

Miscibility studies of azopolymer/poly3-alkylthiophene mixtures in solution and on Langmuir films

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Abstract –The miscibility between an azopolymer and a poly(thiophene) was investigated using UV-Vis and FTIR spectroscopies and in Langmuir films using surface pressure, Brewster angle microscopy (BAM) and Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS). Through FTIR spectra and PM-IRRAS no interactions was observed at the molecular level, while phase segregation was apparent in the BAM images. The results of surface pressure isotherms suggest some degree of interaction for proportions up to 60% of HPDR1-MA. In addition, the Langmuir films formed by the 50 wt% mixture were amenable to form good optical quality LB films, which is relevant for potential applications.

Azopolymers and polythiophenes have been extensively studied due to their functional properties and possibility of applications in opto-electronic devices^{1,2}. The mixture of these polymers can lead to new properties and widen the field of applications, especially if this mixture is processed in the form of nanostructured films such as Langmuir-Blodgett (LB) films. Since the properties of the mixture depend on the molecular-level interactions between the polymers, their miscibility was investigated using UV-Vis and FTIR spectroscopies. In the Langmuir films, the investigation comprised surface pressure measurements, Brewster angle microscopy (BAM) and Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) for the mixture of an azopolymer derived from the dye 4-(N-ethyl-N-(2-methacryloxyethyl) - 4'-nitroazobenzene (Disperse Red 1, DR1), referred to here as HPDR1-MA, with poly(3-dodecylthiophene) (HP3-DodT). The UV-Vis spectra for the 50% HPDR1-MA/HP3-DodT mixture in solution showed maximum absorption at a wavelength intermediate to those obtained for the neat polymers. The immiscibility at the molecular level was confirmed with the FTIR spectrum, which was a superimposition of the spectra of the neat polymers. In Langmuir films, the isotherms of the HPDR1-MA and HP3-DodT showed no clear collapse up to 58 and 30 mN/m and extrapolated area per repeating unit close 25 and 3 Å² respectively, as shown in Figure 1. An analysis of the shape of the isotherms and of the plot of area per molecule at a fixed pressure of 15mN/m as a function of the relative concentration of HPDR1-MA made it possible to infer that proportions lower than 60% of HPDR1-MA did not present interactions. The BAM images for Langmuir films with 30 to 70% of HPDR1-MA indicated phase segregation with small domains of HP-3DodT for any surface pressure, which is clearly seen in Figure 2. The PM-IRRAS features suggested that the structure of the mixed film on the water interface is similar to those of the neat polymers; however, the intensity and orientation of the bands had a stronger influence of HP-3DodT. Even though there was no molecular-level interaction between the polymers, yielding phase segregation, the Langmuir films could be transferred onto glass substrates at 30 mN/m, leading to good optical quality LB films for the mixture with 50 wt% ratio. Significantly, attempts to deposit quality LB films from the neat polymers failed. The UV-VIS. spectrum of the mixed LB films was not shifted in comparison to the spectrum in solution, thus indicating the lack of aggregation in the solid state. The immiscibility between the polymers apparently led to a material with properties of both polymers, which was amenable to LB film fabrication.

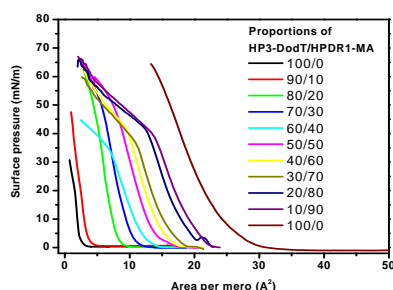


Figure 1: Surface pressure-area isotherms for all proportions of the mixtures

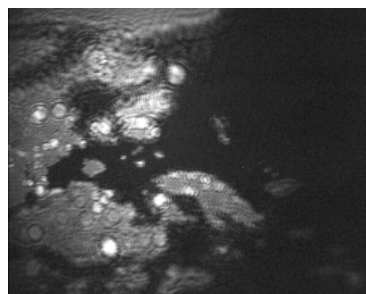


Figure 2 : BAM images showing the phase segregation for 30% HPDR1-MA/HP3-DodT mixture

References

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