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The effect of cross-linking yield of PVK on the vibrational and emissive properties of new copolymer based on vinylcarbazole and phenylene-vinylene units

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The Phenylene-Vinylene (PV) unit's was successfully incorporated in the Vinylarbazole (VC) skeleton using the oxidative way via an anhydrous $FeCl_3$. Dramatic changes in the vibrational and emissive properties are founded by varying the $FeCl_3$ amount in the synthesis way due to the cross-linking of PVK units. SEM analysis showing a modified morphology structures of three compounds. However the percentage of the oxidant account induces the modulation of copolymer properties particularly theirs emissive proprieties. A red shifting of the maximum of photoluminescence, a quenching of luminescence and a fast decay time was observed with increasing of the oxidation yields.

1. Introduction

Block copolymers have attracted an increasing amount of attention in recent years for various organic electronic devices because of their potential advantages [1]. Chemists can design and synthesize a variety of conjugated polymers with different architectures and functional moieties to meet the requirements of these organic devices. One particular approach was the application of donor (D) acceptor (A) system to steer the HOMO and LUMO levels, as well as the band gap of the resulting copolymers, which is an efficient strategy for tailoring the properties of conjugated polymers for nanotechnological applications [2,3]. Their applicability to optoelectronic devices stems from the convenient tunability of properties for example by cross-linking [4,5], and from periodicity related to changing their molecular parameters. Copolymers are widely used for application in the optoelectronic fields in order to benefit from complementary properties [6,7] or to promote specific original optoelectronic behavior [8]. The optoelectronic properties still depends on charge transfer and conjugation length [1,9]. However, for several years we have seen the development of a wide variety of organic copolymers with an interesting properties. In the recent years the non-conjugated poly(*N*-vinylcarbazole) (PVK) stills one of the most widely studied organic semiconductors on account of their photoconductive properties and ability to form charge transfer complexes arising from the electron donating character of the carbazole moiety [10,11]. In the other hand the PPV is the famous polymer used in the optoelectronic devices [12,13] which are very renowned semiconducting polymers and widely applied in OLED. A copolymer strategy consisting in the insertion of PPV block in the *N*-heterocycles is relevant for the design of new conjugated systems. Thus, combining PPV blocks with carbazole units, in a copolymer is particularly attractive to benefit from both the efficient emission feature of PPV and the high hole mobility of PVK. The cross-linking reactions of PVK can be performed by the oxidative way using the anhydrous $FeCl_3$ as oxidant by the radical formation in the benzene ring [14,15]. Here, we study the effect of the degree of the PVK cross-linking as a function of the $FeCl_3$ amount. In this context, we report the elaboration of copolymers based on the PVK and PPV units including the degree of PVK cross-linking. Three copolymers are synthesized by the same way but the difference between these latters is the different yield of oxidative cross-linking of PVK using $FeCl_3$ (250, 750 and 1000 mg). In order to establish better structure properties correlation of the resulting copolymers, some techniques including Infrared and Raman

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spectroscopies, Scanning Electronic Microscopy (SEM), stationary photoluminescence and transient photoluminescence, are performed. To make easy reading of the present paper, we recall briefly the synthesis of PVK-PPV copolymer previously reported [16].

2. Experimental part

2.1. Materials

Poly (9-vinylcarbazole) (PVK) powder (Mw = 1.100.000), ferrichloride (FeCl3), chloroform, methanol, and hydrazine for the synthesis process of the studied copolymers were used as received. The PPV precursor was prepared by addition of 33 ml of tetrahydrothiophenium in the dichloroparaxylene dissolved in methanol. The PPV precursor aqueous solution was dialyzed with the deionized water for several days. The PPV precursor was conserved at 0 °C and in darkness. The concentration of the PPV precursor is about 2.4 mg/ml.

2.2. Preparation of PVK–PPV copolymers

As said before we will recall briefly the synthesis of PVKPPV copolymer. Around 30 mg of PVK were dissolved in 10 ml of $CHCl_3$ and 250 mg of anhydrous $FeCl_3$ were added to this solution. 12.5 ml of PPV precursor were kept in the methanol solvent. The mixture was reserved with agitation in darkness and in an ice bath for three days. The system was kept under reflux at 55 °C for 3 h and washed thoroughly with methanol. The obtained solution was dried under vacuum for 1 h at 80 °C. The resulting copolymers were annealed at T = 200 °C for 3 h under secondary vacuum nearly $4.6 \cdot 10^{-6}$ mbar to ensure the full removal of THT groups, as tetra-hydrothiophene groups (THT) of PPV precursor is known to be removed within a temperature range from 75 °C to 125 °C [17]. The simple EDX analysis before and after annealing the copolymers showing disappearing of PPV precursor (THT) groups (Scheme 1). By increasing the oxidative yield (250, 750 and 1000 mg of $FeCl_3$) the polymerization yield of PVK-PPV was evaluated to be respectively 54.1%, 58.1% and 64%. This increase is due to the PVK cross-linking and the obtained copolymers are named respectively copolymer (a), copolymer (b) and copolymer (c) for 250, 750 and 1000 mg of $FeCl_3$ amount used for each synthesis.

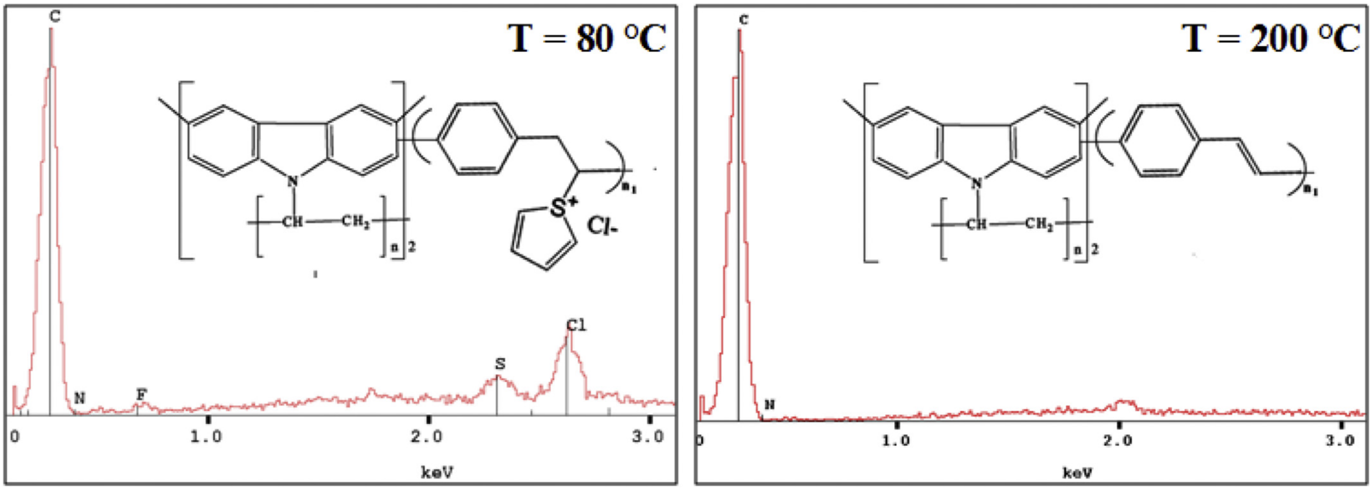
2.3. Experimental

Infrared spectra were obtained with a Brüker Vector 22 Fourier transform spectrophotometer. Samples were prepared in pellets of KBr mixed with the organic compound under study. Raman spectra were registered on a Fourier transform spectrophotometer Brüker RFS 100, using a laser wavelength of 1064 nm with a low puissance of 50 mW. The scanning electron micrography pictures are carried out using the microscope JEOL 6400F which is equipped with a source with field effect making the possibility to obtain an electron beam of a very large smoothness and to thus reach a space resolution of a few tens of nanometers. The diffraction patterns were obtained with a SIEMENS 5000 diffractometer (wavelength Cu Kalpha 40 kV, 30 mA) in Bragg Brentano geometry, the X-ray wavelength (λ = 1.5405 Å). Optical density measurements were carried out at room temperature (RT) using a Cary 5000 spectrophotometer, in the range 200–2200 nm. Continuous-wave (cw) photoluminescence (PL) measurements were collected on a Jobin-Yvon Fluorolog 3 spectrometer using a Xenon lamp (500 W) at room temperature. Time-resolved photoluminescence (TR-PL) experiments, at RT were acquired with a regenerative amplified femtosecond Ti: Sapphire laser system (Spectra Physics Hurricane X). This setup generates 100 fs pulses at 800 nm with a repetitive rate of 1 kHz and a power of 1 W. The laser line is frequency-doubled with a thin BBO crystal to obtain an excitation line λ_{exc} = 400 nm (3.1 eV). The pump energy pulse is controlled to ensure that the excitation density in the sample did not exceed 1017 cm^{-3}, to avoid bimolecular annihilation process and sample photodegradation. TR-PL-3D-maps were obtained with energy emission versus time (range 0–1.2 ns) and intensity in false color. The emission spectra were temporally resolved with a high dynamic range Hamamatsu C7700 streak camera coupled to an imaging spectrograph with a temporal resolution <20 ps and processed using the HPDTA Hamamatsu software.

3. Results and discussion

3.1. IR measurements

All spectra are normalized using the 1485 cm^{-1} band of PVK as reference. The recorded spectra are shown in Fig. 1. This figure represents the absorbance bands of PVK in all copolymers with respect of some absorbance bands of PPV. Firstly, the modification of the intensity ratio between the IR bands in the case of



Scheme 1. EDX analysis before and after annealing treatment.