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Poly(phenoxy-imine)s and poly(phenoxy-ketimine)s: toward new semiconductive polymeric materials

Abstract

Conjugated polymers have attracted widespread interest during the last three decades, because of their useful electronic properties. In this paper we discuss semi-conductive properties of the conjugated polymers with phenylhydrazono (C_6H_5-NH-N=C-(R/H)-) pendent groups, such as poly(phenoxy-imine)s and poly(phenoxy-ketimine)s. These polymers were found to possess the conductivity of 10^{-3}-10^{-2}S/cm. It is supposed that high conductivities of the polymers are due to their phenylhydrazono type structures with π-conjugation with participation of the nitrogen atoms in polymer side groups.

Keywords: conjugated polymers, semi-conductive polymer, poly(phenoxy-imine)s, poly(phenoxy-ketimine)s, oxidative coupling polymerization, gel permeation chromatography

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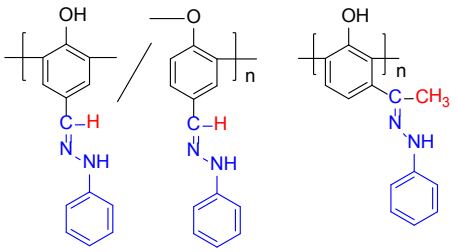
Introduction

Polyphenols have attracted considerable attention due to its conjugated structures, active hydroxyl (-OH) groups. They are promising candidates for a wide variety of applications such as optoelectronics,[1,2] semiconductor,[3] electrochromic,[4] antistatic[5] and antimicrobial[6] materials by adding other functional groups. Efforts were focused to improve the electro-optical properties of polyphenols with longer conjugated segments. Premachandran et al.[7] reported the synthesis of naphthol-based polymers to increase the conjugation lengths in the backbone. The polyphenols with longer conjugation lengths in polymer main chain and pendent groups have also been reported by Kayak et al.[8] However, most of these polymers which possess phenylazo (C_6H_5-N=CH-) pendent groups have not sufficiently semiconductive properties without doping. They had the specific conductivity of 10^{-14}-10^{-16}S/cm at room temperature (as seen in Table 1), the level typical for dielectrics. After doping this type polymer samples by iodine, their increased up to ~10^{-8}-10^{-6}S/cm. In this connection, conductive polymers with higher level of conductivity without doping are of interest. In this work, we discuss semiconductive properties of the polymers obtained by oxidative coupling polymerization of 3-(1-(2-phenylhydrazono) ethyl) phenol (3-PHEP)[9] and 4-((2-phenylhydrazono) methyl) phenol (4-PHMP)[10] by formation of the phenylhydrazono (C_6H_5-NH-N=C(R)-) type structures with π-conjugation with participation of the nitrogen atoms in polymer pendent groups.

Conclusion

According to the gel permeation chromatography (GPC) measurements, poly (4-PHMP) and poly (3-PHEP) have high molecular weight that values change 6,500 to 17,717 depending on the polymers structures.[9,10] The structural analyses show that the prepared polymers consist of C-C and C-O-C coupling systems (Figure 1). Both compounds are readily soluble in highly polar solvents, such as methanol, DMSO, DMF and hence will have film forming properties.

Electrical properties of these polymers were determined with a four-point probe technique at room temperature and atmospheric pressure using Four Point probe Measuring System FPP 470. The pellets were pressed on hydraulic press developing up to 100bar/cm^2. Conductivity measurements of the poly(3-PHMP) was carried out with an electrometer using a four-point probe technique. The conductivity values of poly(4-PHMP) and poly(3-PHEP) were found to be approximately 1.92×10^{-2}S/cm and 5.7×10^{-3}S/cm, respectively. According to these results, poly(4-PHMP) and poly(3-PHEP) have higher conductivity values then other poly(phenoxy-imine)s. Among these poly(phenoxy-imine)s, the highest electrical conductivity; i.e, 5.86×10^{-5}S/cm, was found.[11] The values of electrical conductivity at the range of 10^{-3}-10^{-2}S/cm which were obtained for poly(4-PHMP) and poly(3-PHEP) are compared with the values obtained for o-substituted, m-substituted and p-substituted poly(phenoxy-imine)s in literature (As can be seen in Supplementary Information, (Tables 1-3)). They can be seen that the highest conductivity values belong to poly(4-PHMP) and poly(3-PHEP). This is because of the polyconjugated structures of the polymers with phenylhydrazono pendent groups that increase electrical conductivity values. Having this feature, these polyphenols step forwards in comparison with other imine-substituted polyphenols. The results obtained in this study are compatible with the values in literature.

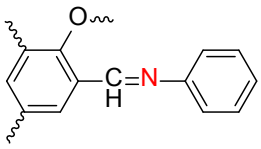
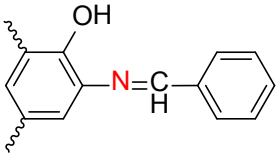
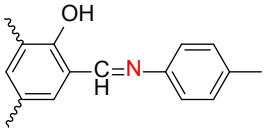
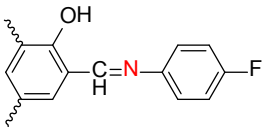
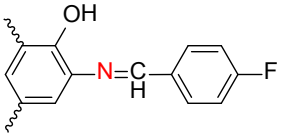
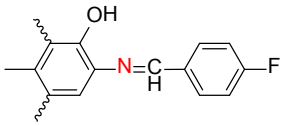
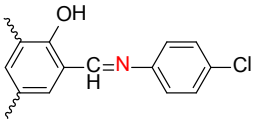
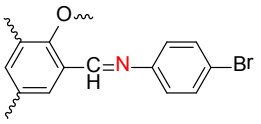
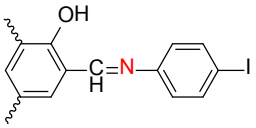
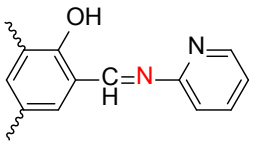
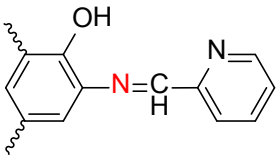
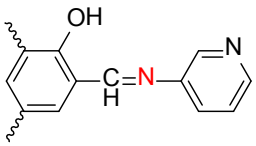
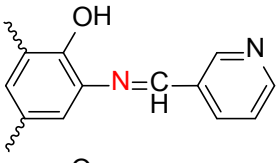
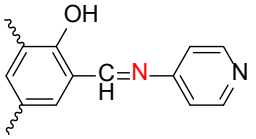
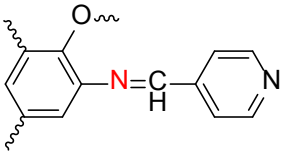
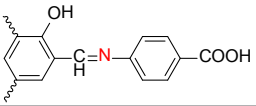


Poly(4-PHMP) (a) Poly(3-PHEP) (b)

Figure 1 The structures of (A) poly(4-PHMP) (B)poly(3-PHEP).

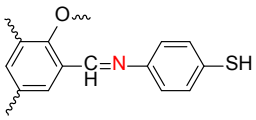
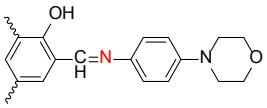
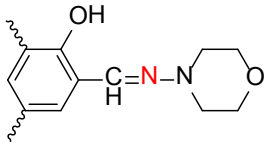
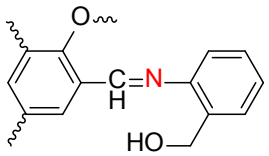
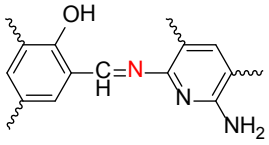
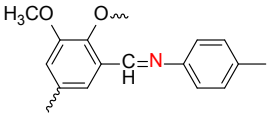
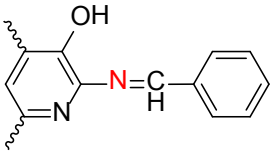
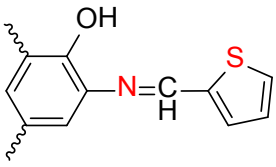
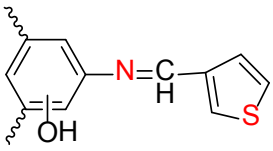
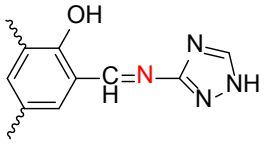
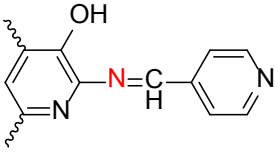
Further work is being carried out in our laboratory to synthesis and characterization of other polyphenols containing phenylhydrazono pendent groups and to investigation of their properties such as conductivity and some properties. These results will be published soon in a full paper.

Table 1 According to the literature data, the synthesized isomeric poly(o-phenoxy-imine)s and their conductivity values

No	Poly(o-phenoxy-imine)s	Undoped S/cm	Doped* S/cm	Lit.	No	Its isomeric structures	Undoped S/cm	Doped* S/cm	Lit.
1		10^{-10}-10^{-9}	5.8×10^{-7}	[12]	1		unmeasured	unmeasured	[13]
2		unmeasured	unmeasured	[14]	2	Not synthesized yet.	unknown	unknown	-
3		10^{-11}-10^{-10}	6.01×10^{-8}	[15]	3		$\sim10^{-10}$	$\sim2\times10^{-6}$	[16]
4	Not synthesized yet.	unknown	unknown	-	4		$\sim10^{-10}$	$\sim2.6\times10^{-5}$	[16]
5		10^{-11}-10^{-10}	5.56×10^{-8}	[17]	5	Not synthesized yet.	unknown	unknown	-
6		unmeasured	unmeasured	[18]	6	Not synthesized yet.	unknown	unknown	-
7		unmeasured	unmeasured	[19]	7	Not synthesized yet.	unknown	unknown	-
8		unmeasured	unmeasured	[20]	8		unmeasured	unmeasured	[21]
9		unmeasured	unmeasured	[22]	9		unmeasured	unmeasured	[23]
10		unmeasured	unmeasured	[24]	10		unmeasured	unmeasured	[25]
11		10^{-11}-10^{-10}	7.82×10^{-7}	[26]	11	Not synthesized yet.	unknown	unknown	-

Citation: Demir HO. Poly(phenoxy-imine)s and poly(phenoxy-ketimine)s: toward new semiconductive polymeric materials. *MOJ Poly Sci.* 2017;1(6):214–218. DOI: 10.15406/mojps.2017.01.00036

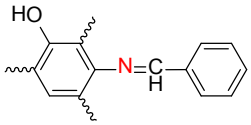
Table Continued..

No	Poly(o-phenoxy-imine)s	Undoped S/cm	Doped* S/cm	Lit.	No	Its isomeric structures	Undoped S/cm	Doped* S/cm	Lit.
12		10^{-11}-10^{-10}	7.91×10^{-10}	[27]	12	Not synthesized yet.	unknown	unknown	-
13		10^{-12}-10^{-8}	7.91×10^{-10}	[28]	13	Not synthesized yet.	unknown	unknown	-
14		unmeasured	unmeasured	[29]	14	Not synthesized yet.	unknown	unknown	-
15		unmeasured	unmeasured	[30]	15	Not synthesized yet.	unknown	unknown	-
16		10^{-12}-10^{-11}	~2.2×10^{-8}	[31]	16	Not synthesized yet.	unknown	unknown	-
17		10^{-8}-10^{-7}	1.07×10^{-5}	[32]	17	Not synthesized yet.	unknown	unknown	-
18	Not synthesized yet.	unknown	unknown	-	18		unmeasured	unmeasured	[33]
19	Not synthesized yet.	unknown	unknown	-	19		10^{-11}-10^{-10}	4.46×10^{-10}	[34]
20	Not synthesized yet.	unknown	unknown	-	20		10^{-11}-10^{-10}	~2.0×10^{-7}	[35]
21		unmeasured	unmeasured	[36]	21	Not synthesized yet.	unknown	unknown	-
22	Not synthesized yet.	unknown	unknown	-	22		unmeasured	unmeasured	[37]

*: These data demostrated the maximum (or saturated) conductivity after iodine doping.

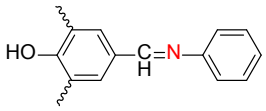
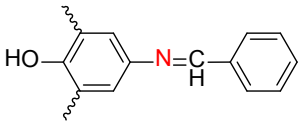
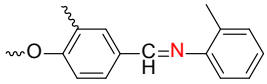
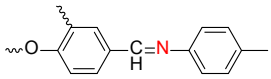
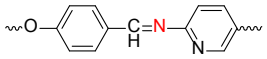
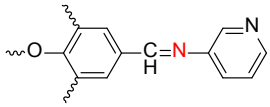
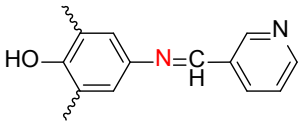
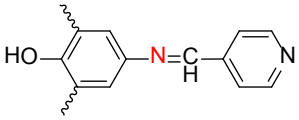
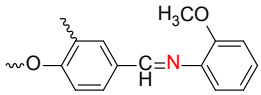
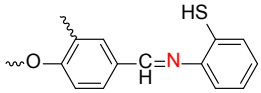
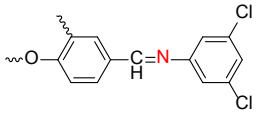
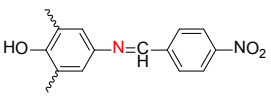
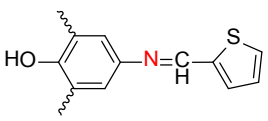
Citation: Demir HO. Poly(phenoxy-imine)s and poly(phenoxy-ketimine)s: toward new semiconductive polymeric materials. *MOJ Poly Sci.* 2017;1(6):214–218. DOI: 10.15406/mojps.2017.01.00036

Table 2 According to the literature data, the synthesized isomeric poly(m-phenoxy-imine)s and their conductivity values

No	poly(o-phenoxy-imine)s	Undoped S/cm	Doped* S/cm	Lit.	No	Its Isomeric Structures	Undoped S/cm	Doped* S/cm	Lit.
1	Not synthesized yet.	unknown	unknown	-	1		unmeasured	unmeasured	[38]

*:These data demostrated the maximum (or saturated) conductivity after iodine doping.

Table 3 According to the literature data, the synthesized isomeric poly(p-phenoxy-imine)s and their conductivity values

No	poly(o-phenoxy-imine)s	Undoped S/cm	Doped* S/cm	Lit.	No	Its Isomeric Structures	Undoped S/cm	Doped* S/cm	Lit.
1		unmeasured	unmeasured	[39]	1		unmeasured	unmeasured	[40]
2		10^{-12}-10^{-11}	2.88×10^{-8}	[41]	2	Not synthesized yet.	unknown	unknown	-
3		10^{-13}-10^{-12}	1.75×10^{-7}	[42]	3	Not synthesized yet.	unknown	unknown	-
4		10^{-8}-10^{-7}	5.40×10^{-7}	[43]	4	Not synthesized yet.	unknown	unknown	-
5		10^{-11}-10^{-10}	3.5×10^{-8}	[44]	5		unmeasured	unmeasured	[45]
6	Not synthesized yet.	unknown	unknown	-	6		unmeasured	unmeasured	[46]
7		10^{-10}-10^{-9}	5.86×10^{-5}	[47]	7	Not synthesized yet.	unknown	unknown	-
8		10^{-11}-10^{-10}	1.89×10^{-9}	[48]	8	Not synthesized yet.	unknown	unknown	-
9		10^{-10}-10^{-9}	1.11×10^{-7}	[49]	9	Not synthesized yet.	unknown	unknown	-
10	Not synthesized yet.	unknown	unknown	-	10		unmeasured	unmeasured	[50]
11	Not synthesized yet.	unknown	unknown	-	11		10^{-10}-10^{-9}	1.55×10^{-5}	[51]

*:These data demostrated the maximum (or saturated) conductivity after iodine doping.

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Conflict of interest

The author declares no conflict of interest.

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