

Polyimines with Electron-Donating and Accepting Groups: Synthesis and Characterization

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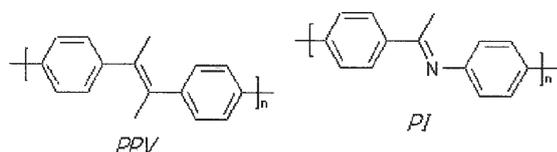
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Novel Schiff base-polymers containing electron-withdrawing groups, such as pyridine or 1,3,4-oxadiazole and carbazole or triphenylamine as electron-donating groups were synthesized via solution polycondensation. Characterization of the synthesized polymeric materials was performed using $^1\text{H-NMR}$, FT-IR spectroscopy, while the electronic properties were studied by UV-vis and fluorescence spectroscopy. The polymers are completely soluble (polymer PI and PIII) or partially soluble (polymer PII) in most common organic solvents such as chlorinated and aprotic polar solvents.

Keywords: conjugated polyazomethines, solution polycondensation, electroluminescence polymers, spectroscopic characterization

The interest for fully aromatic and conjugated polyimines renewed in the last years because aromatic poly(azomethine)s are isoelectronic with poly(*p*-phenylene vinylene)s which are the most known electroluminescent polymers [1] while polyazines are nitrogen-containing analogues of polyacetylene, the most conducting polymer [2]. The researchers have synthesized aromatic polyimines as precursors for conducting polymers by solution polycondensation of aromatic diamine/dialdehyde pairs and also by oxidative polymerization of imine-based monomers containing two oxidizing aromatic end groups (thiophene, pyrrole, naphthalene) [3-9]. Carbazole is a heterocyclic compound that has been used in many polycondensation or polymerization reactions due to the electron-donating character and photoconducting properties. In addition, besides these properties, polyazomethines possess also interesting electro-optical and photochemical properties as well as high thermal stability due to the carbazole and triphenylamine conjugated system [10].

The characteristic structure feature of polyimines is the presence of $-\text{HC}=\text{N}-$ linkages, which are isoelectronic with the $-\text{HC}=\text{CH}-$ groups present in many prototypical conjugated polymers such as polyacetylene and poly(*p*-phenylenevinylene) [11].



The discovery of the electroluminescence in arylenevinylene polymers (PPV) [1] had opened the possibility to use these compounds as active polymeric materials in OLED's but in the same time, grown up the interest for studying other polymers having related structures [12].

We all know that the electroluminescence phenomena involve the formation of a neutral species, called an exciton, through the combination of electrons and holes injected in polymer film between those two electrodes. The exciton can be in the singlet or triplet state according to spin statistics. The maximum quantum efficiency (photons

emitted per electron injected) of light emitting materials, can be risen by improving the injection and charge transport process, recombination and formation of singlet excitons. In order not to disturb the equilibrium established between those two types of charge carriers, the organic material has to be a good electron and hole transporter. Triphenylamine and carbazole are two compounds that possess one nitrogen atom with a free pair of electrons that confer a very strong electron donor character. On the other hand, the electron acceptor character is provided by the pyridine and oxadiazole and the electron density of the aromatic rings is reduced due to the electronegativity of the nitrogen atom. When these compounds are as side chain pendants or in the backbone of the polymers, the polymers achieved very interesting optoelectronic properties. For this, poly-N-vinylcarbazole, was the first organic polymer used in electronography instead of selenium [13]. Polymers that contain electron donor groups are characterized by the holes transport abilities, while electron acceptor groups increase the electron transfer process in the backbone of polymers.

The aim of this paper is to report a preliminary study upon polyimine, synthesis having in their backbone both acceptor (pyridine and oxadiazole) and donor (carbazole and triphenylamine) groups and the charge carrier transport can be assured both by electrons and holes.

Experimental part

Materials

p-Aminobenzoic acid, carbazole, triphenylamine, 2,6-diaminopyridine, hydrazine hydrate, phosphorus pentoxide, *ortho*-phosphoric acid, acetic acid, acetic anhydride, sodium carbonate, hydrated copper azotate hydrated and tin chloride were purchased from Aldrich, Merck or Fluka, and they were used as received. Some solvents used in synthesis of monomers and polymers, as toluene, chloroform, dichloroethane, *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF), were purified and dried, by known methods, used before.

Instruments

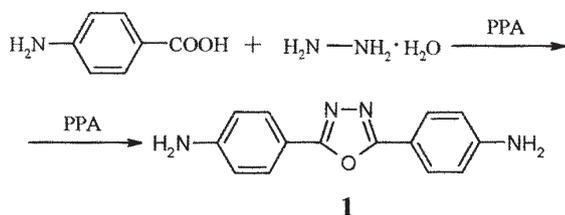
IR spectra were recorded using a spectrophotometer DIGILAB-FTS 2000 and KBr pellets. $^1\text{H-NMR}$ spectra of

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polymers were obtained with a Bruker Avance DRX-400 apparatus in CDCl₃ solution using TMS as an internal standard. UV-vis and fluorescence spectra were obtained using a Specord 200 and Perkin Elmer LS 55 spectrometers, respectively.

Monomers synthesis

2,5-Bis(p-aminophenyl)-1,3,4-oxadiazole (1) was synthesized by treatment of *para*-aminobenzoic acid with a mixture of hydrazine hydrate and polyphosphoric acid.



Firstly, the polyphosphoric acid was obtained and then it was used for synthesis of diamine, as follows.

In a 500 mL round bottom flask equipped with a magnetic stirrer was introduced 100 mL of *ortho*-phosphoric acid (density 1.7 g/dL). The flask was cooled on an ice-water bath and 210.0 g of phosphorus pentoxide was added in portions, with stirring.

After finishing adding the phosphorus pentoxide, the mixture was heated at 150°C for 4 h and then cooled and then 10 g of hydrazine hydrate was added by dropping, for 15 minutes with stirring, while maintaining the flask on ice-water bath. At this mixture it was added 54.8 g *para*-aminobenzoic acid when a brown viscous liquid was observed. After maintaining the reaction mixture at 130 °C for 8 h and then cooled at 70 °C, the mixture was poured, with stirring, in a mixture of ice-water. A powder precipitate was obtained which was filtered and washed with a sodium carbonate solution (400 mL) in order to remove polyphosphoric acid traces. In the final step, the compound was recrystallized from 500 mL ethanol. (b.p.= 259-261°C). Yield: 86%.

¹H-NMR (CDCl₃, δ ppm): 8.00 (2H, d), 7.00-7.50 (2H, d), 5.00-5.50 (4H, -NH₂ groups);

FT-IR (KBr, cm⁻¹): 3350, 3208, 1710, 1600, 1552, 1450, 1210, 835, 750.

4,4'-Diformyltriphenylamine (3) was synthesized using Vilsmyer reaction which consists of treating triphenylamine with a mixture of POCl₃/DMF, in excess. 24 ml (0.258 mol) of phosphorous oxichloride (POCl₃) was added by dropping on DMF solution, at 0 °C. After 1 h the reaction mixture was stirred at room temperature and then was added 5 g (0.024 mol) of triphenylamine dissolved in 30 mL of dichloroethane. After heating at 95 °C for 48 h and then cooled to room temperature, the product was poured in ice-water mixture and then neutralized at pH=7 with NaOH 20% solution. The organic phase that contains the

desired product was extracted with methylene chloride and dried. Finally, a mixture of two formylated compounds, mono and di-aldehyde, were obtained.

The pure compounds were separated by flash chromatography using silica gel and a mixture of ethyl acetate and hexane (1:8) as eluent. After removing the solvent and after recrystallization from acetone, we obtained the pure dialdehyde as a yellow powder with 55.8 yields.

¹H-NMR (CDCl₃, δ ppm): 9.89 (s, -CHO), 7.84 (m, 4H, J = 8.4 Hz), 7.37-7.41 (t, 2H, J = 7.6 Hz), 7.28-7.33 (t, 1H), 7.17-1.19 (m, 6H, J = 8.0 Hz).

FT-IR (KBr, cm⁻¹): 3066, 2803, 2734, 1693, 1609, 1587, 1505, 1494, 1426, 1332, 1292, 1168, 1112, 823, 763, 702, 652, 536, 520, 456, 415.

3,6-Diformyl (N-hexyl) carbazole (4) was synthesized using the same method as we used for derivative (3) (Vilsmyer reaction).

¹H-NMR (CDCl₃, ppm δ): 10.14 (2H, s, -CHO), 8.67 (2H, H_{4,7}, t), 8.08 (2H, t, -N-CH₂-), 1.91 (2H, q, -N-C-CH₂-), 128-1.43 (6H, m, -(CH₂)₆), 0.86 (3H, t, -CH₃).

FT-IR (KBr, cm⁻¹): 726, 751, 766, 806, 857, 886, 905, 1124, 1197, 1241, 1266, 1285, 1305, 1350, 1383, 1438, 1487, 1592, 1626, 1685, 2722, 2857, 2923, 2953, and 3051.

Synthesis of the polyazomethines:

In a 25 mL round bottom flask equipped with a magnetic stirrer, a condenser and inlet-outlet Dean-Stark system, 0.1536 g (0.5 mmol) of 3,6-diformyl(N-hexyl) carbazole, 0.05456g (0.5 mmol) of 2,6-diaminopyridine, 7 mL of DMF and 2 ml of toluene were introduced. The reaction mixture was refluxed at the boiling temperature of toluene in nitrogen atmosphere for 6 h. After cooling at room temperature, the reaction mixture was poured in a large amount of methanol and the polymers precipitate was filtered and dried. The polymers were purified by several precipitations in methanol from chloroform. Using the same procedure we prepared all the polymers.

Results and discussions

Polyimines containing electron acceptor and donor groups with linear structure, were synthesized by solution polycondensation of an equimolar mixture of aromatic dialdehyde (4,4'-diformyltriphenylamine and 3,6-diformyl(N-hexyl)carbazole) and two heteroaromatic diamine, (2,5-bis(p-aminophenyl)-1,3,4-oxadiazole and 2,6-diaminopyridine). The reaction was carried out in homogeneous phase using a polar aprotic solvent (DMF) and the water resulted from reaction, was removed by distillation as azeotrope with toluene. The polycondensation reaction was carried out at 110°C, the boiling temperature of toluene.

In the final step, all polymers were purified by several precipitations in methanol and the precipitate was filtered and dried. In the table 1 are presented some experimental data and polymers characteristics.

Table 1
EXPERIMENTAL DATA AND POLYMER CHARACTERISTICS

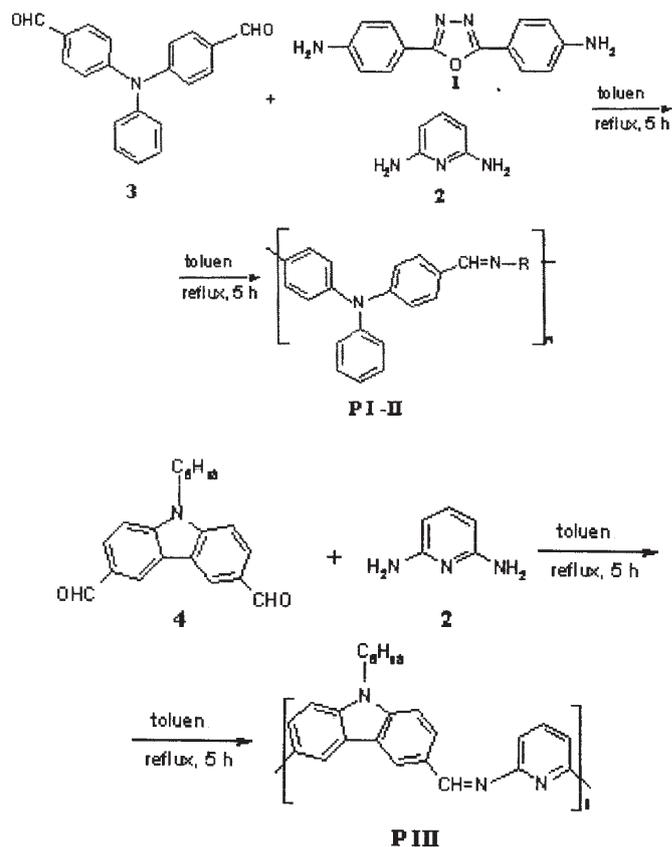
Polymer	Diamine	Yield (η %)		GP ^{a)}	λ _{max} , UV (nm)	λ _{max} , PL (nm), CHCl ₃	
		total yield	soluble fraction			excitation	emission
P I	1	50.20	50.20	6	330, 392	330	450
P II	2	90.60	32.10	9	333, 382	382	458
P III	2	93.16	93.16	8	285, 297, 332, 392	297	446

The polyazomethines were obtained as amorphous solid and highly soluble in chlorinated (chloroform, 1,2-dichloroethane) and strong polar (DMF, NMP, THF) solvents. The PII polymer is making an exception from this behavior and is presenting an insoluble fraction and the yield of the insoluble fraction is much higher than the yield of the soluble fraction. The main drawback in most polyazomethines synthesis is that the polymers are precipitated out of reaction media rapidly, leading to very low molecular weight materials, hardly soluble in any solvents [14,15]. The presence of triphenylamine (TPA) moiety introduces a kinked form of the main chain with benefic effects on polymer solubility, due to the dihedral angle between -N-Ph-CHO units. In spite of using the same diamine (2) in case of polymer PIII it was obtained only soluble fraction and this is due to the alkyl side chain from the dialdehyde (3) structure. By introducing the n-alkyl substituent which contains 6 carbon atoms, it will decrease interchain interactions which have visible results upon solubility properties and processability of polymers.

The structures of all polyazomethine (scheme 1) were confirmed by FT-IR and ¹H-NMR spectroscopy and UV-vis spectroscopy. The molecular weights of these polymers were estimated by GPC (gel permeation chromatography) using as internal standard polystyrene and THF as eluent. Due to the low molecular weights of the polymers, the terminal -CHO (1680 cm⁻¹) group is also observed. Using ¹H-NMR can be also estimated the molecular weights by comparing the ratio of integrals of -CHO ends and the integral of the signal assigned to -CH=N- groups (these signals are very distinct). The significant aspect in the polycondensation of diamine with dialdehyde is the nucleophilic attack of the amine group on the carbonyl bond followed by dehydration of the tetrahedral intermediate. Therefore, the rate of reaction is dependent on the diamine nucleophilicity and the electrophilicity of the carbonyl compound.

So we could compare, for these polymers, the reactivity of the diamine and dialdehyde compounds, used in this study, and we found this, diamine nucleophilicity: (2) > (1) and dialdehyde electrophilicity: (4) > (3). This order explains the lower molecular weight of the polymer I against polymer III.

The FT-IR spectra of all linear polyazomethines (fig. 1) show the typical absorption band localized at 1610 cm⁻¹ which corresponds to vibration of imines' linkage, -CH=N-. The bands at 1586 cm⁻¹ (PI and PII) and 1594 cm⁻¹ (PIII) are due to the double bonds from the aromatic rings, -C=C- and the bands around 800 cm⁻¹, stronger in the case of the polymers with aromatic diamine, and are due to the aromatic C-H out of-plane deformations. These bands remain in the same position and with the same intensity as in the monomers FT-IR spectra.



Scheme 1. Polyazomethines synthesis

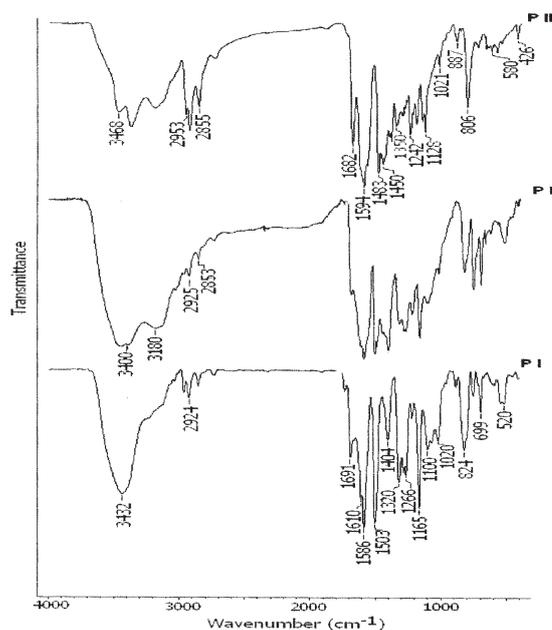


Fig. 1. FT-IR spectra of synthesized polymers

Polymers	δ (ppm)
PI	9.89 ppm (-CHO), 8.44 ppm (-N=CH-), 6.73-8.11 (from the protons of the benzene rings of the triphenylamine or 1, 3, 4-oxadiazole).
PII	9.89 ppm (-CHO), 6.5-8.5 ppm (the protons from benzene rings of pyridine and triphenylamine).
PIII	9.89 ppm (-CHO), 6.50-9.00 ppm (the protons from aromatic rings of carbazole and pyridine), 4.32 ppm (-N-CH ₂), 1.00- 3.50 ppm (the characteristic protons of the -CH ₂ groups from N-alkylcarbazole), 0.86 ppm (the protons of -CH ₃).

Table 2
¹H-NMR CHARACTERISTICS OF THE
POLYMERS WITH AZOMETHINE STRUCTURE

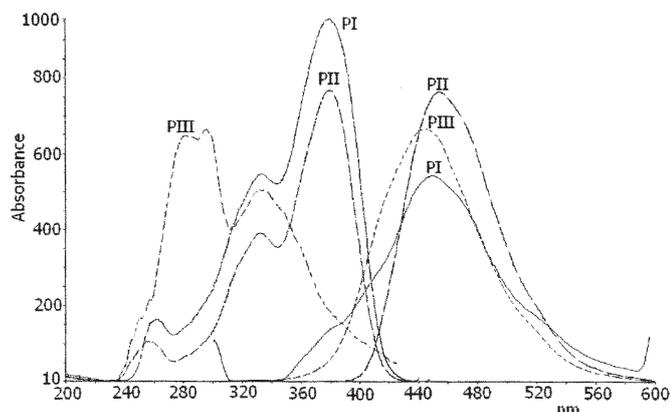


Fig. 2. Excitation – emission spectra of the synthesized polyazomethines

In all polymers's spectra it can be observed the presence of the absorption band at 1691 cm^{-1} due to the unreacted $-\text{CHO}$ functions from the dialdehyde (monomers) and also in $^1\text{H-NMR}$ spectra the peak at 9.89 ppm can be attributed to the same groups. This confirm the presence the $-\text{CHO}$ as an end group for synthesized polymers, and as well that the polymers have low molecular weights (table 2). The absorption bands localized at ~ 830 and $\sim 800\text{ cm}^{-1}$ ($\nu\text{C-H}$ aromatic from benzene rings) and $1260\text{-}1270\text{ cm}^{-1}$ (the stretching vibration of tertiary amine) are present in PI and PII.

From the UV-vis spectra of the polymer solutions in chloroform, it can be observed the presence of the absorption bands at 330 and 392 nm (PI), 333 and 382 nm (PII) and 285 , 297 , 332 and 392 nm (PIII). First absorption bands are due to the $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ in the heteroaromatic rings and those bands at higher wavelength corresponds to $\pi\text{-}\pi^*$ transitions from the conjugated polymer chains.

All the polymers show photoluminescence phenomena by excitation with higher wavelength radiations corresponding to absorption bands from the absorption spectra of the polymers (fig. 2).

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Conclusions

New polyazomethines were synthesized by solution polycondensation of 4,4'-diformyltriphenylamine and 3,6-

diformyl N-hexyl carbazole with two heteroaromatic diamines: 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole and 2,6-diaminopyridine. The synthesized polymers were characterized by spectral methods, as FT-IR, $^1\text{H-NMR}$, UV-vis. The GPC measurements of these polymers exhibit a low molecular weight which can be estimated also by $^1\text{H-NMR}$ spectroscopy, and also from the ratio between the integrals of the signals of $-\text{CH=N-}$ groups and $-\text{CHO}$ end groups, can be calculated the molecular mass and the degree of polymerization which in this case, there is a good correlation between values of molecular weights of polymers determined by both methods.

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