Luminescent Polydibenzothiophene Thin Film Obtained by Glow Discharge Method

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ABSTRACT: This work presents the synthesis by plasma and characterization of luminescent polymer thin films of dibenzothiophene (DBT) by plasma polymerization. The DBT is solid at room conditions and was sublimated and introduced to the plasma reactor to produce the chemical reactions with the vapors. The results indicated the production of polymers with benzene and thiophene rings in the structure as well as methylene groups. The polymer structure was studied by Fourier transform infrared spectroscopy and ^{13}C-CPMAS. The thermal analysis showed a residual mass of 60% at 800°C, which suggests a great thermal resilience in the polymer. The critical superficial tension was calculated with a Zisman plot and was 25 mN/m. The polymer has a fluorescent green emission between 400 and 660 nm and an orange emission between 660 and 850 nm. This effect can be a consequence of the electronic distribution along the structure in aliphatic and aromatic segments with benzene and thiophene rings. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1120–1124, 2012

Key words: plasma; polymerization; dibenzothiophene; photoluminescence; fluorescence; superficial tension

INTRODUCTION

Dibenzothiophene (DBT) is a tricyclic heterocycle with two benzene rings fused to a central thiophene ring; the benzene rings share carbons in *ortho* and *meta* positions with the thiophene ring, see Figure 1(a). It is a planar conjugated structure that can be polymerized giving a conjugated polymer, see Figure 1(b). However, this highly aromatic structure is difficult to polymerize. Conjugated polymers have good optoelectronic applications. Among them, polythiophenes and their derivatives are being regarded as promising materials because of their good thermal and chemical stability, as well as for their electronic and optical properties, and by attaching different functional groups as side chains, a wide range of light emission may be obtained.[1]

Thiophene, pyrrole, aniline, and other aromatic monomers have been polymerized by plasma.[2–12] This kind of polymerization can be handled in one step, without solvents, initiators, or other chemical reagents that could affect the final products.[1,13,14] During the synthesis, the plasma forms a great variety of radicals and ions, as a consequence of the energy transferred by the electrical field. Monomers with only one aromatic ring are relatively stable because of their small cross-sectional collision area and provide 5 or 6 points of union (lateral hydrogen atoms) on each ring. Structures with more rings, as DBT, are less stable because the cross-sectional collision area increases with the number of rings in the structure. Thus, larger structures have more probability to break under the constant collisions in the plasma but provide much more joining points in the polymers, which result in two-dimensional growing structures. One advantage in these mechanisms is that plasma polymers of DBT can be used as a function of their superficial properties. There have been reports of different copolymers and polymers
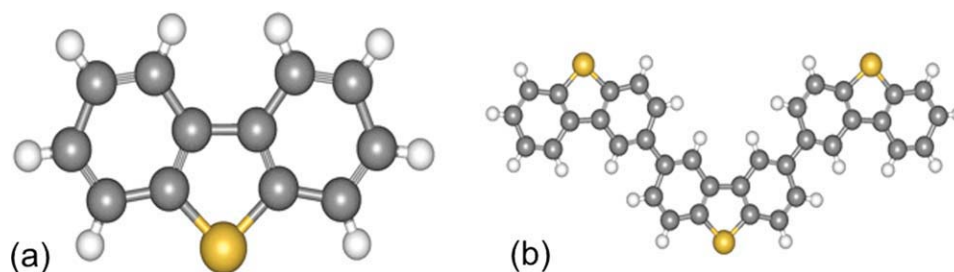
Figure 1 Representation of: (a) DBT and (b) PPDBT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formed with DBT, or some of its derivatives (dioxide and divyniliden), with luminescent properties in blue or green spectra.[15–19]

This work presents a study on the polymerization of DBT in gas phase forming plasmas with its sublimated vapors. The objective is forming superficial layers of polydibenzothiophene (PPDBT) with luminescent emission. The plasma polymerization has the characteristic that, as the energy of polymerization increases, the number of chemical species and the possible combinations among them, increases as well. This effect result in structures around one central polymer backbone derived from the initial monomer.[20–22]

MATERIALS AND METHODS

A schematic representation of the reactor used to polymerize DBT has been presented previously.[23] The reactor is essentially a vacuum chamber with a cylindrical glass tube, 25 cm long and 9 cm diameter, sealed with stainless steel caps at each end. Each cap has three access ports for electrodes, vacuum system, pressure gauges, and gas inlets. The electrodes and caps were connected to a function generator (Wavetek 154) and to a voltage amplifier (ENI A150).

DBT (Aldrich, Toluca, México, 99.0%) is a white semicrystalline powder that was sublimated at 90°C before entering to the reactor. The tubes and connectors of the reactor were heated to prevent condensation of DBT vapors. The plasma was produced with the DBT vapors polymerizing at 13.5 MHz, 10^{-2} Torr, with power between 20 and 24 W, during 60 min in resistive mode. The polymerization started with DBT in gas phase and ended as thin PPDBT films adhered on the reactor walls. The films were swelled and removed from the walls with double deionized water.

Characterization

The structure of PPDBT was studied through solid state nuclear magnetic resonance (^{13}C-NMR) and Fourier transform infrared (FT-IR) spectroscopy. The NMR analysis was made with a Bruker ASX300

spectrometer in a Cross Polarization Magic Angle Spectroscopy experiment (CP-MAS-NMR). The FT-IR analysis was done on KBr tablets with a Perkin-Elmer 2000 spectrophotometer in transmission mode with 64 scans and 4 cm^{-1} resolution. The morphological characteristics were studied by scanning electron microscopy using a PHILIPS XL30 microscope. The superficial energy was evaluated by contact angle, and the critical superficial tension was obtained with Zisman plots using three testing liquids (water, ethylenglycol, and glycerin). As DBT is labile, the thermal stability of PPDBT was studied with a Perkin-Elmer Thermogravimetric analyzer Pyris 1 applying a heating ramp of 10°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSIONS

Structure of PPDBT

Figure 2 shows the FT-IR spectra of DBT and PPDBT deposited on KBr tablets. The FT-IR bands of PPDBT are wide and complex as in many of the polymers synthesized by plasma. The PPDBT spectrum has a band between 3250 and 4000 cm^{-1} that corresponds to the OH stretching, originated on the superficial
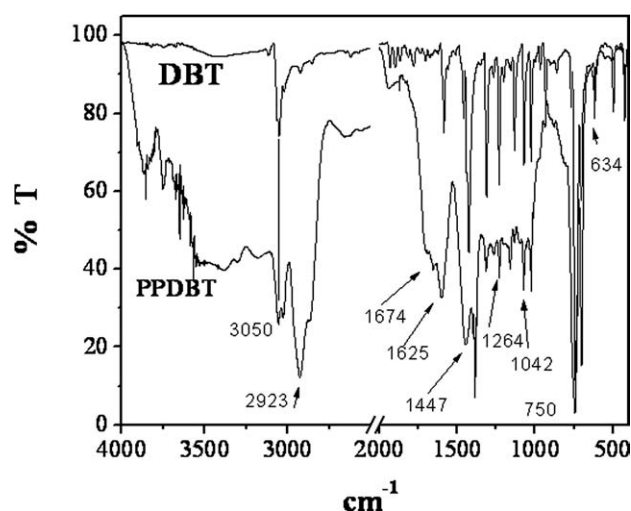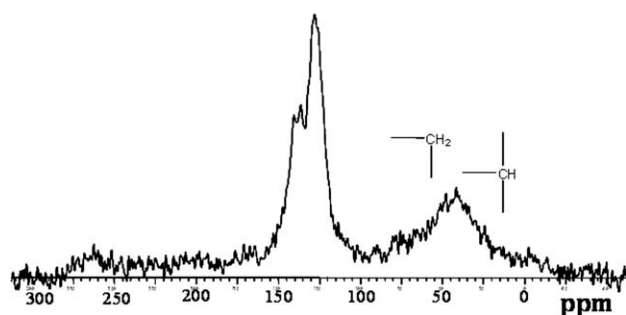

Figure 2 FT-IR spectra of DBT and PPDBT.

Figure 3 NMR spectrum of PPDBT.

oxidation due to the exposition of the films to the atmosphere. The bands at 1674 and 1625 cm^{-1} can be assigned to the superposition of C=C and C=O absorption belonging to the conjugated structure of the thiophene and benzene rings and to the oxidation in the polymer, respectively. The band between 1254 and 1042 cm^{-1} represents C—O and S—O groups, which are another consequence of oxidation.

Another important absorption in PPDBT is the peak at 3050 cm^{-1} corresponding to the aromatic stretching of the C—H groups of DBT rings. This is an indication that the aromatic structure of DBT was incorporated to PPDBT. However, during the plasma polymerization, some rings break and aliphatic C—H groups are detected in the 2923 cm^{-1} peak.

The DBT IR absorption between 500 and 1500 cm^{-1} has many peaks indicating the aromaticity of benzene and thiophene rings, and the substitutions of some hydrogen atoms in both rings. Practically, each of these signals can be also observed in PPDBT in a wide absorption.

Figure 3 shows the CP-MAS-NMR spectrum of PPDBT. In the region between 25 and 75 ppm, a signal of aliphatic carbons (CH and CH$_2$) appears. These carbons may arise from the opening of aro-
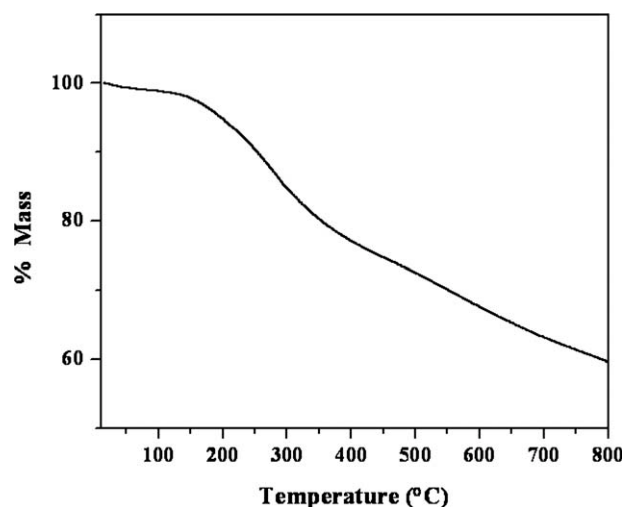
matic rings during the plasma polymerization. These signals reinforce the possibility of aliphatic segments in PPDBT suggested in the 2923 cm^{-1} IR peak.

In the region between 125 and 140 ppm, the principal peak of PPDBT related with aromatic carbons in DBT is observed. The intensity of the aromatic signal is higher than that of the aliphatic carbons, which suggests more participation of aromatic than aliphatic carbons in the structure of the polymers.

Thermal stability of PPDBT

Figure 4 shows the thermogravimetric scans of PPDBT taken from 20 to 800°C. In the first 100°C, approximately 1% of humidity and solvents were released from the polymers. After this, two main decompositions can be seen in the thermal decomposition, which suggests two different structures in PPDBT. The first decomposition starts at around 100°C and ends at approximately 350°C, losing 20% of the initial mass. This loss is probably composed by light polymers of random aliphatic segments.

The second loss starts at 350°C ending after 800°C, which is the limit of the gathered data in the work. In this interval, the loss is also approximately 20% of the initial mass. Independently of the sublimation stage, it should be considered that the boiling point of DBT is 333°C. So, the monomer has a great thermal stability and the polymer should have part of that thermal resistance. In this way, the second loss can be related with the partial vaporization of the aromatic structure of PPDBT, as one thermal decomposition mechanism of the polymer. Another indication of a great thermal stability of PPDBT is that after 800°C, PPDBT has lost only 40% of mass.

Morphology of PPDBT films

Figure 5 shows a micrograph of PPDBT surface. The films have a solid consistence composed by several layers with a total thickness of approximately 3 μm

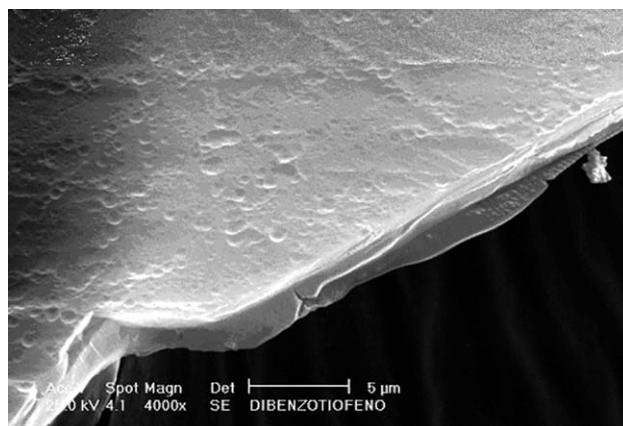**Figure 4** Photoluminescence and absorbance spectra of PPDBT.

Figure 5 Thermal decomposition of PPDBT.

TABLE I
Contact Angles on Glass Modified with PPDBT with Different Testing Liquids

Testing liquid	Contact angle (°)
Water	90 ± 1
Ethylenglycol	64 ± 1
Glycerin	58 ± 1

with a growing rate of 50 nm/min. The layers can be a consequence of small variations in the pressure of the system. Small craters are drawn on a rather homogeneous surface, which could have been originated by the erosion of energetic particles.

Critical superficial energy of PPDBT

To calculate the critical superficial energy, a thin film of PPDBT was synthesized over glass substrates of 25 × 25 mm^2. One drop of water, ethylenglycol, and glycerin was deposited on the polymer in different processes. The contact angle between the liquid and the surface of PPDBT were measured, the data are show in Table I. The values are plotted in Figure 6 to obtain the critical superficial tension of PPDBT with a Zisman plot. Extrapolating the tendency of the angles at $\cos(\theta) = 1$, the minimum superficial tension can be obtained, which is 25 mN/m. At this point, the liquid will completely wet the surface of PPDBT.

Photoluminescence analysis

Figure 7 shows the photoluminescence (PL) and absorbance spectra of PPDBT taken with a Double Spectrophotometer with a He–Cd Kimmon at 325 nm excitation laser. As shown in Figure 7, the material presents an absorption border at approximately 420 nm, decreasing monotonically as the wavelength
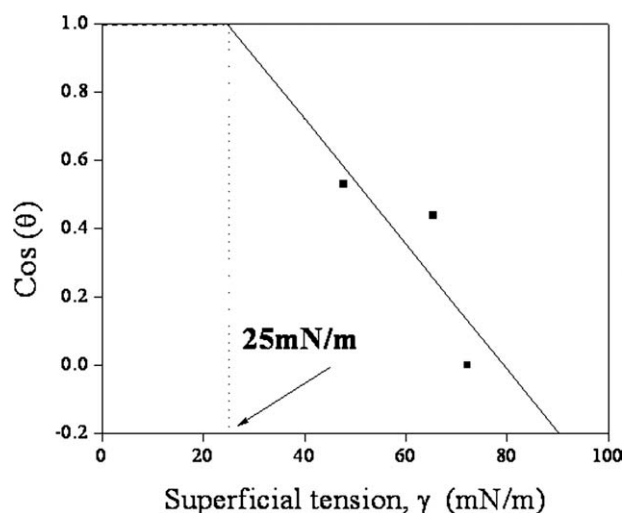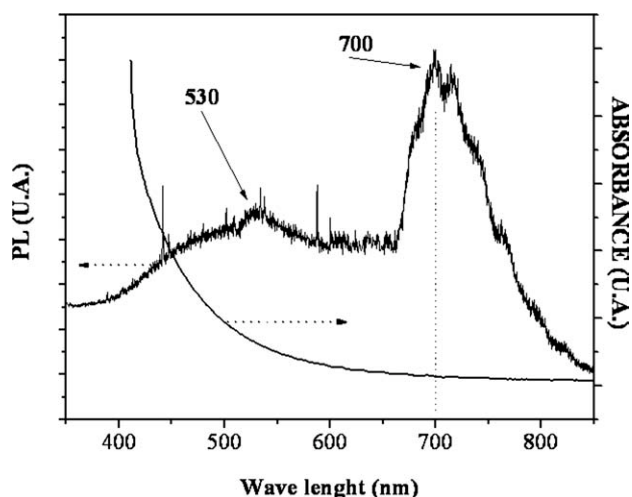
Figure 6 Micrograph of PPDBT films.

Figure 7 Superficial tension of PPDBT.

increases, with a final absorption limit at approximately 700 nm.

The PL spectrum at 325 nm excitation shows that PPDBT emits in the interval between 400 and 850 nm in two regions. The first one is located between 400 and 660 nm with a maximum at 530 nm. The second region is located between 660 and 850 nm with two peaks at 700 and 730 nm. The color of the emission peaks is orange. In the entire interval, the intensity of the signal between 660 and 750 is higher.

Two regions clearly separated in the emission indicate at least two combined structures. One that emits at low level that could be the aliphatic chains and another that emits at high level that can be due to the aromatic rings of thiophene and benzene. The discussion presented above has evidence of these structures based in the participation of carbon atoms.

CONCLUSIONS

This work presents a study on the formation of thin films by plasma polymerization of DBT with the intention to study the luminescent characteristics of the DBT polymers. The analysis of the structure shows that the aromatic character of the monomers represented by the interaction of resonant C—C and C=C bonds is included in the polymers, together with an aliphatic fraction, which result from the high energy collisions of particles in the plasma. The results also show aliphatic carbons and oxygen in C=O and C—O bonds, which can be a consequence of the oxidation at the end of the polymerization with the long-life radicals.

The resonant structure gives the polymer potential of light emission, which was measured in a wide interval of wavelength from 400 to 800 nm centered

in two peaks at 530 and 700 nm. The first one can be associated with the aliphatic fraction of polymers, and the second peak, the most intense emission, with the aromatic segments of PPDBT.

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