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Interfacial Staining of a Phase-Separated Block Copolymer with Ruthenium Tetroxide

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ABSTRACT: We report on an unusual staining phenomenon of a diblock copolymer, poly(ferrocenylsilanes)-*b*-poly(dimethylsiloxanes) (PFS-*b*-PDMS). By a combination of transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis, it is found that when a thin section of diblock copolymer is exposed to ruthenium tetroxide vapor, the interfaces between the PFS and the PDMS microdomains are selectively stained. The effect appears to arise from a delicate competition between reactivity and diffusion. This observation broadens our knowledge of the staining behavior of diblock copolymers and provides a potential route to pattern ordered nanoring arrays using diblock copolymers as a template.

Introduction

Block copolymers in the bulk state can spontaneously self-assemble into periodic structures with long-range order as a result of microphase separation of the constituent blocks.[1] This approach is currently attracting intense current interest as a route to nanostructured materials such as porous membranes, lithographic templates, and photonic band-gap materials.[2] If one of the blocks contains metal centers in the repeat unit, then additional interesting properties may be anticipated because of the novel chemical and physical properties of metallopolymers.[3] For example, polyferrocenylsilanes (PFSs), consisting of alternating ferrocenyl units and silicon atoms in the main chain, possess interesting redox, conductive, preceramic, etch-resistant, and catalytic properties.[4] Well-defined PFS block copolymers with low polydispersity in molar mass can be synthesized via anionic ring-opening polymerization of strained silaferrocenes.[5] Self-assembly of PFS block copolymers in the bulk produces nanostructures with multifunctional PFS microdomains. This topic has been studied in detail both by our research groups and also by other workers.[6]

Transmission electron microscopy (TEM) is the most powerful technique for direct visualization at a high level of resolution of phase-separated structures formed by block copolymers. Obtaining appropriate contrast is often the most important difficulty to overcome when examining block copolymers by TEM. In many block copolymer systems, the poor contrast arises from the fact that generally there is only a small difference in the electron densities of the different polymer phases. This difficulty can be overcome by selectively staining one polymer phase with a heavy-atom-containing reagent, such as osmium tetroxide (OsO_4) or ruthenium tetroxide (RuO_4).[7] OsO_4 is primarily effective as a stain for polymers containing olefinic unsaturated functionalities.[8] RuO_4 is a more vigorous oxidant and can react with both aromatic and unsaturated polymers as well as the amorphous domains of some saturated polymers. This makes RuO_4 a more versatile selective staining reagent to enhance the electron density contrast for TEM studies of block copolymers.[9]

For PFS block copolymers, the electron density of the iron-rich PFS phase has been a useful source of contrast for the examination of unstained TEM images.[5b,6a−f] At times, however, we found that the contrast was insufficient, or we saw features in the image that may be attributed to artifacts. Under these circumstances, selective staining becomes an important tool for understanding TEM images.

Herein, we report an unusual staining phenomenon observed when we exposed thin sections of PFS-*b*-PDMS diblock copolymers to RuO_4 vapor. RuO_4 did not, as expected, stain the easily oxidizable PFS microdomains in the sample. Instead, we found through a combination of TEM and EDX (energy dispersive X-ray) analysis that RuO_4 selectively stained the interfaces between the PFS and the PDMS microdomains.

Experimental Section

Materials. PFS homopolymer was synthesized by anionic polymerization of silicon-bridged [1]ferrocenophane with *n*-butyllithium as initiator. PFS-*b*-PDMS diblock copolymers were synthesized by sequential anionic polymerization of corresponding silicon-bridged [1]ferrocenophane and hexamethylcyclotrisiloxane with *n*-butyllithium as initiator. Molecular weights were determined by gel permeation chromatography (GPC) with a Waters Associates liquid chromatograph equipped with a triple-detector system. The compositions of the diblock copolymers were determined by ^1H NMR. PDMS homopolymer was purchased from Aldrich.

Small-Angle X-ray Scattering. Small-angle X-ray scattering measurements were performed on a Nanostar SAXS system (Cu Kα radiation, $\lambda = 1.54$ Å) from Bruker AXS GmbH with a GADDS area detector. The sample-to-detector distance was set to 0.6 m.

Transmission Electron Microscopy. The diblock copolymer samples were microtomed at −170 °C using a Leica UCT ultramicrotome with a Leica EMFCS cryo-attachment. The sections were collected using 200 mesh carbon-coated copper grids. The bright field transmission electron microscopy (TEM) measurements and energy dispersive X-ray (EDX) analysis images of unstained samples were carried out on a Hitachi S-5200 instrument equipped with an Oxford Instruments Inca EDX system at an accelerating

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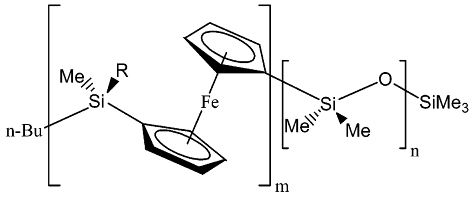
voltage of 30 kV. The bright field TEM, annular dark field TEM measurements, and EDX analyses of stained samples were carried out on a Hitachi HD-2000 instrument equipped with an Oxford Instruments Inca EDX system at an accelerating voltage of 200 kV. EDX analysis was carried out in the line scan mode.

The polymer samples were stained with ruthenium tetroxide as follows: RuO_4 was produced in situ by mixing 0.1% aqueous ruthenium trichloride with 4% active chlorine aqueous sodium hypochlorite. The diblock copolymer thin sections or the homopolymer films were exposed, at ambient temperature, to the vapor of this freshly made ruthenium tetroxide for 10 min to 1 h. *Caution*! RuO_4 is highly toxic.

X-ray Photoelectron Spectroscopy (XPS). The XPS spectra were obtained using a PHI 5500 ESCA system with a monochromated Al Kα source (1486.6 eV). The nominal analysis area is 800 μm^2. The sampling depth is ca. 5 nm. The experimental binding energy values for the stained film were calibrated with respect to binding energy of adventitious surface carbon 1s at 284.8 eV and recorded at a depth of ca. 14 nm. Sputtering was performed using a 3 keV Ar^+ ion beam at an incident angle of 60°. The sputtered depths were estimated on the basis of a sputter rate of 0.6 nm/s, determined using a SiO_2/Si reference sample. The atomic ratio of Ru:O was determined from the relative peak areas of Ru 3p and O 1s due to the overlap of Ru $3d_{3/2}$ and C 1s peaks.

Results and Discussion

Two diblock copolymer samples, a poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFDMS$_{105}$-*b*-PDMS$_{300}$; M_n = 46 000, PDI = 1.01, ϕ = 0.47)[10] and a poly(ferrocenylethylmethylsilane-*b*-dimethylsiloxane) (PFEMS$_{75}$-*b*-PDMS$_{330}$, M_n = 46 000, PDI = 1.1, ϕ = 0.37), were synthesized via sequential anionic ring-opening polymerization according to the literature procedure.[5b] Films of the two samples were prepared by solvent casting from THF solutions of the corresponding block copolymer. Thin sections (ca. 50 nm in thickness) were prepared by microtoming the corresponding film at −170 °C and collected on carbon-coated TEM grids.



PFDMS-b-PDMS R = methyl PFEMS-b-PDMS R = ethyl

Figure 1a shows the small-angle X-ray scattering (SAXS) pattern of the PFDMS$_{105}$-*b*-PDMS$_{300}$ sample, which exhibits peaks at *q* ratios of 1:2:3:4:5:6, as expected for a well-ordered lamellar structure. The bright field TEM−EDX analysis image of the PFDMS$_{100}$-*b*-PDMS$_{300}$ thin section in Figure 1b reveals alternate bright and dark lamellae with the bright domains corresponding to the PFS phase and the darker domains corresponding to the PDMS phase.[11] The thin sections of PFDMS$_{100}$-*b*-PDMS$_{300}$ were stained by exposure to RuO_4 vapor for 10 min. The bright field TEM−EDX analysis image in Figure 1c shows the structure after staining. Black stripes can be clearly seen between gray domains and bright domains. EDX analysis shows that the gray domains correspond to the PDMS phase and the bright domains correspond to the PFS phase. The ruthenium exhibits the strongest intensity at the interfaces between the PFS domains and the PDMS domains, indicating a preferential interfacial staining. This interfacial staining can still be observed when the staining time was increased to 1 h.

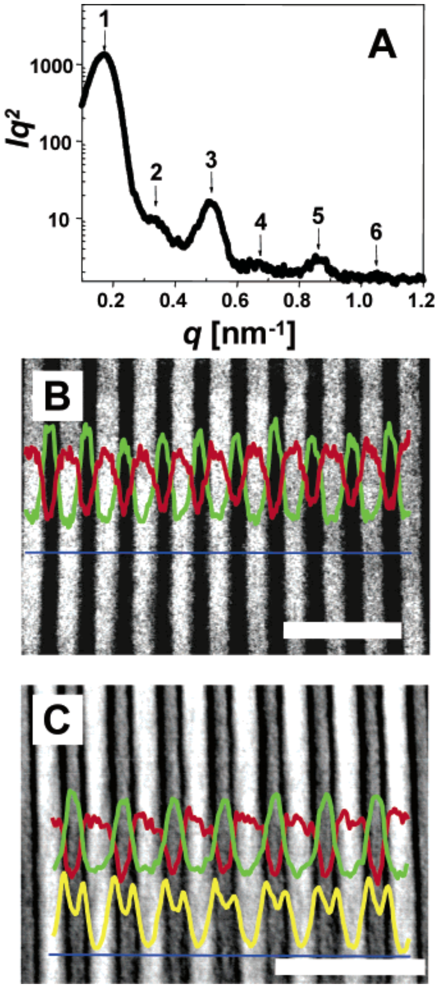


Figure 1. (A) SAXS pattern of a PFDMS$_{105}$-*b*-PDMS$_{300}$ film. (B) Bright field TEM−EDX analysis image of a PFDMS$_{105}$-*b*-PDMS$_{300}$ thin section (iron in red, silicon in green); scale bar: 100 nm. (C) Bright field TEM−EDX analysis image of a PFDMS$_{105}$-*b*-PDMS$_{300}$ thin section after RuO_4 staining (iron in red, silicon in green, and ruthenium in yellow); scale bar: 100 nm.

Loo et al. found when polyethylene-*b*-polyvinylcyclohexane (PE-*b*-PVCH), a semicrystalline−glassy block copolymer, was stained with RuO_4, the amorphous PE regions within the PE microdomains were selectively stained.[9d] Thus, in the TEM micrograph, it appears, although not very clearly, that the interfaces between the PE and PVCH components were preferentially stained. PFDMS homopolymer is semicrystalline.[12] Although the PFDMS-*b*-PDMS block copolymer in bulk appears to be amorphous indicated by the lack of Bragg peaks in its WAXS spectrum (not shown), to further exclude any possible role of crystallinity in our observations in this system, we also examined a diblock copolymer, PFEMS$_{75}$-*b*-PDMS$_{330}$, with an amorphous polyferrocenylsilane block. The SAXS pattern in Figure 2a indicates a hexagonally packed cylindrical structure for PFEMS$_{75}$-*b*-PDMS$_{330}$, corroborated by the bright field TEM−EDX analysis image in Figure 2b, which shows PFEMS cylinders with a diameter of ca. 33 nm dispersed in a PDMS matrix. Figure 2c shows the bright field TEM image of RuO_4 stained PFEMS$_{75}$-*b*-PDMS$_{330}$. One can observe an array of hexagonally packed rings, in which the rings appear darker than the background. Figure 2d shows the annular dark field (*Z*-contrast) TEM image of the same section. The *Z*-contrast TEM image is sensitive to the atomic number of the species shown in the image, where the brighter areas are those containing atoms having a higher atomic number. As indicated by the annular dark field TEM−EDX analysis image in Figure 2e, the stronger contrast for the ordered packed rings resulted

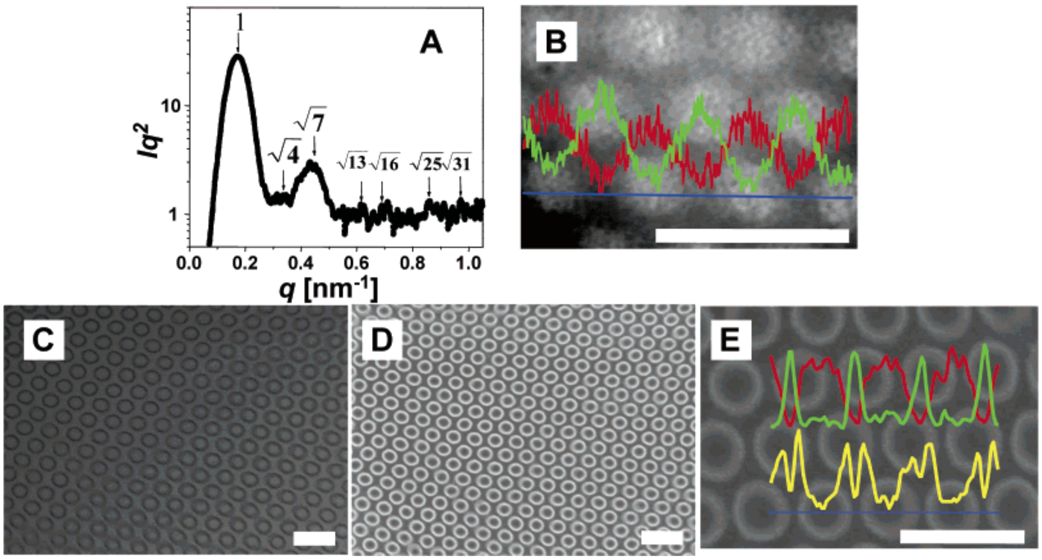


Figure 2. (A) SAXS pattern of PFEMS$_{75}$-*b*-PDMS$_{330}$ film. (B) Bright field TEM−EDX analysis image of PFEMS$_{75}$-*b*-PDMS$_{330}$ thin section (iron in red, silicon in green); scale bar: 80 nm. (C) Bright field and (D) annular dark field TEM image of PFEMS$_{75}$-*b*-PDMS$_{330}$ thin section after RuO$_4$ staining; scale bar: 80 nm. (E) Annular dark field TEM−EDX analysis image of PFEMS$_{75}$-*b*-PDMS$_{330}$ thin section after RuO$_4$ staining (iron in red, silicon in green, and ruthenium in yellow); scale bar: 80 nm.

from the contribution of ruthenium (a relatively high atomic number element), concentrated at the interfaces between the PFEMS domains and the PDMS domains. This result implies that the interfaces between PFEMS and PDMS were preferentially stained after exposure to RuO$_4$ vapor.

The staining by RuO$_4$ is presumably due to the local reduction of RuO$_4$ by the polymer.[7] The presence of localized electron-rich reduced products creates enhanced contrast in TEM imaging. Staining is a dynamic process, controlled by a competition between diffusivity and reactivity. We speculate that RuO$_4$ is more soluble in PDMS than in PFS and that, within the PDMS phase, it is unreactive and diffusively mobile. PDMS is a low-T_g amorphous polymer with excellent gas permeability due to its high free volume and is able to dissolve many nonpolar substances. PDMS is normally considered stable to oxidation, whereas PFS is easily oxidized because of the presence of the ferrocene moiety in the main chain.[4c] We tested the response of PFDMS and PDMS to the staining agent by examining film samples of PFDMS homopolymer (M_n = 25 000, PDI = 1.02) and PDMS homopolymer (M_n = 31 000, M_w = 94 000), prepared by solvent casting from tetrahydrofuran (THF) solution. Under visual inspection, the PFDMS film exposed to RuO$_4$ vapor became gradually darker. When the treated PFDMS film was dissolved in THF, a black precipitate was observed. Size exclusion chromatography (SEC) results (data not shown) reveal obvious degradation of PFDMS upon staining. Under these conditions, PDMS homopolymer was almost unaffected.

To gain insight into the nature of the reaction products of RuO$_4$ and PFS, X-ray photoelectron spectroscopy (XPS) measurements were carried out on PFDMS homopolymer thin films prior to and after staining with RuO$_4$. The thin film was prepared by spin-coating a toluene solution of PFDMS (M_n = 25 000, PDI = 1.02) homopolymer onto a silicon wafer. The results are shown in Figure 3.

The relative binding energy (BE) of the Fe 2p$_{3/2}$ peak at 707.9 eV for the film prior to staining is close to that reported by others for PFDMS[4g] and consistent with the value of 707.8 eV for ferrocene.[13] After staining, both Fe 2p peaks at 707.9 and 720.4 eV became broader, indicating a slight oxidation of the ferrocene moiety. The Si 2p peak shifted to a higher BE (from 100.4 to 102.2 eV) and became much broader, which is indicative of the formation of species with a higher oxidation state. The position of the Si 2p peak at 102.2 eV is close to the range of 102.2−102.4 eV reported for siloxanes.[13] The shoulder at lower BE is consistent with Si 2p for the untreated film. An additional contribution at higher BE may be attributed to silicon dioxide, the BE of Si 2p for which is generally in the range of 103−104 eV. The BE of O 1s at 532.2 eV is also consistent with the range of 532−533 eV reported for siloxanes and silicon dioxide.[13]

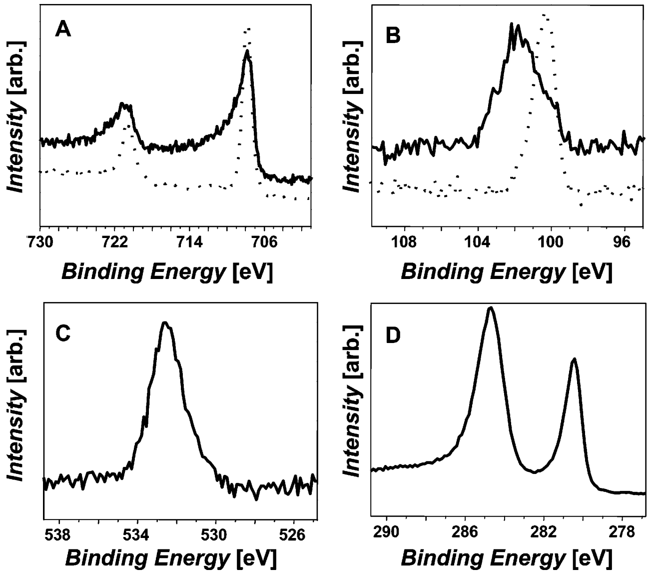


Figure 3. XPS spectra of PFDMS homopolymer thin films. (A) Fe 2p regions prior to staining (dotted line) and after staining (solid line). (B) Si 2p regions prior to staining (dotted line) and after staining (solid line). (C) O 1s region after staining. (D) Ru 3d region after staining, with the peak at ca. 285 eV resulting from the superposition of the C 1s core level from the polymer and the Ru 3d$_{3/2}$ core level.

The BE of Ru 3d$_{5/2}$ at 280.4 eV is near the range for ruthenium in the zerovalent state (279.9−280.2 eV) and that for ruthenium dioxide (280.3−282.1 eV).[13] The binding energy of O 1s for ruthenium dioxide is generally in the range of 529.3−529.4 eV.[13] The absence of an O 1s peak or a peak shoulder in this range ruled out the possibility of ruthenium dioxide formation. Further evidence is available from the atomic ratio of Ru:O, calculated as 3:2. If the reduced product of RuO_4 were ruthenium dioxide, the atomic ratio of Ru:O would be less than 1:2. Therefore, we conclude that ruthenium metal is the reduced product of RuO_4.

We propose the following mechanism for the interfacial staining of PFS-*b*-PDMS block copolymer with RuO_4. When a PFS-*b*-PDMS thin section is exposed to RuO_4 vapor, the RuO_4 is preferentially absorbed into PDMS. Because of the relatively high diffusivity of RuO_4 in PDMS, it rapidly diffuses to the interfaces, where it oxidizes PFS. The consumption of RuO_4 promotes additional diffusion of RuO_4 to the interfaces and further absorption of RuO_4 vapor into the PDMS domains. In this way, the PDMS domains act as reservoirs for RuO_4. At the interfaces, RuO_4 reacts with PFS to form ruthenium particles. As a consequence, the interfaces between PFS and PDMS domains are selectively stained.

Conclusions

We have demonstrated that the interfaces of PFS-*b*-PDMS diblock copolymers can be preferentially stained with RuO_4 vapor. The effect appears to arise from a delicate competition between reactivity and diffusion. To our knowledge, this is the first report of selective staining of a block copolymer interface with RuO_4.[14] This observation broadens our knowledge of the staining behavior of diblock copolymers in the bulk state.

Furthermore, this interfacial staining provides a route to pattern hexagonally packed ruthenium rings using diblock copolymers as a template. Research aimed at exploiting the possibility of transferring the pattern to underlying substrates is underway.

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Supporting Information Available: Figure S1, showing the bright field TEM image and annular dark field TEM image of $PFDMS_{105}$-*b*-$PDMS_{300}$ thin section after RuO_4 staining. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The subscripts refer to the number-averaged degree of polymerization; ϕ refers to the volume fraction in the bulk state of the polyferrocenylsilane block.

(11) In a bright field TEM image of microphase-separated PFS-*b*-PDMS, the electron-rich PFS domains should appear dark. The contrast inversion seen here under electron beam irradiation is the type of observation that prompted these staining experiments. A more detailed analysis of the contrast inversion phenomenon for these samples will be presented elsewhere.

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(14) The staining of the central block in a phase-separated triblock copolymer has been described previously in, e.g., ref 8b.

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