Phase Behavior of Block Copolymer Hybrids

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Nanohybrids of Inorganic and Polymeric Materials

High conductive nanoporous material (400 S/cm upon pyrolysis)

Self-assembly of Block Copolymer

Decreasing Temperature or Concentration

Self-assembly → Nanostructures

Various volume fractions → Various Nanostructured phases

Size

Tens of nanometer

<table>
<thead>
<tr>
<th>Patterns</th>
<th>Spheres</th>
<th>Cylinders</th>
<th>Gyroid</th>
<th>Lamellae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red domain: A block Blue domain: B block</td>
<td><img src="image1" alt="Spheres" /> <img src="image2" alt="Cylinders" /> <img src="image3" alt="Gyroid" /> <img src="image4" alt="Lamellae" /></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume fraction of A block</td>
<td>0~21%</td>
<td>21~33%</td>
<td>33~37%</td>
<td>37~50%</td>
</tr>
</tbody>
</table>

Hybridization by Using BCP as a Template

Diblock copolymer + Ionic Precursors or Inorganic Nanoparticles

Specific Interaction
Dipolar interactions, Hydrogen bonding and Complex formation

Nanostructured hybrids, namely nanohybrids, for functions and complexity
Inorganic/BCP Hybrids

Ex-situ

Self-assembly

In-situ

Self-assembly

: functionalized nanoparticle

: ionic precursor

Time-resolved reduction or oxidation
Phase Behavior of Inorganic/BCP Hybrids

\[ \chi_{AB} = \chi_{PB} > 0 \]

\[ \chi_N = 50 \]

\( P \): particle

\( \Phi \): particle volume fraction

\( f \): diblock copolymer composition

affinity, size and amount of inorganic species

Phase Transformation Induced by Ex-situ Hybridization


Phase Transformation Induced by In-situ Hybridization

Increasing concentration of gold precursors

Poly(4 vinylpyridine)-block-poly(ε-caprolactone)

Strong segregation

$\chi(T) = 103.48/T - 0.062$

→ much easier for hybridization
→ possible to create nanostructures with smaller dimension

Hybridization by Using P4VP-PCL as a Template

1. Specific Interaction
   - Association of nitrogen lone-pair electrons of vinylpyridine and ionic precursors

2. Self-assembling

3. Reduction
The effects of molecular weight and constituent composition on the phase behavior of P4VP-PCL/inorganic nanohybrids.
Association of Ionic Precursors

Before association

After association

Blue shift

Hybrid ratio: Au/N stoichemistry of gold precursor versus nitrogen atom

CH₂Cl₂, 24 hours
Phase Transformation Induced by Hybridization

RuO4 stained samples

\( f_{P4VP} = 0.37 \)

\[ P4VP - PCL \]

\[ \text{Au/N: 1/7} \]

cylinder phase

lamellar phase

unstained
RuO4 stained samples

Au/N: 1/3

Disordered

Segregation: solubility limit

Au/N: 1/1
Phase transformation

$\frac{f_{P4VP}}{P4VP} = 0.37$

P4VP-PCL

Hybrids with High-Mn P4VP Block

How to increase the loading of gold precursors?

$\frac{f_{\text{P4VP}}}{v}=0.38$

**lamellae**

**Diffused lamellae**

- **Au/N: 1/7**
- **Au/N: 1/3**

*Higher Mn (i.e., segregation strength) → high solubility and stability*
Hybrids with Low-Fraction P4VP Block

$f_{P4VP} = 0.24$

Au/N: 1/7

Lower P4VP fraction $\rightarrow$ lower solubility and stability

Au/N: 1/3

gold precursor segregation
SAXS Profiles of Hybrids

**V4C7** \( (f_{P4VP} = 0.38) \)

- **Swelling**

**V2C7** \( (f_{P4VP} = 0.24) \)

- Occurrence of gold precursor segregation

P4VP-PCL with longer P4VP block may play role to stabilize the hybridized morphology so that there is higher solubility limit!
Hybrids for P4VP-rich P4VP-PCL

$V15C5 \ (f_{P4VP}^v = 0.75)$

$\frac{Au}{N}: 1/12$

$f_{P4VP}^v = 0.75$

Disordered morphology even with very low loading of precursors

Strong association: $f_{P4VP}^v_{\text{(hybrid)}} >\!> f_{P4VP}^v_{\text{(neat)}} + f_{\text{gold precursor}}^v_{\text{(neat)}}$
**Effective excluded volume fraction:** $f_{P4VP}^{v}(hybrid) - f_{P4VP}^{v}(neat)$

$$\gamma(z) = \frac{1}{Q} \int_{0}^{\infty} q^2 I(q) \cos(qz) dq$$

**Ideal binary system**

**V4C7** ($f_{P4VP}^{v} = 0.38$)

**V2C7** ($f_{P4VP}^{v} = 0.24$)

Ho, R.-M. *et al.* Macromolecules 2009, 42, 742.
Effective Excluded Volume

Instead of simple swelling by the intrinsic volume of the gold precursors, the association of the gold precursors and the lone pair of the nitrogen in the P4VP profoundly creates extra volume in the P4VP microdomains so as to cause the phase transformation.

<table>
<thead>
<tr>
<th>Code</th>
<th>Loading (Au) V/V</th>
<th>Excluded volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>V4C7-1/7</td>
<td>0.042</td>
<td>0.17</td>
</tr>
<tr>
<td>V4C7-1/3</td>
<td>0.091</td>
<td>0.25</td>
</tr>
<tr>
<td>V2C7-1/7</td>
<td>0.022</td>
<td>0.39</td>
</tr>
<tr>
<td>V2C7-1/3</td>
<td>0.05</td>
<td>0.37</td>
</tr>
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