Polymer 52 (2011) 5897–5903

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Characterization of surface compositions of phase-separated structures in conjugated poly(phenylene vinylene) blends by scanning near-field optical microscopy

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ARTICLE INFO

Article history:
Received 19 July 2011
Received in revised form
20 October 2011
Accepted 23 October 2011
Available online 29 October 2011

Keywords:
Scanning near-field optical microscopy
Conjugated polymer blends
Substrate effect

ABSTRACT

The phase-separated structures in a thin-film conjugated polymer blend, poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene)/poly(methyl methacrylate) (MDMO-PPV/PMMA) was studied by scanning near-field optical microscopy (SNOM), which can probe both of the surface topography and the chemical composition at high spatial resolution. In thin films of MDMO-PPV/PMMA, the PMMA-rich phase with less fluorescent emission appeared as a raised structure while the MDMO-PPV-rich phase with highly fluorescent emission was present as a collapsed phase with a low height. Such the vertical structure of the phase separation was dependent on the solvent quality for each component. On the other hand, the lateral structure was determined by the surface property of the substrate. As the degree of hydrophobic character of the substrate increased, the PMMA domains tended to form a continuous form to a separated spherical form. This evolution arise from a change in affinity between the substrate surface and PMMA, which the hydrophilic substrate has higher affinity to PMMA for maintaining the continuous structures and the hydrophobic substrate with lower affinity to PMMA can not hold the structures continuously.

1. Introduction

Macroscopic properties are greatly dependent on the structure at the length scale from micro- to nano-meters. Polymer blends have attracted a lot of interests because they provide convenience in custom-tailoring the physical or chemical properties by combining different polymeric materials for various end uses. In order to control the properties of polymer blends materials, it is of great importance to understand the phase separation of blend systems [1–12]. Phase separation structures in polymer blends for 3-D bulk system are generally different with those for 2-D thin film system. Recent studies of phase separation in polymer blends have focused on thin films [13–17]. Under spatial confinement, blended thin films with nano- to micro-meter thickness typically form phase-separated structures close to their polymer-air or polymer–substrate interfaces. These structures, with various morphologies and chemical compositions at these interfaces, normally have a broad range of applications, such as lubricants, adhesives, coatings and for lithographic masks. These facts have motivated numerous studies, especially of the causes of the formation of various phase-separated structures in blended thin films. Different factors such as solvent, temperature, film thickness, substrate, blend composition, and the nature of end groups have been examined [13–17]. The polystyrene/poly(methyl methacrylate) (PS/PMMA) blend is the model system for studying structural formation and evolution of a thin film scale with a sub-micron thickness. Its structure and morphology vary with several factors, including solvent solubility as well as film thickness [13,14]. Moderately handling these factors enables the structures to be controlled, widening the range of applications.

Atomic force microscopy (AFM) is commonly utilized to examine surface phase separation in thin-film blends [18–21]. The surface topography of a specimen can be observed with nanometric spatial resolution. The heterogeneity of the surface chemical composition and its correlation with topographic structures are of interest. However, because AFM probes the force between the cantilever tip and the sample surface, the characterization of the chemical composition is generally difficult. Scanning near-field

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doi:10.1016/j.polymer.2011.10.043

optical microscopy (SNOM) has been recently developed as an advanced technology for identifying fine structures in thin films [22–25]. Unlike conventional optical microscopy, SNOM can scan a surface in the same manner as AFM with a force feedback response from the SNOM probe, but the incident light is simultaneously introduced into the SNOM probe. SNOM employs a scanning probe with an aperture in a sub-wavelength size, which generates an optical near-field that is confined near the end of the tip. With SNOM, scanning at a short distance from the surface of the specimen not only determines the topography but also characterize the chemical species unambiguously from optical spectroscopic information with spatial resolution beyond the diffraction limit of light. Therefore, compositional heterogeneity and structural features can be identified by the optical contrast associated with components of the blends.

Conjugated polymers such as polythiophene, polyfluorene and poly(phenylene vinylene) (PPV) have attracted substantial interest because of their particular optical and electrical properties. These special properties of conjugated polymers can be exploited in various developments, especially of advanced devices that must have light-emissive and electron-conducting functions, and they has been extensively studied for the applications in the organic electronics devices such as light emitting diodes, photovoltaics, transistors and lasers [26–29]. The optoelectronics devices of conjugated polymers are mainly fabricated by solution processes. Various properties of the devices are controlled by the combination of a few components of conjugated polymers. Most of the polymer blends undergo phase separation. Understanding and controlling the phase separation of conjugated polymer blends are of great importance for the device construction, since the structure of nanometric length scale has a significant influence on the device efficiency [27–34]. For instance, the phase separation in polymer solar cells importantly affects the device efficiency since the fundamental electronic processes occur at the phase interface [29]. Hence, studying phase separation in conjugated polymer blends would provide important information from the viewpoint not only of academic interest but also of practical application in the organic electronics.

In this study, the phase separation of a thin film in one model conjugated polymer blend system, poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) and poly(methyl methacrylate) (PMMA), was examined to observe/identify directly the phase-separated structures and their compositions at the polymer-air interface using SNOM under high resolution. MDMO-PPV is a conjugated polymer that is widely used for the investigations of optoelectronic devices [35]. The other component in the blends, PMMA, can also be utilized as a dielectric material in thin film transistors or as a host material in polymer light emitting diodes. The relationship of surface topography and the chemical composition in thin film blends of MDMO-PPV/PMMA was directly examined by SNOM. The phase-separated structure of the conjugated polymer blend is discussed in terms of the surface property of the substrate and the solvent quality.

2. Experimental

The SNOM measurements in this work were performed by the α–SNOM (WITec) using a cantilever probe with an aperture diameter of 60nm for scanning the sample surface in contact mode. The conjugated blends were excited through the tip with a 438-nm laser (BCL-015-440, CrystaLaser). The surface topography was simultaneously obtained. The incident laser light was delivered to the sample through the aperture at the cantilever to excite the conjugated polymer blends. The fluorescence of the sample was collected by a microscope objective (0.8NA, 60X, Nikon) behind the sample substrate and detected by a photon counting photomultiplier tube (H8631, Hamamatsu Photonics) after passing through a long-pass filter (LP02-442RS-25, Semrock). All of the SNOM measurements were made at room temperature.

Poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV with a molecular weight of 9.5×10^4 g/mol) and poly(methyl methacrylate) (PMMA with a molecular weight of 3.5×10^5 g/mol) were supplied by Aldrich. Reagent grade toluene was used as a common solvent to dissolve both MDMO-PPV and PMMA. To prepare polymer blend solutions, MDMO-PPV and PMMA were first separately dissolved in toluene at a concentration of 3 mg/ml to yield the individual polymer solutions. Then, blended solutions of MDMO-PPV and PMMA were obtained by mixing the individual polymer solutions in different ratios by mass. Specimens for the SNOM measurement were prepared by spin-coating. Sample films with average thickness around 80–100 nm were prepared by spin-casting the polymer solutions on glass cover slips cleaned by sequential sonication in toluene, acetone and methanol. The resultant films after spin-coating were moved to a vacuum oven at 40 °C for 12 h to remove the residual solvent.

3. Results and discussion

The surface structures and compositions of MDMO-PPV/PMMA blends were identified from SNOM images of specimens. Fig. 1(a) shows the topographic image of the MDMO-PPV/PMMA = 50/50 blend that was spin-cast from toluene. Two structural features, a raised structure and a collapsed structure, were identified.The structural features with height difference in the blends are generally regarded as the structures of different compositions in the blends. However, to elucidate more precisely the compositions of these structures, a fluorescent image was also obtained. Fig. 1(b) presents the SNOM fluorescence image obtained simultaneously with the topography. This image exhibits an optical contrast related to the compositions of the separated phases in the blends. The highly emissive areas in Fig. 1(b) represent the MDMO-PPV-rich phase, while the less emissive regions represent the PMMA-rich phase. The elevated structures with less fluorescence can be identified as the PMMA-rich domains while the structures in the low-lying region with high fluorescence are attributed to the MDMO-PPV-rich domains, which can absorb incident light from the SNOM aperture and fluoresce. Normally, the spin-coating of polymers from the common solvent yields a non-equilibrium structure because the process is too fast for an equilibrium state to be achieved, such structural features as the elevation and the depression of specific phases are suggested to be related to the solubilities of blended components in the solvent [13]. The PMMA may deplete the aromatic toluene solvent more quickly and solidify earlier due to poor solubility than MDMO-PPV. Thereafter, subsequent solvent evaporation cause the solidification/collapse of the MDMO-PPV phase and results in the height difference between the MDMO-PPV and PMMA phases at the polymer-air interface. The blend film from 1,2-dichloroethane showed an opposite topographic feature : the MDMO-PPV and PMMA domains corresponded to the high- and low-lying regions, respectively (the results not shown here). Since the solvent quality of 1,2-dichloroethane is poor for MDMO-PPV and good for PMMA. Therefore, the MDMO-PPV would consume the solvent quickly and solidify earlier to form the raised structure, while the later solidification of PMMA would cause the collapsed structure and result in the height difference between two phases. An estimation of the solubility parameter using the group contribution method [36] also confirms that toluene ($\delta = 17.6$) is a better solvent for MDMO-PPV ($\delta = 17.7$) than it is of PMMA ($\delta = 20.0$), and 1,2-dichloroethane ($\delta = 19.2$) is the better solvent for PMMA than it is of MDMO-PPV, supporting the trend identified in