X-ray Microscopy and NEXAFS Spectroscopy of Macrophase-Separated Random Block Copolymer/Homopolymer Blends

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Received August 20, 1996
Revised Manuscript Received November 13, 1996

Morphological characterization of bulk polymer blends or compatibilized alloys at submicron spatial resolution has almost exclusively relied upon electron microscopy techniques. Since, however, most organic polymers are composed of carbon and light elements, an arsenal of methods to enhance phase contrast has been developed to facilitate discrimination and analysis of property-governing morphological features.[1] For transmission electron microscopy (TEM), chemical modification of polymeric specimens through, for example, functionality-specific incorporation of heavy-metal staining agents (typically OsO_4 or RuO_4) may result in ambiguous results due to an inadequate understanding of the staining reaction or competing reaction kinetics. While microanalytical techniques such as light-element energy-dispersive X-ray mapping[2] and electron spectroscopic (energy-filtered) imaging[3−5] can potentially eliminate the need for chemical modification in TEM and have proven highly valuable in identifying morphological characteristics in unmodified multiphase polymer systems, they are typically only capable of distinguishing among constituent elements. In addition, appropriate steps must be exercised during data acquisition to minimize specimen damage due to electron beam irradiation.

Another microscopy technique recently applied to the morphological characterization of multiphase polymers is X-ray microscopy (XRM),[6−9] in which chemical sensitivity is based on the principles of near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.[10] This technique utilizes a diffractive optical element (zone plate) to focus highly monochromatic soft X-rays in the energy range of 200−600 eV generated by a synchrotron radiation source onto an ultrathin polymer specimen (typically 100−200 nm in thickness). The transmitted flux is detected as a function of specimen position as the specimen is raster-scanned by piezoelectric transducers. A detailed description of the microscope employed in this work is provided elsewhere.[11] The practical spatial resolution of XRM is dictated by zone plate technology, with the smallest available probe presently limited to a full width at half-maximum of about 55 nm, resulting in a minimum feature resolution of about 35 nm.

Recent XRM studies of multiphase polymers have successfully elucidated the morphological characteristics of a binary blend composed of polypropylene (PP) and poly(styrene-*r*-acrylonitrile) (SAN).[6,8] Such blends are expected *a priori* to be highly demixed due to the chemical dissimilarity of the constituent polymers. Moreover, SAN (unlike PP) contains nitrogen, in which case the SAN spatial distribution can be discerned by either XRM or the element-specific techniques mentioned earlier. In this work, we explore the sensitivity of XRM by examining a polymer blend in which the constituent materials are identical in terms of the elements present (C and H only) and, moreover, differ only in terms of their fraction of the same chemical moiety (polystyrene, PS). As a consequence, blends of this type have been found[12,13] to exhibit complex phase behavior that is highly dependent on both blend composition and molecular weight considerations. Results obtained here from XRM are compared with TEM micrographs of the same blend after functionality-specific OsO_4 staining.

The polymers employed in this work were PS with $\bar{M}_n = 120\,000$ and $\bar{M}_w/\bar{M}_n \approx 1.04$ and a "random" diblock copolymer (RBC) synthesized by living anionic polymerization in the presence of *sec*-butyllithium and a potassium alkoxide. A detailed description of the copolymer synthesis and molecular characterization (in terms of monomer sequencing) is provided elsewhere[14−16] and is not addressed, for the sake of brevity, in this communication. The RBC was a poly[(styrene-*r*-isoprene)′-*b*-(styrene-*r*-isoprene)″], (S/I)′-*b*-(S/I)″, copolymer, where the ′ and ″ denote different block compositions, namely, 75/25 and 50/50 (wt %) S/I. The overall composition of the RBC was 68 wt % S, as measured by ^{1}H NMR, and the block lengths were approximately 40 000 each. Two RBC/PS blends, one consisting of 20 wt % RBC and 80 wt % PS and the other 80 wt % RBC and 20 wt % PS, were prepared by solution casting from toluene, as described elsewhere.[13] Upon slow solvent evaporation and subsequent annealing, the resultant films were sectioned in a Reichert-Jung Ultracut-S cryoultramicrotome maintained at −100 °C. Sections for TEM analysis, nominally 100−120 nm in thickness and stained with the vapor of OsO_4(aq) for 90 min, were imaged on a Zeiss EM902 electron spectroscopic microscope operated at 80 kV and $\Delta E = 50$ eV. The XRM analysis was performed on the X-1A Beamline of the National Synchrotron Light Source at Brookhaven National Laboratory.

Shown in Figure 1 is a representative electron micrograph of the 20/80 RBC/PS blend, demonstrating that the blend is, as expected from thermodynamic considerations, macrophase-separated, with the RBC appearing as structureless, slightly ellipsoidal dispersions measuring on the order of 5 μm across. In this micrograph, the isoprene repeat units have been preferentially stained with OsO_4 and consequently appear electron-opaque in transmission. Since isoprene is found in both blocks of the RBC, both blocks are stained with OsO_4 and appear dark in Figure 1. Note also that, since the compositions of the two blocks comprising the RBC are not very different (75/25 vs 50/50 wt % S/I), this styrene−isoprene diblock copolymer is microstructurally disordered,[17] even though the block masses are 40 000 each. This lack of interblock incompatibility explains why the RBC dispersions do not appear as the multilamellar (i.e., "onion"-skin) vesicles typically observed[18] in macrophase-separated block copolymer/homopolymer blends. It is important to realize that not all RBC copolymers composed of styrene and isoprene repeat units are disordered; one RBC with 75/25 and 25/75 S/I blocks of equal length ($\bar{M}_n \approx 80\,000$), for example, has been shown[19] to exhibit distinct, but slightly diffuse, alternating lamellae.

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S0024-9297(96)01268-5 CCC: $14.00

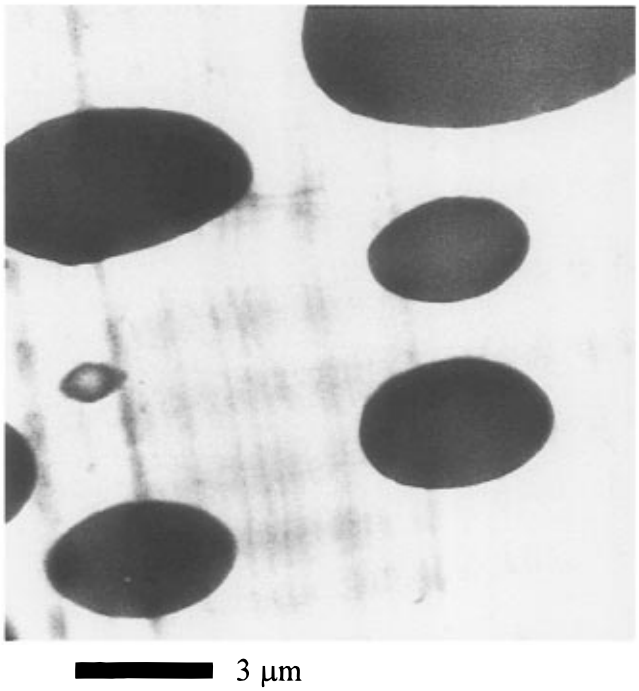

Figure 1. TEM micrograph of the 20/80 (wt %) RBC/PS blend utilized in this study. Electron-opaque (dark) regions correspond to OsO_4-stained isoprene and reveal the spatial distribution of the RBC. This blend has macrophase-separated into discrete RBC dispersions.

X-ray micrographs of thin sections of the same blend acquired without specimen staining are displayed for comparison in Figure 2. The micrograph in Figure 2a was obtained with 285.3 eV X-rays, an energy which is highly absorbed by unsaturated C=C bonds, and the PS appears dark. The RBC dispersions appear lighter than the PS matrix, and their ellipsoidal morphology is apparent. Figure 2b shows an X-ray micrograph acquired at 306.1 eV, an energy not strongly correlated to any specific chemical functionality. It essentially provides a carbon "density" map. Again, the ellipsoidal RBC dispersions are clearly evident, which indicates that they are slightly thinner or less dense than the surrounding matrix. Careful comparison of the two micrographs reveals a higher contrast in Figure 2a relative to Figure 2b due to the presence of more unsaturated C=C bonds on a per carbon atom basis in the matrix.

If the X-ray energy is scanned near an absorption edge while the specimen is held stationary, a NEXAFS absorption spectrum can be obtained from different regions of the same specimen. The presence of absorption peaks depends on both the elements and chemical functionalities comprising the regions analyzed and must be mass-normalized to correct for specimen thickness. Four absorption spectra acquired at the carbon edge from various places in both RBC/PS blends are presented in Figure 3. Figure 3a shows the absorption spectrum of PS from the matrix of the 20/80 RBC/PS blend. The dominant feature of this PS spectrum, which matches well with previously reported spectra of PS,[9−10] is the large absorption peak at 285.3 eV due to π^* absorption of the unsaturated bonds. The next two peaks at 287.5 and 289.5 eV are attributed to C−H σ^* absorption and aromatic $2\pi^*$ absorption, respectively. The remaining broad features located at higher energies are assigned to σ^* absorption of the phenyl group and the C−C backbone. Similarly, Figure 3b displays the absorption spectrum of the RBC from the matrix of the 80/20 RBC/PS blend. Due to the presence of like functional groups, the overall spectral shape of the RBC (Figure 3b) is comparable to that of PS (Figure 3a), but differences are visible, especially between 287 and 289 eV (denoted in each spectrum by an arrow). Unfortunately, a reference spectrum of polyisoprene is unavailable and difficult to obtain. In general, precise energies

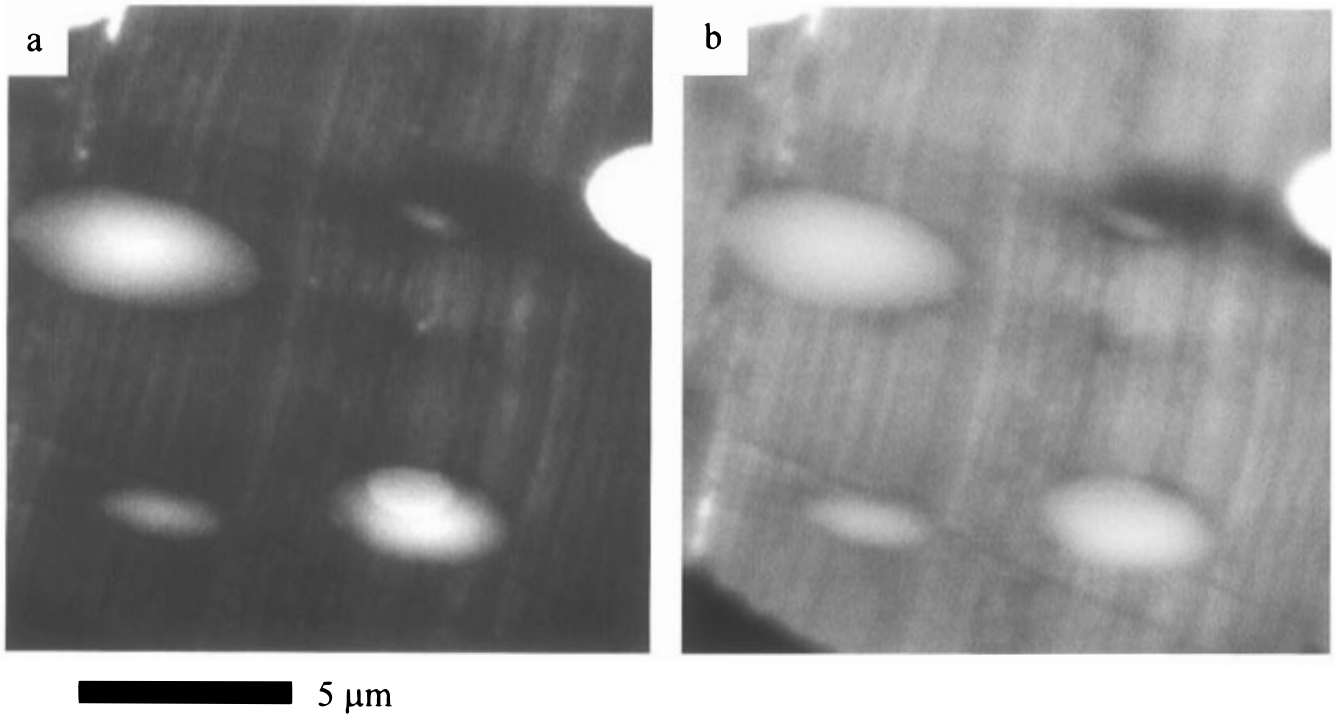

Figure 2. X-ray micrographs of the unstained 20/80 RBC/PS blend acquired at (a) 285.3 eV, where the C=C bonds are highly absorbing, and (b) 306.1 eV, an energy which is nonfunctionality specific and provides a carbon "optical density" map. Both images show the ellipsoidal shape of the RBC dispersions within the PS matrix. The heightened contrast in (a) relative to (b) is due to the presence of isoprene (which absorbs less at 285.3 eV) in the dispersions.

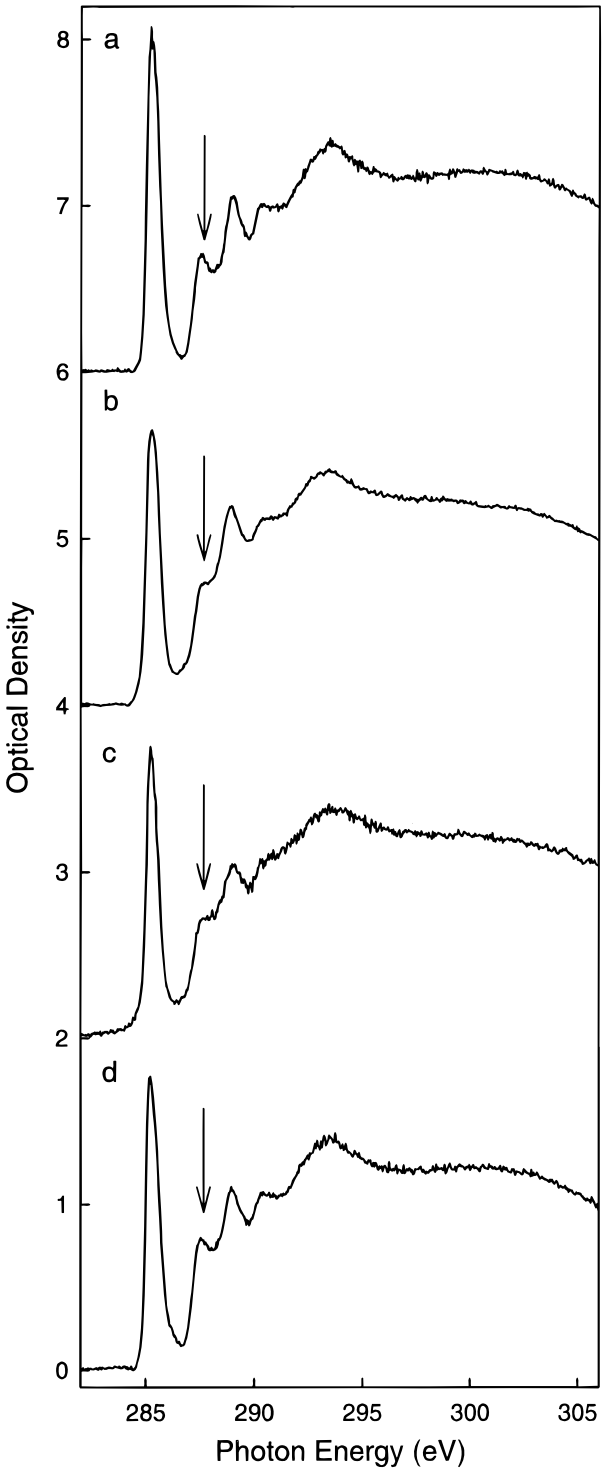

Figure 3. Near-edge X-ray absorption fine structure (NEXAFS) spectra collected from (a) the PS matrix within the 20/80 RBC/PS blend, (b) the RBC matrix of the 80/20 RBC/PS blend, and (c and d) two different dispersions within the 20/80 RBC/PS blend. Spectrum (a) agrees well with previously acquired PS spectra, and differences between (a) and (b) are due to the presence of isoprene units in the RBC. The dispersion corresponding to spectrum (c) is pure or close to pure RBC, while spectrum (d) reveals the existence of PS within a different RBC dispersion. An arrow points to the area in each spectrum where the spectral differences are most obvious. The presence of PS within the dispersions and the nonuniform content among dispersions are only observable with X-ray microscopy. These spectra have been normalized such that the intensity at 281.0 eV is equal to zero and the intensity at 308.0 eV is equal to one with an offset of two between each spectrum.

and intensities of NEXAFS spectral features are difficult to predict due to relaxation of the molecular orbitals during the core-excitation process.[10,20,21] To distinguish the RBC and PS components within the blend, we therefore consider the spectrum in Figure 3b as a "reference" spectrum for the pure RBC.

Absorption spectra acquired from within two different RBC dispersions in the 20/80 RBC/PS blend are provided in Figure 3c,d. The spectrum in Figure 3c is comparable to that presented in Figure 3b, indicating that the dispersion is very similar in composition to the RBC matrix in the 80/20 RBC/PS blend. It can therefore be concluded that this dispersion consists predominantly of the RBC with no significant amount of PS present. However, the spectrum shown in Figure 3d more closely resembles the spectrum of the PS phase provided in Figure 3a, which is particularly obvious if one considers the 287−289 eV energy range (marked by arrows in Figures 3a−d). This similarity indicates the presence of PS within the dispersion. Given the large dispersion size relative to the specimen thickness, contamination by an underlying layer of matrix is unlikely. The spectra in Figure 3c,d demonstrate that the RBC-rich dispersions in the 20/80 RBC/PS blend contain varying amounts of PS and consequently possess a nonuniform composition. This information is only obtainable through XRM, since the OsO_4 staining agent employed in the TEM analysis effectively masks any compositional heterogeneity. It is of interest to note that, according to TEM micrographs, the PS-rich dispersions in the 80/20 RBC/PS blend contain a small fraction of RBC molecules, as evidenced by the presence of an ultrafine microstructure composed of RBC micelles.[13]

In this work, we have examined two block copolymer/homopolymer blends in which the disordered block copolymer contained 68 wt % PS (nonevenly distributed between both blocks) and the homopolymer was neat PS. For the purpose of this study, a random poly(styrene-*r*-isoprene) copolymer could have likewise been used. Electron micrographs of the 20/80 RBC/PS blend, stained with OsO_4 vapor, demonstrate that this blend consists of RBC dispersions in a PS matrix. Complementary X-ray micrographs, obtained at several photon energies specific to different chemical functionalities present in the blend, show virtually identical morphological features without chemical modification (to enhance phase contrast). In addition, XRM absorption spectra indicate the presence of PS in some of the RBC-rich dispersions in the 20/80 RBC/PS blend, a consequence of both the chemical similarity of the constituent materials and the disordered nature of the copolymer. Unlike the micellized RBC molecules residing in PS dispersions in RBC-rich blends, we presently have no evidence to suggest that the PS molecules in the RBC dispersions examined in this study undergo self-organization. Since the chemical moieties in this blend are identical in terms of the elements present, morphological and chemical characterization could only be achieved through functionality discrimination or selective chemical modification (i.e., staining). Thus, XRM constitutes a viable complement to TEM and provides an excellent alternative to blend/alloy characterization when conventional staining may result in ambiguous results.

Acknowledgment. This work was supported by a National Science Foundation Young Investigator Award (DMR 945-8060) (H.W.A.), the National Science Foundation (CMS 941-2361) (R.J.S.), and the Shell Development Co. (R.J.S.).

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MA9612687