



Characterization of new materials poly(Ethylcarbazol-Terphenyl) (PEcbz-Ter) synthesized using AlCl₃ as an oxidant for optoelectronic applications

H. Sadki¹, M. N. Bennani¹, M. Mbarek², K. Alimi², M. Bouachrine^{3*}

¹ Laboratoire de Recherche «Chimie-Biologie appliquées à l'environnement», Faculté des Sciences, Université Moulay Ismail, Meknès, Morocco

² Unité de Recherche, Laboratoire de Matériaux Nouveaux et Dispositifs Electroniques Organiques (U11ES55), Faculté des Sciences, Université de Monastir, Monastir, Tunisia

³ MEM, Ecole Supérieure de Technologie (ESTM), Université Moulay Ismail, Meknès, Morocco

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*Corresponding author: E-mail: bouachrine@gmail.com; (Tel: 00212660736921)

Abstract

In this paper, we report the synthesis and characterization of a new material based on Poly(9-Ethylcarbazole) (PEcbz), and Poly(p-Terphenyl) (PTer); conjugated copolymer containing carbazole moieties either in the main or side chains have attracted much attention because of their unique electronic properties, their high photoluminescence quantum efficiency, and thermal stability. This copolymer was prepared by oxidative copolymerization of PEcbz in the presence of p-Terphenyl monomers in chloroform with anhydrous AlCl₃. First, we describe the route for preparing the new copolymer. Then, we report characterization measurements based on solid state IR absorption, UV-visible absorption, Nuclear Magnetic Resonance (¹³C NMR), photoluminescence spectroscopy (PL), and time resolved photoluminescence decays (PLRT).

Keywords: PEcbz-Ter; IR, UV-Vis- absorption; ¹³C RMN; PL, opto-electronic.

1. Introduction

Recently, more attention has been focused on the organic conducting polymers. Due to their specific properties; these compounds are widely used for opto-electronic device applications, such as organic light emitting diodes (OLEDs) [1-2], field-effect transistors [3-5] (OTFTs), photovoltaic cells [6-8], portable electronic [9], lasers [10-11]. One of the most important factors of controlling physical properties is the band gap, which is a current topic of research. Polymers with a low band gap are desired in optoelectronic applications such as LEDs or solar cells [12].

One of the most important conjugated polymers which allow a very flexible structure and promising properties are copolymers which contain both carbazole and derivatives (Figure 1) and p-Terphenyl (Figure 2) units. This material has proved to be of interest in combining the properties associated with the two different conjugated rings [13] and have attracted much attention because of their unique electronic properties, to their high photoluminescence quantum efficiency, and thermal stability. This family of materials can be prepared by electrochemical or chemical polymerization [14-15]. The necessity of finding new organic materials has caused great concern in scientific community, in this regard. In order to understand well the optical and electronic properties and hence the improvement of such devices in which conjugated polymers are used as active layers, IR spectra can provide structural information. On the other hand, photoluminescence can often be greatly enhanced by increasing the intrinsic stiffness of a polymer backbone or by inducing large bulky side groups to weaken intermolecular interactions. The emission spectrum of a conjugated polymer depends basically on its π - π^* band gap, which can be tailored using different structures [16]. In this paper we present a combined experimental study of the structure, optical and spectroscopic properties of a new copolymer (PEcbz-Ter) based on Poly(9-Ethylcarbazole) (PEcbz), and Poly(p-Terphenyl) (PTer). Then, we report a different characterization IR absorption, UV-visible absorption, Nuclear Magnetic Resonance (¹³C NMR), photoluminescence spectroscopy (PL), and time resolved photoluminescence decays (PLRT).

This work is focused on the characterisation of PEcbz-Ter copolymer using vibrational and optical analysis in order to investigate its properties for an adequate optoelectronic application.

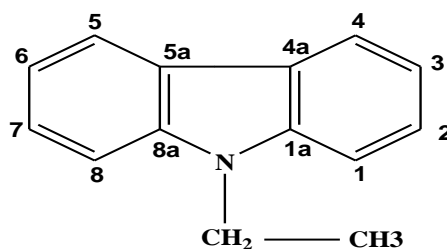


Figure 1: The chemical structure of Poly(9-Ethylcarbazole) (PEcbz).

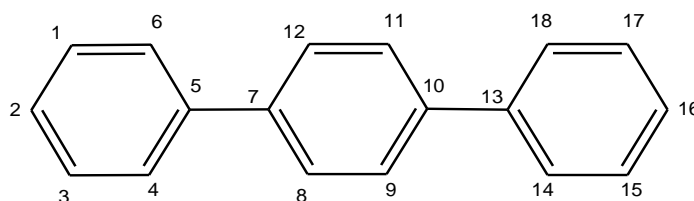


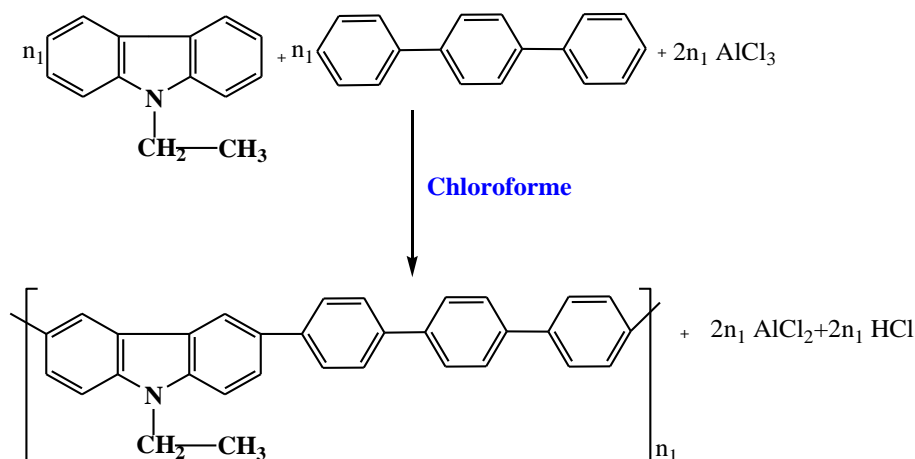
Figure 2: The chemical structure of p-Terphenyl (Ter).

2. Experimental methods

Poly(9-Ethylcarbazole) (PEcbz) powder (97%), p-Terphenyl (Ter) (99%), aluminum chloride Anhydrous (AlCl_3), chloroform CHCl_3 (99%), methanol CHOH (99,9%), used for the synthesis of the studied compounds were purchased from Aldrich chemistry, A Fisher Scientific International and Riedel-deHaën and were purified before use by usual procedures. In this work, the copolymer (PEcbz-Ter) is dissolved and oxidatively polymerized with AlCl_3 . The solvent was Chloroform (HPLC grade). 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. NMR spectra were acquired at room temperature (RT) using a Brüker Avance 500MHz spectrometer operating at 125.7 MHz for ^{13}C , using a 4-mm double-bearing Brüker probehead. All rotors were spun under a dry nitrogen flow. Spectra were referenced to tetramethylsilane (TMS) for ^{13}C (using adamantane as a secondary reference). NMR spectra were acquired using a ramp-amplitude sequence [17], a 2 ms contact time, a repetition time of 2 s and a 15 kHz MAS spinning rate. Continuous-wave (cw) photoluminescence (PL) measurements were collected on a Jobin-Yvon Fluorolog 3 spectrometer using a Xenon lamp (500W) at room temperature. To make paper easy to read, we recall briefly the ultrafast time resolved photoluminescence experiments which were carried out with the regenerative amplified femtosecond laser system installed in University of Nantes. This setup delivers 100 pulses at 1 kHz, 800 nm, and 1 W. Samples were excited at wavelength $\lambda_{\text{exc}} = 400$ nm. The time-resolved emission spectra were spatio-temporally detected with a high dynamic range Hamamatsu C7700 streak camera of temporal resolution <20 ps.

3. Synthesis procedure of the copolymer PEcbz-Ter

The polymerization was been developed by a single procedure to prepare a mixture of PEcbz with p-Terphenyl monomers (Scheme 1). The procedure adopted was to cross link PEcbz by reacting CHCl_3 solution of PEcbz with anhydrous AlCl_3 and to add a known amount of p-Terphenyl with undergo polymerization, and the resulting PTer would subsequently participate in copolymer formation process. The detail of PEcbz-Ter preparation are as follows: 1.95g of Poly(9-Ethylcarbazole) was dissolved in approximately 100 mL of CHCl_3 , and 1.33g of anhydrous AlCl_3 dispersed in 50 mL of CHCl_3 were successively added to the dispersion under stirring. The colour of the solution changed from colourless to dark green, suggesting the oxidation of PEcbz and it's cross-linking. Then 0.23g of p- Terphenyl was added to the mixture. The system was kept under stirring at room temperature for 3 days. Then, an excess of methanol (600–800 mL) was added to the solution for 12 h to remove residual AlCl_3 . The solution was filtered and about 8.6g of a green mass was collected and kept firstly under pressure for 30 min then under vacuum at 80 °C for 48 h. A black powder was obtained in the fully oxidative (doped) state.



Scheme 1: Synthesis of the PEcbz-Ter.

4. Result and discussion

4.1. Infrared results

Figure 3 displays experimental normalized infrared spectrum of the PEcbz-Ter powder in the range of 500-3600 cm^{-1} .

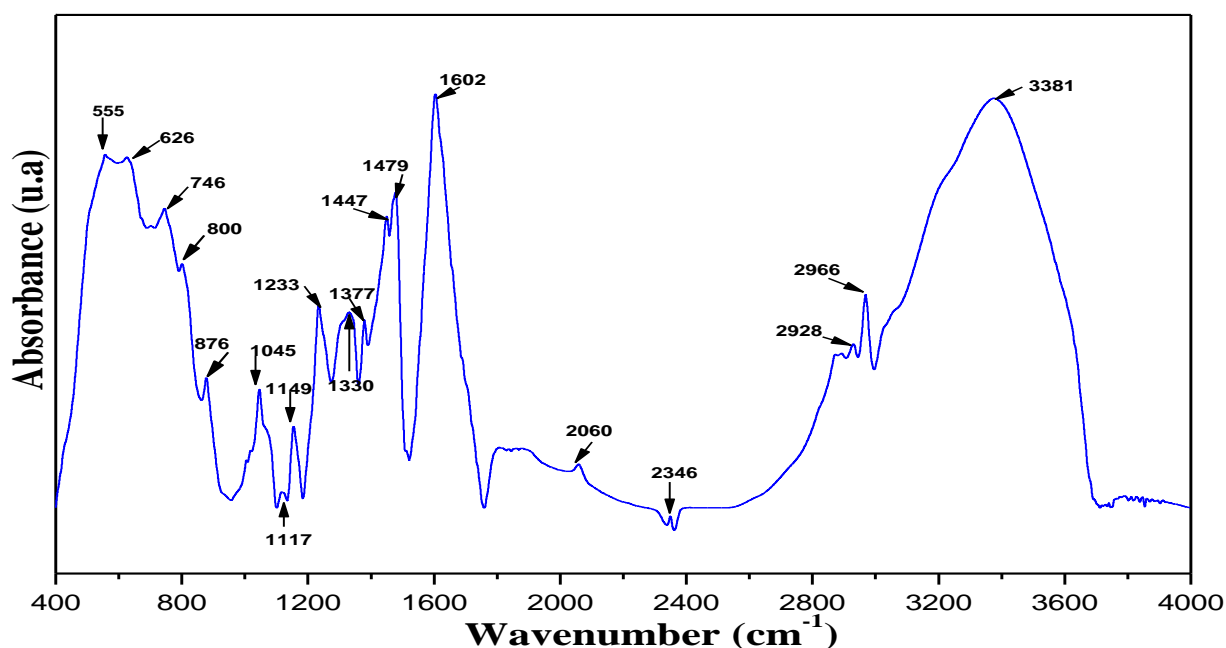


Figure 3: Experimental normalized infrared spectra of PEcbz-Ter copolymer.

The results are depicted in Table 1. Furthermore, two important peaks located at 1454 and 1479 cm^{-1} . These bands were assigned to the aromatic ring and CH_2 rocking of Cbz moiety, respectively, and probably originated from isolated fractions of Cbz units. The combined results show the presence of bands characteristic of PEcbz centered at (746 cm^{-1} , 876 cm^{-1} , 1045 cm^{-1} , 1233 cm^{-1} , 2966 cm^{-1}), which proves that PEcbz is partially cross-linked. More the spectrum IR of PEcbz-Ter show the essential bands characteristic of PTer located at (555 cm^{-1} , 626 cm^{-1} , 1149 cm^{-1} , 1330 cm^{-1} , 1377 cm^{-1} , 1454 cm^{-1} , 1479 cm^{-1} , 1602 cm^{-1}). Finally, when we compare the infrared results of PEcbz-Ter copolymer, we note the presence of the main characteristic bands of the PEcbz, as well as those of PTer. The whole vibrational analyses supported the copolymerization reaction of PEcbz by polymerized of the PEcbz and its grafting into the Skelton of PTer yielding a new compound alternating Ecbz and Ter motives.

Table 1: Infrared Assignments of PEcbz-Ter copolymer

<u>PEcbz-Ter</u>		
Freq (cm⁻¹)	I	Assignments
555	vs	Benzene ring deformation
626	vs	C-H out of plane bend of terminal mono-substituted benzene rings
746	m	CH ₂ Rocking- wagging of ethylene group
800	vw	C-H out of plane deformation the ring aromatic
876	w	C-H out of plane deformation
1045	m	Stretching vibration C-C of Ecbz
1117	vw	C-H in plane deformation
1149	m	C-H in plane deformation of aromatic ring
1233	s	C-N stretching
1330	m	Torsion of C-H of benzene ring of Terphenyl
1377	w	Stretching vibration of C=C bonds of benzene ring (Ter)
1454	vw	Symmetric stretching vibration (C=C) of Ter.
1479	m	C-H deformation in the benzene ring
1602	vs	C=C stretching of Benzene ring (Ter)
2928	vw	-CH ₂ assymmetric stretching
2966	m	-CH ₃ assymmetric stretching
3381	vs	Stretching OH associated with the polymer

vs: very strong; s: strong; m: mean; w: weak and vw: very weak

In order to achieve the relationship between structural properties for this copolymer, we studied their optical characteristics (UV-vis absorption and PL emission).

4.2. Optical absorption and photoluminescence measurements

The absorption spectrum of the new copolymer recorded at ambient temperature in solid state is presented in Figure 4. The synthesized copolymer absorbs both in the visible and UV-Violet region. In the UV region, part of the electromagnetic spectrum with absorption bands centred at 283 and 371 nm and in the visible part the absorption bands centred at around 437, 610 and 850 nm. The one located at 371 nm is attributed to π - π^* transition, due to the presence of PEcbz in the copolymer PEcbz-Ter and the other occurring at 437 nm should originate from a charge transfer state [18]. The effect of the oxidation of the synthesized copolymer is seen in the optical absorption spectrum of PEcbz-Ter, characterized by a wide absorption bands located at 850 (1.46 eV), resulting from the coexistence of polaronic and bipolaronic charge carriers, proving the formation of new backbone resulting from the grafting of Poly(Terphenyl) (PTer) into the skeleton of the cross linked PEcbz. These spectral features are characteristic for organic conducting polymers [19-23]. As mentioned in [24], PVK absorbs entirely in the UV region ($\lambda_{\text{max}} < 350$ nm). So the UV-Vis absorption spectra showed the absorption wavelengths of about 283 nm. The extension of the optical absorption in the case of a copolymer (from 400 nm to 800 nm) shows an increase in the conjugation length. The deduction of the optical gap is judged $E_g = 1.28$ eV, which can be identified by extrapolating the linear portion of the wavelength band of the highest (maximum absorption). Moreover, the energy corresponding to the π - π^* transition depends on the delocalization of the π -electrons system. This delocalization is determined by the effective conjugation length, which depends on the amount of structural and conformational defects in the polymer backbone and the interaction between polymer backbones.

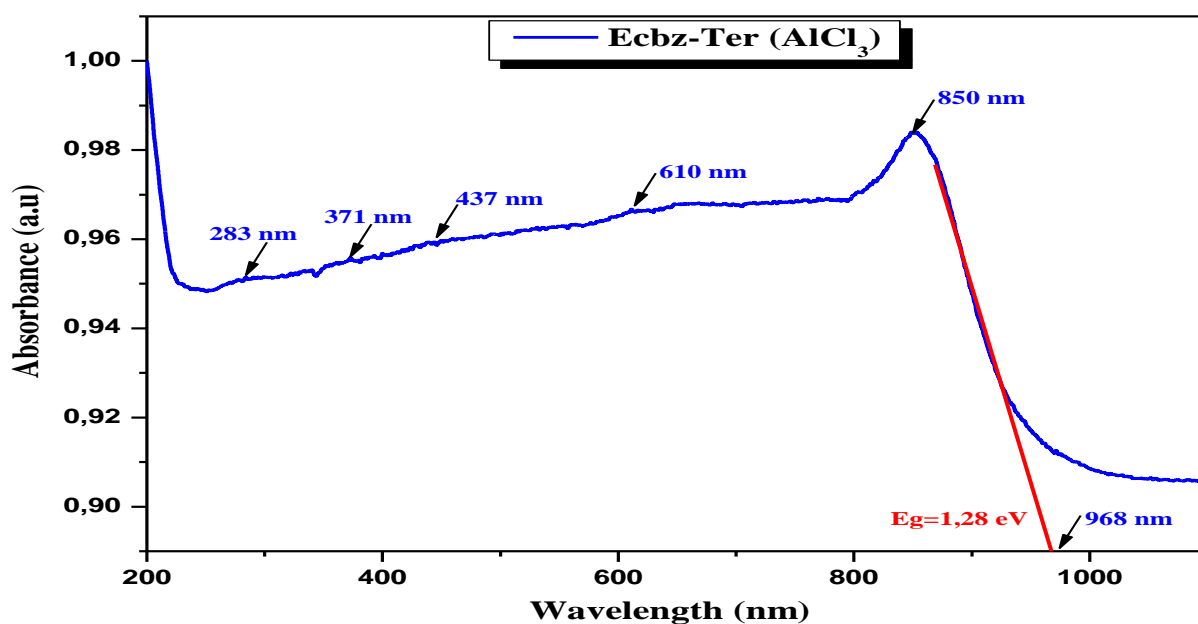


Figure 4: Normalized UV-Visible optical absorption spectra of PEcbz-Ter powder.

Photoluminescence properties of the neutralized copolymer were investigated in powder. The powder was collected between two silica plates and excited at 360 nm. PL spectrum of Ecbz-Ter is presented in figure 5 and characterized by a broad emission situated in the spectral range from 400 to 800 nm, which is constituted of two peaks. This broadening is attributed to the emission from the intramolecular Ecbz excimers. The maximum of the copolymer emission is the more pronounced peaks which appears at 692 nm and is formerly assigned to lower-energy excimers [25]. Lower intensity peak is located at 480 nm, and slightly depend on the polymer composition. So, we can understand that the most interesting feature in these systems is the strong dependence of the excimer emission intensity on the nature of the copolymer composition. The peaks located between 400 and 500 nm are attributed to the poly(Ethylcarbazole) emission [26-30]. On the other hand the redshift compared to the polycarbazole implies an increase of the conjugation length. This increase results from the grafting of Terphenyl units. Kinetically, this means that the exciton migration begins in the PEcbz backbone and continues in the Terphenyl moiety.

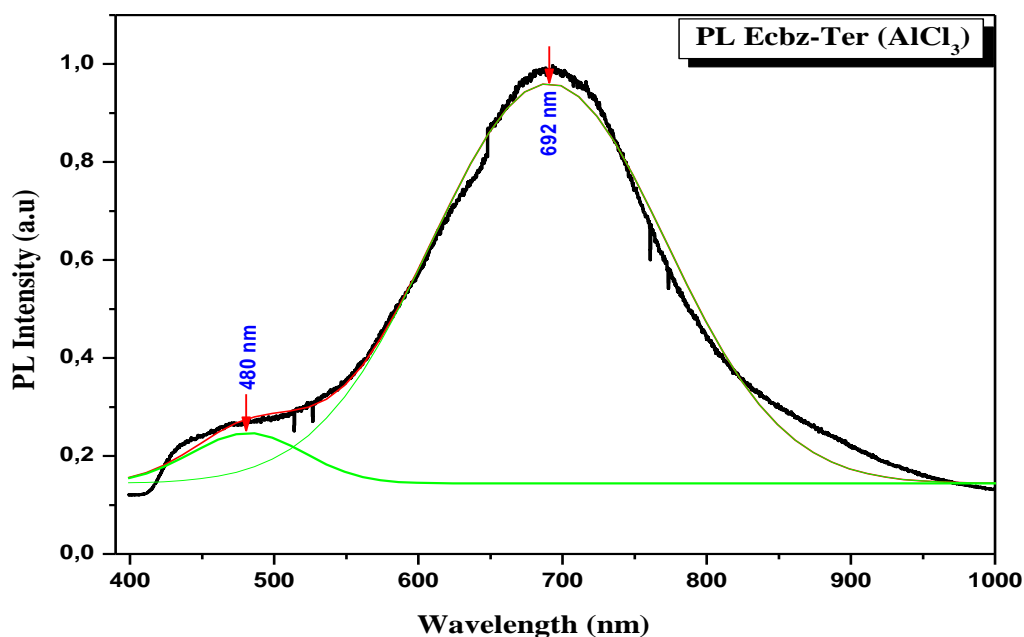


Figure 5: Spectres normalises de photoluminescence du PECbz-Ter (Excitation 360 nm).

4.3. ^{13}C NMR spectroscopy

The ^{13}C NMR spectrum of the studied PEcbz-Ter (Figure 6) confirms the presence of both PEcbz and PTer in the obtained structure since it displays two resonance regions. The first one (0–60 ppm) corresponds to the chemical shift of carbons of the aliphatic chain (ethyl and methyl groups), while the second region located between 100 and 150 ppm corresponds to aromatic carbons of carbazole and benzene rings of Terphenyl. In the aliphatic region, the ^{13}C NMR spectrum displays four resonance band centred at around 13.6- 16.7 ppm and 37.7-57 ppm corresponding respectively, to methyl group ($-\text{CH}_3$) [31] and methylene (CH_2-) carbons - methane ($-\text{CH}-$) of the ethyl groups of PEcbz [32].

In the aromatic region (100-150 ppm), the resonance bands centred at about 109, 126 and 140 ppm are assigned to aromatic carbons of the carbazole rings of PEcbz. In fact, by comparison with CP-MAS ^{13}C NMR spectrum of PVK and that reported in the literature [33], the line centred at 109 ppm correspond to carbons C1 and C8 of carbazole rings, then that at 124 ppm to carbons C3, C4, C4a, C5 and C6 of carbazole rings, the line at 126.7 ppm to carbon C2, C7 and C5a of carbazole rings and the line at 140 ppm to C1a and C8a. In addition, we note a resonance band at 127 ppm is attributed to aromatic carbon $\text{C}=\text{C}$ on Terphenyl ring. This resonance structure confirms well the grafting the reasons for PTer on the chain of PEcbz.

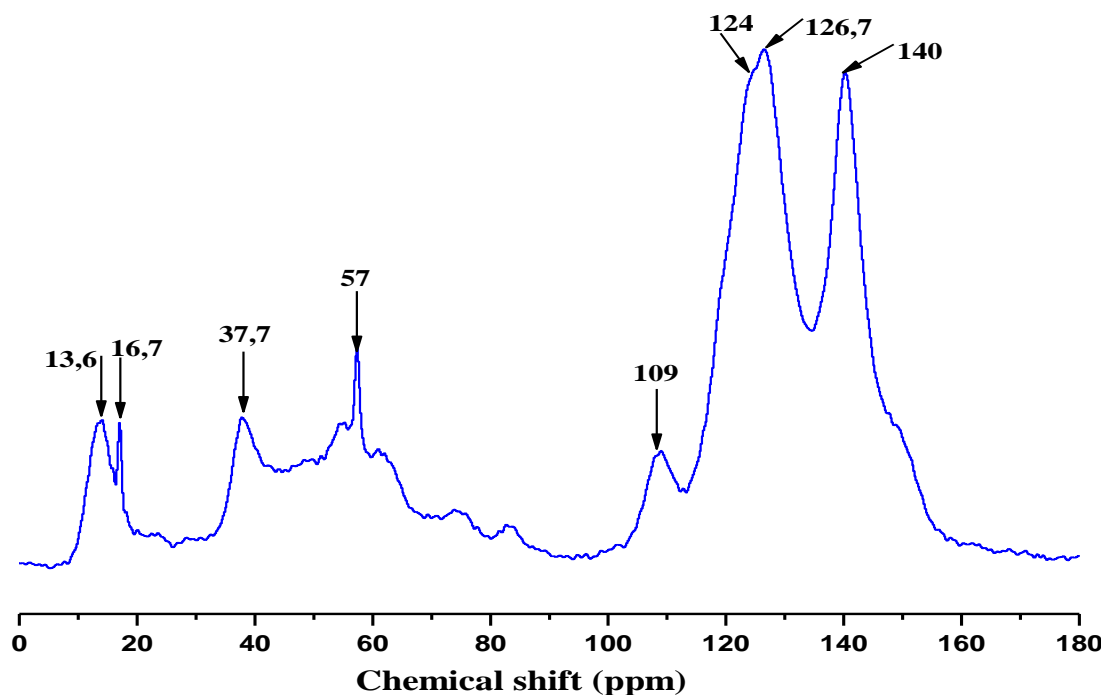


Figure 6: NMR ^{13}C spectra of PEcbz-Ter.

Conclusion

We have developed in this work a single procedure to prepare a new organic conjugated copolymer by oxidative copolymerization from two conjugated compounds N-Ethylcarbazole and Terphenyl. The structural parameters, the characterization measurements based on solide state Nuclear Magnetic Resonance (^{13}C NMR), the IR absorption, the UV-visible absorption, and the photoluminescence spectroscopy. The IR and UV-visible analysis indicate that we have synthesized a new copolymer (PEcbz-Ter) using Ethylcarbazole and p-terphenyl as starting materials. Structural and opto-electronic information obtained during this study and the specific properties suggest this new compound to be a good candidate for optoelectronic applications. Finally, due to the interesting physical and chemical properties of this resulting copolymer many experimental and theoretical effort are now undertaken in our laboratory to study other physic-chemical properties of this new copolymer in order to carry out new electronics components (OLED/PLED) based above.

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