Supramolecular alloying as a facile approach to control crystallinity and morphology in polymer nanostructures

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Length Scales of Self-Assembly

Molecular Structure

Molecular Packing

Nano-Structure

Micro-Structure

Macro-Structure

Chin, S. M. et al. Nat. Commun. 9, 1–11 (2018).

Zhang, S. et al. Nat. Mater. 9, 594–601 (2010).

Freeman, R. et al. Science 362, 808–813 (2018).

Design principles in the field of self-assembly are based on controlling different length scales by encoding information into the chemical structure of a material. When designing a new material, we typically start at the molecular length scales where we synthesize discrete molecules. These molecules then pack together and assemble into different nanostructure morphologies. We can further take these nanostructures and form hierarchical structures at the micron to macroscale using different processing conditions.

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While the field has developed many strategies to control the nano-, micro-, and macro-structures, a remaining challenge in the field is controlling the arrangement of macromolecules at sub-nanometer length scales. Specifically, this requires methods to control the crystal structure of molecules in supramolecular polymers.

Crystal Engineering By Synthetic Modifications

Supramolecular Polymers

Weingarten, A. S. et al. Nat. Chem. 6, 964–970 (2014)

Kazantsev, R. V. et al. Chem 4, 1596–1608 (2018)

Stupp Group: J. Am. Chem. Soc. 139, 6120–6127 (2017)

Covalent Polymers

Winey and Coates Group: ACS Macro Lett. 6, 947–951, (2017)

Recently, promising work has been done to control the crystal structures in supramolecular and covalent polymer systems. For supramolecular polymers, the Stupp group has looked at a class of chromophores that self-assemble in 2D crystals where the crystal structure can be tuned by changing the dipole moment or steric bulk of the chromophores through synthetic modifications. In covalent polymers, the Winey and Coates group showed that crystallinity and lattice spacing of lamellar phases in ionomers could be tuned through sequence defined polymers.

Crystal Engineering By Synthetic Modifications

Supramolecular Polymers

Weingarten, S. et al. Nat. Chem. 6, 964–971 (2014)

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While the use of synthetic modifications is a powerful tool for changing the crystallinity and molecular packing in self-assembled materials, I was interested in developing more facile approaches for controlling crystallinity in supramolecular polymers. In the rest of the presentation, I will borrow concepts from traditional materials science and show how we can control crystal structure and nanostructure morphology of polymeric materials by forming an alloy between covalent polymers and supramolecular polymers.

Supramolecular Alloying: Molecular Design

Chromophore Amphiphile

Supramolecular Alloying: Molecular Design

Experimentally, the nanostructures of these materials can be supported by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The crystal structure can be determined as a 2D oblique lattice (β -phase) by wide angle X-ray scattering (WAXS).

Covalent Polymer Synthesis

Water-Soluble
Polymer

Perylene Monoimide
(PMI) Chromophore

Next, we designed a covalent polymer with a similar structure to the PMI chromophore amphiphile. The structure we chose incorporated a hydrophilic, water soluble polymer functionalized with pendant PMI moieties intended to strongly associate with PMI chromophore amphiphile. The polymer was synthesized by partially functionalizing poly(ethylene-alt-maleic anhydride) with an amine terminated PMI-based chromophore and hydrolyzing the remaining anhydride moieties to yield a random copolymer.

Covalent Polymer Self-Assembly

This polymer can self assemble into narrow, 2D, ribbon-like nanostructures as determined by SAXS and cryo-TEM. WAXS shows that the polymer by itself is semi-crystalline and forms a 2D oblique lattice (α -crystal) with a different unit cell than the PMI chromophore amphiphile.

Supramolecular Alloying: Molecular Design

Co-Crystallization: Experimental Conditions

- ❑ “High” Ionic Strength
→ 50 mM NaCl
- ❑ Constant Charge
→ pH ~7
- ❑ Long Annealing Times
→ 1 h at 95°C, 18 h slow cool

Co-Assembly Ratio

$$\phi = \frac{n_{\text{amphi}}}{n_{\text{amphi}} + n_{\text{poly}}} = \frac{2}{2 + 3} = 0.4$$

$\phi = 0$: covalent polymer

$\phi = 1$: supramolecular polymer

Co-Crystallization of Covalent and Supramolecular Polymer

As ϕ increases from 0 to 1 we observe three distinct phase regimes. From $\phi = 0$ to $\phi = 0.3$, the scattering peaks from the WAXS of the α -crystal phase show an increase in the intensity and decrease in the full width at half maximum (FWHM) indicating an increase in the crystalline domain size. This is indicative of the formation of a substitutional molecular alloy, where the addition of free CA alloys into the α -crystal phase formed by the covalent polymer and increases the α -phase crystalline domain size rather than forming a separate β -phase. As the co-assembly ratio increases from $\phi = 0.4$ to $\phi = 0.6$ we observe a second distinct region in the phase-space where the β -crystal begins to nucleate and emerge in the scattering pattern while the α -crystal phase decreases in intensity. This behavior is indicative of a phase co-existence regime between the α - and β -crystal phases, which is a behavior commonly seen in more traditional metallic and ceramic alloys. Finally, from $\phi = 0.7$ to $\phi = 1$ the β -crystal phase is the only crystal phase detected in the WAXS pattern indicating that the PMI chromophores on the covalent polymer are fully alloying into the β -crystal phase formed by the CA.

Control of the Nanostructure Morphology

In addition to controlling the crystal structure by changing the composition of these supramolecular alloys, we can also change the nanostructure morphology. With increasing ϕ the nanostructures change continuously from narrow, high aspect ratio nanoribbons to wide, low aspect ratio nanosheets. Coarse-grained molecular dynamic (CG-MD) simulations show that the lateral growth of the nanostructures at low values of ϕ is prevented by the covalent polymer backbone, which wraps around the nanostructures and forces them to grow along the chromophore π - π stacking direction. By looking closely at the spatial arrangement of the chromophores in the nanostructures, we also show that they are randomly mixed together forming a substitutional alloy.

Pathway of Co-Crystallization Supramolecular Alloys

To further understand the co-assembly process, we used variable temperature WAXS to characterize the growth of nanostructures during the annealing process. For the VT-WAXS experiments we took pre-annealed nanostructures of CA ($\phi = 1$) and covalent polymer ($\phi = 0$) and mixed them at room temperature. We then annealed these metastable mixtures and used in-situ WAXS to measure the change in crystal structure at different temperatures to characterize the formation of the supramolecular alloy. The VT-WAXS patterns show the initial kinetically trapped state at room temperature contains both the α - and β -phase crystal. As the structures are heated, the β -phase crystal begins to melt between 68 °C and 77 °C then is incorporated into the α -phase crystal as shown by the decrease in the (20) β -phase peak intensity and the subsequent growth of the (20) α -phase peak. CG-MD simulations of the annealing process show the same phenomenon where the β -phase crystal melts into a mixture of monomeric and aggregated CA, which then incorporate into the α -phase of the covalent polymer.

Photocatalytic Hydrogen Production

The β -phase crystal has previously been shown to be excellent photosensitizers for the photocatalytic generation of hydrogen, so we assessed the impact of the alloying composition on the production of hydrogen. Structures at varying values of ϕ were irradiated in the presence of a thiomolybdate cluster, acting as the proton reduction catalyst, and ascorbic acid, which acts both as a source of protons and as a sacrificial electron donor, and measuring the turn over number (TON) of hydrogen produced. We found that the highest TON were measured at $\phi = 0.8$ which showed a two-fold increase in the TON of hydrogen produced relative to the pure CA. The dramatic difference in TON is likely due to higher diffusion of the catalysts and sacrificial electron donor at the $\phi = 0.8$ composition relative to $\phi = 1$ composition. The β -phase at $\phi = 0.8$ can remain solubilized in the acidic catalysis environment while the β -phase at $\phi = 1$ forms a dense, precipitate. The resulting increase in diffusion allows for more interactions between the photosensitizer and the thiomolybdate catalyst leading to an increase in hydrogen production.

Conclusions

Change Crystal Structure

Control Morphology

Improve Hydrogen Catalysis

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