

SYNTHESIS AND CHARACTERIZATION OF SOME ARYLENIMINE POLYMERS CONTAINING N-HEXYL-3,6-CARBAZOLYLDIYL UNITS♦

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Abstract: Two monomers with preformed azomethine structures were obtained by condensation reactions of 1,4-phenylenediamine with 3-formyl-N-hexyl carbazole or 3-formyl-N-hexyl-6-bromo carbazole. The corresponding polymers were synthesized by electropolymerization under galvanostatic conditions (I = ct.). The new structures were characterized by Fourier transform-infrared, ¹H NMR and UV-VIS methods.

Keywords: *conjugated polymers, aryleneimine, electropolymerization, synthesis, characterization*

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INTRODUCTION

Polyazomethines, also called poly(Schiff-base)s, which exhibit an isoelectronic structure to that of poly(*p*-phenylene vinylene)s, have been intensively studied owing to their interesting properties: good thermal stability, mechanical strength, non-linear optical properties, ability to form metal chelates, semiconducting properties, environmental stability and fiber-forming properties, which are associated mainly with their conjugated backbone and the presence of imine sites [1, 2].

Until few years ago, polyazomethines have been synthesized by the simple melt or solution polycondensation reaction of the two comonomers but the reaction is hard to control, is an equilibrium reaction and gives undesirable by-products. After that it was reported a method for synthesis of poly(Schiff-base)s by cation-radical polymerization of monomers containing preformed azomethine groups and aromatic end-groups. The polymerization reaction takes place by chemical or electrochemical oxidation of aromatic ends to cation-radicals followed by their radical-radical coupling.

The modern strategies for synthesis of defect-free poly(*p*-phenylene)s (PPPs) and soluble polyheteroarylenes are based upon nickel- and palladium-mediated cross-coupling reactions, due to largely their preservation of regiochemistry and nearly quantitative yields. [3-5]. In recent years much effort has been focused on the synthesis of soluble conjugated polymers (mainly polyarylenes and polyheteroarylenes) for optoelectronic applications using this method. These type of reactions can be extended for poly(Schiff-base)s synthesis starting from monomers with preformed azomethine groups, carrying bromine final atoms [6].

Carbazole-based polymers are excellent photoconducting materials and show very good hole transport properties. Therefore, the incorporation of both carbazole and fluorene rings in a regular structure along the backbone can improve the performance of light-emitting materials and this has been extensively studied. The kinks introduced by the presence of 3,6-disubstituted carbazoles in the main chain depress the possibility of chain aggregation and increase quantum efficiencies.

Recently, the electrosynthesis of some polymers by dehalogenative organometallic polycondensation using a zerovalent nickel, Ni⁰L_m has been reported [7 – 10]. A complex type NiBr₂·(bipy) (where bipy is 2,2'-bipyridine) was used as a catalytic precursor in order to synthesize various polyconjugated compounds.

The goal of this paper is to present a contribution concerning the synthesis of some poly(Schiff-base)s using monomers like: N,N'-bis(9-hexyl-3-carbazolyl-methylidene) 1,4-phenylene-diamine and N,N'-bis(6-bromo-9-hexyl-3-carbazolyl-methylidene) 1,4-phenylenediamine. The two monomers with preformed azomethine structures were obtained by condensation reactions in order to obtain conjugated heteroarylene polymers. The monomers are crystalline and colored products.

By means of oxidative and dehalogenative coupling reactions corresponding polymers were synthesized. The resulted polymers were soluble in organic solvents (CHCl₃, THF, DMF) owing to the presence of N-hexyl substituents attached to carbazole rings and 3,3'-carbazolyldiyl rings in the main chain.

EXPERIMENTAL

Materials and instrumentation

N-Bromosuccinimide (NBS), N,N-dimethylformamide (DMF), tetrabutylammonium tetrafluoroborate (TBATFB), N,N-dimethylacetamide (DMAc), NiBr₂·(bipy) complex, (all from Aldrich), methanol, chloroform, ethanol (Chemical Company, Romania) are commercially products and were used as received. Toluene was dried by the usual method. 1,4-phenylenediamine (Merck) was purified just before use by recrystallization from water. 3-Formyl-N-hexyl carbazole was synthesized by formylation of N-hexyl carbazole [1]. Fourier transform infrared (FT-IR) spectra were recorded in KBr pellets on a DIGILAB-FTS 2000 spectrometer and UV-Vis absorption spectra were obtained on a Specord M42 Carl Zeiss Jena spectrophotometer in tetrahydrofuran solutions. Melting points were measured with a Boetius microscope. ¹H NMR spectra were recorded on a 400 MHz spectrometer (Brucker AC 400) using deuterated chloroform as a solvent. Synthesis of azomethine monomers (I, II) was performed according to figure 1 and figure 2.

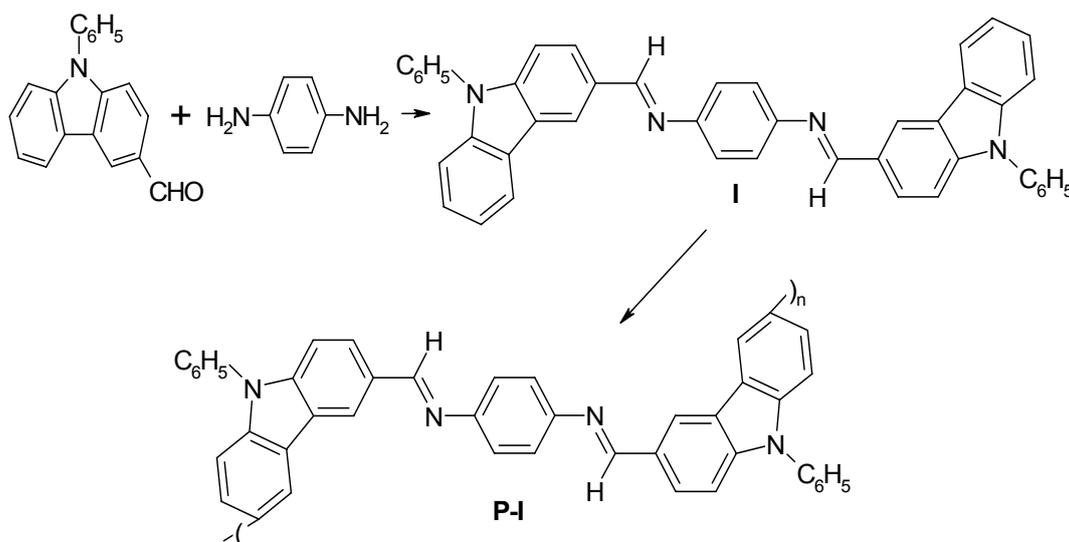


Figure 1. Synthesis of *N,N'*-bis(9-hexyl-3-carbazolyl-methylidene)1,4-phenylenediamine (I) and its polymer (P-I)

3-Formyl-N-hexyl-6-bromo carbazole

To synthesize 3-formyl-N-hexyl-6-bromo carbazole, a two-neck round bottom flask equipped with a magnetic stirrer and a drop funnel was charged with 10 g (35.7 mmol) of 3-formyl-N-hexyl carbazole and 35.86 mL of DMF. A solution of 6.3546 g (35.7 mmol) of N-bromosuccinimide in 21.3 mL of DMF was added to a stirred mixture dropwise. The mixture was stirred for 12 h at room temperature in the absence of light and oxygen, and then was poured into water. The product was filtered, washed with water, and recrystallized from methanol. M.p. = 74 °C.

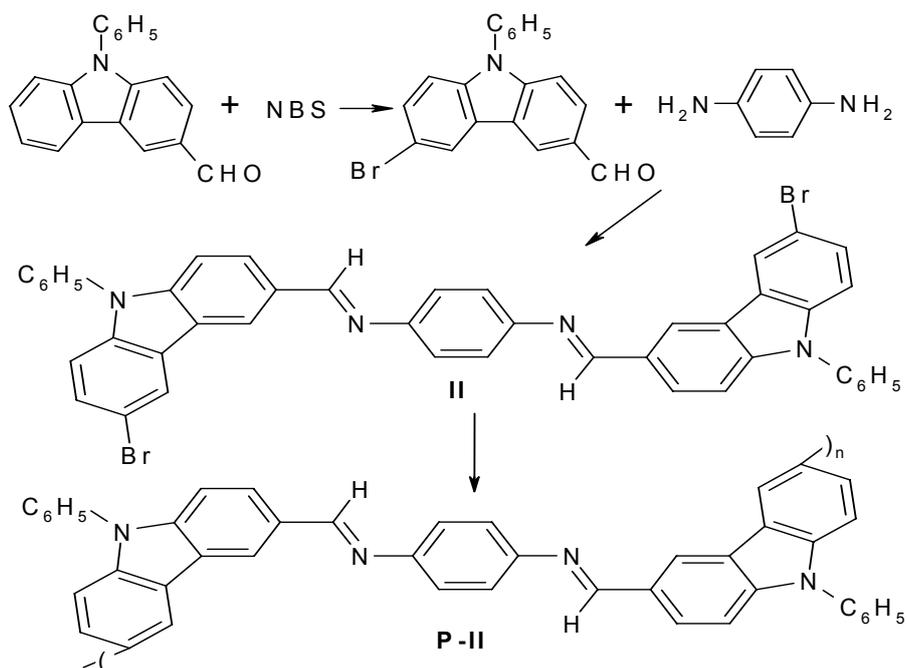


Figure 2. Synthesis of *N,N'*-bis(6-bromo-9-hexyl-3-carbazolyl-methylidene)1,4-phenylenediamine (II) and its polymer (P-II)

Synthesis of monomers

N,N'-bis(9-hexyl-3-carbazolyl-methylidene)1,4-phenylenediamine (I)

A one-neck round-bottom flask equipped with a magnetic stirrer and condenser was charged with 0.9560 g (3.43 mmol) of 3-formyl-N-hexyl carbazole, 0.1856 g (1.71 mmol) of 1,4-phenylenediamine and 20 mL of ethanol. The mixture was refluxed for 3 h and the compound was obtained by precipitation in water. The product was filtered, dried and reprecipitated from chloroform into methanol. M.p. = 128 – 134 °C, yield = 55%.

¹H NMR (400 MHz, CDCl₃): 8.59 (s, 2H, -CH=N-); 8.54 (s, 2H, H₅); 7.96 (d, 2H, H₇); 8.06 (d, 2H, H₄); 7.40 (m, 4H, phenyl and H₂); 7.32 (s, 2H, H₈); 7.18 (d, 2H, H₁); 7.16 (d, 2H, H₆); 4.22 (t, 4H, -N-CH₂-); 1.77 (t, 4H; -N-C-CH₂-); 1.17 (t, 4H; -N-C-CH₂-); 1.17-1.31 (m, 12H, -(CH₂)₃-); 0.76 ppm (t, 6H, -CH₃).

N,N'-bis(6-bromo-9-hexyl-3-carbazolyl-methylidene)1,4-phenylenediamine (II)

A one-neck round-bottom flask equipped with a magnetic stirrer and condenser was charged with 1.8606 g (5.19 mmol) of 3-formyl-N-hexyl-6-bromo carbazole, 0.2807 g (2.59 mmol) of 1,4-phenylenediamine and 20 mL of dry toluene. The mixture was refluxed for 3 h and the compound was obtained by precipitation in methanol. The product was filtered, dried and reprecipitated from chloroform into methanol. M.p. = 135 – 139 °C, yield = 66.6%.

¹H NMR (400 MHz, CDCl₃): 8.69 (s, 2H, -CH=N-); 8.58 (s, 2H, H₅); 8.28 (s, 2H, H₄); 8.15 (d, 2H, H₇); 7.60 (d, 2H, H₂); 7.49 (d, 2H, H₈); 7.38 (s, 4H, H phenyl); 7.26 (d, 2H, H₁); 4.32 (t, 4H, -N-CH₂-); 1.90 (t, 4H; -N-CH₂-); 1.25-1.45 (m, 12H, -(CH₂)₃-); 0.85 ppm (t, 6H, -CH₃).

Polymerization

Electrochemical polymerization was carried out under galvanostatic conditions in a glass cell, containing two compartments separated by a porous glass disk and equipped with Pt electrodes ($1 \times 1 \text{ cm}^2$). Low current densities were used (3 mA). Electrosynthesis was performed in DMAc in the presence of TBATFB as supporting electrolyte and $\text{NiBr}_2 \cdot (\text{bipy})$ as catalyst only for monomer II. The resulting solution was then poured into methanol and methanol / H_2O (2:1, vol.) solutions and one or two polymer fractions were separated.

RESULTS AND DISCUSSION

The electrochemical polymerization, carried out in a glass cell with two compartments, led to polymers separated in two fractions as a function of their solubility; an insoluble fraction in methanol and a fraction that was soluble in methanol, but insoluble in the mixture methanol: water (2:1, vol.). These polymer fractions were colored products: the insoluble fraction in methanol was dark-brown, whereas the soluble fraction in methanol was a yellow-colored product.

Table 1. Electrochemical polymerization of monomers with carbazole rings

Monomer	Monomer concentration (mmol L^{-1})	Molar ratio Monomer/catalyst	Time (h)	Yield (%)	Mn(I)
M-I	20.0	-	35	74.13	4220(1.40)
M-II	12.0	1.57	28	90.66	-
M-II	22.2	1.72	12	64.53	3890(1.45)

Electrosynthesis conditions: solvent = N,N'-dimethylacetamide; concentration electrolyte, TBATFB, 0,1 mol L^{-1} ; current intensity = 3 mA.

Chemical structures of monomers and polymers synthesized are presented in figures 1 and 2 and their FT-IR, NMR and UV-vis spectra are presented in figures 3 - 5. The polymers were soluble in organic solvents as chlorinated (CHCl_3 , CH_2Cl_2), aromatic (toluene) and polar and aprotic solvents (DMF, DMSO, THF). Their solubility was associated with their low molecular weight and was also due their N-alkyl carbazole substituted and kinked structure of the polymers.

The IR spectra of the monomers (figure 3) show the presence of strong absorption bands at 1610 and 1593 cm^{-1} (M-I) and 1610 and 1591 cm^{-1} (M-II) assigned to $-\text{CH}=\text{N}$ and $\text{C}=\text{C}$ vibrations, therefore the dehalogenative polycondensation did not affect the preformed azomethine structure of the monomers. The peaks situated at 800 , 839 and 1200 cm^{-1} for the both monomers are assigned to the out-of-plane deformation of the C-H bonds in the 1,2,4-trisubstituted benzene rings of carbazole nuclei. All these bands were preserved as intensity and very slightly modified as position in the polymer spectra. The decrease of the characteristic absorption of C-Br bond ($\sim 569 \text{ cm}^{-1}$) from the monomer M-II to the polymer P-II confirm the incatenation by dehalogenative polycondensation of the carbazole rings by 3 and 6 positions.

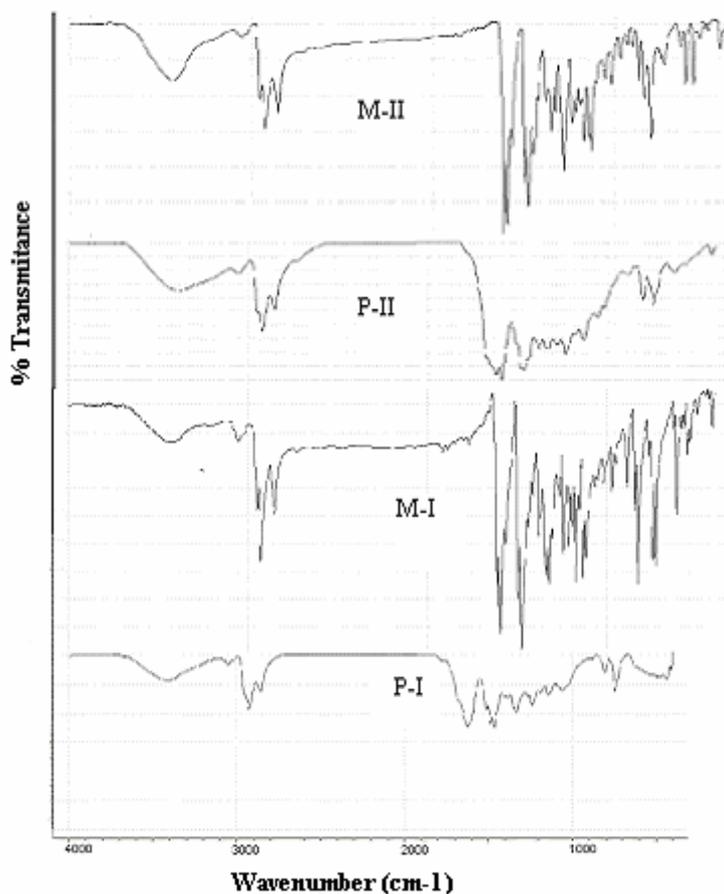


Figure 3. FTIR spectra of monomers (M-I, M-II) and corresponding polymers (P-I, P-II)

The ^1H NMR spectra of the polymers (figure 4) have a complex aspect in the aromatic region not only due to the polydispersity, but also to the possibility that some chains to loose the bromine atoms from the ends during the reaction (the case of polymer P-II). The azomethine protons can be identified at 8.62 ppm for the both polymers.

Figure 5 present the electronic spectra of the monomers and corresponding polymers in THF solution. The UV-VIS spectra show absorption maxima in the range of 260 – 320 nm characteristic to the $\pi\text{-}\pi^*$ transitions in carbazole and phenyl nuclei, and absorptions at higher wavelengths (320-455) can be attributed to $\pi\text{-}\pi^*$ and $\text{n-}\pi$ transitions in imine groups conjugated with aromatic nuclei. Both polymers show UV spectra blue shifted in comparison with the corresponding monomers due to the presence of the neighboring 3,3'-bis-carbazolyldiyl rings that was accompanied by a rotation of the polymer chain and a reduction of conjugation length.

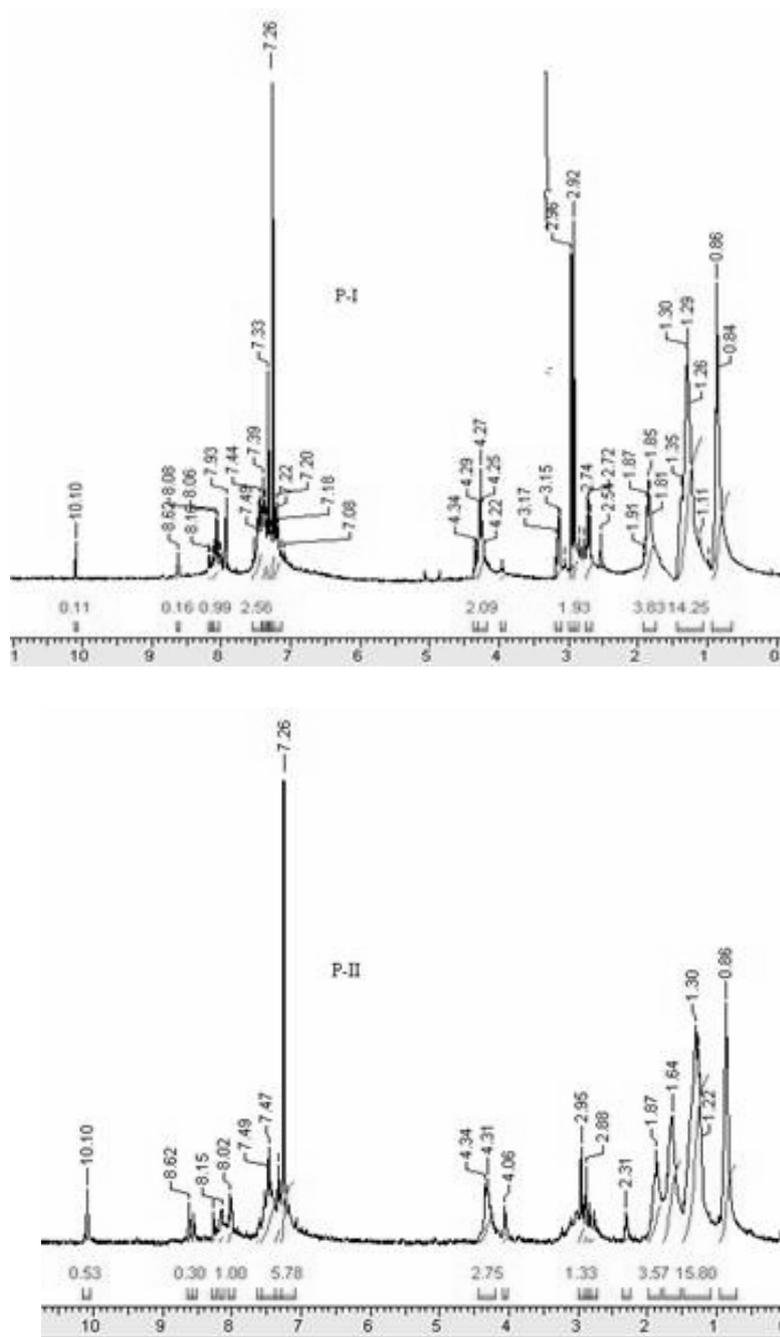


Figure 4. Model ^1H NMR spectra of polymers P-I and P-II

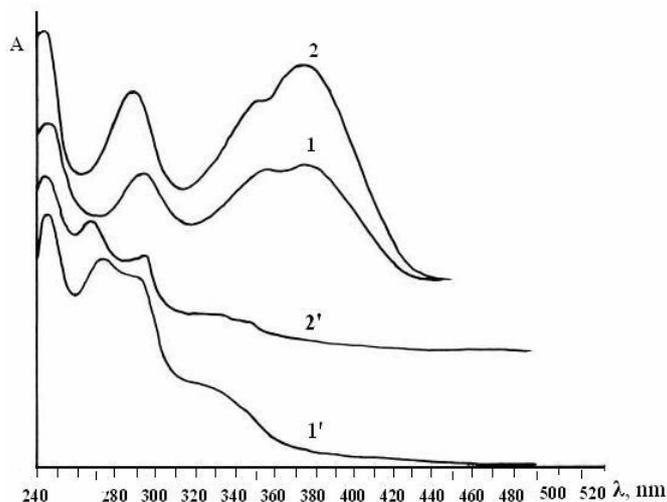


Figure 5. UV-vis spectra of monomers (1) M-II, (2) M-I and polymers (1') P-II, (2') P-I

CONCLUSIONS

To obtain conjugated heteroarylene polymers two monomers with preformed azomethine structure were synthesized and characterized by spectroscopic methods (IR, NMR and UV). These monomers were polymerized by different reactions using oxidative coupling and dehalogenative coupling reactions. The polymers were analyzed by spectroscopic methods that showed that the preformed structure of the monomers is preserved during polymerization. The polymers were soluble in organic solvents due to N-hexyl substituents and presence of 3,3'-carbazolyldiyl rings in the main chain.

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