

Imaging the Phase Segregation in PS/PMMA Copolymer Blends by TOF-SIMS

Overview: Industrial polymer blends are frequently used as lower cost approaches to tailor the chemical and physical properties of the bulk material with the desired surface properties such as lubricity, adhesion or chemical reactivity. In polymer blends, the two-dimensional and three-dimensional structures of the polymer components can be one of the major factors determining the physical properties of the material. Various methods such as cryomicrotomy combined with SPM have been used to observe copolymer structures in 2 and 3 dimensions, as illustrated by Sugihara and coworkers [1]. Often, however, these approaches provide little information concerning the surface and bulk chemistry or molecular composition. Imaging time-of-flight secondary ion mass spectrometry (TOF-SIMS) provides a unique tool to visualize two-dimensional chemical information with a spatial resolution on the order of 100 nm. The recent introduction of liquid metal ion beams incorporating high mass cluster ions such as Au_3^+ , Bi_3^+ and Bi_3^{++} have increased the sensitivity of TOF-SIMS toward molecular and structurally significant ions that now have yields which allow high contrast chemical imaging at a spatial resolution of 100 – 300 nm. In this Note we demonstrate the capability to visualize the chemical inhomogeneities, or phase segregation, of copolymer blends at high spatial resolution. A TRIFT-based TOF-SIMS instrument was equipped with a Bi cluster liquid metal ion gun (LMIG) to produce a high count rate of structurally significant molecular fragment secondary ions for chemical imaging of the sample surface.

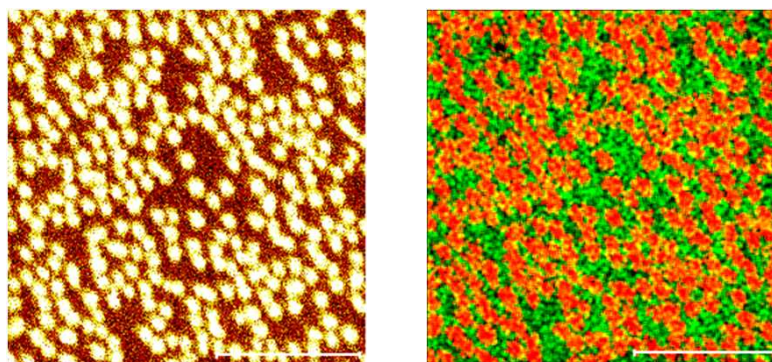


Figure 1. Images of the 30:70 blended copolymer of PS:PMMA. (LEFT) Total Ion image. (RIGHT) False-color overlay of the $\text{C}_4\text{H}_5\text{O}^+$ molecular fragment of PMMA (55 m/z; red) and the C_7H_7^+ molecular fragment of PS (91 m/z; green). Each image is $25\ \mu\text{m} \times 25\ \mu\text{m}$, and the marker is $10\ \mu\text{m}$.

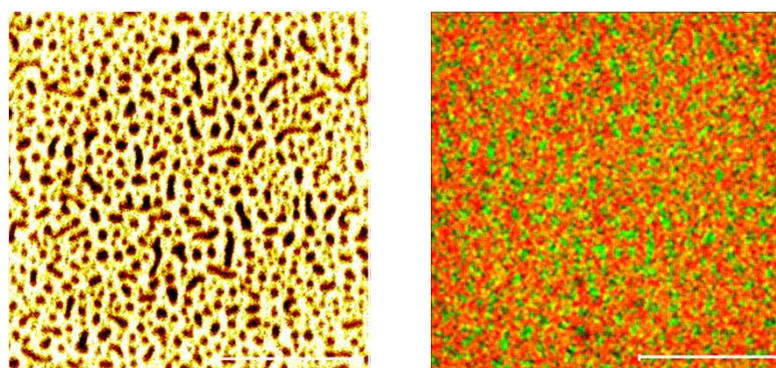


Figure 2. Images of the 20:80 blended copolymer of PS:PMMA. (LEFT) Total Ion image. (RIGHT) False-color overlay of the $\text{C}_4\text{H}_5\text{O}^+$ molecular fragment of PMMA (55 m/z; red) and the C_7H_7^+ molecular fragment of PS (91 m/z; green). Each image is $25\ \mu\text{m} \times 25\ \mu\text{m}$, and the marker is $10\ \mu\text{m}$.

Experimental: Chemical imaging of two different copolymer blends (a. PS:PMMA = 30:70, b. PS:PMMA = 20:80) was performed using samples composed of the copolymer thin film spin-cast onto a silicon substrate. All TOF-SIMS measurements were made on a PHI TRIFT-based instrument. A 60 keV Bi_3^{++} primary ion beam, operating at a DC current of 0.5 nA, was used to acquire images of the copolymer blends in the positive secondary ion polarity. The analytical field-of-view was $25\ \mu\text{m} \times 25\ \mu\text{m}$ with a 256 pixel \times 256 pixel digital raster, and the primary ion dose was maintained well within the static limit, i.e. $< 1 \times 10^{13}\ \text{Bi}_3^{++}/\text{cm}^2$, for each analysis. Charge compensation was easily achieved with $\leq 15\ \text{eV}\ \text{e}^-$ and $\leq 10\ \text{eV}\ \text{Ar}^+$ of the PHI-patented dual-beam charge neutralization system. A raw data stream file was collected to allow further post-acquisition evaluation (i.e. retrospective analysis) of the data.

Results: The total ion image and the polymer specific molecular fragment ion images of the copolymer blends are revealed in Figure 1 and Figure 2. The polymer specific molecular fragment ions used for imaging are the C_7H_7^+ ion of polystyrene and the $\text{C}_4\text{H}_5\text{O}^+$ ion of poly(methyl methacrylate). In each of the total ion images, the PMMA-rich regions produce a greater total ion signal and therefore appear brighter. This difference in contrast between the PS and the PMMA domains is caused by the greater ion yield probability of oxygen containing species produced by PMMA over that of aromatic hydrocarbon species produced by PS. The false-color overlays of $\text{C}_4\text{H}_5\text{O}^+$ (55 m/z; red) and C_7H_7^+ (91 m/z; green) for each copolymer blend show the complementary nature of the polymer phases and also reveal the micron and submicron-scale domains of each blend, specifically of the PS domains in the 20:80 blend. Examined together, these images show that each copolymer blend has a distinct phase segregation behavior. Namely, in the 30:70 blend, the PMMA fraction appears in islands at the surface with rather large domains. However, in the 20:80 blend, the PS fraction has an island structure at the surface but with much smaller domains. These results are in qualitative agreement with a previous report by Sugihara and coworkers [1], but the detailed structure is somewhat different. Ostensibly, the differences arise because the samples prepared for the TOF-SIMS analysis were spin-cast onto Si substrates while those probed by Sugihara, et al., were spin-cast onto polyimide-coated substrates.

Conclusion: A Bi_3^{++} primary ion beam was used on a TRIFT-based TOF-SIMS instrument to observe the domain structure of two PS:PMMA copolymer blends. The utility of the Bi cluster ion beam lies in the ability to achieve high yields of characteristic and structurally significant molecular fragment ions at the 1 μm to the 100 nm scale for the purposes of TOF-SIMS chemical imaging. It was shown that two similar (30:70 and 20:80) blends of PS and PMMA spin-cast onto Si substrates have markedly different phase segregation behaviors.

Acknowledgements and References:

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[1] H. Sugihara, K. Oya, H. Murase, K. Akabori, K. Tanaka, T. Kajiyama and A. Takahara, *Appl. Surf. Sci.* **254** (2008) 3180.



**PHYSICAL
ELECTRONICS**
A DIVISION OF ULVAC-PHI

Physical Electronics USA, 18725 Lake Drive East, Chanhassen, MN 55317
Telephone: 952-828-6200, Website: www.phi.com

ULVAC-PHI, 370 Enzo, Chigasaki City, Kanagawa 253-8522, Japan
Telephone 81-467-85-4220, Website: www.ulvac-phi.co.jp