Synthesis and characterization of a pyridine-containing Schiff base oligomer

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The oligomer of 4-(4-pyridylmethylideneimino)phenol was formed during oxidative polycondensation in aqueous alkaline medium using oxygen as the oxidant. Optimum conditions of the oxidative polycondensation and the main parameters of the process were found. The maximum yield of the oligomer was 52.4%. The product was characterized by elemental analysis, FT-IR spectroscopy, UV-Vis spectroscopy, and ^{1}H NMR spectroscopy. The molecular weight distribution was determined by size exclusion chromatography. Thermogravimetric and differential thermal analyses were carried out for 4-(4-pyridylmethylideneimino)phenol and its oligomer.

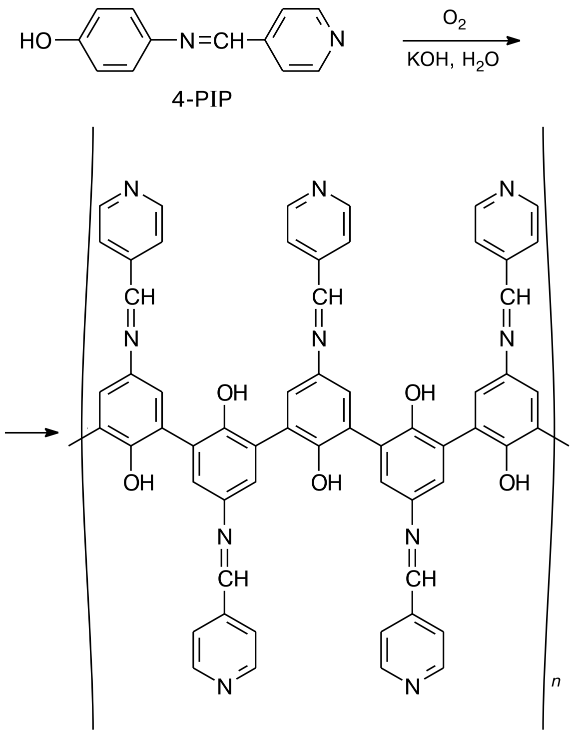
Key words: oxygen, oxidative polycondensation, 4-(4-pyridylmethylideneimino)phenol, Schiff bases, oligomers.

In recent years, Schiff base polymers containing conjugated bonds and active hydroxyl and azomethine groups have been studied.[1] This type of polymers is used in various fields of technology because of several useful properties, such as paramagnetism, semiconductivity, and resistance to high energies.[2,3] Due to this they are used to prepare composites and graphite materials resistant to high temperatures, thermostabilizers, epoxide oligomers, block copolymers, photoresistors, antistatic and flame-resistant materials, and components of electrochemical cells.[4—8] Additional useful properties can be profited by the introduction of other functional groups into these polymer. Schiff bases demonstrate antimicrobial activity against bacteria, yeast, and fungi.[9,10] Polyfunctional oligophenols can be used for purification of industrial waste waters from heavy metals, which is significant for environmental protection. Therefore, it seems reasonable to prepare a polymer-bound chelating ligand capable of complexing with a series of transition metals, which, therefore, can find a wide use.[11]

It is known that oxidative polymerization of phenol derivatives can produce two types of linkages between the monomer units: C—C and C—O—C. The reaction mechanism and coupling selectivity have been studied,[12] and three possible mechanisms affecting the C—C coupling selectivity have been proposed. The polymerization of oligophenols[13] and polyazomethines[14] was found to proceed regioselectively.

In the present work, we investigated the effects of different parameters on the oligomerization of 4-(4-pyridylmethylideneimino)phenol (4-PIP), such as the temperature, time, and initial concentrations of oxy-

Scheme 1



O-4-PIP

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gen and 4-PIP, and determined the optimum reaction conditions (Scheme 1). Synthesized 4-PIP and its oligomers (O-4-PIP) were characterized by the IR, UV, and ^{1}H NMR spectra, elemental and thermogravimetric analyses, and size exclusion chromatography.

Experimental

IR spectra were recorded on a MATTSON 1000 FT-IR spectrophotometer in the range from 400 to 4000 cm^{-1} in KBr pellets. UV spectra in the visible range were obtained on a SHIMADZU UV-1700 instrument in THF. Elemental analysis was carried out on a LECO CHNS 932 analyzer. NMR spectra were measured on a Bruker DPX spectrometer (100.6 (^{1}H) and 400 MHz (^{13}C)) in DMSO-d$_6$ relative to Me$_4$Si as internal standard. Thermal analysis was conducted on a Perkin Elmer Diamond Thermal Analysis instrument. Thermogravimetric and differential thermal analyses were carried out between 20 and 1000 °C with a heating rate of 10 °C min^{-1} under nitrogen. The number-average (M_n) and weight-average (M_w) molecular weights and polydispersity index (PDI) were determined using size exclusion chromatography on a SHIMADZU chromatography using SGX-type columns (7.7×300 mm, pore size of the stationary phase 100 Å and 7 nm, DMF—MeOH (4 : 1, v/v) mixture as eluent, rate 0.4 mL min^{-1}, polystyrene standards, refractive index detector). 4-Aminophenol, 4-pyridinecarbaldehyde, inorganic reagents, and solvents (Merck) were used as purchased. Oxygen was supplied from Muher (Turkey).

4-(4-Pyridylmethylideneimino)phenol. A mixture of 4-pyridinecarbaldehyde (1.0711 g, 0.01 mol) and 4-aminophenol (1.0913 g, 0.01 mol) in EtOH (25 mL) was refluxed for 4 h. The precipitated product was filtered off, recrystallized from EtOH, and dried in a vacuum desiccator. The yield was 93%, m.p. 210 °C. Found (%): C, 72.41; H, 4.11; N, 14.24. $C_{12}H_{10}N_2O$. Calculated (%): C, 72.71; H, 5.08; N, 14.13. UV, λ_{max}/nm: 228, 240, 260, 288, 310, 340. IR, ν/cm^{-1}: 3452 (O—H), 3064 (C—H$_{arom}$), 2999, 2881 (C—H$_{aliph}$), 1600 (CH=N), 1268 (C—O), 1523—1421 (C=C$_{arom}$), 1165 (C=N$_{arom}$). ^{1}H NMR, δ: 6.86 (d, 2 H, H(2), H(6), J = 8.1 Hz); 7.37 (d, 2 H, H(3), H(5), J = 8.1 Hz); 7.80 (d, 2 H, H(3´), H(5´), J = 4.5 Hz); 8.75 (s, 1 H, CH=N); 8.78 (d, 2 H, H(2´), H(6´), J = 4.5 Hz); 9.73 (s, 1 H, OH). ^{13}C NMR, δ: 116.70 (C(2), C(6)); 122.73 (C(3´), C(5´)); 123.92 (C(3), C(5)); 142.48 (C(4´)); 143.89 (C(4)); 151.19 (C(2´), C(6´)); 155.92 (C(1)OH); 158.11 (CH=N).

At ~20 °C 4-PIP is soluble in DMF, THF, DMSO, pyridine, and aqueous KOH. On heating it is also soluble in EtOH, MeOH, acetone, AcOEt, and partially in CHCl$_3$ and CH$_2$Cl$_2$; 4-PIP is insoluble in benzene, xylene, hexane, and heptane.

Oxidative polycondensation of 4-PIP using oxygen. A solution of 4-PIP (0.9912 g, 5 mmol) in 10% aqueous KOH (5 mmol) was placed in a three-necked round-bottom 50-mL flask equipped with a thermometer and a reflux condenser, whose upper part is connected with a tube for oxygen supply. Oxygen was bubbled through the reaction mixture with the rate from 0.6 to 9.6 L h^{-1} at temperatures given in Table 1. At the end of the reaction, the mixture was cooled to ~20 °C and neutralized with 37% HCl (0.410 mL), and the solid product was filtered off and washed with hot distilled water (3×25 mL) to remove mineral salts. The unreacted 4-PIP was removed from the oligomeric product by extraction with AcOEt. The oligomer was dried in an oven at 105 °C. Found (%): C, 71.73; H, 4.84; N, 13.40. $(C_{12}H_8N_2O)_x$. Calculated (%): C, 73.46; H, 4.11; N, 14.28. UV, λ_{max}/nm: 233, 252, 266, 290, 313, 346. IR, ν/cm^{-1}: 3412 (O—H), 2810 (C—H$_{arom}$), 2684, 2613 (C—H$_{aliph}$), 1600 (CH=N), 1240 (C—O), 1550—1448 (C=C$_{arom}$), 1166 (C=N$_{arom}$).

Table 1. Molecular weight distribution of O-4-PIP under different synthesis conditions ([4-PIP]$_0$ = [KOH]$_0$ = 0.34 mol L^{-1})

Entry	v/L h^{-1}	T/°C	t/h	M_n	M_w	PDI
				g mol^{-1}		
1	0.60	80	2	1718	2775	1.62
2	2.40	70	2	1155	1688	1.46
3	2.40	80	2	1915	2816	1.47
4	2.40	80	4	4799	7245	1.51
5	2.40	80	6	35286	38315	1.09
6	2.40	90	2	2085	6900	3.31
7	9.60	80	2	2315	4172	1.80

Note. v is the oxygen flow rate; t is the reaction time; M_n and M_w are the number-average and weight-average molecular weights, respectively; PDI is the polydispersity index.

The oligomer is soluble in DMF, THF, DMSO, pyridine, and aqueous KOH and partially soluble in EtOH, MeOH, and acetone; however, it is insoluble in AcOEt, benzene, xylene, hexane, heptane, CHCl$_3$, and CH$_2$Cl$_2$.

Results and Discussion

Study of the synthesis conditions and molecular weight distribution for O-4-PIP. The oxidative condensation of 4-PIP was carried out in an aqueous alkaline solution, and the color of the reaction mixture turned into brown immediately at the moment of oxygen inlet. The results of 4-PIP oxidative polymerization and the influence of the reaction parameters are presented in Figs 1—3. At the initial concentrations [4-PIP]$_0$ = [KOH]$_0$ = 0.34 mol L^{-1} and the flow rate of oxygen 0.6 L h^{-1} at 80 °C for 2 h the yield of O-4-PIP was 17.4%. The conversion of 4-PIP increases with an increase in the flow rate of oxygen, and at 9.6 L h^{-1} the oligomer yield reaches 33.8% and this value is further retained. The yield also increases with an increase in the initial concentration of 4-PIP. Under the optimum conditions ([4-PIP]$_0$ = [KOH]$_0$ = 0.34 mol L^{-1}, flow rate of O$_2$ 2.4 L h^{-1}, 90 °C, 6 h) the yield of O-4-PIP was 52.4%.

The chromatogram of the sample, which was obtained under the conditions of [4-PIP]$_0$ = [KOH]$_0$ = 0.34 mol L^{-1}, 80 °C, and reaction time 2 h, is shown in Fig. 4. The M_n, M_w, and PDI values are 2164, 3156 g mol^{-1}, and 1.46, respectively. The chromatogram contains two peaks. In the material obtained 4% of the weight belong to low-molecular-weight components (M_n = 308 g mol^{-1}, M_w = 325 g mol^{-1}, PDI = 1.057), and 96% fall onto high-molecular-weight compounds (M_n = 2315 g mol^{-1}, M_w = 4172 g mol^{-1}, PDI = 1.80).

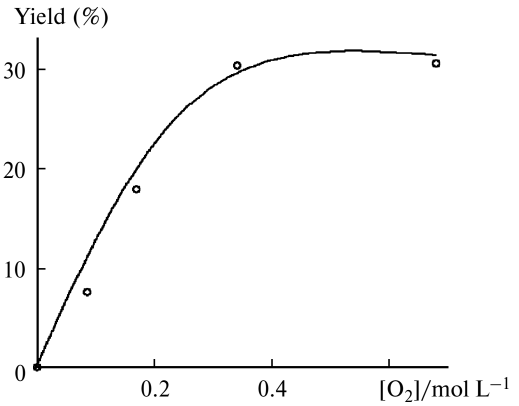

Fig. 1. Plot of the O-4-PIP yield *vs.* oxygen flow rate (80 °C, 2 h, $[4\text{-PIP}]_0 = 0.34$ mol L^{-1}).

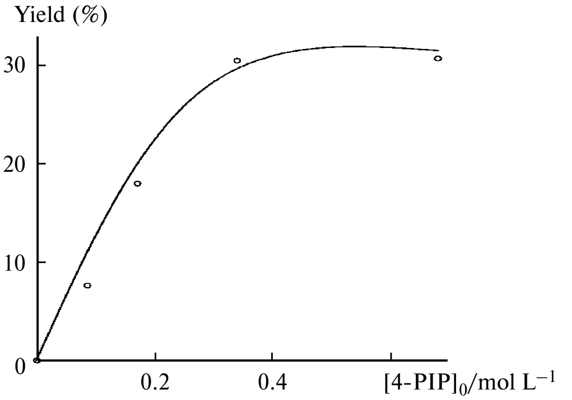

Fig. 2. Plot of the O-4-PIP yield *vs.* initial concentration of 4-PIP (80 °C, 2 h, flow rate of O_2 2.4 L h^{-1}).

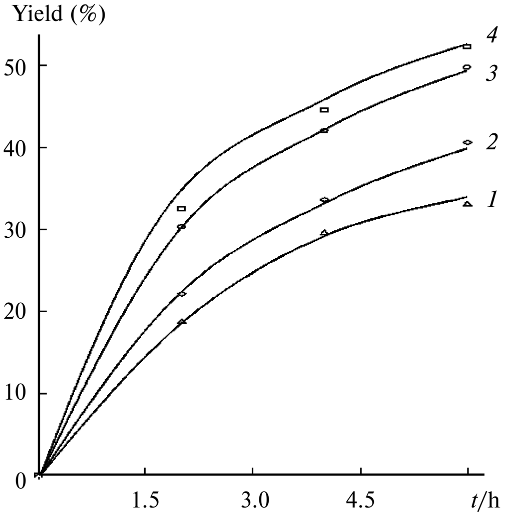

Fig. 3. Plots of the O-4-PIP yield *vs.* reaction time at 60 (*1*), 70 (*2*), 80 (*3*), and 90 °C (*4*) ($[4\text{-PIP}]_0 = 0.34$ mol L^{-1}, flow rate of O_2 2.4 L h^{-1}).

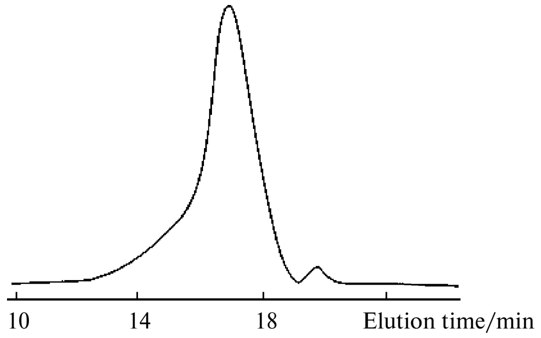

Fig. 4. Chromatogram of O-4-PIP synthesized at 80 °C (flow rate of O_2 9.6 L h^{-1}, 2 h, $[4\text{-PIP}]_0 = [\text{KOH}]_0 = 0.34$ mol L^{-1}).

The plots of the molecular weight distribution in the synthesized O-4-PIP *vs.* oxygen flow rate, temperature, and reaction time are given in Table 1. It is seen that the molecular weight of the prepared O-4-PIP increases with an increase in these parameters.

Spectral characteristics of 4-PIP and O-4-PIP. The UV spectrum of 4-PIP exhibits bands at 228, 240, 260, 288, 310, and 340 nm. The K bands corresponding to the hydroxyl and azomethine groups are observed at 240 and 310 nm, respectively. The R band of the CH=N group lies at 340 nm. The spectrum of O-4-PIP contains bands at 233, 252, 266, 290, 313, and 346 nm. The K bands of the hydroxyl and azomethine groups lie at 252 and 313 nm, respectively, and the R band of the CH=N group is observed at 346 nm.

The IR spectrum of the O-4-PIP oligomer contains characteristic bands of the functional groups: phenolic hydroxyl (3412 cm^{-1}), aromatic CH bonds (3065 cm^{-1}), azomethine group (1600 cm^{-1}), and double bonds (1550 and 1448 cm^{-1}).

The ^{1}H NMR spectrum of O-4-PIP (Fig. 5) represents a superposition of narrow lines, whose chemical shift values do not coincide with the position of lines in

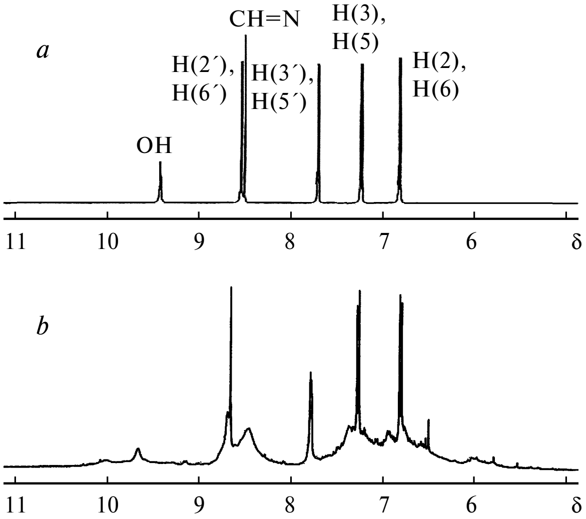

Fig. 5. ^{1}H NMR spectra of 4-PIP (*a*) and O-4-PIP (*b*).

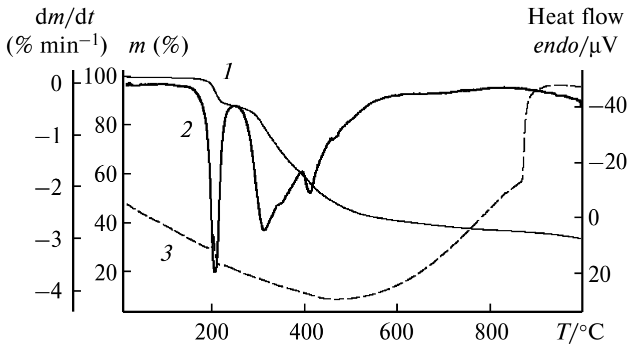

Fig. 6. TGA (*1*), DTG (*2*), and DTA (*3*) curves for 4-PIP. Curve *1*, *f*(*m*); curves *2* and *3*, *f*(d*m*/d*t*).

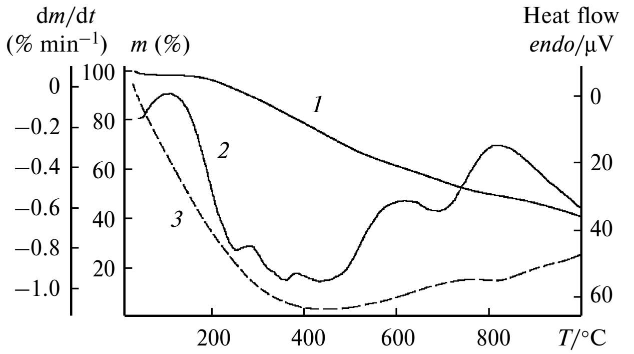

Fig. 7. TGA (*1*), DTG (*2*), and DTA (*3*) curves for O-4-PIP. Curves *1* and *2*, *f*(*m*); curve *3*, *f*(d*m*/d*t*).

the initial 4-PIP, and broad signals. The narrow lines belong, most likely, to low-molecular-weight components, and the broad lines are from high-molecular-weight components. This spectrum provides no clear evidence for the type of linkage of monomeric units; however, published data[15] suggest that coupling occurs at the *ortho*-positions of the phenol fragments (see Scheme 1). Note that the polymers with the azomethine structure containing 1,4-phenylene and 1,5-naphthylene units have been synthesized previously[16] by the polycondensation of dialdehydes with diamines.

Thermal analysis of 4-PIP and O-4-PIP. The thermal analysis curves of the monomer and oligomer are shown in Figs 6 and 7, respectively. For 4-PIP the initial degradation temperature and the temperatures of the 50 and 66.32% weight loss are 195, 460, and 1000 °C, respectively. The thermal decomposition of the monomer proceeds in two stages. At the first stage, 14% of the initial weight are lost in the temperature interval from 170 to 250 °C. The weight loss at the second stage is the highest (46%) and occurs in the 250—600 °C interval. According to the DTA data, the exothermic decomposition of 4-PIP occurs at 204 °C. For O-4-PIP, the initial degradation temperature and the temperatures of the 50 and 57.50% weight loss are 194, 815, and 1000 °C, respectively. The presence of water in O-4-PIP is also seen in the thermogravimetric curves (see Fig. 7): the 2% weight loss is observed in a temperature interval of 100—170 °C, which can be attributed to crystallization (50—150 °C) and loss of coordination water (150—200 °C).

Thus, the synthesized oligomer O-4-PIP exhibits sufficient thermal stability. The results obtained can be used for the development of new functionally substituted polymeric materials.

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