

SYNTHESIS AND MORPHOLOGY OF A CLUSTER-CONTAINING COIL-COIL HYBRID DIBLOCK COPOLYMER

S. Chakraborty¹, Y. Li¹, X. Z. Yan², and Z. Peng^{1*}

¹Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110, USA

²Department of Electrical Engineering, South Dakota State University, Brookings, SD 57007, USA

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Abstract

A coil-coil diblock copolymer containing polyoxometalate clusters covalently linked in one of the coil blocks has been synthesized. The hybrid diblock copolymer (HDCP) and its corresponding cluster-free diblock copolymer (PS-PVP) show very different thin film morphologies both before and after thermal annealing. While PS-PVP appears phase-separated in the pristine film, which is diminished after thermal annealing, the HDCP film shows enhanced cluster aggregation after thermal annealing, leading to isolated domains with sizes around 20 nm.

1 Introduction

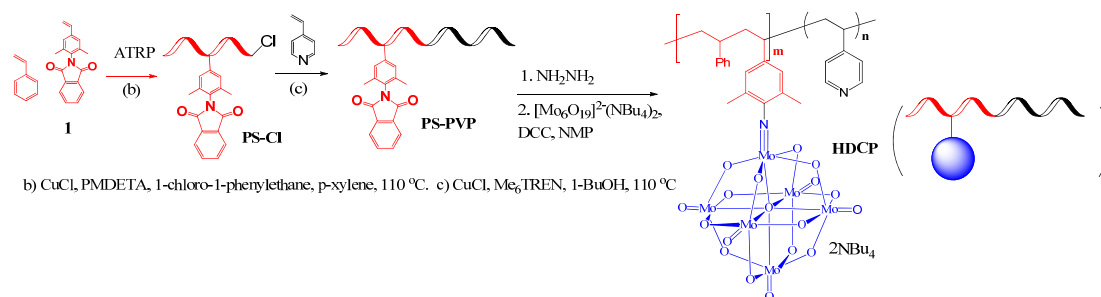
Block copolymers are a fascinating class of materials, exhibiting in many cases predictable and controllable ordered nanometer-size domain structures [1]. The formation of self-assembled multiphase domain structures is due to the incompatibility between the chemically linked different polymer blocks. Depending primarily on the volume fraction, the segment-segment interaction and the length of each block, block copolymers may self-assemble into various morphological structures, including spheres, gyroids, vesicles, cylinders, and lamellae, all of which have been theoretically predicted [2-3] and experimentally observed [4]. With such a unique self-organization process, block copolymers are becoming not only a novel fabrication tool in, for example, nanofabrication and nanolithography [5], but also an attractive vehicle leading to new patterned functional materials [6].

Research on block copolymers has evolved from all organic systems in the early years to hybrid systems lately. In particular, metal-containing block copolymers are drawing increasing attention [7-10]. The incorporation of metals into block copolymers not only affects the self-assembly process, but also brings about novel physical and chemical properties [7-10]. Most metal-containing block copolymers reported so far have metals introduced as coordination complexes. Such copolymers have in most cases discrete mononuclear metal centers. Block copolymers containing metal clusters are still rare [11].

Among various inorganic clusters, polyoxometalate (POM) clusters stand out not only in their structural diversity, but also in the tunability of their many properties, ranging from molecular shape to solubility, charge density to redox potentials [12]. In addition, the molecular nature of POM clusters makes it possible to modify their structures at the molecular level in a rational and controlled version [13]. Indeed, great efforts have been devoted in developing covalently bonded POM-organic hybrids, including POM-polymer hybrids [14]. While all these developments are exciting, research on covalently bonded POM-organic hybrids is still in the stage of focusing on their primary structures. Morphological control on or ordered structures from such hybrid materials is still not well studied [15]. In this presentation, we report the synthesis of a coil-coil diblock copolymer with POM clusters covalently linked to one of the coil blocks. Its self-assembled morphologies of spin-coated films are presented.

2 Results and discussions

Scheme 1 shows the structure and synthesis of the coil-coil hybrid diblock copolymer (HDCP), which is based on a poly(vinyl pyridine)-polystyrene (PVP-PS) diblock copolymer backbone. A macroinitiator PS-Cl was obtained by atom transfer radical polymerization (ATRP) of the monomer mixture of styrene and compound **1** in a 1:1 stoichiometric ratio using $\text{CuCl}/N,N,N',N',N''$ -pentamethyldiethylenetriamine (PMDETA) as the catalyst system and 1-chloro-1-phenylethane as the initiator. The reaction conditions were optimized to ensure that the polymer chain end remains active. The ^1H NMR spectrum of PS-Cl (Figure 1) show aromatic signals distinctive from either monomer **1** (signals a and b) or styrene (signal c). From the integration of those signals, one can conclude that the copolymer composition is close to 1:1, matching the feeding ratio of the two monomers. The propagating chloro-binding methylene protons appear around 4.5 ppm. The number average molecular weight of the PS-Cl, measured by gel-permeation chromatography (GPC), is 3800 with a polydispersity (PD) of 1.1.



Scheme 1. Synthesis of HDCP2.

The macroinitiator was then used to polymerize 4-vinylpyridine. Me_6TREN was employed as the strong coordinating ligand along with CuCl as the catalyst. In addition, a high boiling point solvent 1-butanol was used as the protic solvent. The reaction mixture turned a dark brown color after 1 h. The solution became viscous as the reaction progressed. As the resulting diblock copolymer PS-PVP is soluble in methanol, the reaction mixture was precipitated from hexane after passing through a neutral alumina column. The product was precipitated out from hexane several times to obtain a light brownish white colored copolymer PS-PVP.

The ^1H NMR spectrum of PS-PVP (Figure 1) shows new broad aromatic signals at 8.4 ppm and 6.5 ppm, corresponding to the pyridine protons in the PVP block. The significantly higher integration of PVP aromatic signals than those of the PS block signals indicate that the PVP block may have a higher degree of polymerization. GPC measurements yield a M_n of 6400 and PD of 1.2 for PS-PVP. The higher molecular weight and the lack of bimodal distribution confirm the formation of the diblock copolymer.

The phthalimide protecting group in the mixed monomer block was removed by reacting PS-PVP with hydrazine hydrate to generate free arylamine groups. The complete removal of the phthalimide groups was confirmed by the ^1H NMR spectra of the resulting polymer which shows complete disappearance of phthalimide proton signals a and b. The attachment of hexamolybdate clusters to the flexible block was achieved by our previously-reported method [16]. Excess free clusters were removed by precipitating the hybrid polymer from hot acetonitrile. The resulting cluster attached HDCP is soluble in hot DMF and hot DMSO but insoluble in most other common organic solvents.

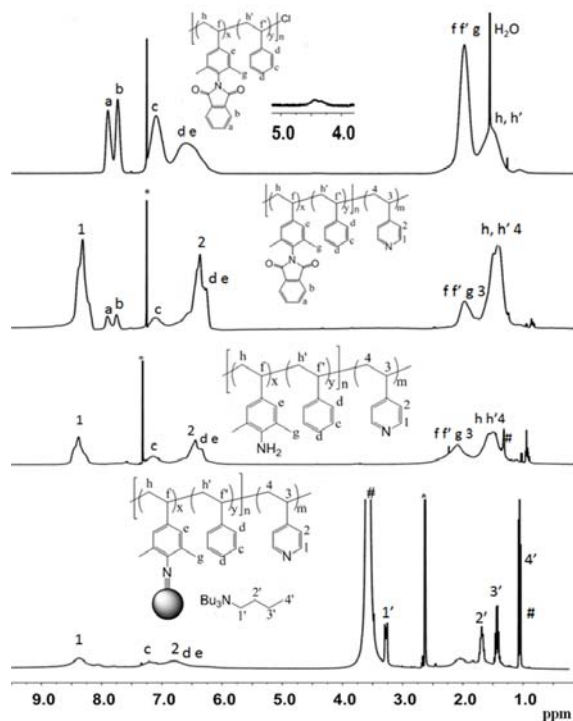


Figure 1. ^1H NMR spectra of PS-Cl, PS-PVP and the amine-deprotected PS-PVP in CDCl_3 , and HDCP in DMSO-d_6 .

^1H NMR spectrum of the HDCP (Figure 1) in DMSO shows broad and relatively weak aromatic signals. Nonetheless, one can still clearly identify signals characteristic of various structural units (for example, signals 1, c, 2, etc.). In the aliphatic region, signals corresponding to the counter ion (tetrabutyl ammonium) are clear and dominant.

The FTIR spectra of PS-PVP, free Mo₆ cluster and HDCP are shown in Figure 2. The PS-PVP shows a sharp and intense peak at 1722 cm⁻¹ which can be assigned to the carbonyl stretching. Two sharp peaks at 1598 cm⁻¹ and 1417 cm⁻¹ are the characteristic ring vibrations of pyridine. Both peaks are seen in the IR spectrum of HDCP. In addition, new peaks at 800 and 950 cm⁻¹, which are characteristic Mo-O stretching vibrations, are shown clearly in the IR spectra of the hybrid DCP. One also notes a side/shoulder peak at 975 cm⁻¹ next to 953 cm⁻¹, which can be seen more clearly when expanded. This peak is attributed to the Mo-N stretching vibration [17]. The observation of this peak is a good indication that Mo₆ clusters are covalently attached to the coil block.

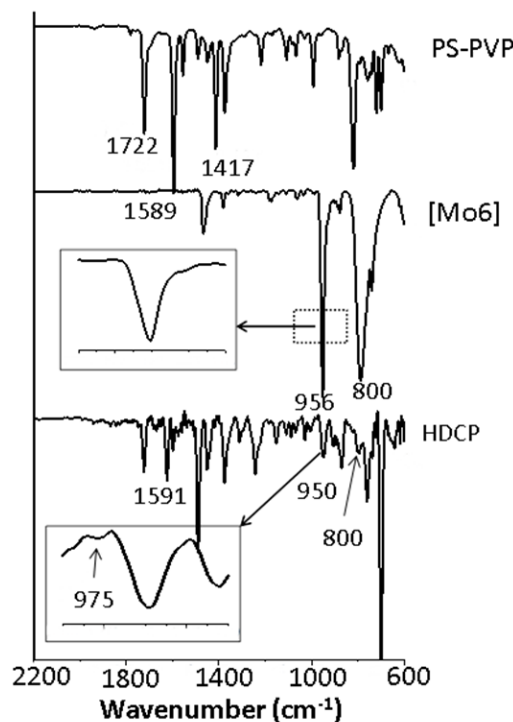


Figure 2. FTIR spectra of the PS-PVP, free Mo₆ cluster and the hybrid DCP.

The covalent attachment of POM clusters has also been confirmed by the UV/Vis absorption spectrum which shows a red-shifted shoulder peak at around 350 nm which is assigned to the ligand-to-metal charge-transfer transition of imido-derivatives of hexamolybdates.

Thin film morphologies of PS-PVP and HDCP were studied using atomic force microscopy (AFM). PS-PVP was dissolved in chloroform whereas the HDCP was dissolved in hot DMF. The solutions were spin-coated onto ITO glass slides at a speed of 600 rpm for 20 s. After taking the AFM images, the samples were annealed at 120 °C for 10 min and the AFM images of the annealed samples were taken again. AFM images were taken in air under ambient conditions using the intermittent contact mode on an Agilent 5500 AFM/SPM microscope. Figures 3 and 4 show the topography and phase images of the pristine and annealed PS-PVP and HDCP films, respectively. Both the topographical (Figure 3a) and phase (Figure 3b) images of the pristine PS-PVP film show clear phase separation, resulting in peanut-shaped aggregates with an average dimension of 100 nm (diameter) x 250 nm

(length). After thermal annealing, the aggregates diminished, leading to a more uniform and smoother film.

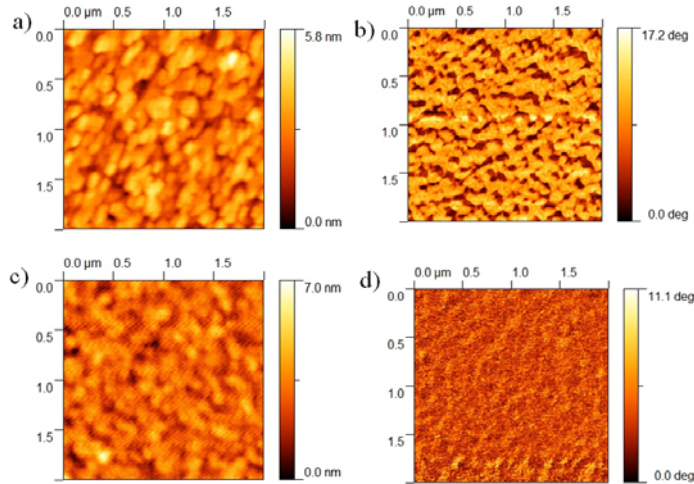


Figure 3. AFM topography (a & c) and phase images (b and d) of a spin-coated PS-PVP thin film before (a & b) and after (c & d) thermal annealing.

The pristine HDCP film, however, shows no phase separation (Figure 4). The surface is smooth with surface roughness less than 2 nm. After thermal annealing, one sees clear particulate aggregates as reflected on the much higher phase contrast. The particles have an average diameter around 20 nm. Such particles are likely aggregates of POM clusters.

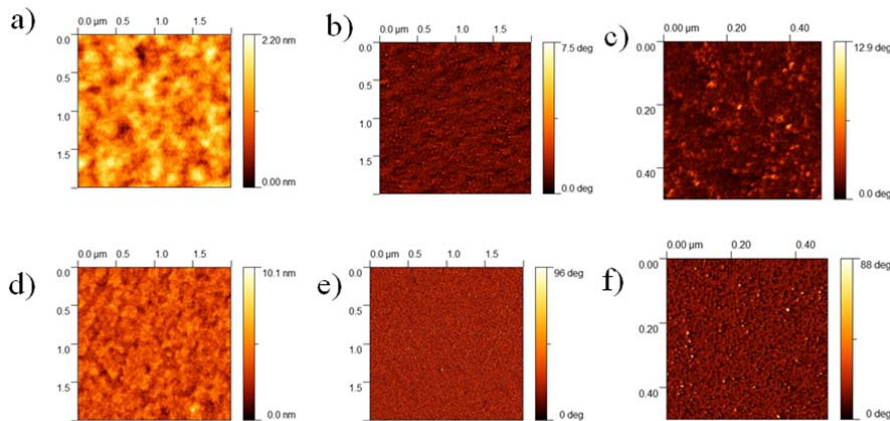


Figure 4. AFM topography (a & d) and phase images (b, c, e and f) of a spin-coated HDCP thin film before (a, b, c) and after (d, e, f) thermal annealing.

3 Conclusions

A polystyrene-poly(vinylpyridine) diblock copolymer was synthesized, where the PS-block was covalently anchored with hexamolybdate clusters. The PS-PVP and the cluster-attached

hybrid diblock copolymer show very different thin film morphologies. Systematic studies on the self-assembled morphologies under different conditions such as pH, annealing temperatures, solvents, etc. are in progress.

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