Supplementary Information for

Dispersity Effects in Polymer Self-Assemblies: A Matter of Hierarchical Control

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Particle Size distribution

DLS

Table S1. The width of the size distribution (± 2 standard deviation) for particles of various Z-average hydrodynamic diameter with increasing dispersity.

<table>
<thead>
<tr>
<th>Z-average (nm)</th>
<th>Size range (± 2 standard deviation, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8.0 – 12.0</td>
</tr>
<tr>
<td>50</td>
<td>40 – 60</td>
</tr>
<tr>
<td>100</td>
<td>80 – 120</td>
</tr>
<tr>
<td>200</td>
<td>160 – 240</td>
</tr>
<tr>
<td>250</td>
<td>200 – 300</td>
</tr>
<tr>
<td>0.05</td>
<td>5.5 – 14.5</td>
</tr>
<tr>
<td>28 – 72</td>
<td>55 – 145</td>
</tr>
<tr>
<td>111 – 289</td>
<td>138 – 362</td>
</tr>
<tr>
<td>0.1</td>
<td>3.7 – 16.3</td>
</tr>
<tr>
<td>18 – 82</td>
<td>37 – 163</td>
</tr>
<tr>
<td>74 – 326</td>
<td>92 – 408</td>
</tr>
<tr>
<td>0.2</td>
<td>1.1 – 19.0</td>
</tr>
<tr>
<td>5 - 95</td>
<td>11 - 189</td>
</tr>
<tr>
<td>21 - 379</td>
<td>26 - 474</td>
</tr>
</tbody>
</table>

Additional definitions regarding the Zimm analysis.

The contrast factor, \( K \), is defined as

\[
K = \frac{4\pi^2 n_{\text{standard}}^2 \left( \frac{dn}{dc} \right)^2}{N_A \lambda^4}
\]

Where \( n_{\text{standard}} \) is the refractive index of the standard used, typically toluene. \( \frac{dn}{dc} \) is the refractive index increment of the sample with increasing concentration, measured in the solvent typically using a differential refractometer. \( N_A \) is Avogadro’s constant and \( \lambda \) is the wavelength of the light source.

The Rayleigh ratio, \( R_0 \) is defined as

\[
R_0 = \frac{I_{\text{sample}} - I_{\text{solvent}}}{I_{\text{standard}}} R_{\theta, \text{standard}}
\]

Where \( I_{\text{sample}}, I_{\text{solvent}} \) and \( I_{\text{standard}} \) are the intensities of the measured scattered light of the sample, solvent and standard at a given angle. \( R_{\theta, \text{standard}} \) is the known Rayleigh ratio of the standard.
Additional Figures

Figure S2. Illustration of how dispersity within a single block can lead to mixed or unpredictable morphologies by altering the packing parameter and particle curvature. A: An A-b-B diblock copolymer with a disperse core-forming block forms a mixture of morphologies with different interfacial curvatures. B: An A-b-B diblock copolymer with a disperse corona-forming block forms small vesicles owing to effective segregation of long and short corona chains into the external and internal faces of the particle. Those with extremely high curvature form spheres as in the study by Eisenberg and co-workers.1 C: A very well defined A-b-B diblock copolymer with near-identical chain lengths and block ratios cannot segregate its chains to pack them effectively and so larger vesicles form.

Suggested additional reading:

Self-assembly

Multiple Morphologies and Characteristics of “Crew-Cut” Micelle-like Aggregates of Polystyrene-b-poly(acrylic acid) Diblock Copolymers in Aqueous Solutions

Building nanostructures using RAFT polymerization
Self-assembly of block copolymers

Comparison of methods for the fabrication and the characterization of polymer self-assemblies: what are the important parameters?

**Polymer Compositional Dispersity**

Copolymerization. I. A Basis for Comparing the Behavior of Monomers in Copolymerization; The Copolymerization of Styrene and Methyl Methacrylate

Nonlinear least squares fitting applied to copolymerization modeling

**Dynamic Light Scattering (DLS)**

*Cumulants analysis for DLS*
Revisiting the method of cumulants for the analysis of dynamic light-scattering data

**Static Light Scattering (SLS)**

*Zimm analysis*
Apparatus and Methods for Measurement and Interpretation of the Angular Variation of Light Scattering; Preliminary Results on Polystyrene Solutions

Accuracy in Multiangle Light Scattering Measurements for Molar Mass and Radius Estimations. Model Calculations and Experiments

*Guinier analysis*

Approximations Leading to a Unified Exponential/Power-Law Approach to Small-Angle Scattering

*Berry Method of analysis*
Thermodynamic and Conformational Properties of Polystyrene. I. Light-scattering Studies on Dilute Solutions of Linear Polystyrenes

**Transmission Electron Microscopy (TEM)**

*Automatic particle counting*
Analysis of Nanoparticle Transmission Electron Microscopy Data Using a Public- Domain Image-Processing Program, Image


Reviews on drug delivery systems

Smart polymers in drug delivery: a biological perspective.

Polymeric Nanostructures for Imaging and Therapy.

Micellar Nanocarriers: Pharmaceutical Perspectives.

Nano-engineering block copolymer aggregates for drug delivery.

EPR Effect

Exploiting the enhanced permeability and retention effect for tumor targeting

A New Concept for Macromolecular Therapeutics in Cancer Chemotherapy: Mechanism of Tumoritropic Accumulation of Proteins and the Antitumor Agent Smancs

The EPR effect: Unique features of tumor blood vessels for drug delivery, factors involved, and limitations and augmentation of the effect

Tumor delivery of macromolecular drugs based on the EPR effect

Macromolecular therapeutics in cancer treatment: The EPR effect and beyond
H. Maeda, *J. Controlled Release*, 2012, 164, 138-144

Effect of size and shape of nanoparticles on properties

The size of liposomes: a factor which affects their targeting efficiency to tumors and therapeutic activity of liposomal antitumor drugs.

The adhesive strength of non-spherical particles mediated by specific interactions

Shaping nano-/micro-particles for enhanced vascular interaction in laminar flows

Polymer particle shape independently influences binding and internalization by macrophages.
Shaping cancer nanomedicine: the effect of particle shape on the in vivo journey of nanoparticles
R. Toy, P. M. Peiris, K. B. Ghaghada and E. Karathanasis, Nanomedicine, 2013, 9, 121-134

References