

Dedicated to the memory of
Professor Candin Liteanu on his 100th anniversary

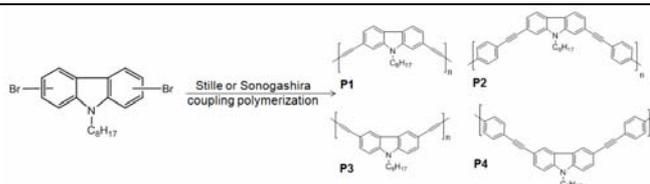
A COMPARATIVE STUDY OF OPTICAL AND ELECTRONIC PROPERTIES OF ARYLENEVINYLENE AND ARYLENEETHYNYLENE POLYMERS CONTAINING 2,7 AND 3,6 DISUBSTITUTED CARBAZOLE UNITS

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New conjugated arylene vinylene, and arylene ethynylene polymers containing disubstituted carbazole group (in 2,7- or 3,6-positions), linked by vinylene (**P1**, **P3**) and 1,4-phenylene ethynylene (**P2**, **P4**) spacers were synthesized by Stille coupling of dibromoderivatives with trans-1,2-bis(tributylstannyl) ethene and by Sonogashira coupling reaction between dibromoderivatives and 1,4-diethynylbenzene, respectively. They were characterized by FTIR and ¹H-NMR spectroscopy and the optoelectronic properties of the polymers as function of carbazole substitution or spacer nature were discussed. Cyclic voltammetry was used to study the redox behavior of thin films deposited on the electrode surface and position of HOMO and LUMO levels was determined.



INTRODUCTION

During the past decades, conjugated polymers have emerged as a novel class of synthetic polymers with highly promising mechanical, optical and electrical properties for advanced technological applications such as light emitting diodes,¹⁻⁴ photovoltaic cells⁵⁻⁷ and electrochromic materials.⁸ Among them, increasing interest has been paid to polycarbazoles (PCzs) because they are the most promising candidates for efficient hole-transporting and photoluminescent materials.⁹⁻¹³ Carbazole is a heterocyclic compound that has

been used in the synthesis of many monomers and polymers because: (a) is a cheaply raw material obtained from distilling of coal, (b) can be easily functionalized at nitrogen atom¹⁴ or 3,6-positions,¹⁵ or in more special conditions at 2,7-positions¹¹ allowing to obtain polymers with various structures,¹⁶ (c) has a low ionization potential and can form cation-radicals, and (d) polymers have good thermal and photochemical stability.¹⁷ Due to these advantages, 3,6-carbazole based polymers have been extensively reported for various optoelectronic devices such as bulk heterojunction polymer solar cells (BHJ-PSCs),¹⁸⁻¹⁹ organic

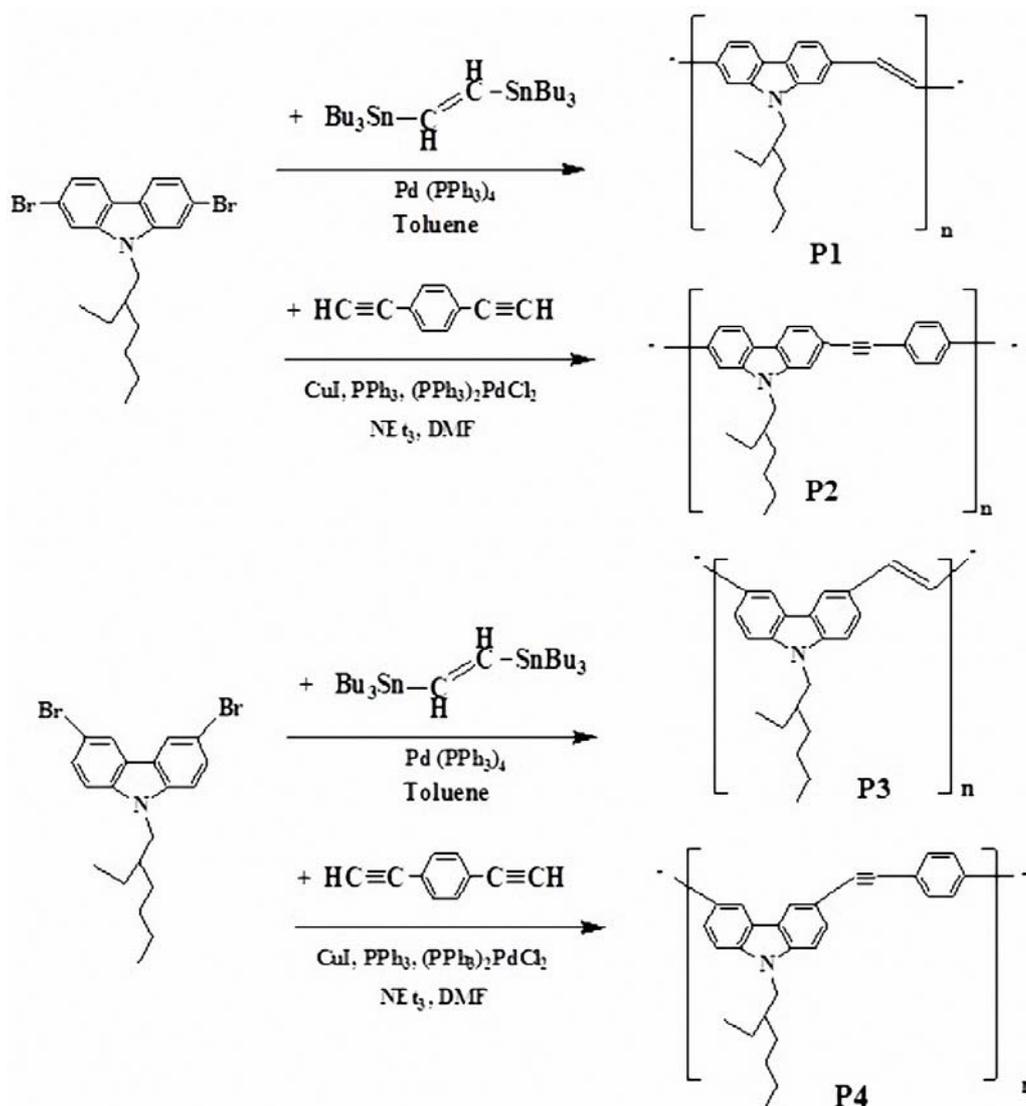
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photoconductors²⁰ and so on. Moreover, carbazole unit functionalized at the 2,7-position was also extensively employed to construct conjugated polymer for various optoelectronic devices, especially for highly efficient BHJ-PSCs.²¹⁻²⁶

The aim of this paper is to report the synthesis and a comparative study of the opto-electrochemical properties of four polymers based on disubstituted carbazole group (in 2,7- or 3,6- positions), linked by two kinds of spacers. Thus, four polymer structures containing *N*-(2-ethylhexyl) 2,7-carbazolyldiyl and *N*-(2-ethylhexyl) 3,6-carbazolyldiyl moieties in the main chain and connected by vinylene (**P1**, **P3**) and 1,4-phenylene ethynylene (**P2**, **P4**) spacers were synthesized.

RESULTS AND DISCUSSION

Two poly(arylene vinylene)s, **P1** and **P3**, were obtained by Stille coupling of dibromoderivatives with *trans*-1,2-bis(tributylstannyl) ethane.²⁷ Arylene ethynylene polymers (**P2** and **P4**) were synthesized by Sonogashira coupling reaction between dibromoderivatives and 1,4-diethynylbenzene²⁸ (Scheme 1). The characterization of polymers (**P1-P4**) was achieved using FTIR and ¹H-NMR spectroscopy. The polymers obtained by Stille coupling polymerization are totally soluble in chloroform, DMF, THF, DMSO and yellow-orange (**P1**) or green (**P3**) colored powders. The polymers obtained by Sonogashira polymerization are partially soluble in chloroform.



Scheme 1 – Synthesis of arylene vinylene and arylene ethynylene polymers containing 2,7-carbazolyldiyl and 3,6-carbazolyldiyl moieties (**P1-P4**).

FTIR AND $^1\text{H-NMR}$ SPECTRA

Chemical structure of polymers **P1-P4** was identified by FT-IR and $^1\text{H-NMR}$ spectroscopy. Fig. 1 gives the IR spectra of polymers. Typical polyCBZ bands at 3023 (**P1**), 3059 (**P2**), 3020 (**P3**), and 3038 (**P4**) cm^{-1} ascribed to the $=\text{C-H}$ stretching vibrations of the aromatic ring, at 2922 (**P1**), 2926 (**P2**), 2926 (**P3**), 2925 (**P4**) cm^{-1} and respectively at 2855 (**P1**), 2858 (**P2**), 2856 (**P3**) and 2857 (**P4**) cm^{-1} , due to the aliphatic CH and CH_2 were observed. In addition a series of bands at 1592-1600 cm^{-1} and 1455-1487 cm^{-1} attributed to the $\text{C}=\text{C}$ bond (stretching) of the carbazole ring, at 1322-1346 cm^{-1} due to the aromatic C-N bonds and at 798-802 cm^{-1} due to the aromatic C-H bending present in the carbazole unit were also observed. FT-IR spectra confirm the vinyl structure of the

polymer **P1** and **P3** by the presence of absorption band located at 954 (**P1**) and 956 (**P2**) cm^{-1} which correspond to the out of plane C-H bending vibration of *trans* vinyl linkage while for polymers **P2** and **P4** and by presence of the absorption band located at 2198 cm^{-1} (**P4**), respectively at 2204 cm^{-1} (**P2**) characteristic for triple bond.

Fig. 2 shows the $^1\text{H-NMR}$ spectra of the polymers that confirm the proposed structure. The spectra are grouped as function of the spacer nature for a better visualization and because the signals of protons appear in same region. The protons of the aromatic rings appear as multiplets between 6.9-8.1 ppm and the signals of the alkyl groups were observed between 0.8-4.2 ppm. For **P1** and **P3** the signals of the vinyl protons appear in the aromatic region.

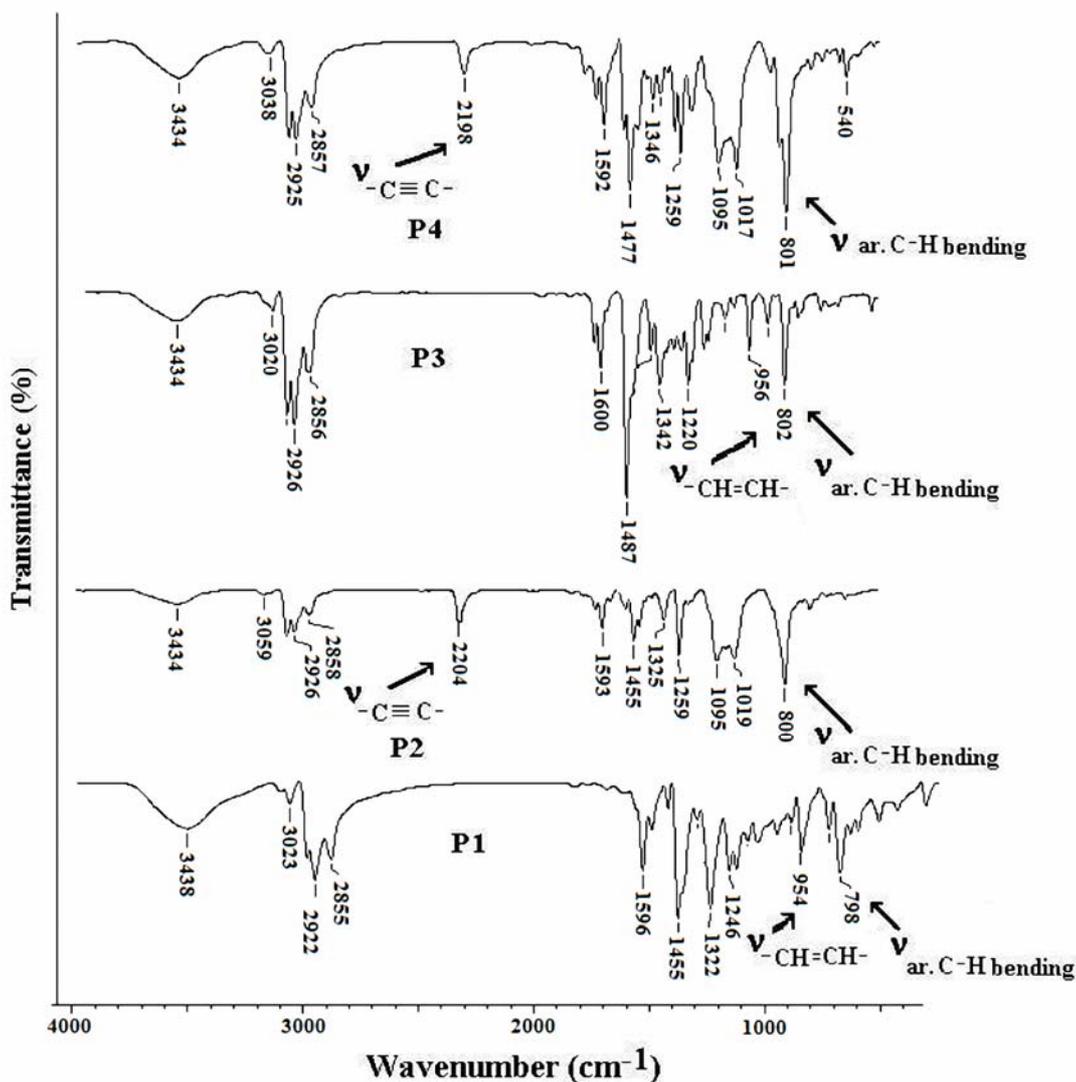


Fig. 1 – FT-IR spectra (KBr pellet) of polymers **P1-P4**.

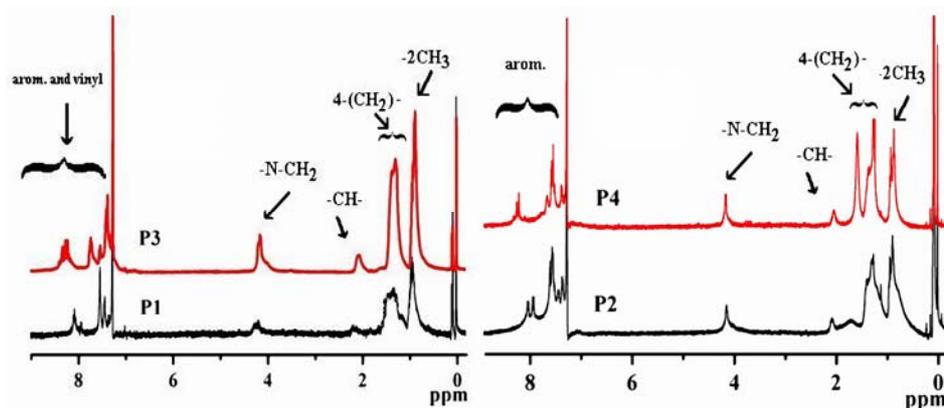


Fig. 2 – $^1\text{H-NMR}$ spectra (CDCl_3) of polymers **P1**- **P4**.

OPTICAL PROPERTIES

The UV-Vis absorption spectra of the polymers were registered in chloroform solution and are depicted in Fig. 3. Relevant optical parameters are summarized in Table 1. The first absorption band position at the shorter wavelength was attributed to the $\pi\text{-}\pi^*$ transitions of the aromatic rings while the next band at longer wavelength was assigned to electronic $\pi\text{-}\pi^*$ transitions of the conjugated backbone.

A comparison of polymers **P1**, **P2** with **P3**, **P4** has evidenced important differences with respect to optical properties, caused by the position of the conjugation connection between carbazoles and vinyl linkage, respectively 1,4-phenylene ethynylene segment. Arylenevinylene polymers show absorptions at higher wavelength than polyaryleneethynyls, due to their different chemical and electronic structure. This behavior could be explained by the fact that carbazole unit functionalized at the 2,7 position shows the conjugation path through biphenylene unit from carbazole and spacer while for polymers with 3,6 disubstituted carbazole units, the conjugation takes place between phenyl units and spacer through lone electron pair of carbazole nitrogen.

The emission spectra of all the polymers were also registered in chloroform solution and were recording by excitation with absorption maxima values found in the UV-Vis spectra. The emission maxima are summarized in Table 2. The maxima of emission in solution are centered around 400-475 nm (Fig. 3 B). The photoluminescence (PL) spectra of the polymers **P1** (473 nm) and **P2** (419 nm) display a red shifting compared to polymers **P3** (446 nm) and **P4** (405 nm) and same behavior observed in UV-Vis absorption spectra can also be seen in the PL spectra of all polymers.

ELECTROCHEMICAL PROPERTIES

Electrochemical properties of the polymers were investigated by cyclic voltammetry (CV) using a three-electrode cell. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the conjugated polymers are important parameters in the design of optoelectronic devices and they can be estimated from the onset of the oxidation and reduction potentials.²⁹ The onset values are estimated from the intersection of the two tangents drawn at the rising oxidation (or reduction) current and the background current in the CVs. The measurements were performed on film samples, which were prepared by the drop casting from dichlorobenzene solution onto the disc platinum electrode and carried out in an acetonitrile solution containing 0.1 M Bu_4NBF_4 with a scan rate of 50 mV/s. Fig. 4 shows the CV curves of polymers **P1**-**P4**. The HOMO and LUMO energy levels of the polymers were determined using ferrocene/ferrocenium (Fc/Fc^+) as an internal standard (the ionization potential of the Fc/Fc^+ is -4.8 eV)³⁰ and its redox potential measured by us is 0.43V versus Ag/AgCl . The energy levels of polymers can be obtained by adding 4.37 V to the values of the redox potential. The onset oxidation potentials ($E_{\text{ox}}^{\text{onset}}$) vs Ag/AgCl were showed in Table 2. Since we couldn't obtain reliable onset reduction potential values for the four polymers, the optical bands gaps (E_g) of the polymers (which were calculated from their absorption band edge) were utilized to estimate the LUMO energy levels based on the relation $E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$. All polymers had relative deep-lying HOMO energy levels which indicated that all of them would have good chemical stability and are attractive candidates for solar cells.

Table 1

Optical absorption data of polymers

Polymer	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)
P1	269, 419	473
P2	260, 366	419
P3	295, 359, 386	446
P4	244, 311, 357	405

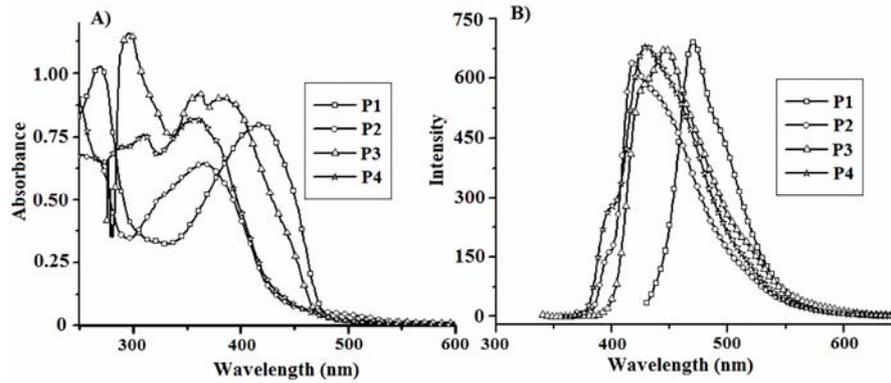
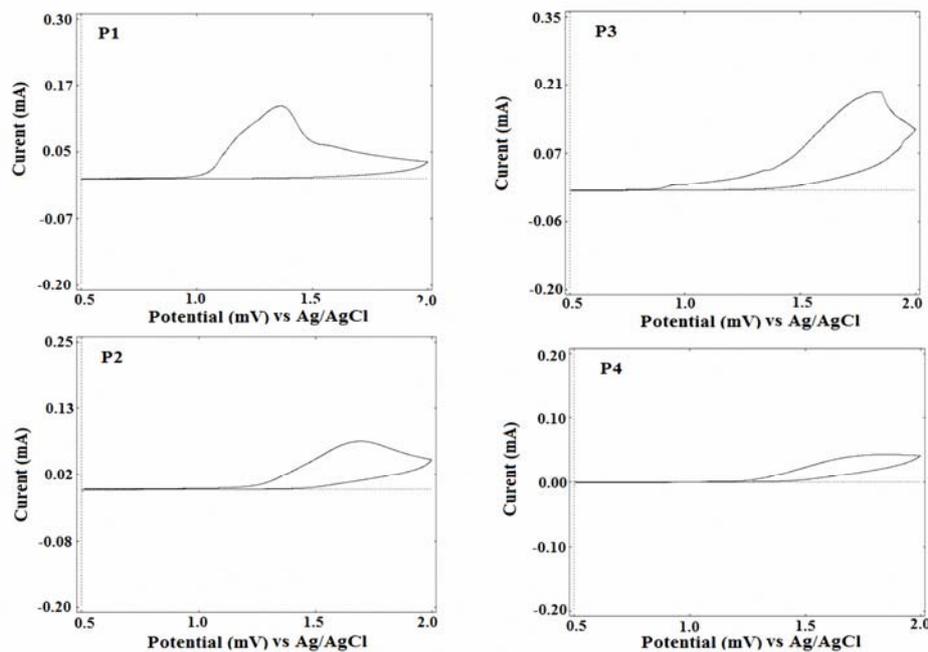
Fig. 3 – Absorption (A) and emission (B) spectra (CHCl_3) of polymers P1-P4.

Table 2

Electrochemical characteristics of polymer

Polymer	$E_{\text{ox}}^{\text{onset}}$ (V) vs Ag/AgCl	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{g}}^{\text{opt a)}}$ (eV)
P1	1.37	-5.74	-2.94	2.80
P2	1.32	-5.69	-2.92	2.77
P3	1.30	-5.67	-2.79	2.88
P4	1.25	-5.62	-2.76	2.86

a) Optical band gap estimated from the onset wavelength of optical absorption, with equation $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$.

Fig. 4 – Cyclic voltammograms of polymers P1-P4 using Bu_4NBF_4 as support electrolyte (10^{-1}M). Scan rate: 50 mV/s.

EXPERIMENTAL

Materials

Carbazole, 2-ethylhexyl bromide, 4,4'-dibromo 2-nitrophenyl, triethylphosphite, NaH, *trans*-1,2-bis(tributylstannyl)ethene, Pd(PPh₃)₄, 1,4-diethynylbenzene, CuI, PPh₃ were purchased from Aldrich and were used without further purification. Triethylamine (from Aldrich) was dried on NaOH pellets and distilled. All solvents (toluene, DMF) are commercial products and purified before use by distillation. N-(2-ethylhexyl)-2,7-dibromocarbazole (**M1**) was prepared starting by 4, 4'-dibromobiphenyl in three steps according to the reported method³¹ and N-((2-ethylhexyl)-3,6-dibromocarbazole) (**M2**) was synthesized by alkylation of carbazole with 2-ethylhexyl bromide in anhydrous DMF and presence of NaH,³² followed by bromination with NBS, using DMF as solvent.³³

Preparation

1) General procedure for poly (arylenevinylene) (**P1** and **P3**):

In a 50 mL two necked-flask were added monomer (**M1** or **M2**) (0.2 g, 0.45 mmol), *trans*-1,2-bis(tributylstannyl)ethene (0.24 mL, 0.45 mmol), and 10 mL dry toluene. The solution was degassed by nitrogen bubbling for 15 min, and then Pd(PPh₃)₄ (5.2 mg, 0.008 mmol) in dry toluene (2 mL) was added. The reaction mixture was degassed again for 30 min. Then the reaction mixture was heated to 90°C and stirred for 48 h. The mixture was precipitated in methanol, filtrated and dried. Yields: 87.23 % (**P1**), 68.66 % (**P3**).

2) General procedure for poly (aryleneethynylene) (**P2** and **P4**):

In a Schlenk tube were introduced 0.086 g 1,4-diethynylbenzene, 0.02g PdCl₂.2PPh₃ (0.03 mmol), 0.01g CuI (0.06 mmol), 0.017g PPh₃ (0.06 mmol), and 3 mL triethylamine. The mixture was stirred in nitrogen atmosphere at 50-60 °C for an hour after that 0.3 g (0.6 mmol) monomer (**M1** or **M2**) dissolved in 5 mL DMF was added. Then the mixture was stirred at 80 °C when the solution color turned out in time from dirty yellow to reddish-orange and some solids are deposited on the flask's walls. After 24 hr the mixture was precipitated in methanol, filtrated and dried. The polymer was separated in two fractions one is insoluble in chloroform and other one, is soluble in chloroform and insoluble in methanol. Yields: 45.29 % (**P2**), 43.97 % (**P4**).

Measurements

FT-IR spectra were recorded in KBr pellets on a DIGILAB-FTS 2000 spectrometer. ¹H-NMR spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer (400 MHz) as solutions in CDCl₃, and chemical shifts are reported in ppm and referenced to TMS as internal standard. UV-Vis and fluorescence measurements were carried out in CHCl₃ solution (spectrophotometric grade), on a Specord 200 spectrophotometer and Perkin Elmer LS 55 apparatus, respectively. The cyclic voltammograms (CV) were recorded using a Bioanalytical System, Potentiostat-Galvanostat (BAS 100B/W). The electrochemical cell was equipped with three electrodes: a working electrode (disk shape Pt electrode, Φ = 1.6 mm), an auxiliary electrode (platinum wire), and a reference electrode (consisted of a silver wire coated with AgCl). Before experiments, Pt electrode was polished between each set of experiments with

aluminium oxide powder on a polishing cloth, and then was sonicated in a mixture of detergent and methanol for 5 min and then rinsed with a large amount of doubly distilled water. The reference electrode (Ag/Ag⁺) was calibrated at the beginning of the experiments by running the CV of ferrocene as the internal standard in an identical cell without any compound in the system (E_{1/2} = 0.43 V versus the Ag/AgCl). Prior to the each experiment, the Bu₄NBF₄ solutions were deoxygenated by passing dry nitrogen gas for 10 minutes. All measurements were performed at room temperature (25 °C) under nitrogen atmosphere.

CONCLUSIONS

In the present paper, four conjugated polymers with linear structure and having 2,7- and 3,6-disubstituted carbazole units in the main chain, connected by two kind of spacers, vinylene (**P1**, **P3**) and 1,4-phenylene ethynylene (**P2**, **P4**) were prepared. The characterization of the polymers was performed using IR and ¹H-NMR spectroscopy and results are in concordance with the structure of polymers. The optical properties showed that carbazole unit functionalized at the 2,7- positions show better optoelectronic properties than carbazole unit functionalized at the 3,6- positions. Cyclic voltammetry measurements showed that all polymers have the HOMO levels with values in the range of -5.74 and -5.62 eV and can be used in optoelectronic applications.

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