

## POMA/PMMA Blends Modified by Dye: Spectroscopic and Morphological Properties

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**ABSTRACT:** Poly(*o*-methoxyaniline) (POMA), a conducting polymer (CP) well known, was used to prepare blends with poly(methyl methacrylate) (PMMA). Conducting polymer keeps absorbance strength within the PMMA matrix. POMA/PMMA blends presented absorption bands regarding the conducting polymer with different intensities and the main band red shifting. However, POMA/PMMA blends showed no photoluminescence (PL) emission. After the hybridization process of the CP with a photoluminescent dye, 2,1,3-benzothiadiazole, POMA/PMMA blends showed new optical properties. PL spectra revealed an emission in the range of 500–550 nm, indicating interaction between the dye and the conducting polymer. The presence of the dye modified the morphological properties of the POMA/PMMA blends. New features have appeared on the surface of the blends prepared with higher concentration of hybridized CP. Blends with lower concentrations of hybridized CP showed their surfaces with POMA globules being covered by PMMA. This morphology replaced the globules and “crystals” on the surface of the blends prepared without the dye. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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### INTRODUCTION

Conducting polymers (CPs) are also known as “synthetic metals” because they have electrical, electronic, magnetic, and optical properties similar to metals.<sup>1</sup> The special properties of these materials are due to their high  $\pi$ -conjugated length and the reversible redox doping process.<sup>2</sup> In recent years, the studies of CP grew significantly along with its promising applications in electronic devices.<sup>3–5</sup> However, the mixtures of two or more polymers can create strategies to produce materials with specific properties of each component of the mixture.<sup>6</sup> Great attention has been given to the investigation of these systems, aiming to develop new materials, because polymer blends are an economical means to develop new resins at low cost.<sup>7</sup> The advantage of mixing CP with insulating polymers is to produce materials with good mechanical properties associated with properties of interest<sup>8</sup> such as absorption, electrical, and photoluminescence (PL). When two amorphous polymers are mixed, it is possible to produce a homogeneous mixture at the molecular level or a mixture with phase separation, i.e., heterogeneous.<sup>4</sup> The miscibility is rare in polymer blends and depends basically on three

parameters: compatibility, relative proportion of the blend composition, and temperature/pressure.<sup>9</sup>

According to this theory, the miscibility of a polymer of high-molecular weight occurs if the mixing process is exothermic.<sup>9</sup> This means that intermolecular interactions between individual polymers lose their intensity, the molecules are “loose” and intermolecular interactions occur between components of the blend, and the excess energy released into the external environment causing heating of the mixture.<sup>9</sup> When the polymer undergoes changes in variables such as temperature, pressure, and composition, there is a phase separation in the metastable and spinodal regions. The metastable region occurs through the mechanism of crystallization, while the region spinodal arises spontaneously through fluctuations in volume, resulting in the formation of co-continuous morphology,<sup>9</sup> i.e., a morphology where the mixture components are part of a single structure, with each phase performing continuously and interwoven/enmeshed.<sup>10</sup>

Several attempts were made to produce materials starting from the mixture of insulating polymers with PC, involving

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formation of composites and blends, including: blends of polyaniline (PANI) with poly(methyl methacrylate) (PMMA) to produce anticorrosion materials,<sup>11</sup> mixture of PANI with poly(3-hydroxybutyrate) (PHB) to prepare a biodegradable material that is also a semiconductor.<sup>12</sup> Besides these applications, the polymer blends have been used in the manufacture of optoelectronic devices.<sup>13</sup> In the past decades,  $\pi$ -conjugated polymers and molecules containing the benzothiadiazole (BT) molecules call attention due to their applications in different areas such as organic light emitting diodes (OLEDs),<sup>14</sup> biologic systems,<sup>15</sup> and solar cells.<sup>16</sup> The advantage of incorporating BT into the molecular systems is due to its electron affinity and intense fluorescence. Because of its ability to shift emission spectra to longer wavelengths and modify the charge transport properties, the BT molecules are used in optoelectronics.<sup>17</sup>

Several different methods have been used to prepare polymeric blends. Previous studies showed the possibility of hybridizing the poly(*o*-methoxyaniline) (POMA) with organic molecules such as deoxyribonucleic acid (DNA) and ribonucleic acid (RNA),<sup>18–20</sup> i.e., there is the possibility of hybridizing the CP with any organic molecule.

Hence, the aim of this work was to prepare POMA/PMMA blends without and with hybridized POMA with the photoluminescent organic compound (BT) and then to compare their spectroscopic and morphological properties. Before mixing the PMMA and the POMA to prepare new blends, the CP was hybridized with the BT, obtaining samples with different properties compared with blends not hybridized.

## EXPERIMENTAL

### Materials

The monomer *o*-methoxyaniline (CAS number 90-04-0), PMMA (CAS number 9011-14-7,  $M_w = 120,000$ ), canfor sulfonic acid (CSA) (CAS number 35963-20-3) and BT (CAS number 273-13-2) were purchased from Aldrich Co., SP, Brazil.

### Synthesis of the POMA

POMA was synthesized according to the literature.<sup>5,21,22</sup>

### Blends Preparation

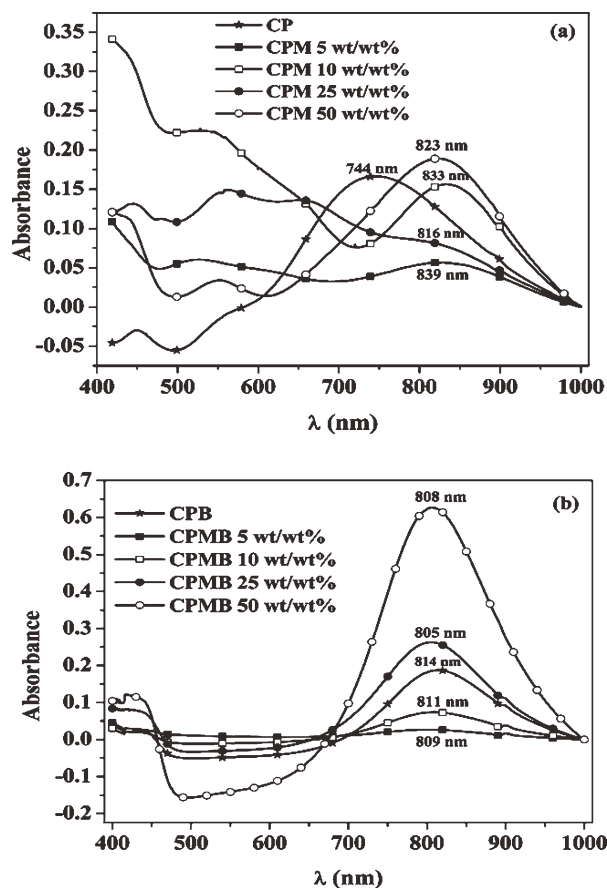
Initially, the POMA/PMMA blends were prepared without dye (BT), where the CP, dissolved in chloroform ( $\text{CHCl}_3$ ) and doped with CSA, was added to the PMMA to produce solutions with concentrations of 50, 25, 10, and 5 wt/wt %, labeled by the following abbreviations CPM 50, CPM 25, CPM 10, and CPM 5, respectively.

To make blends with the dye, 0.05 g of BT was placed in the solution of POMA-CSA. After stirring for 15 min, the PMMA was added to produce solutions with concentrations of 50, 25, 10, and 5 wt/wt %, and labeled by CPMB 50, CPMB 25, CPMB 10, and CPMB 5, respectively, where the letter B refers to BT.

All solutions stirred for 4 h and were deposited on glass surfaces by the spin coating technique at 3000 rpm for 15 s.

### Characterization of POMA/PMMA Thin Films

**Ultraviolet–Visible Spectroscopy.** Optical properties were analyzed by ultraviolet-visible (UV-Vis) absorbance in a spectrometer model Beckman DU-600 in the range 400–900 nm.



**Figure 1.** Absorption spectra of the blends prepared (a) without the presence of the BT and (b) with the presence of the BT.

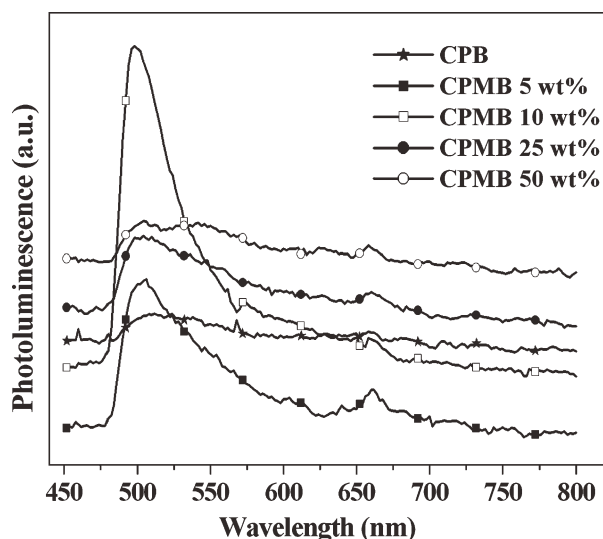
**Spectroscopy of PL.** PL measurements were performed using laser excitation at 405 nm and detected using an optical scanning spectrometer. The PL setup is homemade, slits were 0.10 mm, and scanning speed 1 nm/s.

**Atomic Force Microscopy.** Tapping mode atomic force microscopy (AFM) was performed in a scanning probe microscope Veeco Innova (Instruments, SP, Brazil). Topographic (height) and phase images were recorded simultaneously at room temperature. Commercial antimony (n) doped silicon cantilever probes were used with spring constant in the range of 1–5 N/m were oscillated at their fundamental resonance frequencies, which ranged between 60 and 100 kHz.

## RESULTS AND DISCUSSION

### UV–Vis Absorption

Pure POMA spectrum, in literature, shows three absorption bands at 324–328, 412–417, and 867–881 nm. The first band is attributed to the transition  $\Pi-\Pi^*$  of the aromatic benzoic rings; the second and third bands are justified by polaron- $\pi^*$  transition and  $\Pi$ -polaron transition. Bands at 412–417 and 867–881 nm are related to the doping level and formation of polaron.<sup>23,24</sup> Patil et al.<sup>24</sup> report that a broadening in the POMA absorption band, in the region around 560 nm suggests the formation of phase pernigraniline during polymerization. In this work, the CP, without BT, doped with CSA presented two



**Figure 2.** PL spectra of hybridized pure POMA (CPB) and of its blends (CPMB).

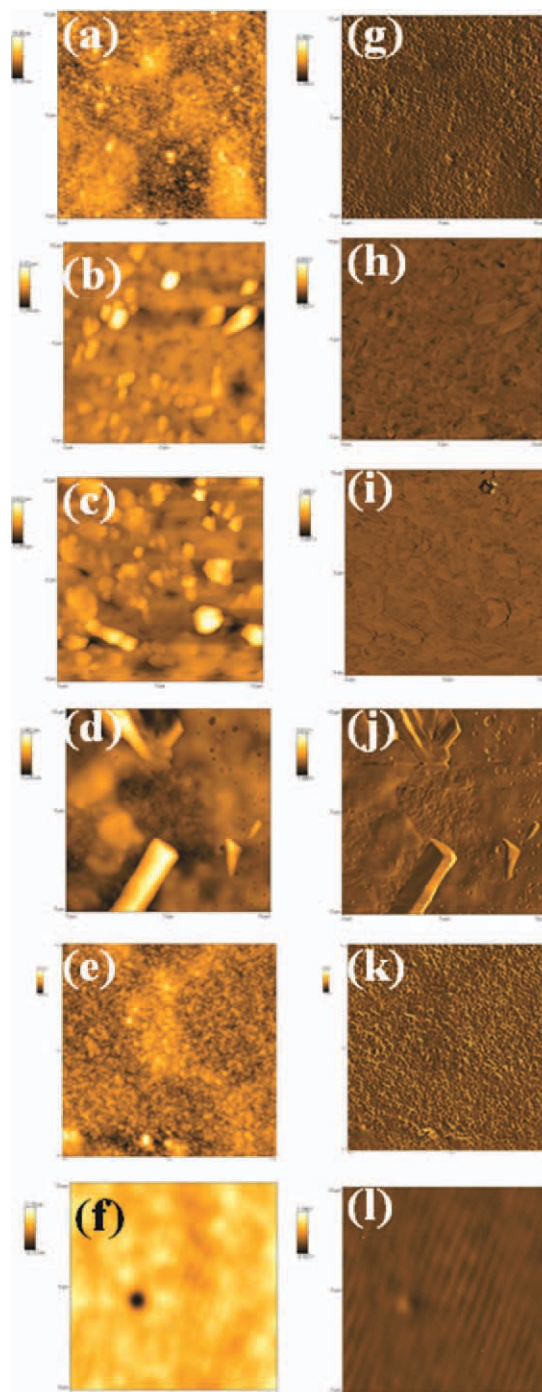
absorption bands and shoulder at 550 nm. The first absorption band occurred at 450 nm and the main band at 744 nm, approximately. All POMA/PMMA blends presented these three bands (including the absorption shoulder at range 519–559 nm) of CP absorption with different intensities and main band red shifting. Blends showed main absorption band in the range 816–839 nm [Figure 1(a)]. This shift may suggest an interaction of POMA with the insulating matrix through van der Waals.

Figure 1(a) shows that the POMA has kept the absorption within the matrix of insulating PMMA, which does not absorb in this region.<sup>25</sup> It is important to say that the POMA did not promote any emergence of electronic transitions of PMMA. The CP only is absorbing in the characteristic region regarding the matrix of PMMA. POMA/PMMA blends prepared with hybridized CP with dye showed different optical properties of absorption, when compared with spectra of the POMA/PMMA blends. The hybridized samples revealed a strong absorption band in the range 600–1000 nm with the maximum absorption in range 805–814 nm, to all samples [Figure 1(b)]. The BT presents two absorption bands, one at 220 nm and other at 310 nm,<sup>26</sup> i.e., it does not absorb in the region of 400 to 1000 nm, keeping the idea of interaction between the POMA and the dye. Other characteristic of the new materials was that the shoulders vanished at wavelengths shorter than 600 nm. The disappearance of absorption bands at lower wavelengths can be explained by interactions between the photoactive molecule (BT) and the CP. These interactions should be van der Waals type, because there was no formation of new compounds.

The samples prepared with hybridized CP produced new materials with wide absorption bands. It can be observed that CPMB 25 and PCMB50 wt/wt % had absorptions higher than the CPB, while blends with low CP concentrations, but same amount of BT, presented small absorption, indicating that the interaction of the dye occurs mainly with CP and not with PMMA.

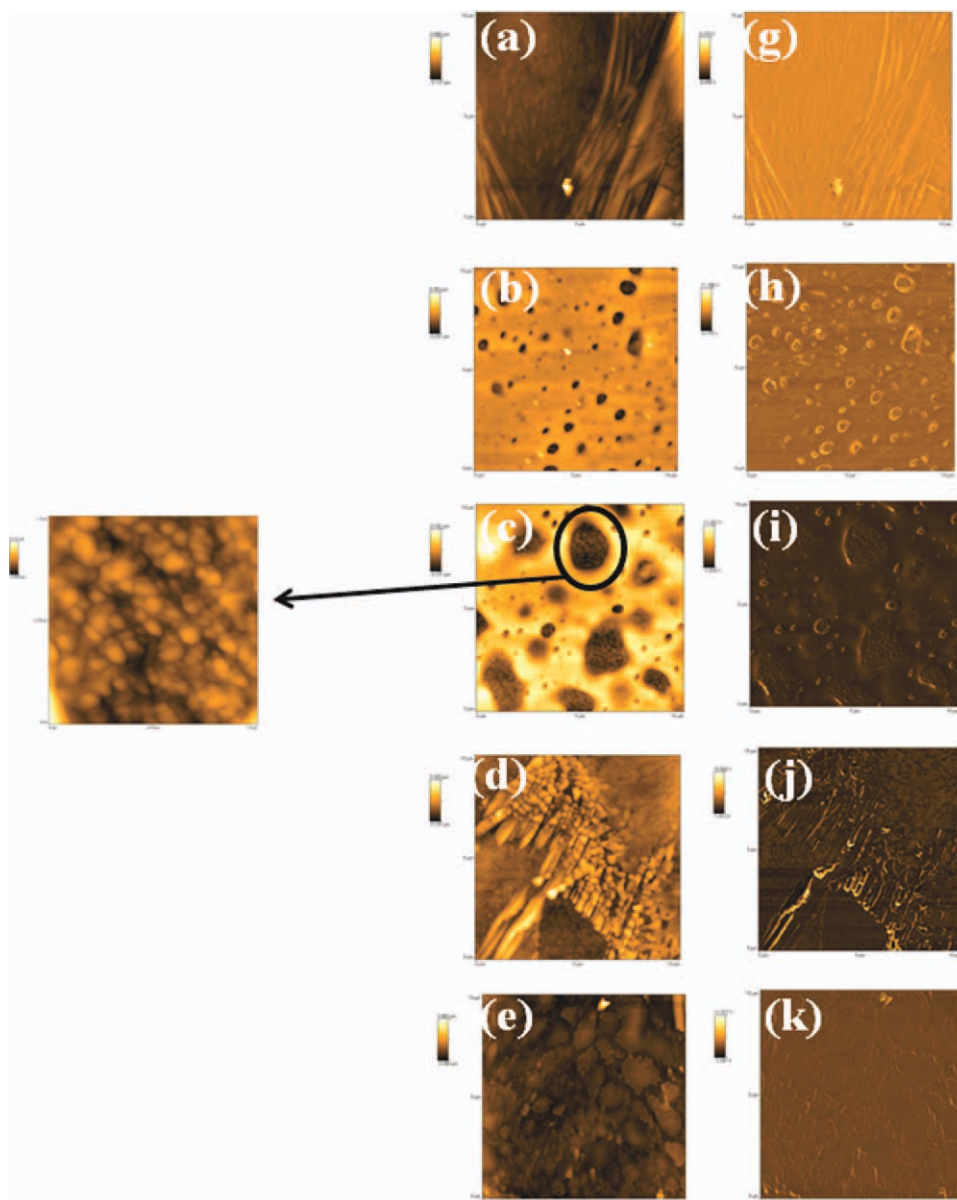
## PL

Figure 2 shows the PL spectra of the hybridized pure POMA (PCB) and of the blends prepared using the CP hybridized with the BT molecule. Hybridized POMA and its blends presented a



**Figure 3.** AFM topographic images of (a) pure POMA (CP), POMA/PMMA blends; (b) CPM 5; (c) CPM 10; (d) CPM 25; (e) CPM 50; and (f) PMMA. Phase images of (g) pure POMA, POMA/PMMA blends; (h) CPM 5; (i) CPM 10; (j) CPM 25; (k) CPM 50; and (l) PMMA. Scanning area:  $10 \times 10 \mu\text{m}^2$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 4.** AFM topographic images of (a) hybridized pure POMA with dye (CPB), POMA/PMMA blends prepared in the presence of dye; (b) CPMB 5; (c) CPMB 10; (d) CPMB 25; and (e) CPMB 50. Phase images of (f) CPB, POMA/PMMA blends; (g) CPMB 5; (h) CPMB 10; (i) CPMB 25; and (j) CPMB 50. Scanning area:  $10 \times 10 \mu\text{m}^2$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

band in the range of 476–550 nm that was attributed to the presence of dye. For comparison, POMA/PMMA blends prepared without BT report no PL emission. The absence of PL in the POMA and consequently in the blends prepared without the dye is due to quinoids/imines groups of the CP chain that quenches the PL from benzoids/amines groups. That is, the light emission by small reduced groups is inhibited by oxidized groups of the CP chain.<sup>27</sup> PL spectrum of the BT molecule in  $\text{CHCl}_3$  presents a band centered at  $\sim 400$  nm. The red shift of this band in the new materials can be justified by the interaction of BT with the CP, causing an increase in  $\pi$  bonds of the dye and consequently its redshift.<sup>6</sup>

It was possible to observe that POMA-CSA-dye/PMMA 10% blends showed more intense PL. A possible explanation for this behavior may be due to fact that at high concentrations, above 10 wt/wt % of the CP, the PL is quenched. In addition, the PL process is competitive, and it is impossible to control the number of electronic decays with light emission, and therefore, it is hard to compare the PL intensity owing to the concentrations of the blends. Then, it is suggested that there are optimal concentrations of CP for the preparation of these blends that can interact with the BT obtaining a better efficiency in the PL intensity.

AFM images of POMA, CPM 50 blend without dye, and PMMA showed small globules on its surface [Figure 3(a, e, f)], while that sample with 5, 10, and 25 wt/wt % of CP showed structures that resemble small crystals [Figure 3(b–d)]. These were originated from recrystallized dopant on the surface of the polymeric blends, after evaporation of the solvent. The phase images [Figure 3(h–k)] of the blends prepared without the hybridized CP did not indicate phase separation between polymers, which is an interesting feature of the polymeric blends. Phase images of the POMA and PMMA [Figure 3(g, l)] showed no color contrast as they are pure samples.

AFM images of the materials obtained with BT showed that the dye modified the morphology of the pure POMA and its blends [Figure 4]. Considering the phase images, again, it was noted that there is no phase separation between polymers [Figure 4(h–k)]. This is an important feature for the photoluminescent blends, because regarding the fabrication of OLEDs from these materials, the phase separation may be responsible for low efficiency and color changing being emitted with the applied voltage.<sup>28</sup> Phase images of hybridized pure POMA [Figure 4(f)] showed no color contrast, suggesting that there is no phase separation between the BT and the POMA.

Topography images revealed that at low concentrations of CP, there are POMA globules being covered by the PMMA matrix [Figure 4(b, c)]. Blends with a high content of hybridized POMA present their surface covered with aggregated globules making structures resembling brushes and islands mostly on the surface of the blends [Figure 4(d, e)]. The morphology of the hybridized CP showed elongated and apparently rigid structures [Figure 4(a)]. This morphology is unusual for this CP.

Crystals on the surface of the blends prepared without BT are responsible for increasing the roughness of the materials as can be seen by the Ra (arithmetic roughness) and Rms (root mean-square average) values [Figure 5(a)]. PCM 5, PCM 10, and PCM 25 blends showed Ra values of 35.6, 54.9, and 69.4 nm; and Rms values of 56.6, 77.1, and 100.3 nm, respectively. On the other side, the samples pure POMA, PCM 50 blend, and PMMA presented Ra values of 10.7, 10.5, and 1.9 nm; and Rms values of 13.6, 13.6, and 2.65 nm, respectively. AFM images show that the samples with crystals on the surface have a significant difference of Ra and Rms values, indicating that in these cases the surfaces are very rough.<sup>29</sup> Although the CPM 50 blend does not present “crystals” of CSA on its surface, it does not mean that this sample does not contain these structures, but only because it was not identified by several scans performed to obtain the morphology of the sample.

Analysis of Ra and Rms values to materials obtained with BT [Figure 5(b)] allowed to observe that the CPMB 10 blend roughness is higher than CPMB 5, CPMB 25, and CPMB 50 blends, and pure POMA. This may be related to the formation of some holes on the CPMB 10 blend with diameters ranging from 1.17 to 2.21  $\mu\text{m}$ , while on the CPMB 5 blend this diameter was 1.05 to 0.62  $\mu\text{m}$ . Despite the higher Ra value for the CPMB 10 sample, probably given by the holes on the surface of the blend, it is possible to make a relationship between the morphology of these blends with the PL efficiency. PL spectrum

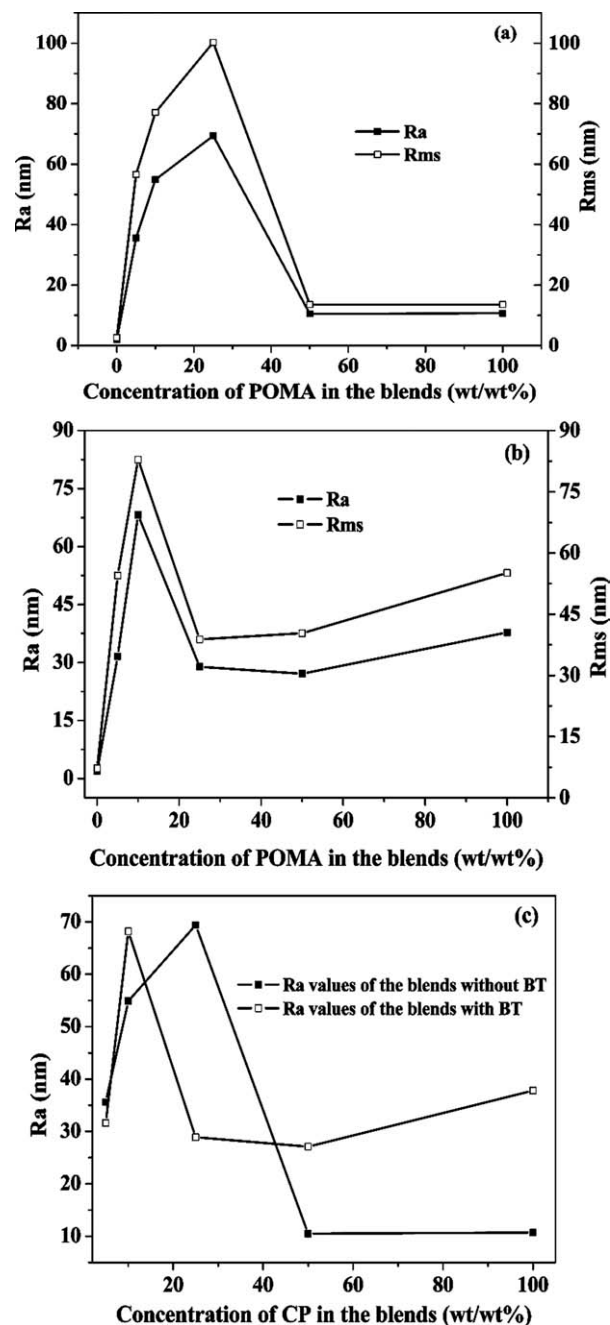
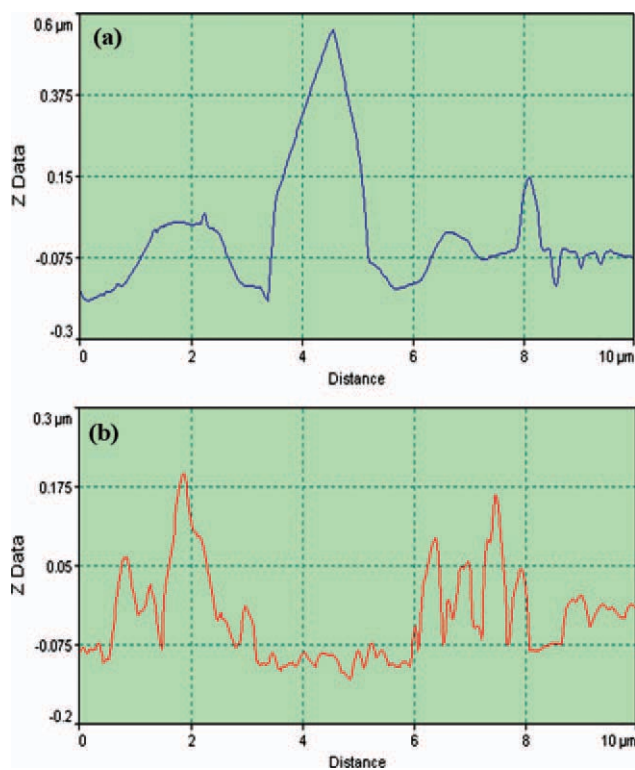


Figure 5. Profile height of the blends (a) CPM 25 and (b) CPMB 25.

[Figure 2] shows that CPMB 5 and CPMB 10 samples are more efficient. In the morphology of these blends, as already mentioned, there are globules of hybridized POMA on the surface covered by the PMMA layer [Figure 4]. This morphology could help to understand the PL efficiency, but it is necessary to consider two points: first, the interaction of the BT molecule occurs, mostly on CP (this was observed in the UV-Vis spectrum, Figure 1); and second, the electronic transitions related to PL occur mainly in the CP chains. So, it is observed that inside the holes on CPMB 5 and CPMB 10, there are globules of hybridized CP with low roughness (13.8 nm, data not shown),



**Figure 6.** Ra and Rms values of the (a) CP, CPM 5, CPM 10, CPM 25, CPM 50 blends and PMMA; (b) CPB, CPMB 5, CPMB 10, CPMB 25, CPMB 50 blends and PMMA; and (c) Comparison of the Ra values of materials prepared without and with the presence of BT. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

compared with the surface of other blends. Inhomogeneous regions, roughness, and holes in the films limit the transport efficiency of charged carriers.<sup>30</sup> In other cases when a surface is smooth, the mobility of charged carriers is more efficiency and consequently the electronic transitions become more intense.<sup>30</sup> In the region inside the hole, i.e., in the region with globules of hybridized CP, the surface is less rough, and perhaps this region is responsible for the highest PL observed.

Comparing the Ra values of the blends prepared with and without hybridized CP, it was possible to observe that the presence of the BT changed significantly the roughness of the blends with 10, 25, and 50 wt/wt % and of the pure CP [Figure 5(c)]. The presence of BT molecules in the CPMB 10 and CPMB 50 blends and CPB (pure POMA) promoted an increase in the Ra values. The blends presented Ra values of 68.2 and 27.1 nm, respectively. These blends prepared without BT showed Ra values of 54.9 and 10.5 nm, CPB sample revealed Ra value of 37.8 nm and sample of CP without BT has Ra value of 10.7 nm.

However, it was verified that in CPMB 5 and CPMB 25 blends, the presence of BT molecules caused a reduction of the roughness on surface. Ra values these blends prepared without the BT were 35.6 and 69.4 nm, respectively, while after hybridization process CPMB 5 and CPMB 25 samples presented Ra values of

31.6 and 28.9 nm, in this order. The difference of roughness between samples prepared without and with the BT occurred probably by appearance of aggregated globules, in hybridized samples, that have heights less than the structure (“crystals”) found on the surface of CPM 25 sample [Figure 6], for example.

In general, it is observed that the BT changes the morphology of the blends; however, this change may be random, increasing the roughness in some samples or reducing in others. Then, it is not possible to say that the BT causes a homogenization process in the samples.

## CONCLUSIONS

Using dye in polymeric blends modifies their optical and morphological properties. Blends prepared without dye showed UV-Vis absorption bands corresponding to the absorption of POMA, however, with different intensities. With the dye, the new materials show a single band and the maximum absorption in range 805–814 nm. Another important characteristic associated with the presence of the dye was the PL emission in the polymeric blends with the maximum in range of 500–550 nm. Small globules and “crystals” on the surface of the blends prepared without BT were substituted by small globules covered by PMMA matrix at samples with low concentration of CP and at samples with higher concentrations of CP. The surface showed clusters of globules and structures that resemble islands and brushes, respectively. Thus, it became evident that the presence of the dye in the polymeric blends completely modified the morphology of the materials. This change in the morphology occurred also in the pure POMA, where AFM images revealed the appearance of elongated features after the hybridization process of the CP.

The presence of the BT in the composition of the blends provides interesting optical properties for the blends, suggesting a possible application in optoelectronic devices such as OLEDs.

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