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# New Organo Soluble and Thermally Stable Schiff Base Polymers by Oxidative Polycondensation

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The Schiff base monomer was synthesized by the condensation reaction between salicyladehyde and p-phenylendiamine. The Schiff base polymers having double azomethine group were prepared by oxidative polycondensation (OP) reaction of monomer in aqueous alkaline medium with NaOCl (P1) and H2O2 (P2) as the oxidants at 90 °C. Cu(II) and Ni(II) complexes of the polymers were synthesized by the reaction of polymer and metal-acetate salts. The monomer and polymers were characterized by elemental analyses, thermogravimertic analyses, DSC analyses, UV-Vis, FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic studies, which revealed that the P1 and P2 polymers synthesized by OP is composed of oxyphenylene (C-O-C;  $P_1 = 77 \%$ ,  $P_2 = 75 \%$ ), phenylene (C-C;  $P_1 = 23 \%$ ,  $P_2 = 25 \%$ ) units. Average molecular weights of polymers were determined by gel permeation chromatography. The polymers were soluble in polar aprotic solvents and aqueous alkaline media. According to the thermogravimetric analyses, Schiff base polymer (P2) exhibited excellent thermal stability with 38 % residual weight at 1000 °C in nitrogen atmosphere. The thermal stability of these polymer systems are found to be in order  $P_2 > P_1$ . As the synthesized polymers were soluble in common solvents such as THF, DMF, DMSO, these properties of polymer are promising for it is environmental and analytical usage.

Key Words: Schiff base polymer, Oxidative polymerization, Soluble polymer, Thermal stability, Metal complexes.

### **INTRODUCTION**

Polymers with highly conjugated chains have attracted much attention in the last few years because they are promising candidates for a wide variety of applications, such as electronics, opto electronics and photonics<sup>1,2</sup>. Schiff base polymers or polyazomethines that are synthesized by polycondensation reaction between diamine or hydrazine with a dialdehyde or diketone<sup>3</sup>.

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On the other hand, chemical or electrochemical oxidation of monomers containing aromatic rings derived from pyrrol, thiophene, furan etc. spaced by azomethine linkage in the main chain is another approach for the preparation of Schiff base polymers. To obtain conjugated polymers with Schiff base structure Simionescu *et al.*<sup>3</sup> tried a strategy. They achieved the preparation of polymers with pyrrol and naphthalene moieties by the oxidative polymerization in the presence of  $(NH_4)_2S_2O_8$  and FeCl<sub>3</sub>·6H<sub>2</sub>O as the oxidative are rarely used to obtain Schiff base polymers.

Polycondensation for Schiff base polymers can be performed in the melt or in the solution using a suitable solvent and catalyst. Melt condensation of such monomers is hard to control and give side reactions that lead to undesirable by products. A major drawback of the Schiff base polymers is their limited solubility in most organic solvents due to their rigid chain structure. Some general methods have been used to overcome limited solubility properties of Schiff base polymers, such as: insertion of flexible bonds between main chain aromatic rings, introduction of pendant group *i.e.* aromatic or alkyl substituents, onto the polymer chain, introduction of structural irregularities like kinks, bents, crankshaft-shaped units<sup>2-8</sup>.

Fortunately, the investigations on the preparation of Schiff base polymers/ oligomers by using oxidative polycondensation (OP) verified that another alternative approach to increase the solubility of Schiff base polymers is use to OP. Because, in contrast to Schiff base polymers prepared by conventional polycondensation reaction, the oligomers obtained by the OP indicated good solubility properties.

Although, OP method is also an oxidative polymerization, the term OP has been specifically used for the polymerization reaction where the oxidants used are NaOCl,  $H_2O_2$  and air  $O_2$ . Due to the reagents used for reaction process, the OP may also be regarded as a good example of environmentally benign or green synthetic process of polymeric materials. The OP is simply the reaction of compounds having phenolic groups and active functional groups (-NH<sub>2</sub>, -CHO, -COOH) in their structure with the above given oxidants. In this method, polycondensation is often carried out in an aqueous alkaline and acidic medium. The polymerization process of the OP is performed under mild reaction conditions without using toxic reagents. Compared with other methods, the OP has important advantages for polymer syntheses such as cheap and simple structured oxidants; ease of product separation from the reaction mixture; enhanced thermal stability of polymers; increased solubility of polymers, release of non-toxic compounds by product (NaCl, H<sub>2</sub>O). One of the target macromolecules for the OP is Schiff base polymers which are difficult to be synthesized by conventional polymerizations. Additionally, oligomers synthesized by the OP have important properties such as, paramagnetism, thermal stability, conductivity and antimicrobial activity<sup>9-14</sup>.

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In previous work<sup>15</sup>, a new Schiff base polymer was synthesized by OP in the presence of NaOCl as the oxidant. The obtained Schiff base polymer exhibited good thermal stability and solubility properties. For these reasons, in this paper, we wish to extend our investigations. In present investigation, the synthesis and characterization of new Schiff base polymer with a double azomethine group and aromatic backbone are reported.

## **EXPERIMENTAL**

The solvents and reagents were purchased from Merck Co. The infrared and UV-Vis spectra were measured by Jasco 300 FT-IR and Shimadzu UV-160, respectively. The FT-IR spectra were recorded using KBr discs (4000-400 cm<sup>-1</sup>). UV-Vis spectrum (200-800 nm) of monomer and polymer were determined by using DMF. Monomer and polymer were characterized using <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra (Bruker AC FT-NMR 400 MHz spectrometer) recorded at 25 °C using deuterated DMSO as solvent. DTA, TG and DSC analyses were performed with a Shimadzu DTA-TGA-50 and DSC thermal analyzer. The thermogravimetric measurements were made between 0 and 1000 °C (in nitrogen, rate 5 °C min<sup>-1</sup>). Average molecular weights of polymers were determined by gel permeation chromatography (GPC). The columns were calibrated using different molecular weight polystyrene standards. The flow rate of the THF was maintained as 1 mL through the experiments and 1 wt. % (10 mg in 1 mL) of polymer solution was filtered and injected for obtaining the GPC chromatograms.

Synthesis of monomer: The monomer was synthesized by common condensation method<sup>16</sup>. p-Phenylenediamine (10 mmol) was dissolved in ethanol (100 mL). This mixture was added into the ethanolic solution of salicyladehyde (20 mmol) at 20 °C. After added the salicylaldehyde, the mixture was stirred magnetically and refluxed for 1 h. The solvent was evaporated under reduced pressure and unreacted phenylenediamine was separated from the mixture by extraction with benzene. The monomer was dried in vacuum desiccator over CaCl<sub>2</sub>. (Colour: Yellow, m.p: 135 °C, Yield: 83 %; UV-Vis in DMSO (nm): 238, 278, 374; FT-IR (KBr, v<sub>max</sub>, cm<sup>-1</sup>): 3435 (-OH str), 2850 (hydrogen bonded -OH), 1641 (-CH=N-str.), 1586 (C=C aromatic), 1286 (phenolic C-O bending), 1042-984 (CH, aromatic), 862-759 (substituted benzene rings); <sup>1</sup>H NMR (DMSO,  $\delta$  = ppm): 6.9-7.7 (m, Ar-H), 13.1 (s, *o*-OH), 9.0 (CH=N, azomethine H); <sup>13</sup>C NMR (DMSO, ppm): 117, 119, 123, 132, 133 and 146 (aromatic ring), 164 (azomethine carbon); Elemental analyses (%), calculated for  $C_{20}H_{16}N_2O_2$  (m.w. = 316.3): C 75.92, N 8.86, H 5.10. Found: C 75.45, N 8.97, H 4.99.

Synthesis of polymers by oxidative polycondensation: Polymers were synthesized through the oxidative polycondensation of monomer with aqueous solutions of NaOCl and  $H_2O_2$ . The Schiff base monomer (0.015)

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mol) was dissolved in an aqueous solution of KOH (10 %, 0.015 mol) and placed into a 50 mL three-necked round-bottomed flask. It was fitted with a condenser, a thermometer and a stirrer, in addition to a funnel containing NaOCl ( $P_1$ ) or  $H_2O_2$  ( $P_2$ ). Solution was heated to 65 °C and then NaOCl or H<sub>2</sub>O<sub>2</sub> (0.015 mol) was added drop-wise over ca. 0.5 h. The reaction mixture was stirred at 90 °C for 5 h. The mixture was neutralized with 0.015 mol HCl (37 %) at the room temperature. Then, unreacted monomer was extracted with CHCl<sub>3</sub>, filtered and dried in an oven at 105 °C. According to spectroscopic and thermal analyses, whereas the similar peaks were observed for P1 and P2 polymers, different thermal behaviours were observed for these polymers. (Colour: Black Yield: 65 %; decomposition point (d.p.): > 300 °C; UV-Vis in DMSO (nm): 278, 300, 360, 400; FT-IR, KBr, cm<sup>-1</sup>: 3331 (-OH str.), 1614 (-CH=N-str.), 1511 (C=C, aromatic), 1280 (phenolic C-O-C, bending), 827-750 (substituted benzene rings); <sup>1</sup>H NMR (DMSO,  $\delta$  = ppm): 6.4-7.8 (m, Ar-H), 10.9 (s, p-OH), 8.9 (CH=N, azomethine H); <sup>13</sup>C NMR (DMSO, ppm): 117, 119, 124, 132, 133, 146 (aromatic ring), 164 (azomethine carbon).

**Synthesis of polymer-metal complexes:** Polymer metal-complexes were synthesized by addition of the nickel(II)/copper(II) acetate (1 mmol, in 25 mL absolute EtOH) to a hot solution of the ligands (1 mmol, in 30 mL THF). The pH was adjusted to 7.0 using alcoholic ammonia (0.01 M). The resulting solutions were stirred and heated on a water bath at 80 °C for 12 h. The resulting product was collected by filtration, washed with EtOH and hot water and finally dried under vacuum at 70 °C. All polymer metal-complexes were isolated as powdered material.

## **RESULTS AND DISCUSSION**

The Schiff base monomer bearing double azomethine group was prepared by known condensation method<sup>16</sup>. The reaction of p-phenylenediamine and salicylaldeyhde resulted in the formation of a Schiff base monomer (Scheme-I). After precipitation of Schiff base monomer, polymers were synthesized by OP reaction in aqueous alkaline medium with NaOCl  $(P_1)$  and  $H_2O_2(P_2)$  as oxidant at 90 °C (Scheme-II). The OP products of the monomer were black colour. The solubility of the polymers was studied at the room temperature at a concentration of 0.1 % (w/v). The obtained polymers were soluble in several polar solvents such as DMF, DMSO, THF and chloroform. However, its solubility in non-polar solvents (benzene, toluene) and hydroxylated solvents (water, methanol, etc.) was almost negligible. On the other hand, when obtained by melt-polycondensation, a major drawback of the Schiff base polymers is their limited solubility in most organic solvents due to their rigid chain structure. This result verified that OP offered new Schiff base polymer having good solubility properties that are clearly advantageous for their technological and analytical applications.

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Scheme-I: Intramolecular hydrogen bonding in the Schiff base monomer



P<sub>1</sub> 97% (C-O-C); 3% (C-C); P<sub>2</sub>, 95% (C-O-C), 5% (C-C)

Scheme-II: Synthesis and the proposed structure of polymers.

Polymer with azomethine groups exhibited dye character since the molar extinction coefficients ( $\epsilon$ ) were over 40000 cm<sup>-1</sup> (max<sub>abs</sub> 0.30)<sup>17</sup>. Aromatic Schiff base monomer containing two azomethine groups show a unique dye-stuff colour due to the high conjugation of azomethine group with aromatic ring. Thus the polymers derived from this monomer displayed black colour. Moreover, the solution of the polymer in DMF and DMSO exhibited a dark black colour.

The number average molecular weights (Mn) and weight average molecular weight (Mw) of the polymers ( $P_1$  and  $P_2$ ) were determined by Gel Permeation Chromatography (GPC) using polystyrene standards (PS). The molecular weights of polymers are given in Table-1. The Mn and Mw values of  $P_1$  and  $P_2$  were found to be 42260, 48520 g mol<sup>-1</sup> and 21670, 21730 g mol<sup>-1</sup>, respectively. The formation of high molecular weights of

#### TABLE-1 REACTION CONDITIONS, GEL PERMEABLE CHROMATOGRAPHY (GPC) MOLECULAR WEIGHTS AND T<sub>2</sub> OF POLYMERS

Polymer	Time (h)	Yield (%)	M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)	*M <sub>w</sub> /Mn	**T <sub>g</sub> (°C)
$\mathbf{P}_{1}$	20	60	42.260	21.670	1.95	220
$\mathbf{P}_{2}$	14	55	48.520	21.730	2.23	160

\*Determined by GPC using polystyrene standards as reference in THF.

\*\*Determined by DSC at 5 °C/min heating range.

polymers suggests that the OP conditions used for the synthesis are highly effective. The Mn, Mw and PS values of the  $P_2$  are higher than those of  $P_1$ . The chromatogram of polymers showed bimodal distributions for solution of polymers. This indicates the formation of one type of polymers in the  $P_1$  and  $P_2$  synthesis. These results corroborate the assumptions made on the basis of <sup>1</sup>H NMR spectra.

It has been known that aromatic polyazomethines or Schiff base polymers are naturally coloured yellow, orange, red and brown. The relatively low colouration is explained by the lack of coplanarity of the aromatic ring structures with the azomethine units and the consequent low conjugation of double bonds along the polymer chain. On the other hand, Kim et al.<sup>18</sup> proposed that the reason of the observed brown colour of Schiff base polymers were related with the extension of  $\pi$ -electron conjugation along the polymer chain. Likewise, the OP of Schiff base monomer afforded the corresponding polymer with brown or black colour suggesting the extension of  $\pi$ -electron conjugation along the chain. It is known from the UV-Vis spectra of the Schiff base polymers that these polymers indicate the  $\pi \rightarrow \pi^*$  transition absorption band at about 300 nm. Similarly, in this study, in the spectra of the monomer, aromatic band at 278 nm are attributed to benzene  $\pi \rightarrow \pi^*$ transitions. The band at 238 nm was attributed to conjugation between benzene ring and non-bonding electrons of nitrogen in the azomethine group. The band at 374 nm was assigned to the imine  $\pi$ - $\pi$ \* transition in the Schiff base monomer. After the OP reaction, however, the spectra of the polymers changed ranging from 20 to 40 nm compared to those of monomers (Fig. 1). Absorbance of the polymer shifted into a longer wavelength than monomer due to the high conjugation with aromatic ring. Polymer exhibited a broad UV absorption band with maximum value at 273 and a shoulder from 360 and 400 nm.

In the FT-IR spectra of monomer, the stretching vibration band of phenolic OH group and azomethine group were observed at 3435 and 1610 cm<sup>-1</sup>, respectively. Also, the sharp absorption band at 750 cm<sup>-1</sup> of monomer



Fig. 1. UV-Vis spectra of monomer (1) and polymer (2)

was because of four neighboring C-H groups of the aromatic ring. It is known that after polycondensation reaction, due to increasing molecular weight, the FT-IR spectra of polymer become broaden. This fact is also proven in the FT-IR spectra of polymer prepared in this work. As seen in FT-IR spectra, the main peaks of polymer become to broaden. In the structures of polymers, stretching vibration bands of phenolic hydroxyl groups were observed to be intense with wide bands in 3385-2600 cm<sup>-1</sup> region. The band of the azomethine group of the P<sub>1</sub> was observed at 1614 cm<sup>-1</sup>. This band was also consistent with other results. Because, it was found that almost all Schiff base polymers exhibited<sup>3</sup> the azomethine absorption band at 1640-1601 cm<sup>-1</sup>.

The stretching frequency observed at 2745 and 2710 cm<sup>-1</sup> for monomer shows the presence of O–H…N intramolecular hydrogen bond, which is in agreement with the literature<sup>19</sup>. The infrared spectra of the polymer did not show these bands, which may be explained by participation on hydroxyl sites in polymerization. These data can be attributed to oxyphenylene (C-O-C linkage) units chain of the polymer. As being different from monomer, the FT-IR spectrum of polymer showed the new absorption band aroused at 1281 cm<sup>-1</sup>, indicating to the asymmetric vibrations of the C-O-C linkages. A comparison of the polymer spectrum with that of the monomer indicates that the monomer absorption peaks intensity at 827 and 750 cm<sup>-1</sup> decreased after polycondensation.

In order to identify the structures of monomer and polymers, the <sup>1</sup>H NMR spectra were recorded in DMSO- $d_6$ . The <sup>1</sup>H NMR spectrum of the monomer shows sharp peaks at 6.9-7.7, 9.0 and 13.1 ppm, respectively.

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These peaks can be ascribed to the aromatic ring, azomethine (-CH=N-) and hydrogen bonded azomethine nitrogen with -OH protons of monomer, respectively. The peak at 3.40 ppm is assigned to the H<sub>2</sub>O impurity in the DMSO- $d_6$  reagent. It is known from the literatures that the Schiff base polymers obtained by conventional melt or solution polycondensation exhibited signals in the range 8.1-8.8 ppm due to the azomethine proton with broadening<sup>9</sup>. The <sup>1</sup>H NMR spectrum of the P<sub>1</sub> also showed the broad singlet signal at 8.8 ppm corresponding to the azomethine proton, the multiplet broaden signal around 6.6-7.8 ppm indicating the aromatic protons. The disappearing of o-hydroxy proton of the P<sub>1</sub> can be attributed to the complete polymerization reaction via hydroxyl groups. The broadening of the peaks in the spectrum is attributed to polymerization. This indicates that aromatic ring protons are at low rates participating in the coupling reaction. In the <sup>1</sup>H NMR spectrum of the monomer, the integral ratio of the aromatic ring protons to azomethine proton is about 4.30, whereas it is 3.30 for the polymer, indicating that aromatic ring protons are at very low rates participating in the coupling reaction. In addition, the integral ratio of the azomethine protons to hydroxyl protons for monomer and polymer is 1.18 and 4.91, respectively. This indicates that hydroxyl group is participating at highest rate in the polymerization reaction. The detailed analysis of <sup>1</sup>H NMR spectral data suggest that there is 77 % C-O-C (oxyphenylene) and 23 % C-C-(phenylene) type coupling type coupling in the polymer  $(P_1)$  structure.

<sup>1</sup>H NMR spectrum of the P<sub>2</sub> showed broad peaks compared to monomer centered at 6.9-7.7 ppm. The singlet at 10.9 ppm attributed to the proton of the hydroxyl group disappeared in the spectrum of the P<sub>2</sub>. The disappearing of hydroxyl proton of the P<sub>2</sub> can be attributed to the complete polymerization reaction *via* hydroxyl sites (C-O-C). In the <sup>1</sup>H NMR spectrum of the monomer, the integral ratio of the aromatic ring protons to azomethine proton is about 4.20, whereas it is 3.15 for the polymer, indicating that aromatic ring protons are participating at very low rates in the coupling reaction. In addition, the integral ratio of the azomethine protons to *o*-hydroxyl proton for monomer and P<sub>2</sub> is 1.21 and 4.82, respectively, indicating that this hydroxyl group is also participating at highest rates in the polymerization reaction. The detailed analysis of <sup>1</sup>H NMR spectral data suggest that there is 75 % C-O-C type coupling, while the remaining 25 % coupling is in the form of C-C type coupling in the P<sub>2</sub> structure. These observations were consistent with their assigned chemical structure.

The <sup>13</sup>C NMR spectrum of the monomer showed signals at 119, 122, 128, 133, 134, 151, 156, 164 and 167 ppm, respectively. A signal at 167 ppm is assigned to the azomethine carbon atom of the monomer. The signal at 164 ppm is attributed to hydroxyl group carbon atom. Polymer is being

similar to monomer; the <sup>13</sup>C NMR spectrum of  $P_1$  indicated broad signals at 120, 123, 125, 130, 152 and 167 ppm, respectively. The chemical shift of carbon that is bonded to hydroxyl group is 164 ppm for monomer, whereas it is 152 for  $P_1$ , indicating that hydroxyl oxygens are participating in the polymerization reaction. The presence of imine group in the *para* position of the C-4 of the phenyl ring appears 130 ppm, while other aromatic carbons show distinct peaks at 120, 123 and 125, respectively.

<sup>13</sup>C NMR spectrum of P<sub>2</sub> indicates signals at 118, 121, 126, 132, 133, 150 and 165 ppm, respectively. A signal at 165 ppm is assigned to the azomethine carbon atom of the P<sub>2</sub>. The chemical shift of carbon that is bonded to hydroxyl group is 164 ppm for monomer, whereas it is 150 for P<sub>2</sub>, indicating that hydroxyl oxygens are participating in the polymerization reaction. These similarities of <sup>13</sup>C NMR spectra of monomer and polymers (P<sub>1</sub> and P<sub>2</sub>) can be attributed to protection of all structures of monomer during OP reaction except hydroxyl group. The presence of imine group in the *para* position of the C-4 of the phenyl ring appears 132 ppm, while other aromatic carbons show distinct peaks at 118, 121 and 126, respectively. According to the FT-IR, <sup>13</sup>C NMR and <sup>1</sup>H NMR data, polymerization of P<sub>1</sub> and P<sub>2</sub> is occur dominantly in the form of C-O-C type coupling. Structure of polymer can be given as in **Scheme-II**.

The thermal behaviour of the Schiff base polymers was studied by thermogravimetric techniques at temperature range of 20-1000 °C in nitrogen atmosphere (Figs. 2 and 3). The data from the thermogravimetric analyses indicated that the decomposition of the polymers proceeds in two steps. The mass loss of the polymers in the range of 20-110 °C is due to the water molecules in the structure. After the removing of hydrated waters, the weight loss of polymers began at 240 °C, which is lower than the temperature (270 °C) for monomer. An interesting observation is that the monomer has a higher stability than the corresponding polymers. The behaviour clearly indicates that polymers in the present study, which provide C-O-C type coupling, exhibit frail chemical C-O-C bonds to the phenyl rings. The introduction of C-O-C type bonds in the polymer backbone probably results in a lowering of first thermal degradation point. On the other hand monomers have more rigid chemical bonds in the molecular structure than that have corresponding the polymers. In addition, polymers were completely decomposed at the temperature around 1000 °C, whereas monomer was completely decomposed at 380 °C.

The samples were heated to 280 °C at 5 °C/min to record the thermal transitions. After eliminating of water molecules between 70-110 °C, 5 and 50 % weight loss temperature of P<sub>1</sub> were 230 and 540 °C, respectively. In the first DSC heating cycle, the water molecules were lost at the temperature around 100 °C. The P<sub>1</sub> was heated to 110 °C to vapourize the water molecules,



then cooled down to room temperature and heated again. The DSC heating curve of  $P_1$  showed an endotherms at 270, 380 and 470 °C followed by decomposition of the polymer. This may be due to the phase transition of polymer. The glass transition temperature of polymers was observed at 220 °C ( $P_1$ ) and 160 °C ( $P_2$ ), respectively. The melting point of polymers was not observed. It suggests that all polymers are highly amorphous.

First thermal decomposition point of Schiff base polymer is lower than the corresponding monomer because of easily breaking of C-O-C bonds. This can be explained cleavage of polymeric ligand units from polymer backbone occurs at lower temperature when compared to decomposition of monomer. However, as expected, polymers at the higher temperatures have greater thermal stabil-ities compared to the parent monomer, probably due to the formation of new bonds during the decomposition in the polymer backbone. In addition, this behaviour can be explained with the conjugated structure of main chain of polymer backbone.

Whereas  $P_2$  had the 42.2 % carbon residue at 1000 °C,  $P_1$  had the 32.2 % carbon residue at 1000 °C (Fig. 2). This can be explained by thermal stability of  $P_2$  higher than  $P_1$ . It is also interesting to note that all polymers were in undoped form and this fact explains higher residues quantities. The residue is supposed to be graphite like polymer material. Therefore, it is important to select suitable materials having the appropriate thermal shock resistance. This polymer residue may be used to candidate material for the thermally resistant materials. For this reason, these properties of polymer may be useful for graphite materials technologies. It has been found that polymers containing double azomethine group possess thermal stability and can be used for technological applications.

To show the polymeric ligand property of polymer, the polymer metal complex was synthesized by the reaction of polymer and metal-acetate salts. Polymer-metal complexes were synthesized by dissolving in THF solution which was then treated with an alcoholic solution of Cu(II)/Ni(II) acetate. The pH was adjusted to 7.0 using alcoholic ammonia (0.01 M). After the reaction, polymer metal complex with black colour was obtained. It was stable in room temperature. Elemental analyses showed that the metal:ligand ratio of the polymer-metal complexes is 1:1. The solubility property of polymer metal complex was completely different than that of polymer. The polymer metal complex was insoluble in aqueous alkaline, THF, DMSO and DMF solvents while the polymer was soluble in these solvents. Also, polymer metal complex was insoluble in ethanol, 1,4-dioxane, chloroform and acetone. The insolubility of polymer metal complex was in relation with the formation of metal oxygen and metal nitrogen bonds between polymer and metal ion. This fact was also proven in the FT-IR spectrum of polymer metal complex. In the FT-IR spectrum of polymer (P<sub>1</sub>) metal complex (not shown), the stretching vibration bands of -OH groups shifted to 3424 cm<sup>-1</sup>. Also, like -OH vibration bands, the azomethine band shifted to 1602 cm<sup>-1</sup>. These results suggest that polymer synthesized by oxidative polycondensation reaction is suitable candidate for the preparation of polymer metal complexes.

## Conclusion

The new soluble Schiff base polymers having double azomethine group were synthesized by oxidative polycondensation (OP) method. The synthesized polymers contain hydroxyl and double azomethine group at every repeat unit, which can be difficult to achieve by conventional polycondensation method. According to the FT-IR, <sup>13</sup>C NMR and <sup>1</sup>H NMR data,

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polymerization of  $P_1$  and  $P_2$  is occur dominantly in the form of C-O-C type coupling. These groups are known to be suitable electron donors to prepare polymer metal complexes. As the synthesized polymers were soluble in common solvents such as THF, DMF, DMSO, these properties of polymer are promising for it is environmental and analytical usage. An interesting observation is that the monomer has a higher stability than the corresponding polymers. The introduction of C-O-C type bonds in the polymer backbone results in a lowering of first thermal degradation point. These polymer residues may be used for the thermally resistant matters. It has been found that polymers containing double azomethine group possess high thermal stability and can be used for technological applications. In addition, it is expected that the synthesized polymer can be used as antistatic, conductive, antimicrobial agent as well as polymeric ligand for polymer-metal complexes.

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