using BRUKER DRX-400 AVANCE spectrometer at 400 MHz. All chemical shifts are reported in δ units downfield from TMS. The TG was performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in nitrogen atmosphere with a heating rate of 20 ºC/min in the temperature span of 30–750 ºC.

Preparation of sal-2,5-Clan

A solution of 2,5-dichloroaniline (4.05g, 0.025mol) in 25 mL methanol was added drop-wise to a methanol solution of salycilaldehyde (3.05 g, 0.025 mole) under stirring condition. The reaction mixture was then refluxed for 2 h and when the solution color turned yellow we allowed the solution to cool at room temperature over-night. The appeared crystals are filtered, washed with cold methanol and dried at room temperature. Yield: 91.8%. M.P.: 176°C. FT-IR (KBrpellet, cm^{-1}): 1613 (s, C=N). ^{1}H-NMR (DMSO-d_6, δ(ppm)): 6.98-7.04 (m, 2H), 7.37-7.40 (dd,1H), 7.45-7.50 (ddd, 1H), 7.62 (d, 1H), 7.67-7.70 (dd, 1H), 7.77 (d, 1H), 9.06 (s, 1H), 12.86(S, 1H).

Preparation of PDCBAP polymer

Sal-2,5-Clan (0.242 g, 0.001 mol) is dissolved in an aqueous KOH solution (10 wt %, 0.112g, 0.002 mol) and warmed in a 50 mL three-necked round bottom flask at 40°C followed by drop-wise addition of NaOCl for about 20 min. The mixture was then neutralized with 0.174mL HCl (37 wt %) at room temperature. The products were filtered, washed with hot water, and dried at room temperature. Yield: 72.21%. M.P.: >400°C. FT-IR (KBr pellet, cm^{-1}): 1620 (s, C=N), 1470 (Ar-O-Ar). ^{1}H-NMR (DMSO-d_6, δ(ppm)): 6.92-6.96 (3, 2H), 7.01-7.03 (dd,2H), 7.06 (d, 1H), 7.30-7.39 (m, 2H), 7.48-7.52 (m, 2H),7.56 (d, 1H), 7.63-7.66 (dd, 2H),10.27 (s, 2H).

Results and discussion

Polymer was a dark brown powder and it was completely soluble in highly polar organic solvents such as DMF and DMSO, partly soluble in methanol, and ethanol, and insoluble in$CHCl_3$ and acetone. The monomer, sal-2,5-Clan, was a yellow crystalline and soluble in

all the above mentioned solvents. Table 1 shows the solubility of the monomer and its polymer indifferent solvents.

Table 1. Solubility test results of sal-2,5-Clan and PDCBAP

Solvents	**DMF**	**DMSO**	**Methanol**	**Ethanol**	**Acetone**	**Chloroform**
sal-2,5-Clan	+	+	+	+	+	+
PDCBAP	+	+	±	±	-	-

+: soluble, ±: partially soluble, -: insoluble

The oxidization of the parent compound sal-2,5-Clan in the presence of NaOCl in aqueousalkaline medium are given in Table 2. The yield of PDCBAP is 52.17% under the reaction conditions such as time= 14 h, $[NaOCl]_0$= 0.12, $[KOH]_0$ = 0.1 M and T = 90°C (sample no.8), while the change of $[NaOCl]_0$ to 0.50, keeping other parameters unaltered (sample no. 11),the yield of PDCBAP become 36.12%. Table 2 shows that increase in the concentration of KOH and NaOCl have lowered the yield of PDCBAP.

FT-IR spectra

In the FT-IR spectrum of sal-2,5-Clan, the absence of stretching bands for NH_2 and C=O groups of the corresponding amine and aldehyde along with the appearance of new strong peaks at 1613 (monomer) and 1620 cm^{-1}(polymer) have suggested the formation of new imine (C=N) functionality [2,5]. Also, the phenolic–OH stretching is observed in 3435 cm^{-1}. The weak band at 3000 $cm^{-1}$is assigned to C-H aromatic stretching vibrations. FT-IR peaks of polymer are broadened due to the poly-conjugated structure. Appearance of new broad peak at 1470 cm^{-1}in the FT-IR spectrum of PDCBAP confirmed the formation of Ar-O-Ar ether bond.

Table 2. The parameters of OP reaction of sal-2,5-Clan

No.	**T(°C)**	**Time(h)**	**[sal-2,5-Clan)] (M)**	**[KOH](M)**	**[NaOCl](M)**	**Yield (%)**
1	60	7	0.02	0.10	0.24	45.12
2	60	7	0.02	0.20	0.24	37.20
3	70	7	0.02	0.20	0.24	36.33
4	70	10	0.02	0.10	0.24	44.15
5	80	10	0.02	0.15	0.24	48.15
6	90	14	0.02	0.15	0.12	50.91

7	80	10	0.02	0.10	0.12	38.35
8	90	14	0.02	0.10	0.12	52.17
9	90	14	0.02	0.25	0.12	48.73
10	90	14	0.02	0.10	0.30	36.60
11	90	14	0.02	0.10	0.50	36.12

^{1}H-NMR spectra

^{1}H-NMR spectrum of sal-2,5-Clan show one peak as singlet at 12.86 ppm, assigned to OH proton. The absence of signal for -OH in the ^{1}H-NMR spectrum PDCBAP confirmed the formation of Ar-O-Ar ether bond. Also,sal-2,5-Clan which show one peak as singlet at 9.06 ppm has been assigned to –CH=N- (imine proton) that shifted downfield to 10.28 ppm in PDCBAP. In addition, the absence of aromatic hydrogen (about 7.8 ppm) in the ^{1}H-NMR spectrum of PDCBAP suggests the formation of new C-C and C-O-C functionality [3,5] (Fig. 1). This indicates that the hydroxyl group is involved in the formation of free radical leading to polymer formation [4].

Thermal analysis

TG/DTA curves of sal-2,5-Clan and PDCBAP are presented in Fig. 2. The weight losses of sal-2,5-Clan and PDCBAP at 740°C are found to be 2.7%and 62%, respectively. PDCBAP has demonstrated higher resistance against temperature thansal-2,5-Clan and thus more stable than sal-2,5-Clan with regard to thermal decomposition.

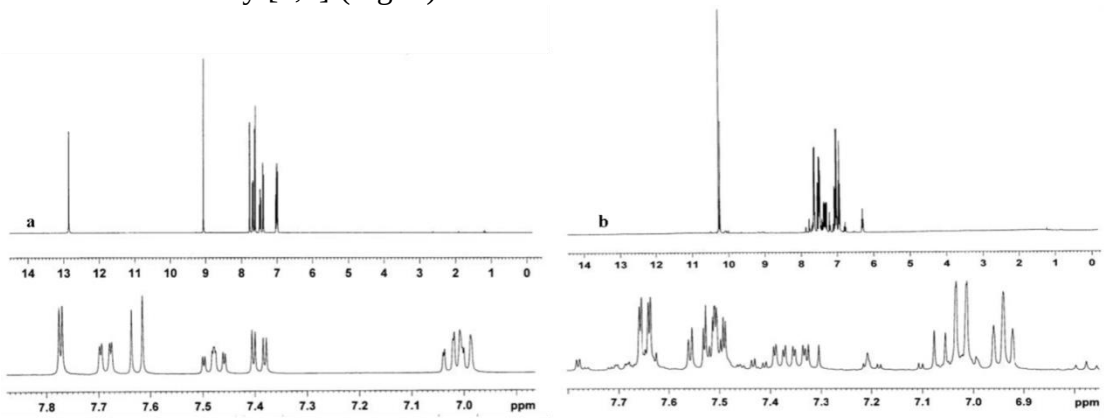

Figure 1. ^{1}H-NMR spectrum of a) sal-2,5-Clan and b) PDCBAP

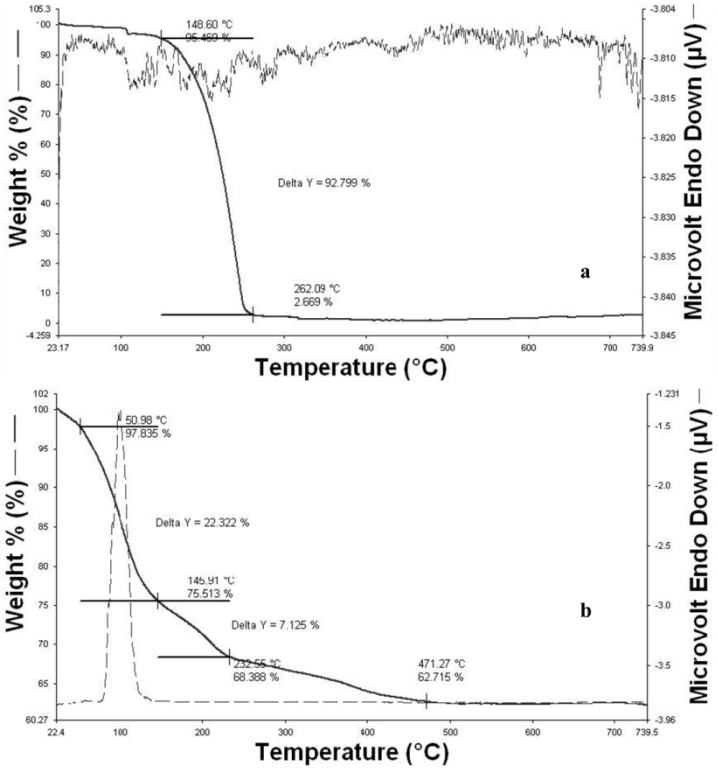

Figure 2. TG/DTA curves of a) sal-2,5-Clanand b) PDCBAP

Conclusion

Poly-2-(2,5-dichlorobenzylideneamino)phenol has been synthesized using oxidants such asair and NaOCl in an aqueous alkaline medium. The yield of polymer is found to 52.17% forNaOCl oxidant. FT-IR and $_1$H-NMR spetra of polymer indicates the formation of Ar-O-Arbond during oxidative polycondensation of sal-2,5-Clan. According to TG/DTA curvesPDCBAP demonstrated higher resistance against temperature than sal-2,5-Clan.

Acknowledgments

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