Selective Doping of Lead Ions into Normally Aligned PEO Cylindrical Nanodomains in Amphiphilic Block Copolymer Thin Films

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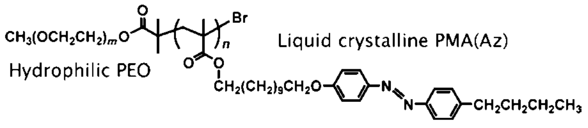
Hexagonally arranged nanocylindrical arrays of polymer-complexed multivalent metallic ions were fabricated by performing template process with amphiphilic diblock copolymer consisting of poly(ethylene oxide) and liquid crystalline poly(methacrylate) with azobenzene mesogen (PEO-*b*-PMA(Az)). The block copolymer exhibits PEO hexagonal cylindrical microdomains perpendicular to the substrate. Lead ions were selectively diffused into the PEO microdomains to generate the lead-doped nanocylinder array, of which size, shape, and alignment can be controlled by the block copolymer thin film as a template.

A control of shape and arrangement of metal or metal oxide particles at nanometer scale has attracted a great deal of attention for investing conventional nanotechnologies and devises such as lithographic micro/nanopatterning, high-density magnetic storage media, superconducting applications with singular functions based on nanosize and quantum effects of the components.[1] A rich variety of periodic microdomain structure of block copolymer with a resolution of a few nanometers has been recognized as an excellent candidate to produce the structure-controlled nanomaterials via templating process.[2] The metal ion or its precursor, which has chemical interaction specific to one of the polymer segments in the block copolymer, can be selectively incorporated into one of the microdomains and successively converted to the corresponding metal or metal oxide in the microdomains. In this approach, the original nanostructure of the block copolymer is crucial in the templating process. The polymer design, therefore, is of prime importance for the preparation of reliable block copolymer template for a wide range of applications. Our research group has devoted the past several years to exploiting the block copolymer template with well-aligned hexagonal cylinder microdomain (HCM) structure by utilizing an amphiphilic liquid crystalline block copolymer, PEO-*b*-PMA(Az) (Scheme 1).[3] The PEO self-segregates to form the HCM surrounded by the PMA(Az) matrix. We report herein the simple procedure for the three-dimensional (3D) nanostructure formation of Pb source, bis(2,4-pentanedionato)-lead(II) ($Pb(acac)_2$) or lead(IV) tetraacetate ($Pb(OAc)_4$), which was complexed selectively with the PEO microdomains (Figure 1E).



Scheme 1. PEO-*b*-PMA(Az).

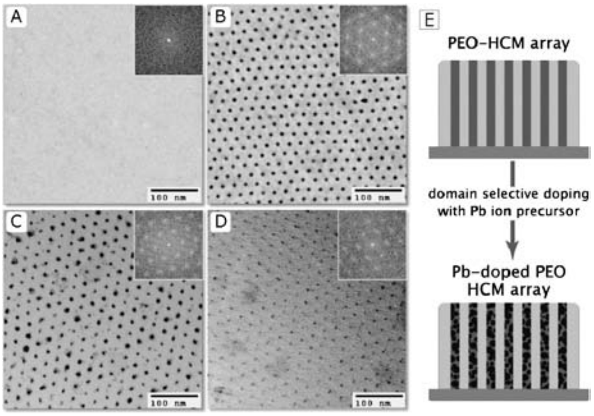


Figure 1. TEM images of **BC1** thin films (A) without staining, (B) with RuO_4 staining; (C) obtained in the vapor process and (D) the immersion process for domain-selective doping of $Pb(acac)_2$. The FFT images are indicated in insets. (E) Schematic illustration of domain-selective doping.

A series of PEO-*b*-PMA(Az) was synthesized as we reported previously.[3a] To examine the microdomain size, two block copolymers with different molecular weights (M_w) and volume fractions of PMA(Az) block ($VF_{PMA(Az)}$) were used: **BC1** ($M_w = 32600$, $VF_{PMA(Az)} = 0.85$, PEO_{114}-*b*-$PMA(Az)_{56}$, $M_w/M_n = 1.07$) and **BC2** ($M_w = 80500$, $VF_{PMA(Az)} = 0.75$, PEO_{454}-*b*-$PMA(Az)_{123}$, $M_w/M_n = 1.08$). The thin films were prepared with thickness of 100 nm. The thin films were anealed at 140 °C for 24 h. The templating processes for Pb ions were carried out in both vapor-exposure and solution immersion processes.[4] In the former process, the annealed thin film was exposed to the vapor of $Pb(acac)_2$ at 95 °C under 0.08 Torr for 30 min. For the latter process, the thin film was immersed into methanol solution of $Pb(OAc)_4$ for 24 h, so-called immersion process.

No structural feature was observed in the TEM image of pure **BC1** film even after the thermal treatment (Figure 1A), while the film stained with RuO_4 as the conventional staining reagent gave a clear image of (001) plane of PEO–HCM array structure with average diameter (*d*) of 8 nm and average distance between cylinders (*D*) of 25 nm, visualized as black part (Figure 1B). This TEM image shows typical nanostructure of the PEO-*b*-PMA(Az) film as our standard sample, in which PEO–HCMs are aligned perpendicularly to the film interfaces.[5] The fast Fourier transform (FFT) shown in the inset consisting of six distinct spots also supported high quality of the ordered nanostructure. Similar nanostructures were found in the **BC1** films treated with $Pb(acac)_2$ under the vapor process (Figure 1C) and the immersion process (Figure 1D) without staining. The HCMs were preserved in small size distribution with the structural parameters, (d, D) = (10, 26 nm) and (6, 26 nm) in Figures 1C and 1D, respectively. The TEM images indicate that the Pb(acac)$_2$ can selectively decorate the PEO–HCM[4] from the central part, which leads to the prediction of this selective doping mechanism as follows. In both processes, the Pb(acac)$_2$ was selectively diffused into the PEO–HCM owing to the hydrogen and coordination bondings with the EO units.[6] Such specific chemical interactions can make the interfaces between the Pb(acac)$_2$-doped PEO domain and the PMA(Az) matrix rather sharp and well defined. The darker contrast over the whole image of the sample obtained by the vapor process might result from the amount of Pb(acac)$_2$ doped into the PEO cylinders, more than that in the case of the immersion process, leading to a larger cylinder diameter. Moreover, the decomposition or dissociation of the metal complex might be responsible for the darker contrast in the vapor process, although the doping process was carried out at the temperature lower than the decomposition temperature at 159 °C under 1 Torr. The lone pairs of oxygen in the PEO block possibly play an important role as coordination sites to the central metals of acac complexes to dissociate the coordination bonding with acac ligand and then to newly associate with the oxygen of PEO.[7]

The immersion process is essentially vulnerable to the doping efficiency as the TEM image showed weak contrast. However, it is worth while mentioning that the immersion process can be applied for various kinds of metal ions, organometallic compounds, and organic molecules, which scarcely sublime. Fortunately, the PEO-*b*-PMA(Az) film has the strong resistivity in polar solvent to keep the nanostructure with little damage. We demonstrated the Pb(OAc)$_4$ doping with the same manner, using the **BC2** film as template. The **BC2** thin film exhibited the PEO–HCM arrays with $d = 28$ nm and $D = 48$ nm (Figure 2A). A relatively wide size distribution and poor orderness of the PEO domain arrangement rather than those of **BC1** have been realized as the inherent nanostructure formed from the PEO-*b*-PMA(Az) with a higher molecular weight of PEO segment. Since it has been known that Pb(OAc)$_4$ is strong oxidant, the Pb^{IV} ion is gradually reduced in methanol or in the film during the diffusion around the PEO domains.[8] After the treatment of **BC2** film with Pb(OAc)$_4$, XPS analysis was conducted to characterize the change of ionic valency (Figure 2B). The main peaks in the Pb4f region were detected at 138.7 eV (Pb4f$_{7/2}$) and 143.5 eV (Pb4f$_{5/2}$), which are higher binding energies than those of Pb^{II} ion but lower than those of Pb^{IV} ion. The result implies that the Pb^{II} ion generated in the doping process interacts with the oxygen of PEO through the coordination bonding.[9] Along this line, the PEO-domain selective doping can be extended to a wide range of metal ion precursors, which form the coordination bonding with the oxygen in PEO, such as Li, Al, Ti, Fe, Co, Sn ions, and so on. The satellite peaks at 137.4 eV (Pb4f$_{7/2}$) and 142.2 eV (Pb4f$_{5/2}$) were identified as PbO or Pb metal.[10] These products might be attributed to hydrolysis consuming a little amount of water in the reaction system and subsequent reduction of the resulting metal oxide with the free acetic acid.

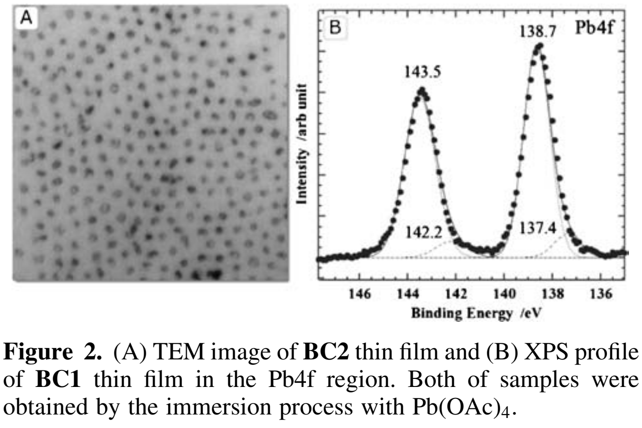


Figure 2. (A) TEM image of **BC2** thin film and (B) XPS profile of **BC1** thin film in the Pb4f region. Both of samples were obtained by the immersion process with Pb(OAc)$_4$.

In conclusion, we successfully demonstrated the versatile templating process of the amphiphilic diblock copolymer, PEO-*b*-PMA(Az), to produce the HCM array nanostructure consisting of multivalent Pb ion hybrids. The PEO effectively acted as coordination site to the Pb ions, which was essential for the domain selective doping. All of the processes involved the material transport between heterogeneous phases, i.e., gas or liquid phase to solid phase. Therefore, the block polymer film can serve us more reliable 3D template with well-ordered PEO cylindrical nanochannels. The metal Pb nanocylinder array could be fabricated by thermal decomposition or hydrogen-reduction process, which enables to reduce the Pb ion in PEO cylinders as well as to remove the template. It has been limited so far to fabricate the Pb-based 3D nanoarchitectures we proposed here by the methods previously reported; templating of block copolymer sphere, lamellar, or micelle array in their monolayer film,[11] synthesis of block copolymer covalently bearing organometallic complex,[12] utilization of aggregation formed between polymer and metal precursor in solution.[13] The quantitative analyses such as ICP, QCM, and other spectroscopic studies are undergoing. The resulting Pb-doped HCM array structure will provide prototype materials to explore nanostructure-specific functions in optical, magnetic/superconducting applications.

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