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Photoluminescence analysis of a polythiophene derivative: Concentration and temperature effects

J. Castrellon-Uribe*, M. Güizado-Rodríguez, R. Espíndola-Rivera

Centro de Investigación en Ingeniería y Ciencias Aplicadas, CIICAp, (IICBA), Universidad Autónoma del Estado de Morelos, UAEM, Av. Universidad No. 1001, Col. Chamilpa, C.P. 62209 Cuernavaca, Morelos, Mexico

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ABSTRACT

In this work, the photoluminescence properties of a PA copolymer, which is a polythiophene derived from 3-OT and (*S*)-(-)-1-(4-nitrophenyl) pyrrolidin-2-il) methyl 2-(thiophen-3-yl) acetate, were investigated. The optical response of the copolymer dissolved in a toluene solution and of the copolymer film under the optical excitation was analyzed. Besides, the temperature dependence of photoluminescence (PL) of the PA copolymer (solution and film) was examined. The PL behavior of the solution-phase copolymer (diluted and concentrated solutions) under 365 nm (UV light) excitation is reported. Moreover, the copolymer films were obtained using the spin coating technique. The PL of the copolymer films under 488 nm (blue light) irradiation was studied at different excitation powers. Finally, we examined the PL signal temperature dependence of the copolymer film. We determined that the maximum PL signal peak of the copolymer corresponds to 626 nm and has a temperature sensitivity of approximately 11×10^{-3}/°C, with a minimum ascending and descending temperature hysteresis between 22 °C and 50 °C.

1. Introduction

The development of new materials with non-linear optical properties (NLO) has been one of the main objectives of research and development in the field during the past few decades due to their important applications primarily in photonics [1]. In recent years, conducting polymers (CPs), such as polypyrrole (PPy), polyaniline (Pani), polythiophene (PTh) and their derivatives, have been investigated because of their chemical and electro-optical properties for the development of gas and chemical sensors [2–4]. The CPs are synthesized using chemical or electrochemical processes, and their molecular chain structure can be conveniently modified via copolymerization or structural derivations. Currently, the research has been focused on the thiophene-based polymers due to their structural versatility, solubility upon functionalization and environmental stability. In addition, the functionalized polythiophenes combine interesting nonlinear optical (NLO) [5–10] and photoluminescence (PL) properties [11–15]. Fluorescence is a photoluminescence in which the molecular absorption of a photon triggers the emission of a photon with a longer wavelength (less energetic). Currently, the luminescence properties of conjugated polythiophenes are of considerable interest due to their potential applications in light-emitting diodes (LEDs) [16,17], organic solar cells [18–21] and optical chemical sensors [22–25].

In this work, the photoluminescence properties of the PA copolymer (solution and film) under optical excitation were investigated. First, the synthesis of the novel copolymer was performed and was reported in Ref. [26]. Next, the absorbance of the copolymer dissolved in a toluene solution at different concentrations was measured and their photoluminescence was analyzed. Besides, the photoluminescence signal temperature dependence of the copolymer in a toluene solution was examined. Later, the copolymer films were obtained using the spin coating technique. Next, the copolymer film was optically excited at 488 nm, and the photoluminescence signal that was generated at 620 nm was monitored at different optical powers. Moreover, the films were exposed to different temperatures (20 °C–50 °C) under a constant optical excitation, and the PL signal variations of the films were monitored to determine their optical sensitivity. Finally, a morphologic study of the copolymer films was performed to determine the surface damage due to laser radiation and temperature.

* Corresponding author.
E-mail addresses: jcastrellon@uaem.mx (J. Castrellon-Uribe), marisolguizado@uaem.mx (M. Güizado-Rodríguez).

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2. Experimental procedure

2.1. Synthesis and physicochemical characterization of the PA copolymer

The PA copolymer, structure in Fig. 1, was synthesized according to the previously reported polymerization procedure [26]. This procedure involves an oxidative polymerization of 3-octylthiophene and (*S*)-(-)-1-(4-nitrophenyl) pyrrolidin-2-il) methyl 2-(thiophen-3-yl) acetate in the chloroform and nitromethane solution of $FeCl_3$. Soluble yield was 15%, monomer ratio was 88% for 3-OT and 12% for functionalized thiophene, molecular weight was $\overline{M_n}$ = 11,000 g/mol, $\overline{M_w}$ = 117,000 g/mol, PDI = 10.6. Thermal stability: T_d = 474 °C, weight loss = 71%. The ^{1}H NMR signals, Fig. 1, showed the configurations of diads (HT = 68%, HH = 32%) and triads (HT-HT = 50%, TT-HT = 15%, HT-HH = 18%, TT-HH = 17%). ^{1}H NMR (200 MHz, $CDCl_3$, TMS), 3-octylthiophene: δ = 6.98 ($H_{4'}$), 2.79, 2.60 (H_α), 1.66, 1.26, 0.87, 0.07 ($H_{\beta-\theta}$). Functionalized thiophene: δ = 8.06 ($H_{17,19}$), 7.00 (H_4), 6.60 ($H_{16,20}$), 3–4.5 ($H_{6,9,10,12}$), 2.0 ($H_{13,14}$) [26]. The physicochemical properties of the PA copolymer, such as regioregularity (diads and triads), molecular weight distribution (Mn and Mw) and thermal properties (T_d), are similar to those found in the PT that was synthesized using the same regioselective method [5,10]. The synthesized PA copolymer has a low molecular weight and a large polydispersity. Additionally, in the copolymer, the incorporation of functionalized thiophene, with a push–pull chromophore as pendant group, is considerable (12%). Finally, the polythiophene derivative has a good thermal stability [26].

2.2. Optical measurements

2.2.1. PA copolymer in a toluene solution

To investigate the photoluminescence properties of the PA copolymer in a toluene solution, the following procedure was used. First, the optical absorbance of the copolymer dissolved in toluene at different concentrations was measured using a tungsten halogen light source. The concentrations of the copolymer were: [0.005–0.025 mg/mL] and [0.5–2.5 mg/mL] of the diluted and concentrated solutions, respectively. Then, the absorption spectra were monitored and analyzed at room temperature in the 250–900 nm wavelength region.

Subsequently, in a second optical experiment, the copolymer photoluminescence in a toluene solution was investigated. A UV lamp with a 4 W output was used to irradiate the solution-phase copolymer. The PL signal was observed up to approximately 580 nm (yellow light) when the copolymer was excited using a 365 nm wavelength. The PL signal of different copolymer concentrations (diluted and concentrated solutions) was monitored and analyzed at room temperature. Later, in a third optical experiment the PL signal behavior of the solution-phase copolymer, when it was exposed to different temperatures (20 °C–50 °C) was investigated. The fluorescence spectra were recorded using a spectrometer (Ocean Optics, Dunedin, Florida, USA).

2.2.2. PA copolymer in films

Additionally, the photoluminescence properties of the PA copolymer film were investigated. First, a PA copolymer toluene solution (60 mg/mL) was used to deposit thin films via spin coating at approximately 5000 rpm on glass substrates (corning glass). The films were characterized using AFM (nano scope IV multimode scanning probe microscope). Then, the absorption spectra of the films with thicknesses of approximately 200 nm for a concentration of 60 mg/mL were measured at room temperature for the wavelength interval from 300 nm to 650 nm. After that, the PL of the copolymer film was measured. The generated PL signal was observed up to approximately 630 nm (red light) when the films were excited with a laser at 488 nm (blue light). Likewise, the PL behavior was studied at different excitation optical powers (5–20 mW). The PL signal of the films was analyzed at room

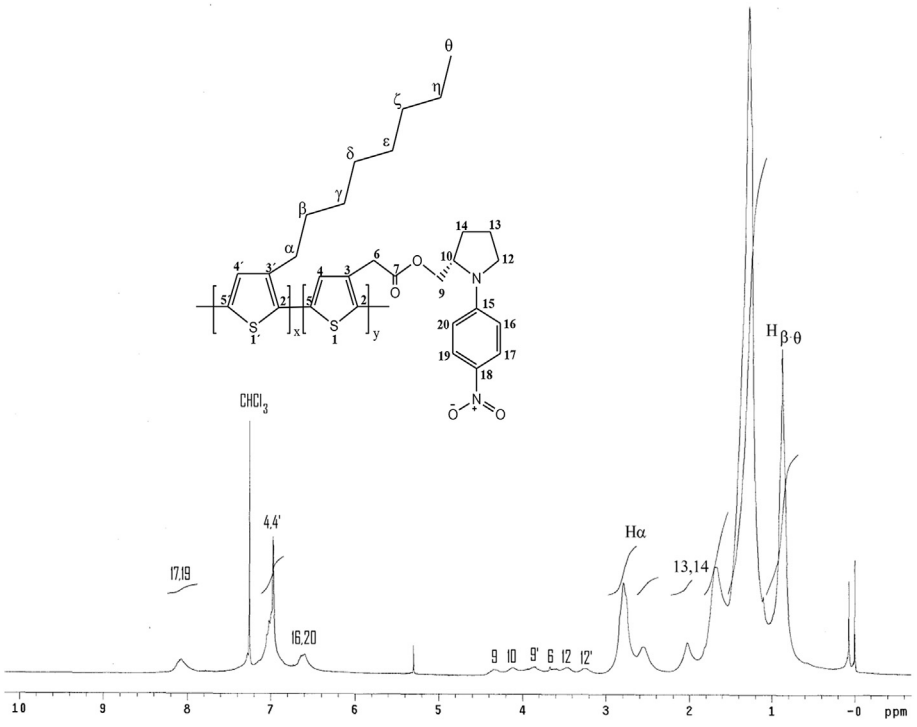

Fig. 1. ^{1}H NMR spectrum of PA copolymer and its structure.