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Visualizing Surface Phase Separation in PS-PMMA Polymer Blends at the Nanoscale using Tip-enhanced Raman Spectroscopy

Phase-separated polymer blend films are an important class of functional materials with numerous technological applications including solar cells [1], coatings [2], and biotechnology [3]. These technologies are underpinned by precise control of phase separation at the nanometer length-scales, which is highly challenging to visualize using conventional analytical tools. In this work, we show that tip-enhanced Raman spectroscopy (TERS), in combination with AFM, confocal Raman spectroscopy, and XPS, is a sensitive nanoanalytical method to determine lateral and vertical phase-separation in polystyrene (PS)-poly(methyl methacrylate) (PMMA) polymer blend films (Figure 1a) [4]. Correlative topographical, molecular, and elemental information obtained using the combination of techniques is able to reveal a vertical phase separation of the polymers within the top ca. 20 nm of the blend surface in addition to the lateral phase separation in the bulk. Furthermore, complementary TERS and XPS measurements reveal the presence of PMMA within 9.2 nm of the surface and PS at the sub-surface of the polymer blend as schematically illustrated in Figure 1b. These results show that correlative topographical, molecular, and elemental information can provide a complete picture of the lateral and vertical phase separation in polymer-blends, which cannot be determined by any single technique alone. This work demonstrates the potential of TERS to be a powerful complementary analytical tool for nanoscale polymer characterization.

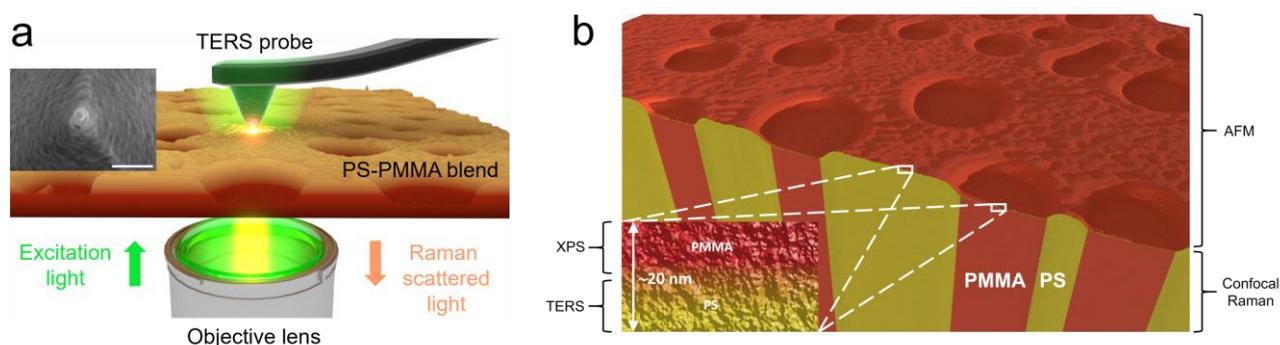


Figure 1: (a) Scheme of the transmission-mode AFM-TERS setup used for AFM, confocal Raman and TERS measurements in this study. Inset displays a SEM image of a representative Ag-coated TERS probe. Inset scale bar: 300 nm. (b) Schematic illustration of the proposed PS-PMMA blend structure based on the correlative AFM, confocal Raman, TERS and XPS measurements. Laterally phase-separated PS and PMMA domains revealed by AFM and confocal Raman imaging are covered with a continuous surface layer of vertically phase-separated PMMA and PS revealed by XPS and TERS, as shown in the inset.

References

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