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Core-crosslinked block copolymer nanorods as templates for grafting $[SiMo_{12}O_{40}]^{4-}$ Keggin ions† ‡

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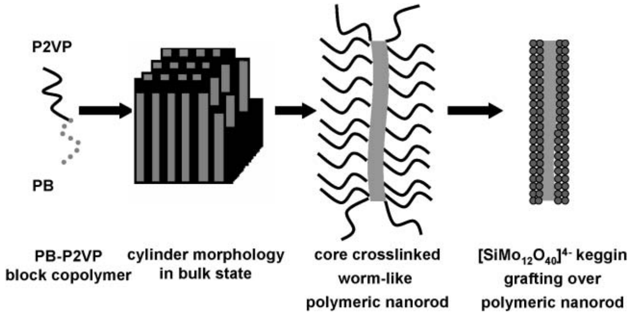
Core-crosslinked PB-P2VP block copolymer nanorods are used as templates for the synthesis of Keggin-type heteropolyoxometalate (POM) nanostructures by grafting $[SiMo_{12}O_{40}]^{4-}$ Keggin ions on the template.

The organic template-directed synthesis of inorganic materials has attracted world wide attention due to the ability of organics to self-assemble into a variety of micelle nanostructures with well-defined shape and size.[1–3] An important class of organic templates used for the synthesis of materials is the amphiphilic block copolymers.[4] However, block copolymer micelles are very sensitive to the reaction conditions. Change in pH, temperature, solvent, or ionic strength can lead to micelle transformation or disintegration. For example, when polybutadiene-block-poly(2-vinylpyridine) (PB-P2VP) with 80% PB is dissolved in THF, worm-like micelles are formed in solution. Addition of water or protonation leads to a micelle transformation thus leading to undesired changes in the template morphology (see ESI‡). Hence, the use of polymeric micelles to synthesize inorganic materials with desired morphologies is not always possible due to the dynamic nature of micelles. The micelle stability is especially important for the synthesis of materials which ask for changes in reaction conditions.

In this communication, we present a novel synthesis strategy for the development of inorganic nanostructures using core-crosslinked stable polymer templates. Scheme 1 summarizes this novel approach for the synthesis of desired inorganic nanostructures. Firstly, a block copolymer is synthesized which microphase-separates into a well-defined cylindrical bulk structure. Generally, adjusting the volume fractions and molecular weight of the block copolymer allows a facile tunability of the dimensions and shapes of the desired polymeric template. Secondly, it is possible to freeze the dynamics of the polymeric nanostructures by crosslinking the core, shell or even the surface.[5] In the present study, the core of the micelles is crosslinked and the resultant polymeric micelles are stable and resistant to changes in reaction conditions. Thirdly, protonation or quaternization can be performed at controllable rate to achieve charge matching between the polymer template and inorganic complexes. Fourthly, anionic inorganic precursors are grafted on the charged template and the inorganic/organic nanocomposite will precipitate. Please note, that when using an acidic inorganic precursor, quaternization of polymer template and grafting of the corresponding anion take place simultaneously.



Scheme 1 Synthesis of $[SiMo_{12}O_{40}]^{4-}$ Keggin nanostructures using core-crosslinked PB-P2VP worm-like polymer template and $H_4[SiMo_{12}O_{40}]$.

Keggin-type heteropolyoxometalates (POM) were chosen as inorganic precursors due to the following reasons. Polyoxometalates (POM), the discrete metal-oxygen cluster compounds mainly of transition metals, exhibit fascinating properties and applications.[6] The properties of the POMs, particularly of the Keggin-type, depend mainly on the nature of the counter cation and the composition of the POM anion.[7] POMs with high surface areas and controllable nanostructures are of interest in a variety of applications such as high performance catalysts (acid and redox), sensor devices and electrodes (due to their high ion conductivity, electron density, rapid and reversible oxidative-reductive processes).[7,8] But, POMs present relatively small surface areas, the surface area of commercial $H_4SiMo_{12}O_{40}$ is 4 $m^2\ g^{-1}$, which hinders accessibility to the active sites and as a result the applications of POMs are limited.[7] Hence, there is a great demand to develop POM materials with high surface area.

The efficiency of the POMs can be increased by two approaches. (1) using high surface area solids as supports to disperse POM and (2) developing composite materials with POMs as building blocks. Mesoporous silica materials like MCM-41 or SBA-15 have very high surface area (*ca.* 800–1000 $m^2\ g^{-1}$) and these materials were used as supports for the dispersion of POM.[9,10] There are also reports using carbon, silica gel, titanium gel, aluminium, *etc.* as solid supports for the dispersion of POM.[11] Even though, the accessible surface area for POMs can be increased by these methods, limitations rely on low POM loading, leaching of the active sites into the reaction medium and pore blocking in porous supports. Another approach involves the synthesis of POM nanocomposites using organic surfactants or polymers.[12,13] However, the accessible surface area is lower and the organic templates need to be removed to allow free access to the POM

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active sites but the hybrid structures tend to collapse during the template removal.[12] Neumann and co-workers used polymeric micelles to synthesize POM nanoparticles and observed improved catalytic activities for the developed POM nanostructures.[14] All together, these results indicate that the synthesis of chemically and physically well defined, discrete POM nanostructures with a highly accessible surface area is of great interest. But the synthesis of POM nanostructures requires the control of various reaction parameters like pH, temperature, ionic strength, *etc*. Hence, the templating micelles should be stable and resistant to changes in the reaction parameters.

To prove our concept, a well-defined PB-P2VP block copolymer with 30 wt % PB and a molecular weight of 2.0×10^5 g mol^{-1} was synthesized by anionic polymerization (see ESI‡). The weight fractions are chosen in such a way that it forms a cylindrical morphology in the bulk state with PB-cylinders embedded in a P2VP matrix. The unsaturated PB-cores were crosslinked using a commercial photointiator to lock the cylindrical structure. The core-crosslinked cylinders exhibit worm-like morphologies when dissolved in THF or acetone. The block copolymer nanostructures were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), and Fourier transform infrared (FTIR) measurements.

The TEM images of the core-crosslinked PB-P2VP worm-like polymer template are shown in Fig. 1. The core-corona structure of the worm-like polymer template is revealed due to the different electron penetrability of the PB core and P2VP corona. The diameter of the PB core is approximately 40 nm and the P2VP corona extends *ca.* 35 nm around the PB-core. The total diameter of the worm-like polymeric rods is *ca.* 110 nm. As sonication is necessary for the dissolution of the crosslinked PB-P2VP template, worm-like polymer rods with different lengths are observed. Fig. 2 shows the SEM image of worm-like polymer rods, where the smooth surface of the polymer cylinders can be observed.

The Keggin-type POM nanostructures can be synthesized by adding the PB-P2VP worm-like polymer solution to the $H_4SiMo_{12}O_{40}$ (POM) solution. Experimental details are provided in the ESI.‡ When neutral polymer rods in THF are added to the POM solution (which is a heteropolyacid) the 2-vinylpyridine units in the arms will be protonated, while the POM-anions are simultaneously grafted onto the template. Thus formation of the inorganic–organic nanocomposites is driven by strong Coulombic interactions between the 2-vinylpyridinium arms of the core-crosslinked PB-P2VP worm-like micelles and the inorganic POM anions. The polymer–POM nanocomposite is referred hereafter as POM-1. The produced POM-1 was characterized using SEM, EDX, TEM, FTIR, X-ray diffraction (XRD) and N_2 sorption measurements.

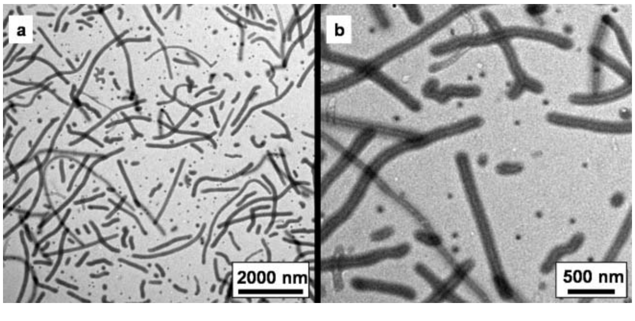


Fig. 1 TEM images of the core-crosslinked PB-P2VP worm-like polymer template at different magnifications.

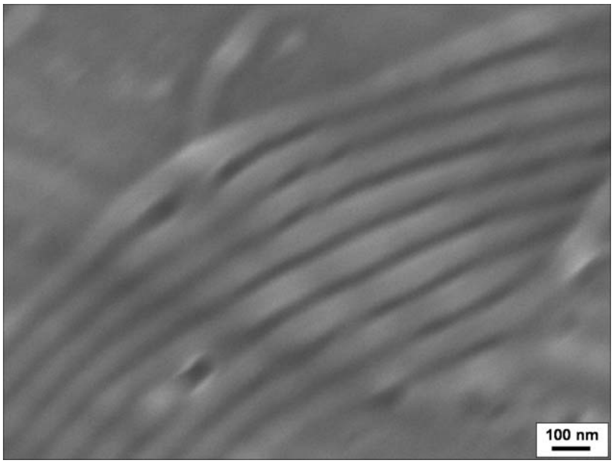
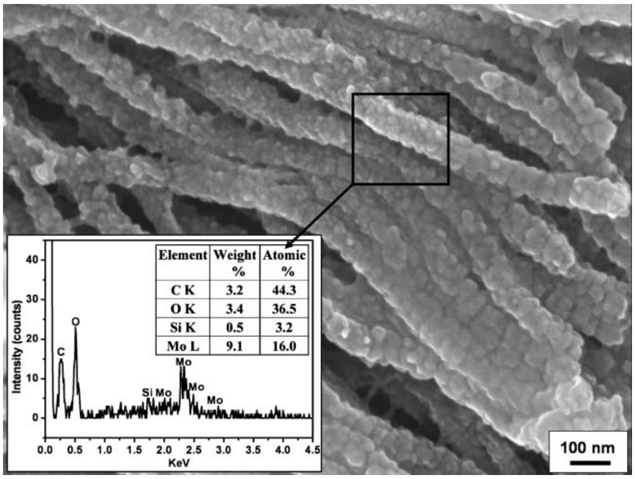


Fig. 2 SEM image of the core-crosslinked PB-P2VP worm-like polymer template.

The formation of POM-1 can be directly observed by SEM and TEM. In comparison to the pure polymer nanorods (Fig. 2), the surface of the POM-1 is rough (Fig. 3). The surface roughness of the POM-1 is due to the grafting of $[SiMo_{12}O_{40}]^{4-}$ Keggin around the polymer template. The selected area EDX spectrum clearly shows the presence of Si, Mo and C and confirms the grafting of $[SiMo_{12}O_{40}]^{4-}$ Keggin around the template. The surface roughness due to the presence of $[SiMo_{12}O_{40}]^{4-}$ Keggin POM around the polymer template becomes also obvious when comparing the TEM images of the pure polymer template (Fig. 1) with POM-1 (Fig. 4). The interaction of the inorganic $[SiMo_{12}O_{40}]^{4-}$ Keggin POM with the P2VP block of the core-crosslinked PB-P2VP worm-like polymer template also changed the dimensions of the resultant composite nanostructures. In the absence of the $[SiMo_{12}O_{40}]^{4-}$ Keggin POM anions, the P2VP corona of the core-crosslinked PB-P2VP worm-like polymer rods is stretched (*ca.* 35 nm around the core). Addition of $[SiMo_{12}O_{40}]^{4-}$ Keggin POM



Element	Weight %	Atomic %
C K	3.2	44.3
O K	3.4	36.5
Si K	0.5	3.2
Mo L	9.1	16.0

Fig. 3 SEM image of the $[SiMo_{12}O_{40}]^{4-}$ Keggin POM grafted onto core-crosslinked PB-P2VP worm-like polymer template (inset: EDX spectrum).

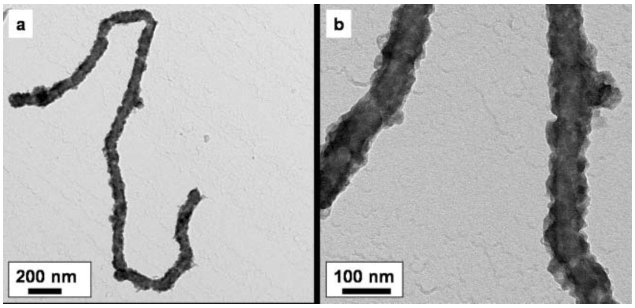


Fig. 4 TEM images of the $[SiMo_{12}O_{40}]^{4-}$ Keggin POM-grafted onto core-crosslinked PB-P2VP worm-like polymer template at different magnifications.

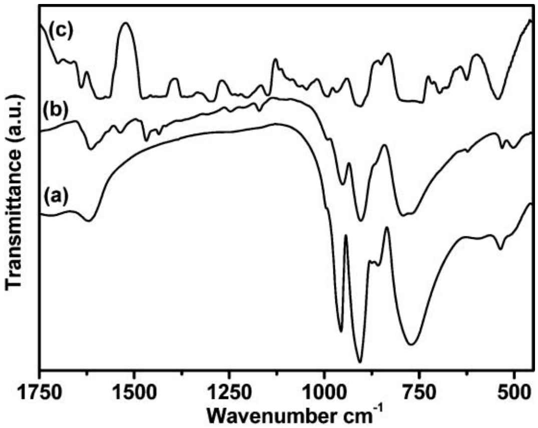


Fig. 5 FTIR spectra of the (a) pure $H_4[SiMo_{12}O_{40}]$ Keggin POM, (b) POM-1 and (c) core-crosslinked PB-P2VP worm-like polymer template.

caused the complexation of the 2-vinylpyridine units in the arms with the Keggin anions and as a result the P2VP corona shrinks from initial *ca.* 35 nm to *ca.* 15–20 nm. The $[SiMo_{12}O_{40}]^{4-}$ Keggin POM-grafted worm-like polymer rods exhibit overall diameters in the range of *ca.* 60–65 nm, significantly smaller than the initial pure worm-like polymer rod.

The grafting of $[SiMo_{12}O_{40}]^{4-}$ Keggin POM over wormlike polymer rods was further verified by FTIR analysis. FTIR spectra of the pure $H_4SiMo_{12}O_{40}$ Keggin POM, POM-1 and core-crosslinked polymer rod template are shown in Fig. 5. It has been widely reported that the Keggin-type heteropolyoxometalates show four characteristic bands, which are the fingerprint of the Keggin structure.[15] There are four kinds of oxygen atoms in $H_4SiMo_{12}O_{40}$ (O_a—oxygen in SiO_4 tetrahedra, O_d—terminal oxygen atom to Mo, O_b—corner sharing oxygen and O_c—edge sharing oxygen) and these characteristic bands were observed at ν_{as} (Mo–O_d) -952 cm^{-1}, ν_{as} (Mo–O_b–Mo) -794 cm^{-1}, ν_{as} (Mo–O_c–Mo) -864 cm^{-1} and ν_{as} (Si–O_a) -902 cm^{-1}. The FTIR spectrum of the POM-1 corresponds well to the superposition of the spectra of the pure Keggin type heteropolyoxometalates and PB-P2VP polymer rod template which is clear evidence that the Keggin structure stayed intact when being grafted onto the worm-like polymer rods.

In addition, wide-angle powder XRD patterns of the pure $H_4[SiMo_{12}O_{40}]$ Keggin POM, core-crosslinked worm-like polymer template and POM-1 were recorded (see ESI‡). In contrast to the pure $H_4[SiMo_{12}O_{40}]$ Keggin POM, XRD patterns of POM-1 do not show any characteristic peaks for $H_4[SiMo_{12}O_{40}]$. This amorpous nature is an indication of the very high degree of dispersion of Keggin POM in the polymer matrix.[10d] The N_2 sorption measurements of POM-1 show that the developed Keggin POM nanostructures have a 37 m^2 g^{-1} surface area, whereas the commercially available POM ($H_4SiMo_{12}O_{40}$) only has a 4 m^2 g^{-1} surface area.

In conclusion, we presented a novel approach for the grafting of Keggin-type heteropolyoxometalates around the core-crosslinked PB-P2VP worm-like polymer templates. The produced POM-1 exhibit high dispersion, improved surface area and are thus expected to be useful in catalytic, electrochemical and biotechnology related applications. An investigation of the properties of the POM-1 is ongoing together with steps aimed at the synthesis of other metal oxide nanostructures. The method appears to be generally applicable. For instance, $[PMo_{12}O_{40}]^{3-}$ Keggin-type POM nanostructures can be synthesized following the same procedure (see ESI‡).

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