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Support Information

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

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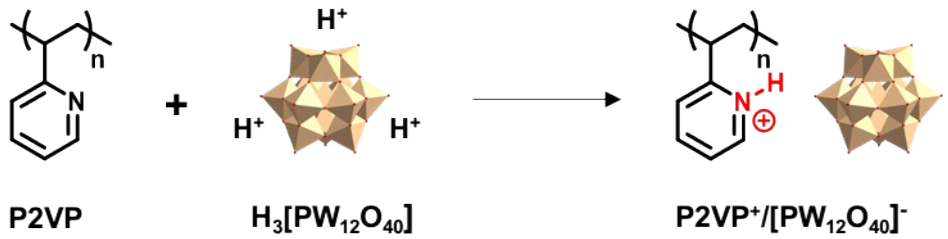
Schematic illustration of the electrostatic interaction between P2VP and $H_3PW_{12}O_{40}$



Scheme S1. The illustration of the electrostatic reaction between P2VP and $H_3PW_{12}O_{40}$

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

The method was similar to that in previous references[1,2].

$$f_{\mathrm{VP/PW}}=\frac{\sum V_{\mathrm{P2VP}}+\sum V_{\mathrm{PW}}}{\sum V_{\mathrm{PS}}+\sum V_{\mathrm{P2VP}}+\sum V_{\mathrm{PW}}}$$

$$=\frac{\sum m_{\mathrm{P2VP}}/\rho_{\mathrm{P2VP}}}{\sum m_{\mathrm{PS}}/\rho_{\mathrm{PS}}+\sum m_{\mathrm{P2VP}}/\rho_{\mathrm{P2VP}}+\sum N_{PW}*v_{PW}}$$

and $N_{\mathrm{PW}}=N_{\mathrm{a}}*\sum m_{\mathrm{PW}}/M_{PW}$

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

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

ρ_{PS}[3]	1.06 g/cm^3
ρ_{P2VP}[2]	1.145 g/cm^3
v_{PW}[2]	0.599 nm^3

Simulation method of phase behaviors of PS-*b*-P2VP/$H_3PW_{12}O_{40}$ complex

Phase behavior of PS-*b*-P2VP/$H_3PW_{12}O_{40}$ 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 $V = Lx \times Ly \times Lz$ 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 $Eij = \varepsilon ij k_B Tref$ is assigned for the pair of components i and j, where ε_{ij} is the reduced interaction energy, k_B is the Boltzmann constant, $Tref$ is a reference temperature. A, B, C, and S represents PS, P2VP, $H_3PW_{12}O_{40}$ and solvent, respectively. The pair interactions were set as ε_{AB} =2.0, ε_{BC}=-2.0 for short chain and -6.0 for long chain, ε_{AC}=1.0, ε_{AS} =-0.1, ε_{BS}=-1.0, ε_{CS}=-1.0, and the interactions between identical monomers ε_{ii}= 0.0. Define the volume concentration of the complex as Φ, $\Phi = \frac{V_A + V_B + V_C}{V_A + V_B + V_C + V_S}$=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[7,8], 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

$$S(q) = L^{-3}\sum_{i,j} e^{iq.r_{ij}}\sigma(r_i)\sigma(r_j)$$

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

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

with $0 \le n_r \le L_r$ 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 $<Rg^2>$ 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).

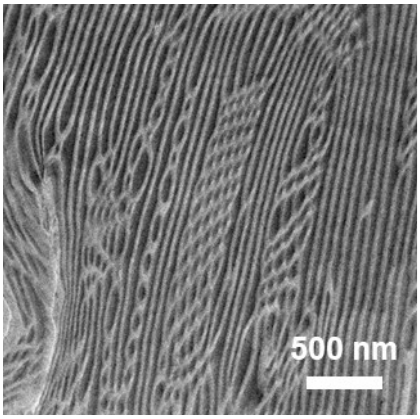


Fig. S1. TEM image of PS-*b*-P2VP (130k-b-130k)/$H_3PW_{12}O_{40}$ complex at $f_{VP/PW}$=0.63

Reference:

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