

# Nanoscale Patterning of Barium Titanate on Block Copolymers

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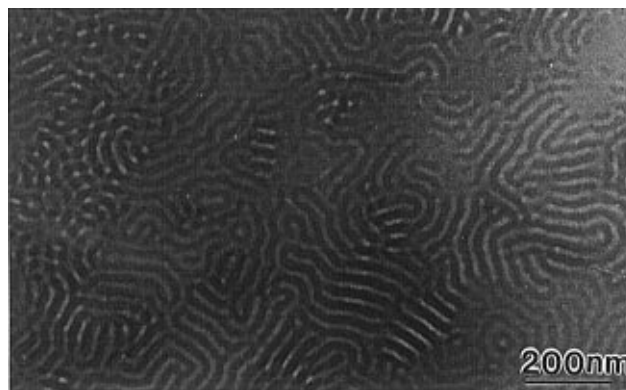
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A triblock copolymer of polystyrene–polybutadiene–polystyrene (Kraton D1102) has been used to pattern barium titanate precursor with nanoscale modulations. The copolymer self-assembles to yield cylindrical polystyrene nanodomains in a polybutadiene matrix. The preorganized thin films of polymer are then selectively OH-functionalized *in situ* on the unsaturated carbon bonds in the polybutadiene matrix with antistereochemistry. Anchoring the barium titanate precursor onto the hydroxylated polymer thin films is possible only in the *trans*-1,2 polybutadiol matrix through the condensation between the barium titanium double alkoxides and the hydroxyl groups. The regioselective deposition of the barium titanium double alkoxides on the original polybutadiene matrix of the Kraton thin films was verified by transmission electron microscopy and electron energy loss spectroscopy. The spacing of the coordinated barium titanium double alkoxide pattern was ~23 nm, equivalent to the interdomain spacing of the original polybutadiene matrix.

## Introduction

The length scales defining structure and organization determine the fundamental characteristics of a material. Unique, size-dependent properties are observed especially when the dimensions of a phase are confined to the nanometer scale (<100 nm).<sup>1</sup> Many useful size-dependent phenomena in optics, electronics, and magnetism are exhibited by nanosized clusters of metals and semiconductors.<sup>2</sup> However, in spite of the potential of nanostructured materials, their development has been partially hindered by an inability to process them for commercial applications. A promising fabrication approach is the self-assembly methodology used by biogenic systems. Especially in the processing of organic/inorganic nanocomposites (i.e., bone, teeth, and shells), the approach used by nature offers a significant opportunity to design materials through the self-assembly of organic molecules into complex structures on the scale of 1–100 nm.<sup>3</sup> Organization of inorganics on these length scales is difficult; but, self-assembling organic structures can assist the formation of nanostructured inorganics by catalytically or epitaxially inducing specifically patterned organic/inorganic composites through controlled nucleation and growth of the inorganic phase.

The recent development of a family of nanostructured organic/inorganic composites formed by templating surfactant liquid crystalline structures is an excellent example of utilizing self-assembly to design periodic structures in the 1–10 nm length scale.<sup>4</sup> The extension of the



**Figure 1.** TEM bright-field image of the terrace region of the osmylated (stained) annealed thin film of Kraton. The cylindrical nanodomain spacing of PS (light) in Kraton is 10 nm, and the interdomain spacing of PB (dark) is 23 nm. The average molecular weight is 71 000 and the PS:PB ratio is 28:72.

length scale up to 100 nm is desirable and it may be possible to achieve this with the use of other surfactant systems.<sup>5</sup> An attractive alternative approach is to use block copolymers that spontaneously self-assemble to yield nanodomains of lamellas, cylinders, or spheres at length scales of 10–100 nm (Figure 1).<sup>6</sup> These are ideally suited to the design of periodic structures and can be used to form organic/inorganic nanocomposites.<sup>7–9</sup> The orientation of nanodomains can be further influenced by the substrate surface. Registration between layers influences the interfacial coordination which propagates into the phase-mixed region. At equilibrium, an organized array is formed everywhere and the periodicity of the nanodomain orientation is well established.<sup>10–12</sup>

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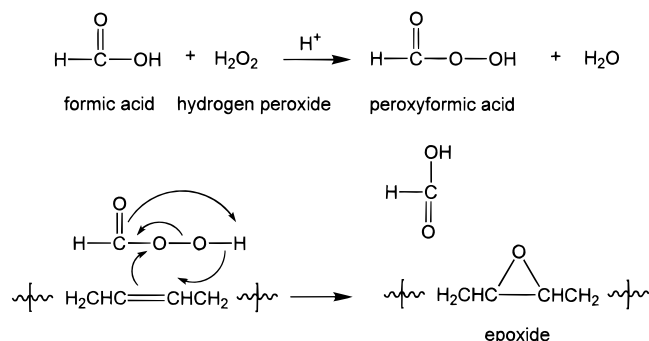
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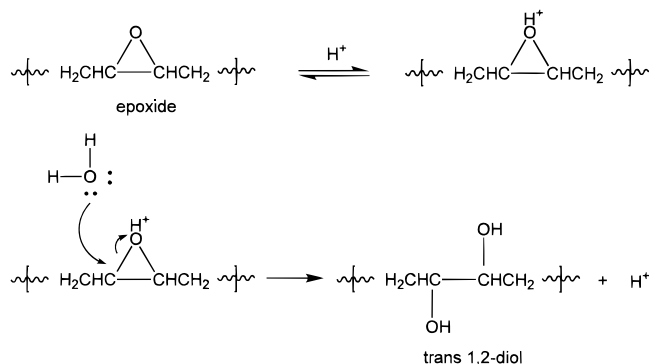
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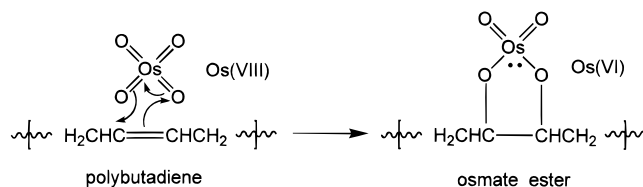
**Figure 2.** Peroxyformic acids are thought to transfer the oxygen farthest from the carbonyl group to the unsaturated carbon in PB through a rather complex one-step mechanism without carbonation intermediates.<sup>20</sup>



**Figure 3.** Hydroxylation of epoxides to 1,2-diols. Acid-induced epoxide ring opening takes place by S<sub>N</sub>2 attack of a nucleophile on the protonated epoxide.<sup>22</sup>

Toward the goal of forming nanostructured composites with periodic patterns, we have successfully localized coordinated barium titanium double alkoxides regioselectively onto polybutadiene (PB) interdomains within a polystyrene (PS)–polybutadiene–polystyrene triblock copolymer, Kraton D1102 (Shell Chemical Co., Houston, TX) thin film. The structure of Kraton was preserved throughout the chemical reactions. Barium titanate (BaTiO<sub>3</sub>), a dielectric and a ferroelectric, was selected as the inorganic phase because it is used extensively in multilayer capacitors, thermistors, and electrooptic devices<sup>13,14</sup> and its low-temperature (<100 °C) synthesis, an essential requirement for coupling with polymers, is well understood.<sup>15</sup>

Kraton, with cylindrical domains of PS in a PB matrix, was chosen as the organic template for many reasons: (i) The geometry of the nanodomains and the domain sizes can be varied predictably by adjusting the length of each block and the total molecular weight.<sup>6</sup> (ii) The unsaturated carbon bonds in PBs provide reactive sites (Figures 2 and 3).<sup>16</sup> The works of Cohen and co-worker and of Saito and Ishizu have shown respectively that it is feasible to have metal loadings<sup>7,8</sup> and ion exchange<sup>9</sup> in the nanodomains. (iii) The thickness of the block copolymer template can be engineered by spin casting and reactive ion etching.<sup>17</sup> (iv) The orientation of the nanodomains can be aligned by an electric field.<sup>18</sup> (v) The work of Liu and co-workers has shown that the substrate surface orients the cylinders into well-ordered arrays in triblocks but not in diblocks.<sup>11</sup>



**Figure 4.** Osmate ester formation. Osmium in its +8 oxidation state is electronegative and therefore attracts electrons. The osmium in the osmate ester gains a pair of electrons after electrophilic addition to the  $\pi$ -electrons of the unsaturated carbon of PB. The oxidation state is reduced to +6.<sup>19,22</sup>

The important features of our approach are that (i) the interdomains of PB in the preformed solid thin films are chemically OH-functionalized *in situ*. A thorough investigation is needed later to find out whether this technique can also work for millimeter-thick films; (ii) the barium titanate precursors are solely localized within and reacted to the interdomains of PBs in solid thin films by condensation. However, it is unclear at this point whether the precursors are diffused through the interdomains of PBs, the nanodomains of PSs, or the interfaces of PBs/PSs; and (iii) the barium titanate precursors can be polymerized among themselves with the presence of the ambient moisture by condensation. A noteworthy precedent of the solid phase chemistry of preformed films is the staining of samples of block copolymeric thin films with osmium tetroxide for characterization by transmission electron microscope (TEM). Osmium tetroxide selectively attacks the unsaturated carbon bonds and forms cyclic osmate esters (Figure 4),<sup>19</sup> enhancing the contrast of TEM images.

In this study, the procedure of Margaritis and Kalfoglou,<sup>20</sup> developed to epoxidize the unsaturated bonds of carbons of polybutadiene in bulk solution, was extended to Kraton in solid–liquid phase. The feasibility for solid–liquid phase chemistry of this sort is reminiscent of the surface-selective hydroxylation of polypropylene polymeric layers studied by McCarthy and Lee,<sup>21</sup> who introduced hydroxyl groups, olefins, ketones, and esters at room temperature to the surface of the thin layers with chromium(VI) oxide held in acetic acid/acetic anhydride solution. Schematics of the mechanisms of epoxidation<sup>20</sup> and hydroxylation<sup>22</sup> are shown in Figures 2 and 3, respectively. The idea of reacting barium titanium double alkoxide with the hydroxyl groups on the hydroxylated Kraton thin films was based on the work of Shin *et al.*,<sup>23</sup> who have uniformly titanated a monolayer of hydroxyl-functionalized 1-(trifluoroacetato)-16-(trichlorosilyl)hexadecane on single crystalline silicon using 0.3 M titanium isopropoxide in anhydrous 2-propanol under dry nitrogen. A more sophisticated way, of course, is to synthesize pedigreed hydrocarbon/hydroxy triblocks, thereby eliminating the *in situ* epoxidation and hydroxylation on the unsaturated blocks of Kraton. However, our primary concern here is just to demonstrate the viability of nanoscale patterning of barium titanate precursors on a block copolymeric template with the use of the hydroxyl groups.

## Experimental Procedures

Thin (<50 nm) films of Kraton were prepared by spin casting (Spin Coater; Model CB 15, Headway Research, Inc., Garland,

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TX) a 1 wt % Kraton/toluene solution with a rotational speed of 2500 rpm on a 22 mm  $\times$  22 mm cover glass which had previously been spun cast with a layer of 10 vol % aqueous detergent solution (Mr. Clean, Proctor and Gamble, Cincinnati, OH) and coated with a layer of amorphous carbon. Film thicknesses were measured by ellipsometry (Model L116C, Gaertner, Inc., Chicago, IL). Films were scored into small pieces with a diamond knife and lifted off from the cover glass surface by dipping the film-coated cover glass into doubly distilled water. Gold TEM specimen grids (SPI Supplies, West Chester, PA) were then used to pick up the floating Kraton thin films, and the samples were annealed for 24 h at 130 °C under vacuum to obtain phase separation.

Analytical TEMs (CM 20 and CM 200 FEG, Philips Electronic Instruments, Mahwah, NJ), and a Fourier transform infrared spectrometer (FTIR) (IR 44, IBM Instruments, Inc., Danbury, CT) were used to characterize thin films of Kraton and functionalized thin films of Kraton. In addition, an electron probe microanalyzer (EPMA) (SX 50, Cameca Instruments, Stamford, CT) was used on 16 different points of the barium titanated thin film of Kraton for wavelength-dispersive X-ray spectroscopic analysis.

For transmission FTIR studies, thicker films were needed to give enough signal throughput. Thick films (70 nm) of Kraton were processed by spin casting 1 wt % Kraton/toluene solution directly on 0.375 mm thick silicon wafers with a rotational speed of 1000 rpm. Annealing for 24 h at 130 °C was performed immediately afterward.

Both gold TEM grids and silicon wafers were utilized as supporting substrates because they are chemically inert. Gold TEM grids with annealed thin films of Kraton and silicon wafers with annealed thin films of Kraton were prepared and subjected to one of three treatments: (i) osmylation, (ii) epoxidation-hydroxylation-barium titanation, and (iii) direct barium titanation.

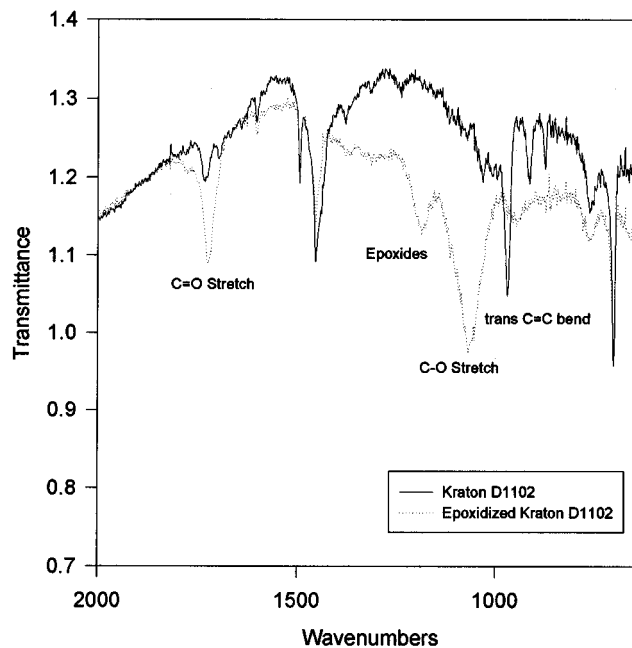
**(1) Osmylation.** Osmylation of the polybutadiene was used to enhance the contrast between PS and PB and thus to bring out the general morphology of an annealed thin film of Kraton. An annealed thin film of Kraton on a gold TEM grid was placed at the center of a glass petri dish. A few drops of an aqueous 4 % osmium tetroxide solution (Polysciences, Warrington, PA) were applied around the sample. The petri dish was covered for 1 h at room temperature prior to a detailed TEM study of the osmylated sample.

**(2) Epoxidation-Hydroxylation-Barium Titanation.** Epoxidation-hydroxylation-barium titanation was used to demonstrate the feasibility of nanoscale patterning of coordinated barium titanium double alkoxides on a preorganized block copolymeric template. The annealed thin films of Kraton on both a gold TEM grid and a silicon wafer were epoxidized-hydroxylated together in 0.974 g of 85 wt % formic acid (J. T. Baker Inc., Phillipsburg, NJ) to which 2.04 g of 30 wt % hydrogen peroxide (J. T. Baker Inc.) was slowly added within 2 h below 20 °C. The mixture was agitated by a stream of N<sub>2</sub> for 10 h more below 20 °C, prior to TEM and FTIR studies. The two hydroxylated samples were then reacted with a barium titanium double alkoxide solution, BaTi(OR)<sub>6</sub>, where R = CH<sub>2</sub>CH(CH<sub>3</sub>)OCH<sub>3</sub> (Gelest Inc., Tullytown, PA), under dry nitrogen for 1 h at 60 °C. To stop the reaction, samples were rinsed with a copious amount of anhydrous 2-propanol (Aldrich Chemical Co., Inc., Milwaukee, WI). TEM, electron energy loss spectroscopy (EELS), EPMA, and transmission FTIR techniques were used to thoroughly characterize the barium titanated samples.

**(3) Direct Barium Titanation.** Alternatively, an attempt was made to form patterned coordinated barium titanium double alkoxides directly to verify the presence and the necessity of having hydroxyl groups on the films to react with the barium titanium double alkoxide solution. Annealed thin films of Kraton on both gold TEM grids and silicon wafers were immersed in the barium titanium double alkoxide solution under dry nitrogen for 1 h at 60 °C. A copious amount of anhydrous 2-propanol was used again to rinse the samples, which were then characterized by TEM, PEELS, and transmission FTIR.

## Results and Discussion

The film spun cast from a 1 wt % Kraton/toluene solution with a rotational speed of 2500 rpm had a thickness of



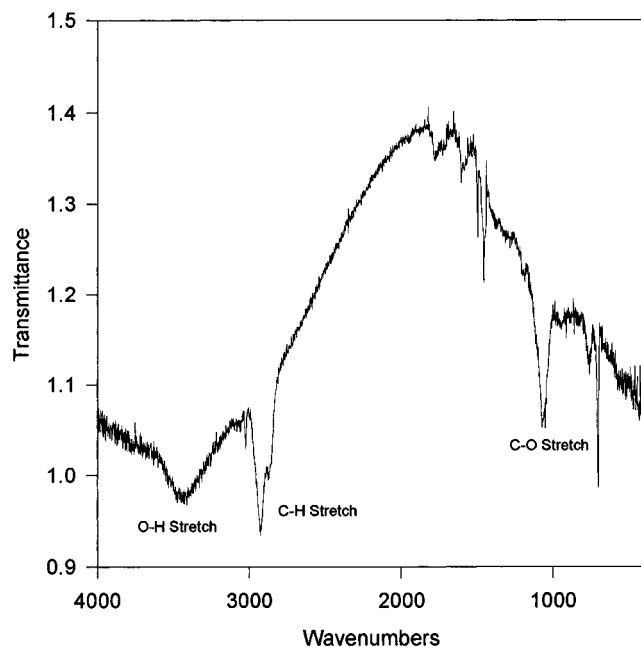
**Figure 5.** Transmission FTIR spectra of the annealed and the epoxidized thin films of Kraton.

42.5 nm as measured by ellipsometry. The specific concentration of the Kraton/toluene solution and the optimized rotational speed of spin casting to fabricate a monolayer of Kraton thin films were not determined; islands and holes were therefore observed under TEM. However, the TEM image of the terrace region of the annealed osmylated film in Figure 1 and a series of tilting experiments indicated that the film had a cylindrical morphology.

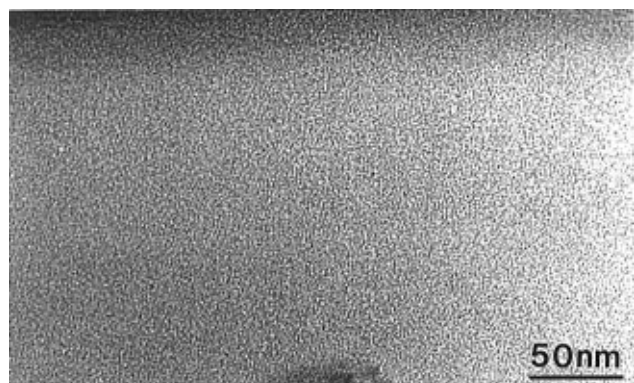
Transmission FTIR spectra were taken respectively of the plain, the epoxidized, and the hydroxylated thin film of Kraton to confirm that solid phase epoxidation-hydroxylation did indeed take place. After epoxidation (Figure 5), the bands of the double-bond stretching vibration near 940–980 cm<sup>-1</sup> disappeared, a new C–O stretching absorption band is observed centered near 1050 cm<sup>-1</sup>, and the 1240–1260 cm<sup>-1</sup> band assigned to epoxides appears. The strengthening of C=O bond stretching in the vicinity of 1710–1730 cm<sup>-1</sup> also suggests the formation of a cross-linking bridge<sup>24</sup> as the by-product of epoxidation. After hydroxylation (Figure 6), a broad OH stretching band near 3400–3600 cm<sup>-1</sup> appears. TEM images of the plain, the epoxidized, and the hydroxylated thin film of Kraton looked all the same with no detectable pattern (Figure 7).

Unlike Figure 7, the TEM image of the terrace region of the thin film of barium titanated Kraton shown in Figure 8 has a pattern. Similar to osmylation, heavy atoms of barium and titanium give rise to this contrast due to electron scattering. In addition, EELS microanalyses were also performed. Since EELS deals with the inelastically scattered electrons and measures the amount of energy lost by individual electrons during their transmission through a specimen, it is very sensitive to detect and quantify light elements ( $Z < 13$ ) with short acquisition times, and high-energy resolution better than 0.7 eV. By examining the primary energy transfer event, EELS microanalyses further verified the presence of carbon, titanium, oxygen, and barium within the patterned thin films as shown in Figure 9. The spacing of the barium titanated nanodomains is 23 nm, which agrees exactly with the original interdomain spacing of the PB matrix.

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**Figure 6.** Transmission FTIR spectrum of the hydroxylated thin film of Kraton.

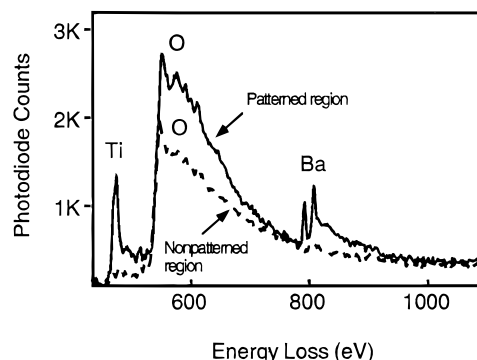


**Figure 7.** TEM bright-field image of the terrace region of the plain annealed thin film of Kraton.

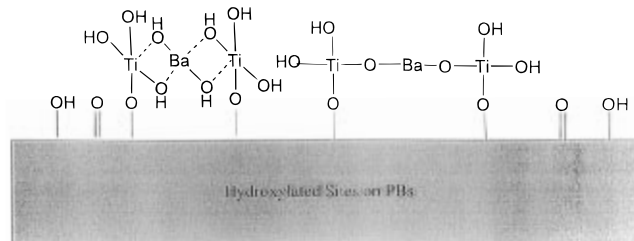


**Figure 8.** TEM bright-field image of the terrace region of the coordinated barium titanium double alkoxide doped thin film of Kraton. The cylindrical nanodomain spacing of PS (light) is 10 nm, and the barium titanated interdomain spacing (dark) is 23 nm.

We were unable to remove this pattern by rinsing the thin film of barium titanated Kraton with anhydrous 2-propanol. Electron diffraction further showed that the patterned area is amorphous. All these observations point to the feasibility of the regioselective deposition of the coordinated barium titanium double alkoxides. However, not all the regions of the films were successfully barium



**Figure 9.** EELS analyses on patterned and non-barium titanated areas of the coordinated barium titanium double alkoxide doped thin film of Kraton.



**Figure 10.** Proposed condensation mechanism of barium titanation. Barium titanium double alkoxide molecules, Ba-Ti(OR)<sub>6</sub>, where R = CH<sub>2</sub>CH(CH<sub>3</sub>)OCH<sub>3</sub>, are localized at the OH-functionalized sites in the PB interdomains. The alkoxide ligands ORs are also exchanged by the OHs when the double alkoxides are exposed to ambient moisture. They are either polymerized further to form organometallic oligomers or coordinated to form complexes. Along with the terminal OHs, C=O sites are also present in the PB interdomains due to the undesired formation of cross-linking bridge.<sup>24</sup>

titanated, as evidenced by the lack of a pattern in some regions. EELS microanalyses (Figure 9) on such regions showed only the presence of oxygen but no titanium and barium. One explanation for incomplete reaction is that some areas may be very rich in carbonyl groups. Consequently, we have not yet performed the cross-sectional TEM characterization of the films since random sampling makes it difficult to find the barium titanated regions in a cross-sectional view. Reaction conditions need to be optimized to form uniformly patterned films.

Because the Kraton film is localized with the coordinated barium titanium double alkoxides, its transmission FTIR spectrum does not show a strong band centered at 550 cm<sup>-1</sup> and a second band starting near 450 cm<sup>-1</sup> as in the case for crystalline BaTiO<sub>3</sub>.<sup>25</sup> The spectrum looks exactly the same as the one of the hydroxylated film of Kraton in Figure 6. The presence of the broad OH-stretching band near 3400–3600 cm<sup>-1</sup> following barium titanation suggests that not all of the hydroxyl groups were reacted with the barium titanate precursor and the precursor might be hydrolyzed by the ambient moisture. A proposed condensation mechanism of barium titanation is shown in Figure 10. The reaction is assumed to occur via a ligand exchange of the terminal OH of the hydroxylated Kraton film with an alkoxide ligand. The EMPA showed that the atomic ratio of Ba:Ti:O is around 1.0:1.3:8.0. The atomic percentage of O is high because the hydroxylated Kraton film has a high content of OH. Furthermore, the TEM images of the control experiment suggest that, without the presence of the hydroxyls on the thin film of Kraton, a regioselective pattern does not form on the thin films. This supports the anchoring role of hydroxyls for the formation of a barium titanated pattern.

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By comparing Figures 1 and 8, it is seen that the definition of the coordinated barium titanium double alkoxide pattern is not as sharp as the osmylated version. The diffuseness of the coordinated barium titanium double alkoxide pattern is most likely due to the inherent polymerization characteristics of barium titanium double alkoxide molecules. The formation of oligomers of alkoxides in the free alkoxide solution and the hydrolysis of the deposited barium titanium moieties induced by ambient moisture may have occurred prematurely and complicated the molecular interactions at local reactive sites. Although all chemicals used were anhydrous, treated with freeze-pump-thaw, and the reaction environment was kept under dry nitrogen, we have not yet been able to totally suppress the undesired condensation between alkoxides caused by the ambient moisture thereby preventing uncontrolled aggregation. Crystalline  $\text{BaTiO}_3$  was not observed to result from our process. Normally, either a hydrothermal process under strongly alkaline conditions in the temperature range of 40–160 °C<sup>15</sup> or high-temperature annealing at ~600 °C<sup>26</sup> is needed to process crystalline  $\text{BaTiO}_3$ . Further, the immersion of our barium titanated films into alkaline aqueous solutions resulted in some loss of patterning. Similarly, high-temperature annealing cannot be used to avoid decomposition of the polymer.

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## Conclusions

We have demonstrated the feasibility of a biomimetic approach using self-patterned triblock copolymeric thin films of Kraton as templates to localize the coordinated barium titanium double alkoxides. All the chemistry employed is in solid-liquid phase and three steps are needed: (i) film preparation and annealing, (ii) epoxidation-hydroxylation, and (iii) barium titanation. Hydroxyl groups are sites for the attachment of barium titanium double alkoxides. TEM and EELS analyses showed that the coordinated barium titanium double alkoxides were regioselectively deposited on the OH-terminated PB nanodomains of Kraton thin film. The resultant cylindrical film morphology and the spacing of the barium titanated nanodomains of 23 nm closely match with the original interdomain spacing and pattern of Kraton thin film.

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