Support Information

Modulation of Thermodynamic and Kinetic Inverted Phase Behavior of Block Copolymers by Inorganic Polyoxometalates

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Schematic illustration of the electrostatic interaction between P2VP and H₃PW₁₂O₄₀

Scheme S1. The illustration of the electrostatic reaction between P2VP and H₃PW₁₂O₄₀

Calculation method for volume fraction of P2VP/PW phase ($f_{VP/PW}$)

The method was similar to that in previous references.

\[
f_{VP/PW} = \frac{\Sigma V_{p_{VP}} + \Sigma V_{PW}}{\Sigma V_{PS} + \Sigma V_{p_{VP}} + \Sigma V_{PW}}
\]

\[
= \frac{\Sigma m_{p_{VP}} / \rho_{p_{VP}}}{\Sigma m_{PS} / \rho_{PS} + \Sigma m_{p_{VP}} / \rho_{p_{VP}} + \Sigma N_{PW} * \rho_{PW}}
\]

and \( N_{PW} = N_a * \sum m_{PW} / M_{PW} \)

$m$ is the mass of corresponding matter, $\rho$ is density. $N_{PW}$ is the number of PW molecules, $\rho_{PW}$ represents the volume of one PW molecule, $M$ is the molecule weight of PW. The specific values were summarized in Table. S1.

<table>
<thead>
<tr>
<th></th>
<th>( \rho_{PS}^3 )</th>
<th>( \rho_{p_{2VP}}^2 )</th>
<th>( \rho_{PW}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.06 g/cm³</td>
<td>1.145 g/cm³</td>
<td>0.599 nm³</td>
</tr>
</tbody>
</table>

Table. S1. The corresponding values in calculating $f_{VP/PW}$. 

S2
**Simulation method of phase behaviors of PS-b-P2VP/H$_3$PW$_{12}$O$_{40}$ complex**

Phase behavior of PS-$b$-P2VP/H$_3$PW$_{12}$O$_{40}$ complex was investigated by simulated annealing method with the ‘single-site bond fluctuation’ model$^{4,5}$. The model and simulation algorithm were reviewed and a detailed description could be found elsewhere$^6$.

A simple cubic lattice of volume $V = L_x \times L_y \times L_z$ was used. Several boxes with different sizes are used for a system with a given composition to calculate the average period$^7$. Periodic boundary conditions are applied in all three directions. The bond length is set to be 1 and $\sqrt{2}$ lattice spacing, and each site has 18 nearest neighbor sites. The energy of the system is calculated by taking account of the pair interactions between different species on two nearest neighbor sites.

Interaction energy $E_{ij} = \varepsilon_{ij} k_B T_{\text{ref}}$ is assigned for the pair of components $i$ and $j$, where $\varepsilon_{ij}$ is the reduced interaction energy, $k_B$ is the Boltzmann constant, $T_{\text{ref}}$ is a reference temperature. A, B, C, and S represents PS, P2VP, H$_3$PW$_{12}$O$_{40}$ and solvent, respectively. The pair interactions were set as $\varepsilon_{AB}=2.0$, $\varepsilon_{BC}=-2.0$ for short chain and -6.0 for long chain, $\varepsilon_{AC}=1.0$, $\varepsilon_{AS}=-0.1$, $\varepsilon_{BS}=-1.0$, $\varepsilon_{CS}=-1.0$, and the interactions between identical monomers $\varepsilon_{ii}=0.0$. Define the volume concentration of the complex as $\Phi$, $\Phi = \frac{V_A + V_B + V_C}{V_A + V_B + V_C + V_S} = 0.8$ was set to investigate the phase behaviors. Where $V_A = n_{AB} \times N_A$, $V_B = n_{AB} \times N_B$, $V_C = n_C \times N_C$, $n_{AB}$ and $n_C$ are the number of AB diblock copolymer chain and C molecules, respectively, and $N_A$, $N_B$, $N_C$ is the length of each A-block, B-block and C chain, respectively. In the study we set $N_A = N_B = 3$, $N_C = 2$ for PS-$b$-P2VP(50k-$b$-50k), and $N_A = N_B = 6$, $N_C = 2$ for PS-$b$-P2VP(130k-$b$-130k).
The period $d$ was obtained by calculating the static collective structure factor $S(q)$. $S(q)$ was obtained according to the literature, and label the sites with a spin-type variable $\sigma(r_i)$ which is 1 for A monomers, 0 for B and C monomers and solvent molecules. Then calculate the collective structure factor $S(q)$ as

$$S(q) = L^{-3} \sum_{ij} e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \sigma(r_i)\sigma(r_j)$$

The sum here is spread over all lattice points. Given a finite lattice and the boundary conditions implemented here, only a set of discrete $q$ vectors are physically meaningful; these are

$$q = 2\pi \frac{n_x n_y n_z}{L_x L_y L_z}$$

with $0 \leq nr \leq Lr$ for $r=x, y, z$. The structure factor for all these $q$ vectors and average over those of equal length were calculated to obtain the spherical structure factor $S(|q|)$, and $S(q)=S(|q|)$.

All the $<R_g^2>$ values are measured in the unit of the value of the corresponding ideal Gaussian chain (with the value of $(N + 1)(N - 1)b_0^2/6N$, where $b_0^2 \approx 1.6667$ is the square of the average of all the allowed bond length and $N$ is the corresponding chain length).

Fig. S1. TEM image of PS-b-P2VP (130k-b-130k)/$\text{H}_3\text{PW}_{12}\text{O}_{40}$ complex at $f_{VP/PW}=0.63$
Reference: