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Synthesis and Characterization of Polysalicylaldehyde (PSA) by Oxidative Polycondensation of Schiff base Compound [(2,4-dichlorophenylimino)methyl]-phenol

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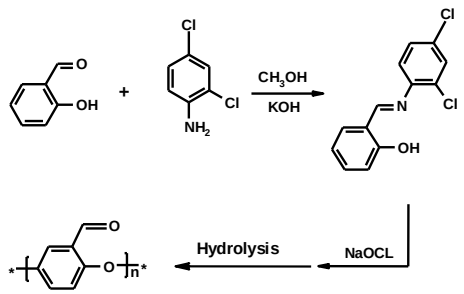
Abstract

In this paper, polysalisylaldehyde (PSA) has been synthesized from the oxidative polycondensation (OP) of 2-[(2,4-dichlorophenylimino)methyl]-phenol (sal-2,4-Clan) with NaOCl in an aqueous alkaline medium between 50 and 90°C and characterized by ^{1}H-NMR, FT-IR, UV-Vis and TGA/DTA techniques. The conversion of PSA was 61.23% in optimum conditions such as $[sal\text{-}2,4\text{-}Clan]_0$ = 0.02, $[KOH]_0$= 0.1 $[NaOCl]_0$ = 0.12 mol/L at 90°C for 10 h. Additionally, the crystal structure of sal-2,4-Clan has been determined by single-crystal X-ray crystallography.

Keywords: Polysalisylaldehyde; Oxidative polycondensation; X-ray crystallography.

1. Introduction

The OP method is one of the best methods for preparation of polymer compounds including -OH group and active functional groups such as -NH_2, -CHO and –COOH. The main advantage of this method is the use of easily found, cheap, and simple structured oxidants. Until now, many studies on polymerization and reaction mechanisms of polyphenols by oxidative polycondensation method have been reported [1-5]. In this paper, we report the synthesis of PSA from the OP of sal-2,4-Clan as new precursor (Scheme 1).



Scheme 1. Chemical structure and preparation of sal-2,4-Clan and PSA

2. Experimental

2.1. Materials and Instruments

All solvents and reagents were have been purchased from Merck Co. and used as received. Infrared spectra are recorded using KBr disk on a FT-IR (Perkin–Elmer) spectrometer. ^{1}H-NMR spectra are measured on a BRUKER DRX-400 AVANCE spectrometer at 400 MHz. All chemical shifts are reported in δ units downfield from TMS. UV-Vis absorption spectra were recorded on a JASCO V-570 spectrophotometer; λ_{max} in nm. Thermal studies have been 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 of30–750 ºC.

2.2. Preparation of sal-2,4-Clan

A solution of 2,4-Dichloroaniline (4.05g, 0.025mol) in 25 mL methanol is added drop-wise to a methanol solution of salycilaldehyde (3.05 g, 0.025 mole) under stirring condition. The reaction mixture is then refluxed for 2 h when the solution color turns yellow and allowed the solution to cool at room temperature over-night. The suitable crystals are filtered, washed

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with cold methanol, and dried at room temperature. IR (KBr pellet, cm^{-1}): 1616 (s, C=N). ^{1}H-NMR (DMSO-d^6, δ(ppm)): 6.98-7.03 (m, 2H), 7.44-7.49 (ddd, 1H), 7.53-7.56 (dd, 1H), 7.65 (d, 1H), 7.67-7.69 (dd, 1H), 7.77 (d, 1H), 9.02 (s, 1H), 12.91 (S, 1H). UV-Vis (DMSO, λ_{max} in nm): 400, 340.

2.3. Preparation of PSA

Sal-2,4-Clan (0.242 g, 0.001 mol) was dissolved in an aqueous solution of KOH (10 wt %, 0.112 g, 0.002 mol) and placed into a (50 mL) three-necked round bottom flask. After heating to 40°C, NaOCl was added drop wise for about 20 min. The reaction mixture was stirred at the different temperatures and time intervals. The mixture was then neutralized with 0.174 mL HCl (37 wt %) at room temperature. The products are filtered, washed with hot water, and dried at room temperature. IR (KBr pellet, cm^{-1}): 1659 (s, C=O). ^{1}H-NMR (DMSO-d^6, δ(ppm)): 7.12 (d, 1H), 7.51-7.54 (dd, 1H), 7.56 (d, 1H), 10.24 (s, 1H). UV-Vis (DMSO, λ_{max} in nm): 420, 325.

2.4. Crystallographic analysis

A single crystal with the dimensions 0.37 mm × 0.12 mm × 0.11 mm of sal-2,4-Clan is chosen for X-ray diffraction study. Crystallographic measurements are done at 120 K with four circle CCD diffractometer Gemini of Oxford diffraction, Ltd., with graphite-monochromated Mo *K*α radiation (λ = 0.07107 Å). The crystal structures are solved by direct methods with program SIR2002 [6] and refined with the Jana2006 program package [7] by full-matrix least-squares technique on F^2.. Hydrogen atoms are mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice they are nevertheless kept in ideal positions during the refinement. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as 1.2-1.5U_{eq} of the parent atom. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

Table 1. Crystallographic data of sal-2,4-Clan.

Empirical formula	$C_{13}H_9NOCl_2$
Formula weight	266.1
Crystal system, Space group	Monoclinic, $P2_1/c$
a (Å)	4.70390 (10)
b (Å)	12.8101 (4)
c (Å)	19.2614 (6)
β (°)	91.782 (2)
V ($Å^3$)	1160.08 (6)
Z	4
μ (mm^{-1})	0.54
R_{int}	0.035
S	1.71
$R[F^2>2\sigma(F^2)]$	0.031
$wR(F^2)$	0.036
Parameter	157
Independent reflections	2544
Reflections with $I > 3\sigma(I)$	1982
Restraint	1
$\Delta\rho_{max}$, $\Delta\rho_{min}$ ($eÅ^{-3}$)	0.30, -0.20

3. Results and discussion

The oxidation of the parent compound sal-2,4-Clan in presence of NaOCl in aqueous alkaline medium are given in Table 2. The yield of PSA is 61.23% under the reaction conditions such as time = 14h, $[NaOCl]_0$ = 0.12, $[KOH]_0$ = 0.1 M and T = 90°C (sample no. 9). Table 2 shows that increase in the concentration of KOH and NaOCl have lowered the yield of PSA.

Table 2. The parameters of OP reaction of sal-2,4-Clan

Sample no.	T (ºC)	Time (h)	[sal-2,5-Clan)] (M)	[KOH] (M)	[NaOCl] (M)	Yield of PDCBAP (%)
1	60	7	0.02	0.20	0.24	48.17
2	60	7	0.02	0.20	0.12	48.44
3	70	7	0.02	0.25	0.12	48.11
4	80	10	0.02	0.20	0.24	52.33
5	80	10	0.02	0.30	0.24	47.98
6	80	10	0.02	0.15	0.24	56.14
7	80	14	0.02	0.10	0.12	60.79
8	90	14	0.02	0.10	0.12	60.77
9	90	14	0.02	0.10	0.12	61.23
10	90	10	0.02	0.10	0.12	61.22
11	90	14	0.02	0.15	0.24	59.19

3.1. ^{1}H-NMR, FT-IR and UV-Vis spectra

^{1}H-NMR spectra of sal-2,4-Clan and PSA in DMSO-d^6 are presented in figures 1 and 2, respectively. The ^{1}H-NMR spectrum of sal-2,4-Clan shows one singlet in the region of 12.91 ppm which are assigned to OH proton and the peak at 9.02 ppm has been assigned to –CH=N- (imine proton). The absence of these peaks in the ^{1}H-NMR spectrum of PSA suggested hydrolysis of sal-2,4-Clan and formation of new C-O-C functionality [1-5].

The absence of vibration peaks related to NH_2 and C=O groups of amine and aldehyde in the FT-IR spectrum of sal-2,4-Clan and appearance of new strong peak at 1613 (monomer) and 1620 cm^{-1} (polymer) have suggested formation of new imine (C=N) functionality [6,7]. In the FT-IR spectrum of polymer, the peaks also broaden due to the poly-conjugated structure. Appear of new broad peak at 1470 cm^{-1} in the FT-IR spectrum of polymer indicating the Ar-O-Ar ether bond formation.

The UV-Vis spectra are measured in DMSO. There are two peaks at 400 and 340 for sal-2,4-Clan and 420 and 325 for PSA, attributed to the π-π* and n-π* transition, respectively.

3.2. Crystal structure of sal-2,4-Clan

Crystallographic measurements were done at 120 K with four circle CCD diffractometer Gemini of Oxford diffraction, Ltd., with mirrors-collimated Mo *K*α radiation. The molecular structure of sal-2,4-Clan was determined by single crystal X-ray diffraction and the asymmetric unit is shown in figure 4 [8,9]. The title compound sal-2,4-Clan crystallizes in the monoclinic with space group $P2_1/c$ and is non-planar. The bond distances of N1=C6 (1.277(2) Å) and N1-C10 (1.4091(19) Å) are consistent with double and single bonds, respectively [8,9].

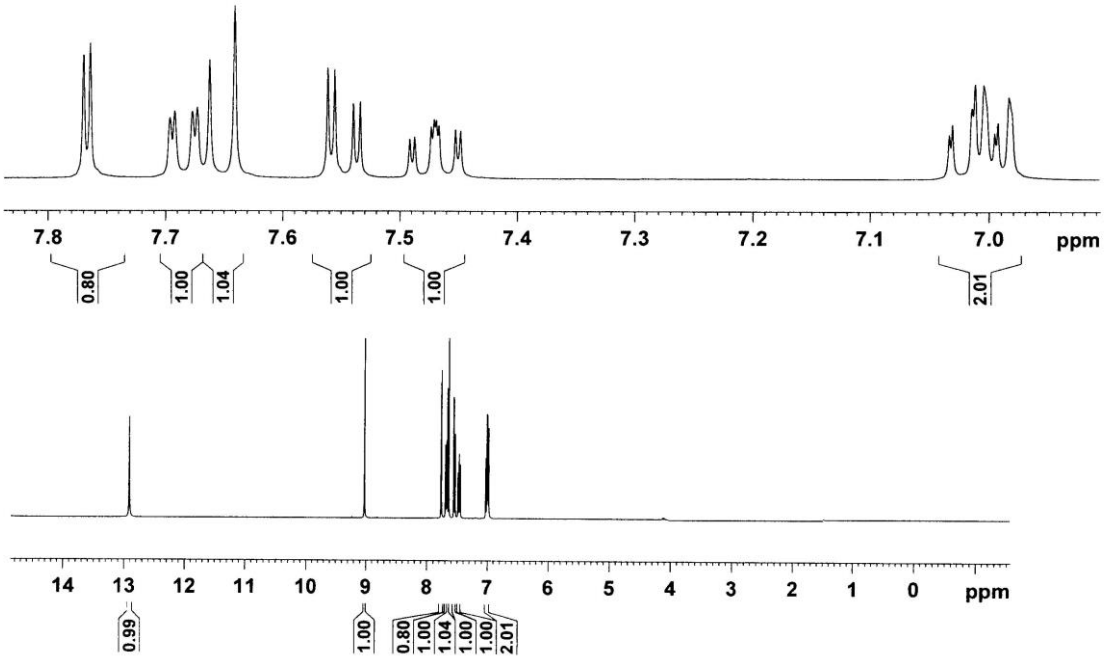

Fig1. [1]H NMR spectrum of sal-2,4-Clan

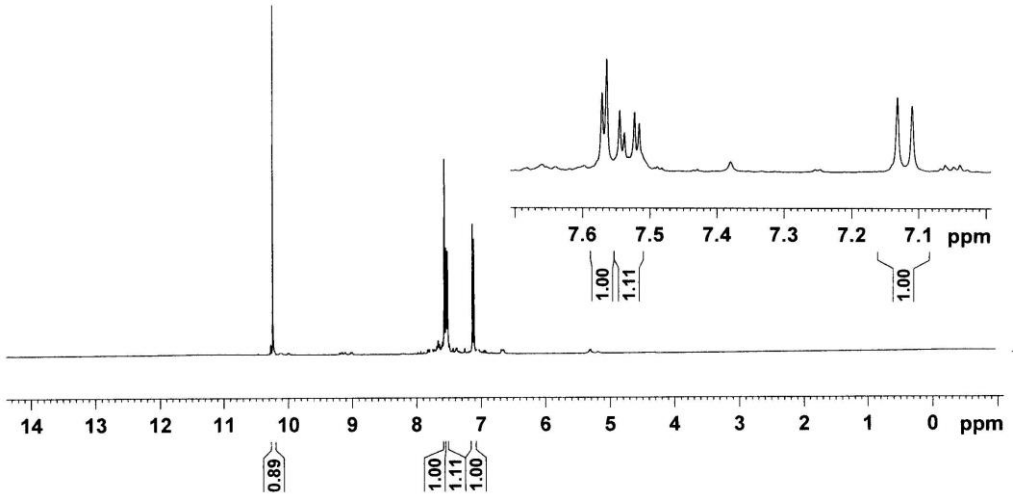

Fig 2. [1]H-NMR spectrum of PSA

3.3. Thermal analysis

TG/DTA curves of sal-2,4-Clan and PSA are presented in Fig. 4 and Fig. 5 respectively. The weight losses of sal-2,4-Clan and PSA at 740°C are found to be about 9% and 70%, respectively. PSAP has demonstrated higher resistance against temperature than sal-2,4-Clan and thus more stable than sal-2,4-Clan with regard to thermal decomposition.

4. Conclusion

PSA has been synthesized by OP method from Schiff base compound sal-2,4-Clan in an aqueous alkaline medium. The yield of PSA was found to be 50.9% for oxidants such as air and NaOCl in an aqueous alkaline medium. The yield of polymer was found to 72.21% for the best optimum conditions, $[\text{sal-2,4-Clan}]_0$ = 0.02, $[KOH]_0$= 0.1 $[NaOCl]_0$ = 0.12 mol/L at 90°C for 10 h. FT-IR and [1]H-NMR spetra of polymer indicates the Ar-O-Ar ether bond formation during OP of sal-2,5-Clan.

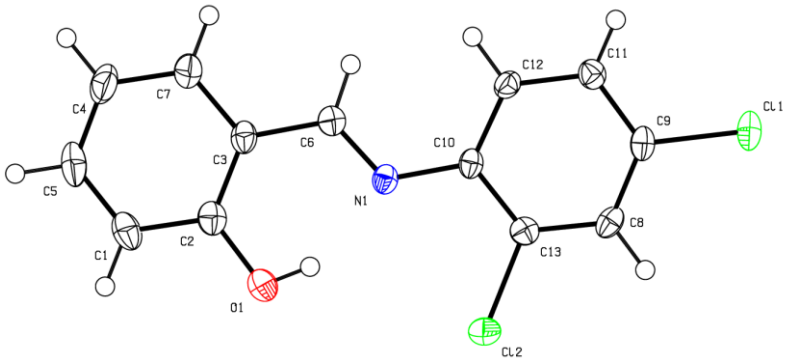

Fig 3. Molecular structure of sal-2,4-Clan.

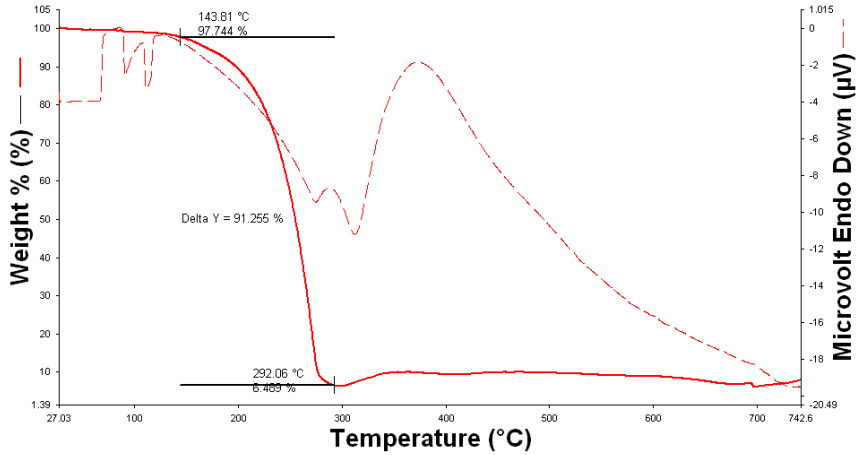

Fig 4. TG/DTA curve of sal-2,4-Clan

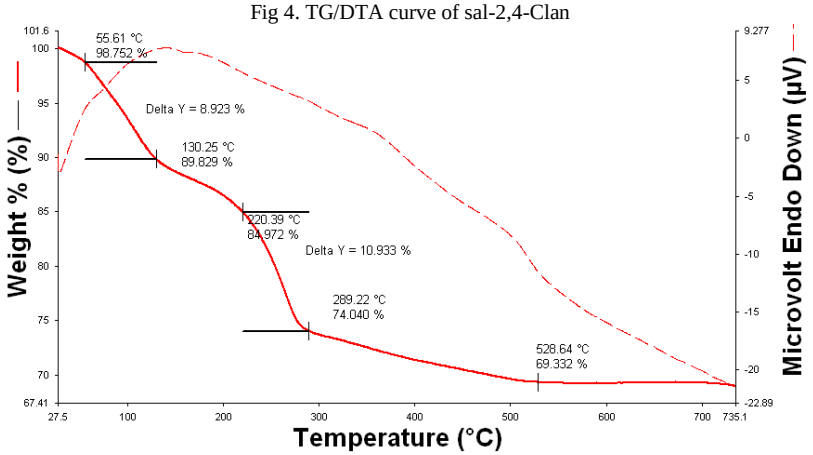

Fig 5. TG/DTA curve of PSA

5. Acknowledgements

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سنتز و شناسایی پلی‌سالیسیل آلدهید بوسیله اکسایش تراکمی ترکیب باز شیف ((۲،۴–دی کلروفنیل-ایمینو)متیل)فنول

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چکیده:

در این مقاله، پلی‌سالیسیل آلدهید (PSA) بوسیله اکسایش تراکمی (OP) ترکیب ((۲،۴- دی کلروفنیل‌ایمینو) متیل) فنول با NaOCl و در محلول مایی نمک قلیایی بین دمای۵۰ تا ۹۰ درجه سلسیوس تهیه و به کمک تکنیک‌های ^{1}H-NMR، FT-IR، UV-Vis و TGA/DTA شناسایی شد. بازده تبدیل در شرایط بهینه $[sal\text{-}2,4\text{-}Clan]_0 = 0.02$، $[KOH]_0 = 0.1$ و $[NaOCl]_0 = 0.12$ mol/L، در دمای ۹۰ درجه سلسیوس و مدت زمان ۱۰ ساعت، ۶۱،۲۳٪ می‌باشد. بعلاوه، ساختار بلوری ترکیب sal-2,4-Clan به کمک پراش پرتو ایکس تک بلور تعیین شد.

لغات کلیدی: پلی‌سالیسیل آلدهید، اکسایشی تراکمی، بلورنگاری X-ray

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