



Dedicated to Professor Bogdan C. Simionescu  
on the occasion of his 65<sup>th</sup> anniversary

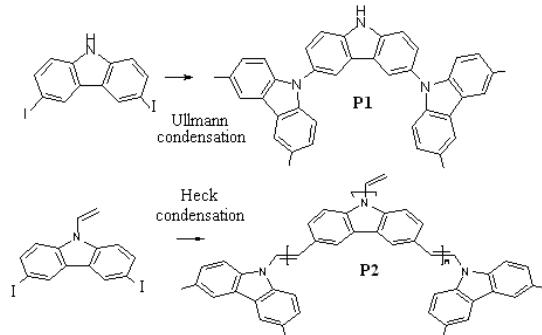
## SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF TWO BRANCHED CARBAZOLE-BASED POLYMERS

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Two branched carbazole-based polymers having arylene- and arylenevinylene-type structure respectively, were synthesized by copper- or palladium-catalyzed self- polycondensation of AB<sub>2</sub> carbazole monomers. The self-Ullmann C-N polycondensation of 3,6-diiodocarbazole led to a branched polymer containing about 15 trisubstituted carbazole (at 3,6 and N-positions) nuclei included in the polymer chain. The self-Heck polycondensation of 3,6-diido- or 3,6-dibromo-N-vinylcarbazole led to a branched polyarylenevinylene with trisubstituted carbazole nuclei at 3,6 and N- positions. Both polymers were amorphous materials and soluble in organic solvents and their optical and electrochemical properties were comparable with those of similar polymers with linear structure.



### INTRODUCTION

There is a considerable interest in conjugated polymers due to their applications in many electrical and optoelectronic devices,<sup>1</sup> such as organic photoconductors,<sup>2,3</sup> organic light emitting diodes,<sup>4-9</sup> field effect transistors,<sup>10,11</sup> solar cells,<sup>12-14</sup> sensors and protective coatings against oxidizing agents or electromagnetic waves, etc.<sup>1</sup>

Carbazole is a heterocyclic compound that has been used in the synthesis of many monomers because: (a) is a cheap raw material obtained from distilling of coal, (b) can be easily functionalized at nitrogen atom or 3,6 positions or in more special conditions at 2,7 positions allowing to obtain polymers with various structures<sup>15</sup> (c) has

a low ionization potential and can form cation-radicals, and (d) polymers have a good thermal and photochemical stability.<sup>3</sup> Carbazole-based polymers, such as poly(N-vinylcarbazole), are very known due to their photoconducting properties and high electron-donating character and have been used in xerography.<sup>2</sup> Polymers are good hole-transporting materials with interesting electro-optical and photochemical properties as well as high thermal stability due to the conjugated system.<sup>3</sup> In the most polymers, carbazole moieties were positioned as N-substituted groups. Other conjugated polymers containing carbazole ring linked in the main polymer chain by 3 and 6 positions, i.e. poly(3,6-carbazoles), have been synthesized in the last years by chemical or electrochemical oxidation<sup>16-21</sup>

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while poly(2,7-carbazoles) have been synthesized by multi-step methods.<sup>22-25</sup> On the other hand, dendrimers containing carbazole units have also synthesized using more laborious methods and studied as electronic materials for OFET, sensors, OLED, etc.<sup>26-34</sup> Recently, Li *et al.* have synthesized hyperbranched carbazole-based polymers by coupling reactions using mixtures of monomers through A<sub>4</sub>+B<sub>2</sub> or AB<sub>2</sub>+A<sub>2</sub>+B<sub>2</sub> approaches.<sup>33,35</sup> These methods are more convenient and facile because they use one-pot and single reaction procedure.

Previously, we have synthesized for other purposes vinyl monomers, 3,6-dihalogeno-N-vinyl carbazole and its intermediate, 3,6-dihalogeno-NH-carbazole. These compounds could be considered also as AB<sub>2</sub> monomers for Heck and respectively, Ullmann self-condensation reactions. The aim of this communication is to present two simple and direct methods for synthesis of carbazole-based branched polymers by copper- or palladium-catalyzed condensation of the two monomers and some photophysical properties of branched polycarbazoles and polycarbazolylvinylanes.

## RESULTS AND DISCUSSION

The two starting AB<sub>2</sub> monomers, 3,6-diido 9H-carbazole and 3,6-diido N-vinylcarbazole or (3,6-dibromo N-vinylcarbazole), were obtained by iodination (bromination) of carbazole at reactive positions 3 and 6. The vinyl group was introduced by intermediate of dihalogenated β-hydroxyethylcarbazole derivatives (obtained using ethylene oxide), followed by changing of the -OH group with chlorine and finally, dehydrochlorination with

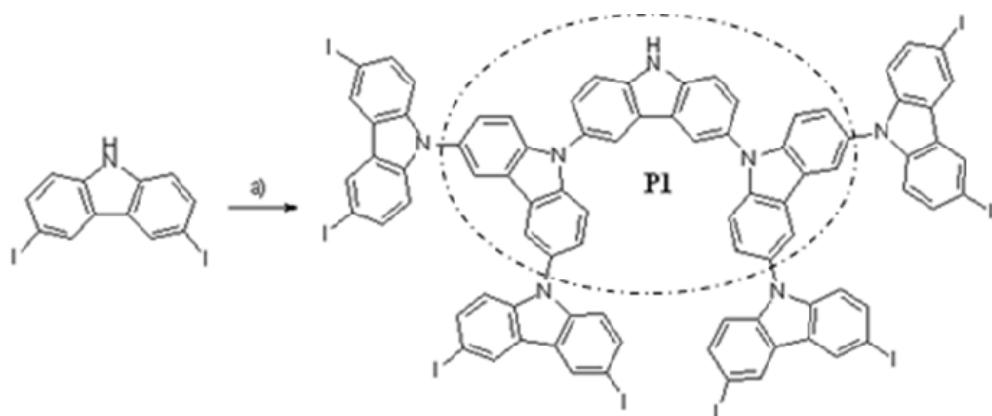
KOH. The spectral data have confirmed the structure and purity of the monomers.

The branched N-carbazolyl 3,6-diyl polymer (**P1**) was synthesized by the self-Ullmann C-N coupling reaction of 3,6-diido 9H-carbazole in dry decalin using copper powder/KOH as catalyst and 18-crown-6 as phase transfer agent (according to Scheme 1). The polymer has a molecular weight: Mn= 3665; Mw=5880; PDI= 1.60, which corresponds to about 15 carbazole units linked in the branched molecule.

The branched vinylcarbazole polymer (**P2**) was synthesized by a Heck self-condensation using 3,6-diido N-vinylcarbazole or 3,6-dibromo N-vinylcarbazole and two palladium catalysts [Pd(OAc)<sub>2</sub> and PdCl<sub>2</sub> (PPh<sub>3</sub>)<sub>2</sub>]. The best yields were obtained using diido monomer and Pd(OAc)<sub>2</sub> as catalyst. It is evidently that 3,6-dibromo N-vinylcarbazole consistently gave lower yields of branched polymer under analogous conditions used for diido derivative due to lower reactivity of bromine vs iodine derivatives in Heck condensations. The iodine ends were capped with N-vinylcarbazole when an oligomer with Mn=7000, Mw=25000; PDI = 3.57 was obtained (Scheme 2).

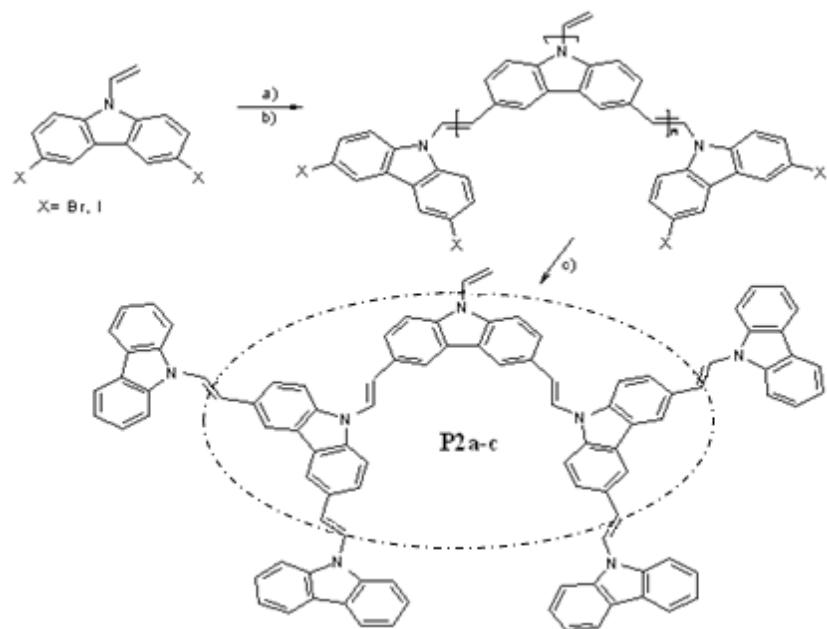
For comparison, a linear 3,6-(N-hexyl)carbazolyl vinylene polymer (**P3**) (Scheme 3) was used and its synthesis was previously presented.<sup>36</sup>

The <sup>1</sup>H-NMR spectra of the branched carbazole polymer **P1**, (Fig. 1) showed aromatic protons on a wide range (6-8.5 ppm) due to both of the branched and random structure and hindered rotation and shielding effects, associated with the bulkiness of carbazole groups. A broad slight signal at about 9.1-9.2 ppm could be assigned to –NH- protons from some linear 3,6-disubstituted carbazoles units.

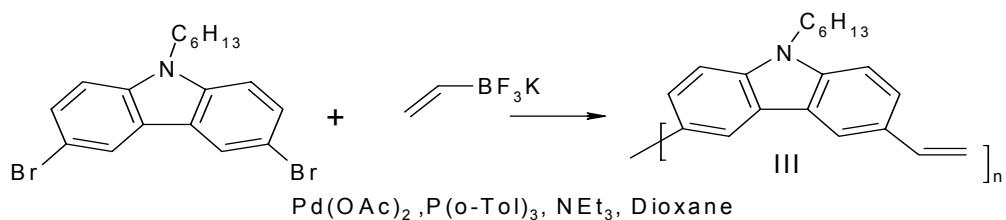
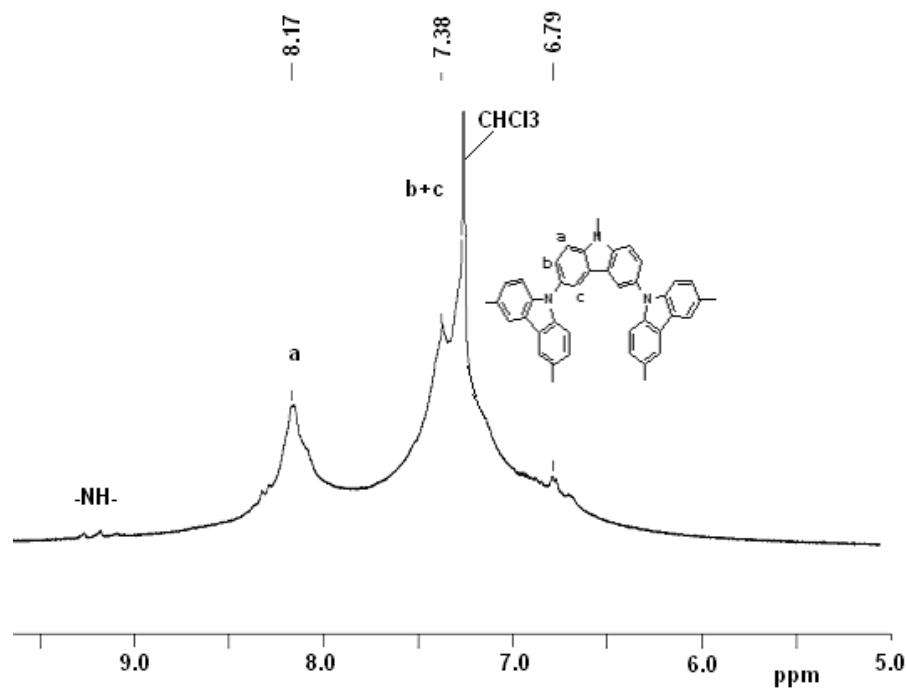


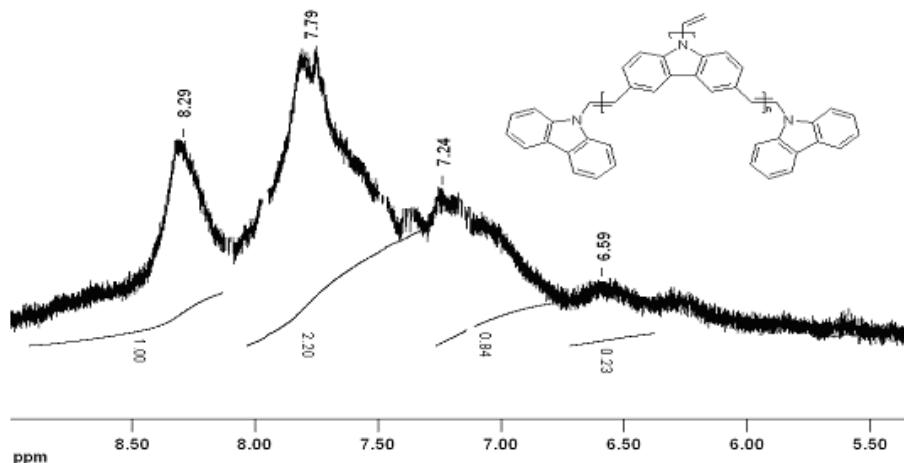
Scheme 1 – Synthesis of branched N-carbazolyl 3,6-diyl oligomer **P1**.

<sup>a</sup> Reagents and conditions: decalin, copper powder, KOH solid, 24 hr, 170 °C, nitrogen.

Scheme 2 – Synthesis of branched vinylcarbazole polymers **P2**.

Reagents and conditions: (a)  $\text{Pd}(\text{OAc})_2$ ,  $\text{P}(\text{o-tol})_3$ ,  $\text{DMF}$ ,  $\text{NEt}_3$ , reflux, 24 hr, (b)  $\text{PdCl}_2(\text{PPh}_3)_2$ ,  $(\text{nBu})_4\text{NI}$ ,  $\text{K}_2\text{CO}_3$ ,  $100^\circ\text{C}$ , 27 hr (c)  $\text{NVK}$ ,  $100^\circ\text{C}$ , 8 hr.

Scheme 3 – Synthesis of linear poly(N-hexyl)carbazolyl vinylene oligomer **P3**.Fig. 1 –  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz) of **P1**.

Fig. 2  $^1\text{H}$ -NMR spectrum ( $\text{CDCl}_3$ ) of **P2c**.

The  $^1\text{H}$ -NMR spectra of branched vinylene carbazole polymer (Fig. 2) showed also aromatic protons together vinylene protons on a wide range (5-8.5 ppm) assigned to aromatic and vinylene protons. These two spectra have reminded about the spectrum of poly(N-vinyl carbazole), where also signals were observed in the aromatic region, between 5-8.5 ppm which correspond to aromatic protons shifted at high field due to shielding effect introduced by bulky carbazole groups.<sup>37</sup>

The optical properties of oligomers were investigated by UV-Vis and fluorescence spectroscopy in diluted N,N'-dimethylformamide solution. Typical spectra of some polymers are presented in Fig. 3. All polymers showed wide absorptions between 250-500 nm, small red-shifted compared to those of the starting monomers, with maxima at 282, 290 and 330 nm for **P1**, 286, 293, 330 and 340 nm for **P2** and 320, 334, 400 (sh) for **P3**. This behavior is explained by extension of conjugation from monomers to polymers, however the conjugation is limited due to the torsion angle between carbazole rings induced by high sterical hindrances. The UV absorption edge of **P2** is positioned at longer wavelength than those of **P1**. The vinyl linkage as a spacer between carbazole rings has reduced the sterical hindrances and allowed a better conjugation between them. The linear polymer (**P3**) has a more distinct peak at 334 nm with a shoulder at 400 nm because has a less random structure.

The emission spectrum of **P1** has almost a symmetrical shape with a maximum at 385 nm while spectra of **P2** and **P3** are asymmetrical, red-shifted vs spectrum of **P1**, having maxima at 365, 385 and 420 (shoulder) nm for **P2b**, 370, 410 (sh.) and 440 nm for **P2a**, 425 and 443 nm for **P3**. Poly(N-vinylcarbazole) shows fluorescence emission peaks at 350, 370 and 420 nm which corresponds to the monomer fluorescence, the

partial overlap excimer and the sandwich excimer.<sup>38</sup> Based on these assumptions we can suggest that in **P1** the fluorescence is mainly due to the carbazole rings in non-aggregated state, the branched and crowded structure doesn't allow formation of excimer aggregates. The presence of vinylene linkages between carbazole moieties reduces sterical hindrances and allows formation of both types of excimers in **P2** and **P3**.

Cyclic voltammetry is a very useful method that reveals the electron transfer during the electropolymerization and also evidences the redox properties of the electroactive polymer films. The electrochemical behaviour of three polymers **P1**, **P2** and **P3**, as solid thin film deposited on the platinum electrode surface from chloroform solution was studied (Fig. 4). The cyclic voltammograms of polymer **P1** revealed that the oxidation process of the polymer starts at 1.297 V and an anodic peak appears at 1.606 V, which corresponds to the oxidation of the carbazole units at nitrogen sites and doping. On the reverse scanning, **P1** exhibits a reduction process of oxidised species and dedoping, all process being reversible. On the other hand, an effect of the cycle numbers on the peak intensity is observed, the film becomes less electroactive, which is probably linked to less ingress of tetrafluoroborate anions from the electrolyte to compensate for the positive doping charge. A very similar behaviour was observed for **P2** that shows a reversible redox process with an oxidation peak at 1.567 V, and a decrease of the current intensity as the cycle numbers increases. The linear carbazole-based polymer (**P3**) is characterized by two oxidation peaks at 1.206 V and 1.755 V, and the reduction peaks can not be clearly localized. A crosslinking of the polymers during the electrochemical studies was not observed because carbazole groups are substituted at reactive positions (3 and 6).

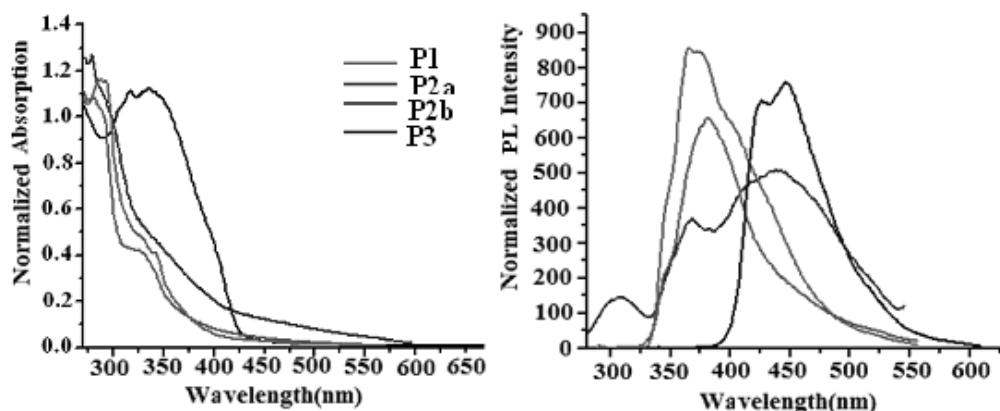


Fig. 3 – UV-Vis absorption (a) and photoluminescence (b) spectra of polymers **P1-P3** ( $10^{-5}$  mol/l) in diluted DMF solution.

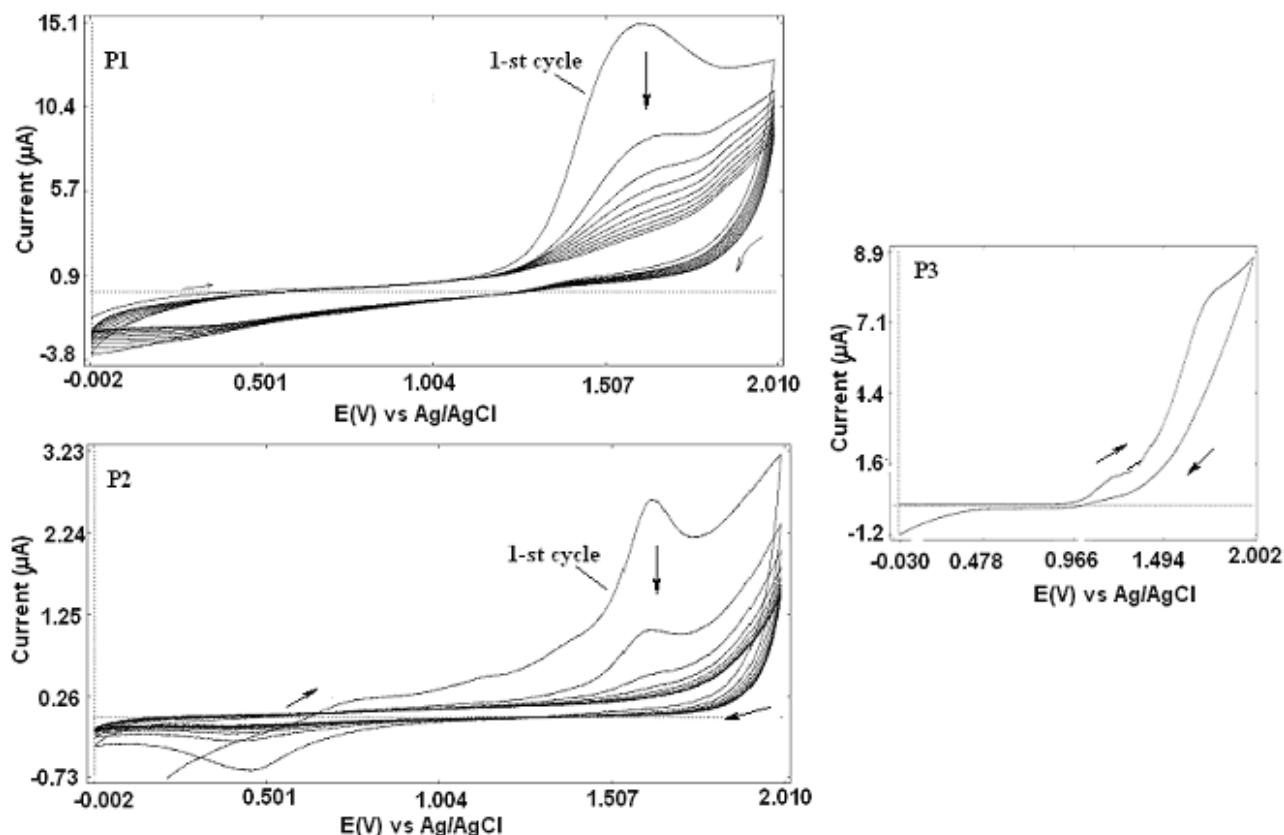


Fig. 4 – Cyclic voltammograms of **P1**, **P2** and **P3** using  $\text{Bu}_4\text{NBF}_4$  as support electrolyte ( $10^{-1}\text{M}$ ). Scan rate: 50 mV/s.

## EXPERIMENTAL

### Materials

N,N-Dimethylformamide (Aldrich) was dried by distillation over  $\text{CaH}_2$ . Triethylamine (Aldrich) was dried by maintaining a week over KOH and distillation on  $\text{CaH}_2$ . Palladium (II) acetate, tri-o-tolylphosphine, and copper powder are from Aldrich source. Other reagents and solvents were commercially purchased and used as received.

3,6-diido-9H-carbazole was synthesized from carbazole by iodination using  $\text{KIO}_3/\text{KI}$  and recrystallized from absolute ethanol, according to the method of Tucker.<sup>39</sup>  $M_p = 215\text{-}216^\circ\text{C}$ .

3,6-Diido N-vinyl carbazole was synthesized by dehydrochlorination of  $\beta$ -chloro-N-ethyl-3,6-diiodocarbazole.<sup>40</sup> Yield= 89 %.  $M.p.=189\text{-}190^\circ\text{C}$ .

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 8.28 (s, 2H,  $\text{H}_4$ ), 7.72 (d, 2H,  $\text{H}_2$ ), 7.38 (d, 2H,  $\text{H}_1$ ), 7.16 (m, 1H,  $-\text{CH}=$ ) and 5.54 and 5.24 (d, 2H, trans and cis  $=\text{CH}_2$ )

FT-IR: 800 (v C-H aromatic 1,2,4-trisubstituted benzene), 1640 (v  $\text{C=C}$  vinyl)

3,6-Dibromo N-vinylcarbazole was synthesized by dehydrochlorination of  $\beta$ -chloro-N-ethyl-3,6-dibromocarbazole.<sup>40</sup> Yield = 78.4%.  $M.p.=152\text{-}154^\circ\text{C}$

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 8.08 (s, 2H,  $\text{H}_4$ ), 7.50-7.55 (m, 4H,  $\text{H}_2$  and  $\text{H}_1$ ), 7.16 (m, 1H,  $-\text{CH}=$ ) and 5.53 and 5.25 (d, 2H, trans and cis  $=\text{CH}_2$ )

FT-IR: 800 (ν C-H aromatic 1,2,4-trisubstituted benzene), 1640 (ν <sub>c=c</sub> vinyl)

3,6-Dibromo-N-hexyl carbazole was synthesized by alkylation of carbazole with *n*-tetradecylbromide in dried acetone, followed by bromination with NBS, using DMF as solvent.

<sup>1</sup>H-NMR (400 MHz, ppm, CDCl<sub>3</sub>): 8.12 (s, 2H), 7.53 (d, 2H), 7.24 (d, 2H), 4.21 (t, 2H, -N-CH<sub>2</sub>-), 1.81 (t, 2H, -N-C<sub>2</sub>H<sub>5</sub>-), 1.24 (m, 6H, -(CH<sub>2</sub>)<sub>3</sub>-), 0.87 (t, 3H, -CH<sub>3</sub>).

#### Synthesis of branched carbazole oligomer (P1) by self-Ullmann condensation of 3,6-diiodo-9H-carbazole

3,6-Diiodo-9H-carbazole (0.838g, 2 mmol), decaline (15 ml), powdered anhydrous KOH (1.344 g, 24 mmol) and copper powder (1.2 g) and 18-crown-6 (25 mg) were introduced sequentially into a Schlenk tube under nitrogen atmosphere and the resulting mixture was refluxed for 24 h. The inorganic compounds were removed by filtration and the filtrate was poured into a large amount of methanol to precipitate a brown polymer. The precipitate was filtrate, dried and purified by dissolving in chloroform and precipitation with methanol. Yield = 52.1%

#### Synthesis of branched vinylcarbazole polymer (P2a-c) by Heck polycondensation

**P2a:** 0.15 g 3,6-Diiodo N-vinyl carbazole, 0.113 g Pd(OAc)<sub>2</sub>, 0.154 g tri-*o*-tolylphosphine, 5 mL triethylamine and 5 mL N,N-dimethylformamide were introduced in a 25 mL two-necked round bottom flask. The red-brown mixture was stirred at 80 °C for 24 hr under nitrogen atmosphere. After 24 hr, 0.1 g N-vinylcarbazole was added to the reaction mixture (for capping the iodine atoms) and the reaction was carried out for another 8 hr. The mixture was cooled at room temperature and poured into a large amount of methanol and the precipitate was collected by filtration and dried at 40 °C *in vacuo* to afford polymer **P2a**. Yield: 83.4%

**P2b:** 3,6-Diido N-vinyl carbazole (0.1706 g), 0.0137 g PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 0.161 g tetrabutylammonium iodide and 0.0083 g K<sub>2</sub>CO<sub>3</sub> were introduced in a round bottom flask, in nitrogen atmosphere, and 5 mL dried DMF were added. The mixture, orange colored, was stirred and maintained at 100 °C for 27 hr. After 27 hr, 0.1 g N-vinylcarbazole was added to the reaction mixture and the reaction was carried out for another 8 h. The polymer was separated by precipitation in methanol. The product was precipitated into methanol several times. Yield = 0.0588 g.

**P2c:** 3,6-Dibromo N-vinylcarbazole (0.272 g), 0.0275 g PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 0.323 g tetrabutylammonium iodide, 0.129 g K<sub>2</sub>CO<sub>3</sub> and 7 mL DMF were introduced in a round bottom flask and stirred at 100 °C for 27 hr. The green solution was cooled and poured into methanol. The oligomer traces were filtrated and dried. Yield = 0.0244 g.

#### Synthesis of linear vinyl carbazole polymer (P3)

A mixture consisting of 0.5 g (1.22 mmol) of 3,6-dibromo-*N*-hexyl carbazole, 0.174 g (1.2987 mmol) of potassium vinyltrifluoroborate, 0.0145 g (0.065 mmol) of Pd(AcO)<sub>2</sub>, and 0.0987 g (0.3245 mmol) of P(*o*-Tol)<sub>3</sub>, 5 ml triethylamine and 10 ml dioxane were introduced in a 25 mL two-necked round-bottom flask. The reaction mixture was refluxed for 24 h. After cooling to room temperature, the solution was poured into a large amount of methanol (100 mL).

The obtained solid was filtered off and dried and then dissolved in a minimum amount of chloroform and reprecipitated in methanol, leading to a solid product as a yellow-orange powder with 67.7% yield. The molecular weight is Mn=22850 and DP<sub>I</sub>=1.47.

#### Characterization

UV-visible and fluorescence measurements were obtained on a Specord M42 Carl Zeiss Jena spectrophotometer using quartz cells (10 mm) and a Perkin Elmer LS 55 apparatus (Perkin Elmer, Norwalk, CT, USA), in N,N dimethylformamide solutions. <sup>1</sup>H-NMR spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer (400 MHz) in CDCl<sub>3</sub> with TMS as internal standard. The reported melting points were determined on a Boetius microscope and are uncorrected. The relative molecular weights were determined by gel permeation chromatography (GPC) using polystyrene standards for the calibration plot and N,N'-dimethylformamide as solvent. 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). Polymer films were deposited on working electrode from chloroform solution and solvent removed at room temperature and films were dried in *vacuo*. 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<sup>+</sup>) 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<sub>1/2</sub> = 0.425 V versus the Ag/AgCl). Prior to the each experiment, the Bu<sub>4</sub>NBF<sub>4</sub> solutions in acetonitrile were deoxygenated by passing dry argon gas for 10 minutes. All measurements were performed at room temperature (25 °C) under argon atmosphere.

#### CONCLUSIONS

In summary, two novel branched, amorphous and soluble carbazole-based polymers have been synthesized by copper-catalyzed Ullmann condensation of 3,6-diiodocarbazole and palladium-catalyzed Heck polycondensation of 3,6-diiodo- or 3,6-dibromo-*N*-vinylcarbazole. The synthesis is very simple, in a single step method. The characterization of the synthesized polymers was performed using <sup>1</sup>H-NMR spectroscopy and the obtained data are in accordance with the polymer structure, while the electronic properties were studied by UV-Vis and photoluminescence spectroscopy and cyclic voltammetry. The polymers are soluble in most common organic solvents and can be deposited as thin films on supports for electronic applications.

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