Synthesis, Characterization, Conductivity, Band Gap, and Kinetic of Thermal Degradation of Poly-4-[(2-Mercaptophenyl) Imino Methyl] Phenol

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ABSTRACT: The oxidative polycondensation reaction conditions of 4-[(2-mercaptophenyl) imino methyl] phenol (2-MPIMP) were studied in an aqueous acidic medium between 40 and 90°C by using oxidants such as air, H_2O_2, and NaOCl. The structures of the synthesized monomer and polymer were confirmed by FTIR, ^1H NMR, ^{13}C NMR, and elemental analysis. The characterization was made by TGA-DTA, size exclusion chromatography (SEC) and solubility tests. At the optimum reaction conditions, the yield of poly-4-[(2-mercaptophenyl) imino methyl]phenol (P-2-MPIMP) was found to be 92% for NaOCl oxidant, 84% for H_2O_2 oxidant 54% for air oxidant. According to the SEC analysis, the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index values of P-2-MPIMP were found to be 1700 g mol^{-1}, 1900 g mol^{-1}, and 1.118, using H_2O_2; 3100 g mol^{-1}, 3400 g mol^{-1}, and 1.097, using air; and 6750 g mol^{-1}, 6900 g mol^{-1}, and 1.022, using NaOCl, respectively. According to TG analysis, the weight losses of 2-MPIMP and P-2-MPIMP were found to be 95.93% and 76.41% at 1000°C, respectively. P-2-MPIMP showed higher stability against thermal decomposition. Also, electrical conductivity of the P-2-MPIMP was measured, showing that the polymer is a typical semiconductor. The highest occupied molecular orbital, the lowest unoccupied molecular orbital, and the electrochemical energy gaps (E'_g) of 2-MPIMP and P-2-MPIMP were found to be −6.13, −6.09; −2.65, −2.67; and 3.48, 3.42 eV, respectively. Kinetic and thermodynamic parameters of these compounds investigated by MacCallum-Tanner and van Krevelen methods. The values of the apparent activation energies of thermal decomposition (E_a), the reaction order (n), pre-exponential factor (A), the entropy change (ΔS^*), enthalpy change (ΔH^*), and free energy change (ΔG^*) were calculated from the TGA curves of compounds. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1234–1243, 2009

Key words: poly-4-[(2-mercaptophenyl) imino methyl] phenol; band gap; conductivity; kinetic; thermal analysis

INTRODUCTION

The polyazomethine or oligomers attracted attention in the early 1960s[1] as promising conducting or semi-conducting new materials. The polyazomethine which included azomethine (—CH=N) and active hydroxyl (—OH) groups have been used in various fields. They have useful properties such as paramagnetism, electrochemical cell, and resisting materials to high energy. Because of these properties, they were used to prepare composites with resistance to high temperature, graphite materials, epoxy oligomer and block co-oligomers adhesives, fotoresists, and antistatic materials.[2–8] Poly- or oligo-azomethine compounds had been synthesized with the oxidative polycondensation reaction by using oxidants such as air, H_2O_2, and NaOCl in an aqueous acidic medium at various temperatures.[9] Many studies on oxidative polymerization and reaction mechanisms of polyphenols and azomethine oligomer have been reported.[10,11] These compounds were improved by adding other functional groups to their structures, which imparts new properties. Because of azomethine (—CH=N) and hydroxyl (—OH) groups, these types of compounds may be used as antimicrobial agents. The antimicrobial properties of 4-(4-aminophenyl)morpholine were studied by Panneerselvam et al.[12] Also, because of these groups, azomethine oligomer or polymers have the capability of coordination with different transition metal ions and they can be used for cleaning of transition metals in the industrial waste waters. Therefore, the synthesis of oligomer or polymer–metal complex compounds is important at analytic and environmental chemistry. It seemed advantageous to attempt to design and prepare oligomer-bound chelating ligand, which would be able to form complexes with a variety of transition metals and therefore have a large range of applications. The thermal decomposition behaviors of some metal complex compounds were studied by El-Shekeil et al.[13] and Kaya and Bilici.[14]

Kinetics methods

Nonisothermal methods have been extensively used for the study of the kinetics and mechanism of condensed phase reactions.[15] In general, most methods of kinetic analysis of thermoanalytical data begin with the Arrhenius' equation:

$$k = A \exp(-E_a/RT) \quad (1)$$

and a rate expression

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

In eq. (2), $f(\alpha)$ is a so-called kinetic function that depends on the reaction mechanism, where α represents the fractional conversion (increasing from 0 to 1) in the solid reactant during the course of the reaction. If $f(\alpha) = (1 - \alpha)^n$, and with a constant temperature increase, $dT/dt = \beta$ (where β is the heating rate in °C min^{-1}), integration of Eq. (2) leads to

$$g(\alpha) = \int_0^\alpha \left[\frac{1}{(1-\alpha)^n}\right] d\alpha = \frac{A}{\beta} \int_{T_o}^T \exp\left(\frac{-E_a}{RT}\right) dT \quad (3)$$

where n is reaction order. For the special case $n = 1$,

$$\int_0^\alpha \left[\frac{1}{(1-\alpha)^n}\right] d\alpha = -\ln(1 - \alpha) \quad (4)$$

For n not equal to zero or unity,

$$\int_0^\alpha \left[\frac{1}{(1-\alpha)^n}\right] d\alpha = -\frac{1 - (1-\alpha)^{1-n}}{1 - n} \quad (5)$$

Several techniques using different approaches have been developed for solving the integral of eq. (3).

The Coats-Redfern method[16]

The following equation can be obtained by using an asymptotic approximation for resolution of eq. (3):

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \left(\frac{E_a}{RT}\right) \quad (6)$$

The authors supposed that $\ln(1 - \frac{2RT}{E_a}) \to 0$ for the Doyle approximation,[17] obtaining in natural logarithmic form:

$$\ln g(\alpha) \cong \ln\left[\frac{AR}{\beta E_a}\right] - \frac{E_a}{RT}$$

The apparent activation energy of thermal decomposition for each decomposition mechanisms can be obtained from the slope of a plot of $\ln[g(\alpha)/T^2]$ versus $1000/T$.

The MacCallum-Tanner (MC) method[18]

MacCallum and Tanner method provides an approximation integrated from the rate of degradation as a function of temperature. The rate of degradation can be thus expressed as

$$\log g(\alpha) = \log\frac{AE_a}{\beta R} - 0.4828 E^{0.4351} - \left(\frac{0.449 + 0.217 E_a}{10^{-3} T}\right) \quad (7)$$

A plot of $\log g(\alpha)$ versus $1/T$ can give E from the slope, and A from the intersection of the Y axis.

The van Krevelen (vK) method[19]

The integration method used by van Krevelen is expressed as

$$n \neq 1 \quad \ln g(\alpha) = \ln\left[\frac{A(0.368/T_m)^x}{\beta(x+1)}\right] + (x + 1)\ln T \quad (8)$$

here $x = E_a/RT_m$, and T_m is the temperature at the maximum rate of weight loss. Therefore, E can be obtained from the slope of a plot of $\ln g(\alpha)$ versus $\ln T$. In the equations above, $g(\alpha)$, β, T_m, E_a, A, R, and k are the integral function of conversion, heating rate, DTG peak temperature, activation energy (kJ mol^{-1}), pre-exponential factor (min^{-1}), gas constant (8.314 J mol^{-1} K^{-1}), and specific rate constant, respectively. The kinetic parameters were calculated from the linear plots of the left-hand side of kinetic equations [eqs. (6) and (7)] against $1/T$; for vK equation [eq. (8)] the left-hand side is plotted against lnT. The E_a and A values were calculated from the slope and intercept of the straight lines, respectively.

In this article, we have investigated the effects of different parameters such as temperature, time, air O_2, initial concentrations of NaOCl, H_2O_2, and acid for the preparation of poly-4-[(2-mercaptophenyl) imino methyl] phenol. 2-MPIMP and P-2-MPIMP were characterized by spectral and thermal analyses and by size exclusion chromatography (SEC) techniques. The electrochemical energy gaps (E'_g) of monomer and polymer were calculated from cyclic voltammograms measurements. The electrical properties of polymer doped and undoped with I_2 were determined by four-point probe technique at a room temperature and atmospheric pressure. The kinetic and thermodynamic parameters of thermal degradation of monomer and polymer were investigated by MC and vK methods.

EXPERIMENTAL

Materials

2-Aminothiophenol and 4-hydroxybenzaldehyde were supplied from Fluka Chemical (Germany). Tetrahydrofurane
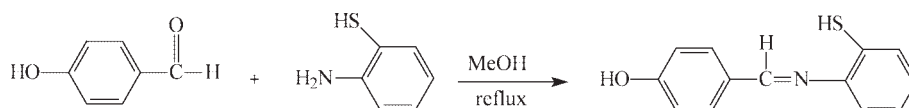
Scheme 1 Synthesis of 4-[(2-mercaptophenyl) imino methyl] phenol.

(THF), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), benzene, acetone, ethyl acetate, hexane, heptane, H_2O_2 (30% aqueous solution), KOH, HCl (37%), CCl_4, and $CHCl_3$ were supplied from Merck Chemical (Germany) and they were used as received. Sodium hypo chloride (NaOCl), (30% aqueous solution) was supplied from Paksoy Chemical (Turkey).

Preparation of 4-[(2-mercaptophenyl) imino methyl] phenol

4-[(2-Mercaptophenyl) imino methyl] phenol (2-MPIMP) was prepared by the condensation of 4-hydroxybenzaldehyde (1.22 g, 0.01 mol) with 2-aminothiophenol (1.25 g, 0.01 mol) in methanol (25 mL), achieved by boiling the mixture under reflux for 3 h at 70°C (Scheme 1). The precipitated 4-[(2-mercaptophenyl) imino methyl] phenol (2-MPIMP) was filtered, recrystallized from methanol, and dried in vacuum desiccator (yield 90%).

Calcd. for 4-MPIMP: C, 68.12; H, 4.80; N, 6.11; S, 13.97. Found: C, 68.00; H, 4.69; N, 5.96; S,13.84. FTIR (cm^{-1}): v(O—H) 3357 s, v(C—H Phenyl) 3090 m, v(C—H aliphatic) 2925 s, v(C=N) 1598 s, v(C=C phenyl) 1586, 1478, v(C—O) 1283 s, v(S—H) 2587 s. ^{1}H NMR (DMSO): δ ppm, 10.30 (s, 1H, —OH), 8.02 (s, 1H, —CH=N—), 6.98 (d, 2H, Ar-Haa'), 7.98 (d, 2H, Ar-Hbb'), 7.06 (d, 2H, Ar-HcHf), 7.48 (t, 1H, Ar-Hd), 7.37 (t, 1H, Ar-He), 7.40 (d, 1H, Ar-Hf), 3.61 (s, 1H, —SH). ^{13}C NMR (DMSO): δ ppm, 161.04 (C1-ipso), 116.59 (C2,6), 129.54 (C3,5), 134.65 (C4-ipso), 167.98 (C7), 154.25 (C8-ipso), 122.47 (C9), 124.59 (C10), 122.79 (C11), 125.31 (C12), 126.84 (C13-ipso).

Synthesis of poly-4-[(2-mercaptophenyl) imino methyl] phenol (2-MPIMP) with NaOCl, H_2O_2, and air in aqueous acidic medium

P-2-MPIMP was synthesized via oxidative polycondensation of 2-MPIMP with solution of NaOCl (30%, in water), H_2O_2 (30%, in water), and air oxidants,[9] respectively (Scheme 2). 2-MPIMP (2.29 g, 0.01 mol) was dissolved in an aqueous solution of HCl (1*M*, 3

mL) and placed into a 50-mL three-necked round-bottom flask. It was fitted with a condenser, thermometer, and stirrer and, in addition, a funnel containing NaOCl. After heating to room temperature, NaOCl were added drop by drop over about 20 min. The reaction mixtures were stirred at various temperatures and durations (Table I). Air was passed into an aqueous solution of HCl (1*M*, 3 mL) before being sent through the reaction tube to prevent water loss in the reaction mixture and the neutralizing of CO_2 in the air to KOH. The mixture was neutralized with KOH (1*M*, 3 mL) at room temperature. Unreacted monomer was separated from the reaction products by washing with ethanol. For the separation of mineral salts, the mixture was filtered and washed in 25 mL of hot water for three times and then dried in a vacuum oven at 60°C.

Calcd. for P-2-MPIMP: C, 68.72; H, 3.97; N, 6.17; S, 14.10. Found: C, 68.59; H, 3.75; N, 5.98; S, 13.92. FTIR (cm^{-1}): v(O—H) 3408 s, v(C—H phenyl) 3065 m, v(C—H aliphatic) 2925 s, v(C=N) 1603 s, v(C=C phenyl) 1583, 1481 s, v(C—O) 1284 s, vC(Ar)—O—C(Ar) and C(Ar)—O—H 1224 m, vC(Ar)—O—C(Ar) 1107 m, v(S—H) 2588 s. ^{1}H NMR (DMSO): δ ppm, 10.20 (s, 1H, —OH), 9.40 (s, 1H, —CH=N—), 6.96 (d, 2H, Ar-Haa'), 7.94 (d, 2H, Ar-Hbb'), 8.06 (d, 1H, Ar-Hc), 7.49 (t, 1H, Ar-Hd), 7.41 (t, 1H, Ar-He), 7.98 (d, 1H, Ar-Hf), 3.90 (s, 1H, -SH). ^{13}C NMR (DMSO): δ ppm, 161.04 (C1-ipso), 116.57 (C2,6-terminal), 115.73 (C2,6-ipso), 129.51 (C3,5), 134.57 (C4-ipso), 167.95 (C7), 154.18 (C8-ipso), 122.47 (C9), 124.49 (C10), 122.75 (C11), 125.35 (C12), 126.88 (C13-ipso), new peak 130.13.

Electrical properties

Conductivity was measured on a Keithley 2400 Electrometer. The pellet was pressed on hydraulic press developing up to 1687.2 kg cm^{-2}. Iodine doping was carried out by exposure of the pellet to iodine vapor at atmospheric pressure and room temperature in a desiccator.[7]
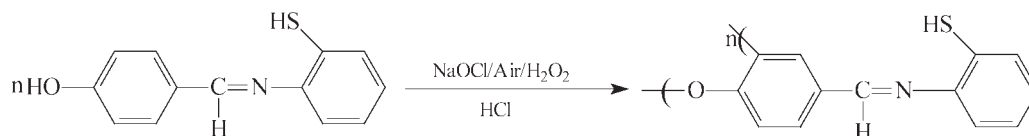
Scheme 2 Synthesis of poly-4-[(2-mercaptophenyl) imino methyl] phenol.

TABLE I
Oxidative Polycondensation Reaction Parameters of 2-[(2-Mercaptophenyl) imino methyl] Phenol (2-MPIMP)[a] with NaOCl (Sample Numbers: 1–17), H_2O_2 (Sample Numbers: 18–27) and Air O_2 (Sample Numbers: 28–36) in Aqueous HCl

Sample number	$[HCl]_o$ (mol L^{-1})	$[NaOCl]_o$ (mol L^{-1}), H_2O_2 (mol L^{-1}), or air O_2 (L h^{-1})	Temp. (°C)	Time (h)	Yield of P-2-MPIMP (%)
1	0.15	0.05	40	5	66
2	0.15	0.05	50	5	81
3	0.15	0.05	60	5	85
4	0.15	0.05	70	5	78
5	0.15	0.05	80	5	29
6	0.15	0.05	90	5	38
7	0.15	0.05	60	3	65
8	0.15	0.05	60	10	92
9	0.15	0.05	60	15	57
10	0.15	0.05	60	20	45
11	0.075	0.05	60	3	35
12	0.20	0.05	60	3	60
13	0.25	0.05	60	3	49
14	0.3	0.05	60	3	45
15	0.15	0.1	60	5	58
16	0.15	0.15	60	5	47
17	0.15	0.025	60	5	72
18	0.15	0.75	50	5	74
19	0.15	0.75	60	5	78
20	0.15	0.75	70	5	80
21	0.15	0.75	80	5	69
22	0.15	0.75	90	5	58
23	0.15	0.75	60	10	84
24	0.15	0.75	60	15	65
25	0.15	0.75	60	20	49
26	0.15	0.375	60	5	54
27	0.15	1.5	60	5	62
28	0.15	8.5	40	5	23
29	0.15	8.5	50	5	32
30	0.15	8.5	60	5	40
31	0.15	8.5	70	5	46
32	0.15	8.5	80	5	39
33	0.15	8.5	90	5	29
34	0.15	8.5	70	10	54
35	0.15	8.5	70	15	49
36	0.15	8.5	70	20	43

[a] The initial concentration of 2-MPIMP was 0.15 mol L^{-1}.

Electrochemical properties

Electrochemical properties of monomer and polymer were determined by CH instruments 660B cyclic voltammetry in $0.1M$ tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as supporting electrolyte. The voltammetric measurements were carried out for oligomer in acetonitrile and DMSO, respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the 2-MPIMP and P-2-MPIMP were determined from the onset potentials of the n-doping (ϕ'_n) and p-doping (ϕ'_p), respectively, as described in the literature.[20,21]

Solubility and characterization techniques

2-MPIMP is a yellow color powder and is completely soluble in polar organic solvents such as methanol, ethanol, acetone, THF, acetonitrile, ethylacetate, 1-butanol, chloroform, DMF, and DMSO. 2-MPIMP is insoluble apolar organic solvents such as in heptane and hexane. P-2-MPIMP is a light brown powder and is completely soluble in organic solvents such as chloroform, DMF, and DMSO. P-2-MPIMP is partly soluble in acetone, ethylacetate, THF, and dioxane. P-2-MPIMP is insoluble in ethanol, methanol, acetonitrile, 1-butanol, heptane, and hexane. Solubility testing and spectral and thermal analyses measurements of polymer were made from Table I sample no. 8 product.

The infrared spectra were measured by Perkin–Elmer Spectrum One FTIR system. The FTIR spectra were recorded using ATR attachment (4000–550 cm^{-1}). 2-MPIMP and P-2-MPIMP were characterized by using ^1H NMR and ^{13}C NMR spectra (Bruker Avance DPX-400 and 100.6 MHz, respectively) recorded at 25°C by using deuterated DMSO as a solvent and tetramethylsilane was used as internal standard. Thermal data were obtained by using Perkin-Elmer diamond thermal analysis. The TGA-DTA measurements were made between 10 and 1000°C (in N_2, rate 10°C/min). The M_n, M_w, and polydispersity index (PDI) values were determined by SEC techniques (Shimadzu). For SEC investigations, we used an SGX (100 Å and 7-nm-diameter loading material) 3.3 mm i.d. × 300 mm column, DMF/methanol (v/v, 4/1, 0.4 mL min^{-1}) as eluent, and polystyrene (PS) standards. A refractive index detector (at 25°C) was used to analyze the product.

RESULTS AND DISCUSSION

Synthesis of P-2-MPIMP

The optimum reaction conditions of 4-[(2-mercaptophenyl) imino methyl] phenol were investigated in an aqueous acidic medium by using air, H_2O_2, and NaOCl as oxidant. When 2-MPIMP interacted with these oxidants in an aqueous acidic medium, brown phenoxy radicals immediately precipitated in the solution medium. The oxidative polycondensation reaction conditions of 2-MPIMP with 30% NaOCl solution in an aqueous acidic medium are given in Table I. The yield of P-2-MPIMP was 92% at conditions such as $[2\text{-MPIMP}]_0 = 0.05$, $[HCl]_0 = 0.15$, and $[NaOCl]_0 = 0.05$ mol L^{-1}, at 60°C for 10 h. It is seen that in Table I, the yield of polymer decreased in increasing of reaction temperature. But the yield of

TABLE II
The Number Average Molecular Weight (M_n), Weight Average Molecular Weight (M_w), Polydispersity Index (PDI), and % Values of Oxidative Polycondensation Products of P-2-MPIMP

| | Molecular weight distribution parameters | | | | | | | | | | | | | | | |
| | Total | | | Fraction I | | | | Fraction II | | | | Fraction III | | | |
Compounds	M_n	M_w	PDI	M_n	M_w	PDI	%	M_n	M_w	PDI	%	M_n	M_w	PDI	%
P-2-MPIMP[a]	6750	6900	1.022	800	950	1.188	70	1400	2400	1.714	10	97,900	100,000	1.022	20
P-2-MPIMP[b]	3100	3400	1.097	1000	1100	1.100	75	8000	9900	1.125	15	74,000	79,700	1.077	10
P-2-MPIMP[c]	1700	1900	1.118	850	1000	1.177	65	1200	1600	1.333	30	85,000	90,000	1.059	5

[a] NaOCl oxidant.
[b] Air O_2 oxidant.
[c] H_2O_2 oxidant.

polymer increased in increasing of reaction times at the same reaction temperatures. At the same conditions, when initial molar amount of NaOCl increased, the yield of P-2-MPIMP changed from 74 to 65%. The yield of P-2-MPIMP was 37% at conditions such as $[2\text{-MPIMP}]_0 = [\text{NaOCl}]_0 = 0.05$ mol L^{-1} and $[\text{KOH}]_0 = 0.15$ mol L^{-1}, at 60°C for 10 h. The oxidative polycondensation reaction conditions of 2-MPIMP with air in aqueous alkaline medium are given in Table I. The yield of P-2-MPIMP was 54% at the reaction conditions such as $[2\text{-MPIMP}]_0 = 0.05$ mol L^{-1}, $[\text{HCl}]_0 = 0.15$ mol L^{-1}, and air (flow rate = 8.5 L h^{-1}), at 70°C for 10 h. As seen from Table I, the yields of these reactions were dependent upon temperature, time, and initial concentrations of NaOCl and HCl. For the yield of P-2-MPIMP, NaOCl was a better oxidant to H_2O_2 and air at the same conditions. On the basis of temperature, time, and initial concentrations of HCl and NaOCl oxidant, the yield of P-2-MPIMP has changed.

Structure of P-2-MPIMP

On the basis of SEC chromatograms, the M_n and M_w of P-2-MPIMP were calculated according to a PS standard calibration curve and are given in Table II. The M_n, M_w, and PDI values of P-2-MPIMP were found to be 1700 g mol^{-1}, 1900 g mol^{-1}, and 1.118, using H_2O_2, and 3100 g mol^{-1}, 3400 g mol^{-1}, and 1.097, using air, and 6750 g mol^{-1}, 6900 g mol^{-1}, and 1.022, using NaOCl, respectively. When reaction temperatures and reaction times increased, molecular weight distribution (MWD) of P-2-MPIMP increased, but the yield of P-2-MPIMP decreased. With the increase of polymerization time, temperatures, and oxidant concentrations, the molecular weight and MWD of P-2-MPIMP increased. Because of the increasing molecular weight, together with the broadening of the polydispersity, NMR analyses fail to give valuable information for the characterization of these compounds.
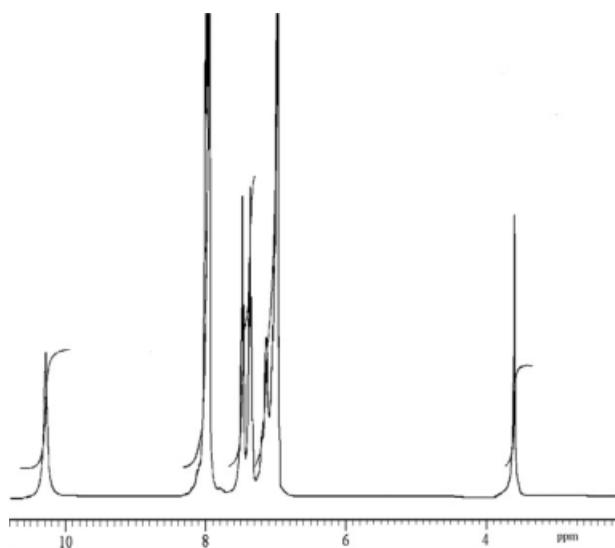
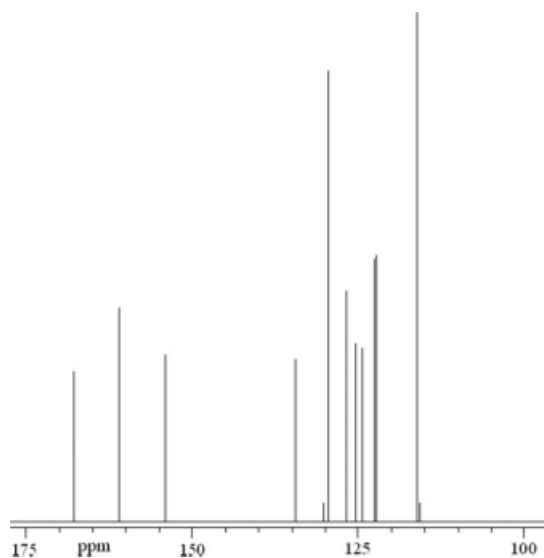Figure 1 ^{1}H NMR spectrum of 4-[(2-mercaptophenyl) imino methyl] phenol.
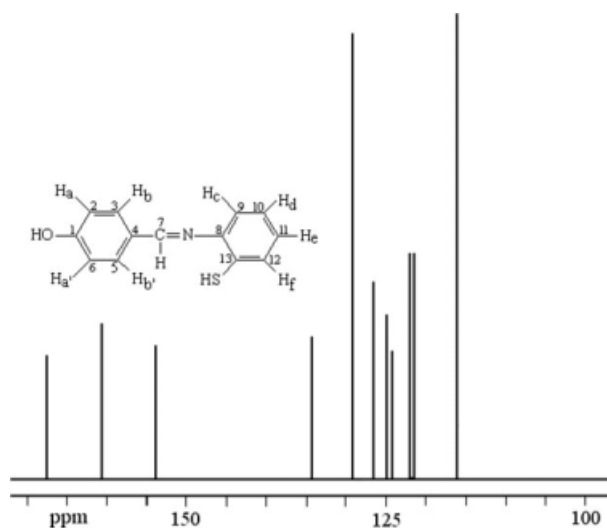
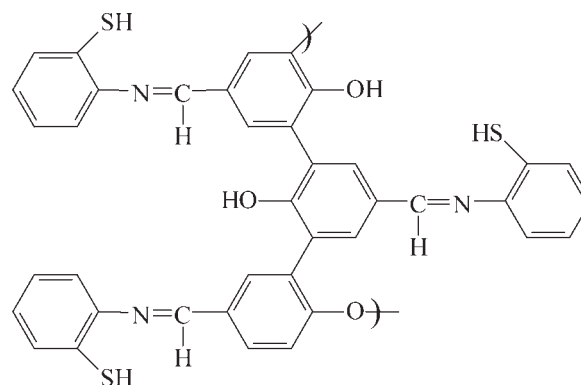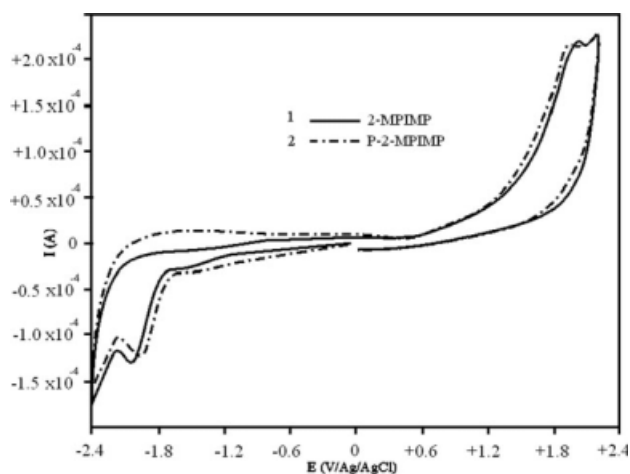Figure 2 ^{13}C NMR spectrum of 4-[(2-mercaptophenyl) imino methyl] phenol.
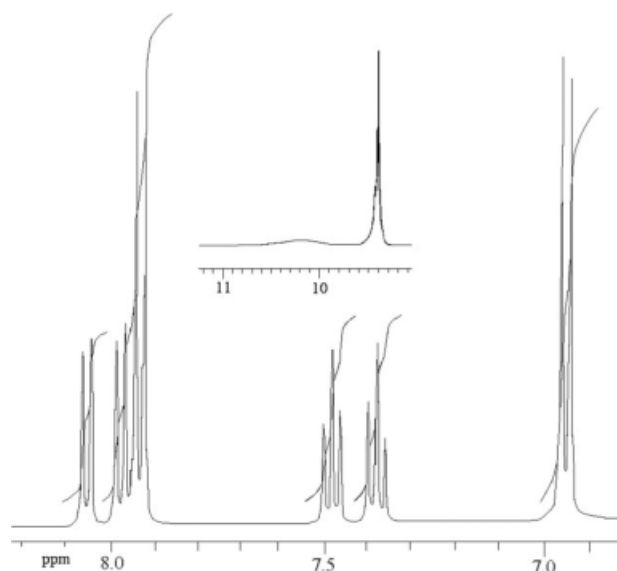
Figure 3 ^{1}H NMR spectrum of poly-4-[(2-mercapto-phenyl) imino methyl] phenol.

Scheme 3 The structure of poly-4-[(2-mercaptophenyl) imino methyl] phenol.

At the FTIR spectra of oxidative polycondensation product of 2-[(4-mercaptophenyl) imino methyl] phenol are only different by reduction of band strength and number of bands from the FTIR spectra of 2-MPIMP. From the FTIR spectra of 2-MPIMP and P-2-MPIMP, bands of —OH and —CH=N groups were observed at 3357 and 1598 cm^{-1}, and 3408 and 1603 cm^{-1}, respectively. Also, from the FTIR spectra of P-2-MPIMP, C(Ar)—O—C(Ar) and C(Ar)—O—H bending vibrations were observed at 1224 and 1107 cm^{-1}, respectively. To identify the structures of monomer and polymer, the ^{1}H NMR and ^{13}C NMR spectra were recorded in DMSO-d_6.

^{1}H NMR and ^{13}C NMR spectra of the monomer and polymer are given in Figures 1–4. From the ^{1}H NMR spectra of 2-MPIMP and P-2-MPIMP, the signals of —OH, —CH=N, and —SH groups were observed at 10.30, 8.02, and 3.61 ppm and 10.20, 9.40, and 3.90 ppm, respectively. Other phenol derivatives were also polymerized, and the results were reported at the literatures.[22] Crosslinking in polymer structure is expected in those cases where the ortho and para positions in the corresponding monomer structure are unsubstituted.[22] ^{1}H NMR, ^{13}C NMR, and FTIR spectral results of P-2-MPIMP have indicated that the linkage between any two adjacent phenyl rings is largely at ortho position and oxyphenylene. However, this type of linkage may strain the polymer backbone in such a manner that the phenyl rings are out of plane with respect to the adjacent rings. The peak values of C2,6 carbon atoms of monomer and polymer were observed at 116.59 and 115.73 ppm, respectively. The new peak was observed at 130.13 ppm in the ^{13}C NMR spectrum of polymer. The

Figure 4 ^{13}C NMR spectrum of poly-4-[(2-mercapto-phenyl) imino methyl] phenol.


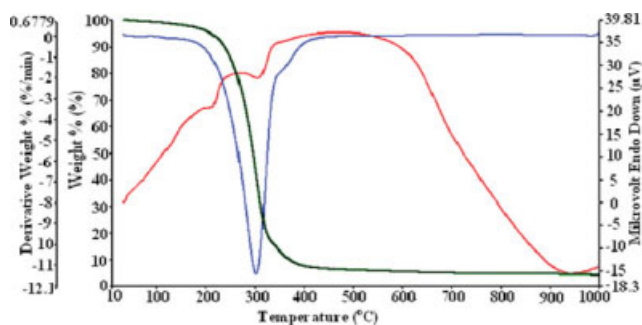**Figure 5** Cyclic voltammograms of 2-MPIMP (1) and P-2-MPIMP (2).
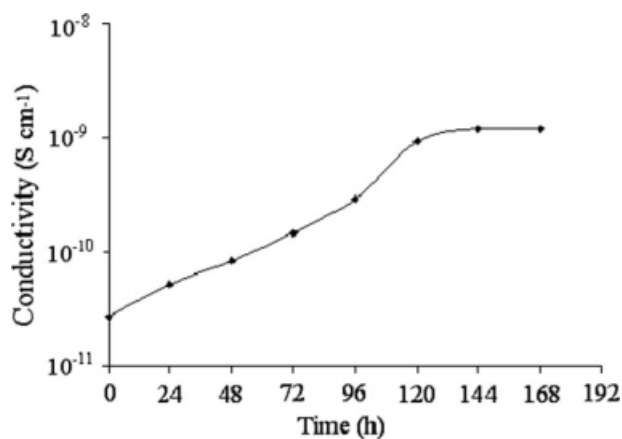
Figure 6 Electrical conductivity of I_2-doped poly-4-[(2-mercaptophenyl)imino] methyl phenol versus doping time at 25°C.

hydroxyl groups are involved in the formation of free radicals, leading to polymer formation and, based on the proton integration of hydroxyl peak, C—O—C coupling system appeared at the structure of polymer. Thus the phenyl rings in the polymer appears to be linked primarily at ortho position and oxyphenylene. The reaction mechanisms of oligo/polyphenols on the coupling selectivity has been studied by Ayyagari et al.[22] and Kaya and Bilici,[23] and three possible reaction mechanisms were proposed for the C—C and C—O—C coupling selectivity. The interconversion combinations of radical units of Schiff base monomers have been proposed in the literature[24] (Scheme 3).
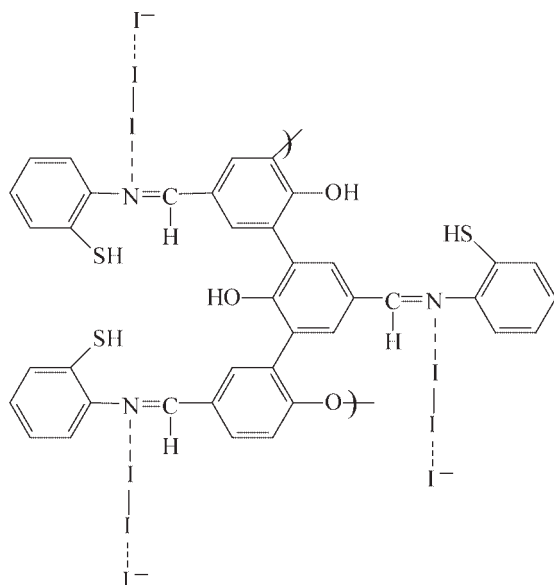
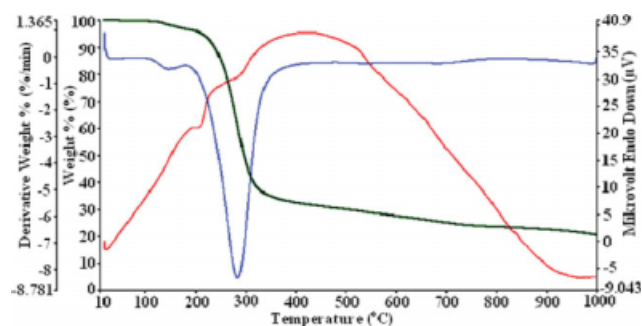**Scheme 4** Coordination of iodine during P-2-MPIMP doping.

Figure 7 TGA-DTG-DTA curves of 4-[(2-mercaptophenyl)imino] methyl phenol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Electrochemical Properties of 2-MPIMP and P-2-MPIMP

The voltammograms of 2-MPIMP and P-2-MPIMP were carried out in acetonitrile and DMSO, respectively. The HOMO and LUMO energy levels and electrochemical energy gaps (E'_g) of monomer and polymer were determined from oxidation and reduction onset values and are shown in Figure 5. The onset potentials of the n-doping (ϕ'_n) and p-doping (ϕ'_p) can be used to determine the HOMO and LUMO energy levels of monomer and polymer.[21] The HOMO and LUMO energy levels and electrochemical energy gaps (E'_g) of 2-MPIMP and P-2-MPIMP were found to be between -6.13, -6.09; -2.65, -2.67; 3.48 and 3.42 eV, respectively.

P-2-MPIMP has conductivities of 10^{-11} to 10^{-10} S cm^{-1}. When doped with iodine, conductivities of the compounds could be increased. Figure 6 shows the doping results of P-2-MPIMP with iodine for the various times at 25°C. The structures of P-2-MPIMP showed significant differences in conductivity. This effect may possibly be due to all of them actually belonging to the same class of polymer. In the doping

Figure 8 TGA-DTG-DTA curves of poly-4-[(2-mercaptophenyl)imino] methyl phenol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thermodynamic and Kinetic Parameters Obtained by the Different Methods 2-MPIMP and P-2-MPIMP

Compounds	Stage	Methods	n	E_a (kJ mol^{-1})	ln A (s^{-1})	ΔS^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	r^a
2-MPIMP	I	vK	0.3	47.06	14.25	−131.90	42.27	118.12	0.99918
		MC	0.5	51.05	10.52	−162.85	46.29	139.92	0.99915
P-2-MPIMP	I	MC	0.3	51.07	15.37	−122.39	46.39	115.18	0.99911
		vK	0.3	52.55	10.94	−159.18	47.87	137.33	0.99744

[a] r: correlation coefficients of the linear plot; n: order of reaction.

of P-2-MPIMP with iodine, it was found that the conductivity of P-2-MPIMP first increases greatly with doping time, but then tends to level-off. The increasing conductivity could indicate that a charge-transfer complex between P-2-MPIMP and dopant iodine is continuously formed. Consequently, Figure 6 not only shows the conductivity/doping time relationship but also indicates how quickly the doping reaction takes place. The experimental results showed that a longer doping time is needed to obtain the maximal conductivity. As a result, the conductivity/doping time curve varies with doping conditions. To exclude the influence of doping conditions, the conductivity of doped polymer has been related with doping extent (shown in Fig. 6). The maximal or saturated conductivity values of P-2-MPIMP were found to be 1.8 × 10^{-9} S cm^{-1}. Nitrogen is an electronegative element and it is capable of coordinating iodine ions. Coordination of iodine during P-2-MPIMP doping is as follows (Scheme 4): On the nitrogen atom, the coordination of iodine with Schiff base polymers and pyridine solutions had been suggested in the literatures as follows.[7,25–27]

Thermal analyses

The thermal degradations of 2-MPIMP and P-2-MPIMP were studied using TGA-DTG-DTA analyses in N$_2$ medium, and the thermal analyses results and the curves of these analyses are given in Figures 7 and 8, respectively. The initial degradation temperatures of 2-MPIMP and P-2-MPIMP were found to be 259 and 239°C, respectively. According to these values, the initial degradation temperature of 2-MPIMP was higher than that of P-2-MPIMP. Because of C—O—C coupling formation, initial degradation temperature of polymer was lower than monomer in the TGA measurements. This result demonstrated the degradation of C—O—C bond at lower temperature than C—C bond. The initial degradation temperature of P-2-MPIMP was lower than poly-2-[(4-mercaptophenyl) imino methyl] phenol (257°C).[28] The reason for this is formation of C—C coupling bonding at high amount at the structure of polymeric product. The weight losses of 2-MPIMP and P-2-MPIMP were found to be 95.93% and 76.41%, respectively, at 1000°C. This poly-

mer formed high amounts of carbine residue, i.e., 23.59% at 1000°C. According to DTG curve, T_{max} values of 2-MPIMP and P-2-MPIMP were 300 and 282°C, respectively. According to DTA analysis of 2-MPIMP, endothermic peaks were observed at 214 and 307°C. According to TG analysis, although initial degradation temperature of P-2-MPIMP was lower than monomer, it was more stable than monomer with respect to temperature and thermal decomposition. Because of long conjugated band systems, polymers demonstrated higher resistance against high temperature with respect to monomer.

Kinetic and thermodynamic parameters

TGA experiments could be performed to determine the thermal behavior of monomer and polymer and to suggest degradation processes and kinetic parameters. The vK and MC methods were used for kinetic analysis. These methods are based on a single heating rate (10°C min^{-1}). From the TG curves, the reaction order (n), the activation energies of thermal decomposition (E_a), entropies (ΔS^*), enthalpy change (ΔH^*), free energy change (ΔG^*), pre-exponential factor (A), and the linearization curves of the thermal degradation of monomer and polymer have been elucidated by the methods mentioned earlier. The thermodynamic parameters and results are given in Table III. As seen in Table III, the value of correlation coefficients of linearization curves of monomer and polymer are ∼ 1.00 and the values of reaction orders are around zero for the compound.
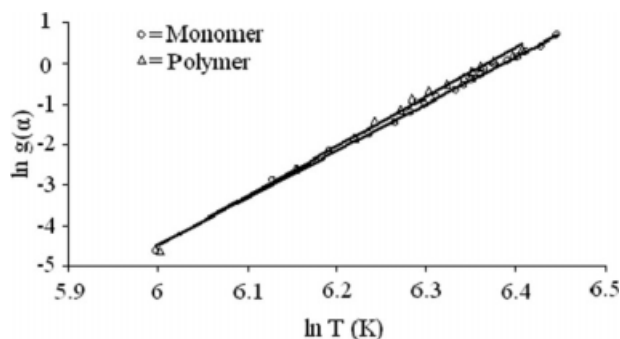

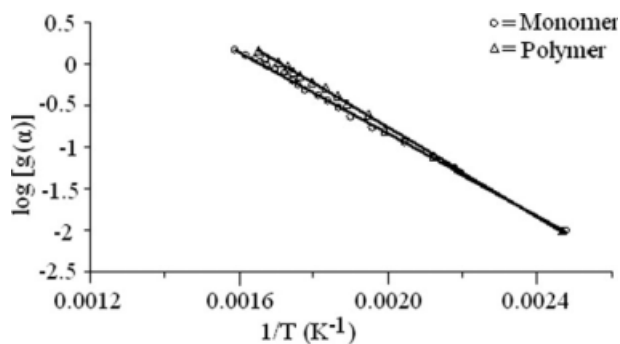**Figure 9** vK plots of monomer and polymer.

Figure 10 MC plot of monomer and polymer.

Using the investigated methods, determination of the pre-exponential factor and reaction order is possible from the expression of $g(\alpha)$ in eq. (3) and $n \neq 1$:

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n}$$

The results are in good agreement with the values obtained from each method. The results indicate that the values of all methods are comparable. The kinetic data obtained by different methods agree with each other. The enthalpy (ΔH^*), entropy (ΔS^*), and the Gibbs free energy (ΔG^*) changes of monomer and polymer were calculated using the following relations[29]:

$$\Delta S^{\#} = 2.303 \log\left(\frac{Ah}{kT}\right) R$$

$$\Delta H = E_a - RT$$

$$\Delta G^{\#} = \Delta H - T\,\Delta S^{\#}$$

where h is the Planck constant, T is the temperature, and A is the pre-exponential factor.

Figures 9 and 10 show Arrhenius plots determined by vK and MC methods in nitrogen for weight loss thermograms at 10°C min^{-1}. The activation energies of thermal decomposition can be calculated from the slopes of the ln $g(\alpha)$ against ln T plot and are given in Table III. The activation energies of thermal decomposition (E_a) of monomer and polymer were found to be 47.06, 51.05 ; and 52.55, 51.07 kJ mol^{-1}, respectively, by the vK and MC methods from thermal curves. Brown et al.[30] had examined the actual experimental results for the thermal decompositions of ammonium perchlorate and calcium carbonate from the isothermal and nonisothermal data sets provided, based on a hypothetical simulated process. The kinetic parameters had been calculated by nonisothermal data corresponding to thermal and thermo-oxidative degradation of polymers and polymeric materials.[31,32] Vyazovkin et al. had examined the kinetics parameters for the thermal

degradation of PS, poly(propylene), and polyethylene in TGA experiments studied under nitrogen.[32]

CONCLUSIONS

Poly-4-[(2-mercaptophenyl) imino methyl] phenol was synthesized by using air, H$_2$O$_2$, and NaOCl in an aqueous acidic medium. The yield of P-2-MPIMP was found to be 92, 84, and 54% for NaOCl, H$_2$O$_2$, and air oxidant, respectively. The H$_2$O$_2$ and NaOCl oxidants demonstrated high activities for the polymerization of 2-MPIMP by the oxidative polycondensation reaction in air. The ^{1}H-NMR and ^{13}C-NMR spectral analyses of polymer have demonstrated bonding of unite from both *ortho* carbons and oxyphenylene of phenol ring at the oxidative polycondensation of 2-MPIMP. The optical band gap value of monomer was higher than that of polymer. This is due to the azomethine group which is an electron donor. Because the HOMO increased more than the LUMO, the electrochemical band gap values were observed to be lower. The observed band gaps are sufficiently low to make this monomer and polymer highly promising for photovoltaic applications. According to thermal analysis results, polymer has demonstrated high stability against thermal degradation. The reaction order (n), the activation energies of thermal decomposition (E_a), entropies (ΔS^*), enthalpy change (ΔH^*), free energy change (ΔG^*), pre-exponential factor (A), and the linearization curves of the thermal degradation of monomer and polymer were calculated by the vK and MC methods from the TGA curves.

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