Electronic Supplementary Material (ESI) for Chemical Society Reviews.

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.

	Size range (± 2 standard deviation, nm)				
Z-average / *Đ*	10 nm	50 nm	100 nm	200 nm	250 nm
0.01	8.0 – 12.0	40 – 60	80 – 120	160 – 240	200 – 300
0.05	5.5 – 14.5	28 – 72	55 – 145	111 – 289	138 – 362
0.1	3.7 – 16.3	18 – 82	37 – 163	74 – 326	92 – 408
0.2	1.1 – 19.0	5 - 95	11 - 189	21 - 379	26 - 474

Additional definitions regarding the Zimm analysis.

The contrast factor, *K*, is defined as

$$K = \frac{4\pi^2 {n_{standard}}^2 (\frac{dn}{dc})^2}{N_A \lambda^4}$$

Where $n_{standard}$ is the refractive index of the standard used, typically toluene. *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 λ is the wavelength of the light source.

The Rayleigh ratio, R_θ is defined as

$$R_\theta = \frac{I_{sample} - I_{solvent}}{I_{standard}} R_{\theta,\, standard}$$

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

Additional Figures

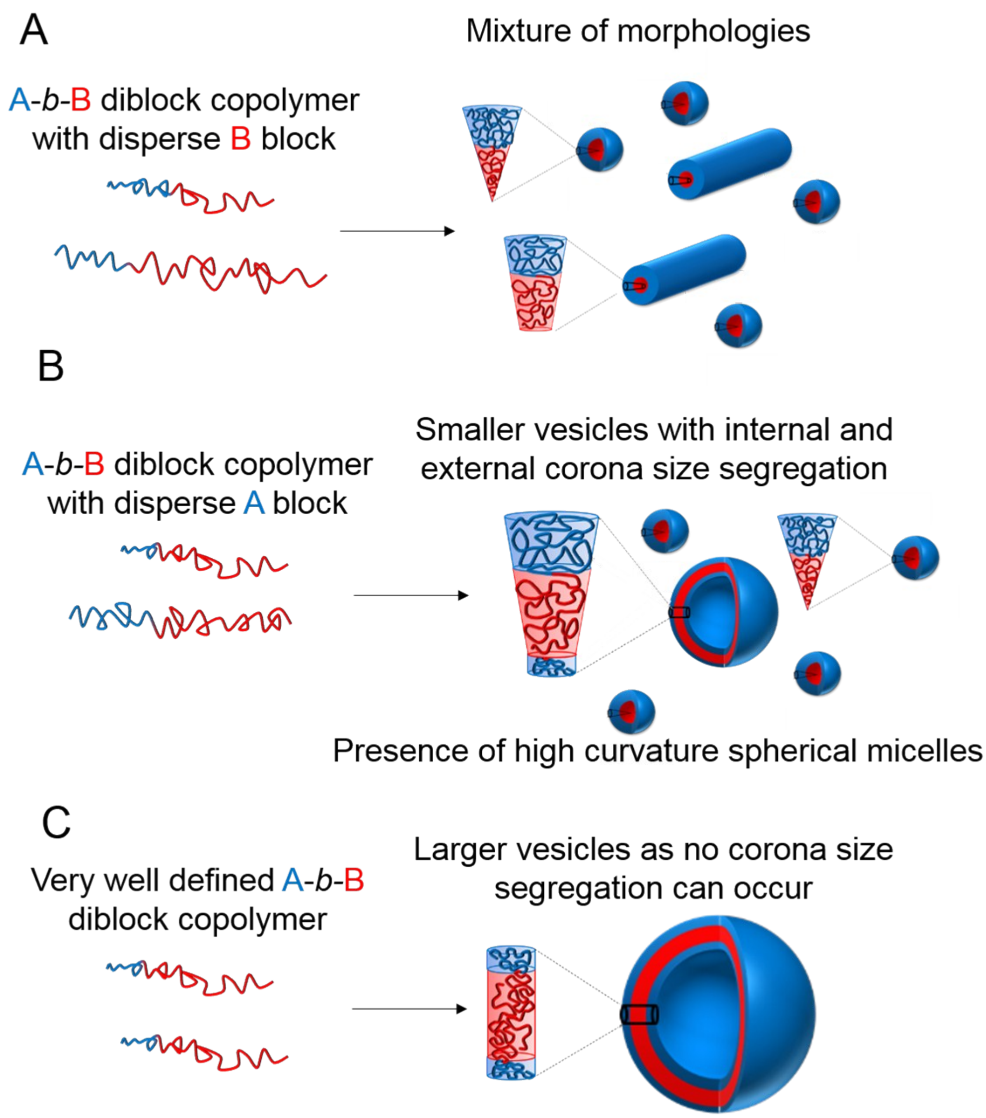

Figure S2. Illustration of how dispersity within a single block can lead to mixed or unpredictable morphologies by altering the packing parameter and particle curvature. **A**: An A-*b*-B diblock copolymer with a disperse core-forming block forms a mixture of morphologies with different interfacial curvatures. **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
L. Zhang and A. Eisenberg, *J. Am. Chem. Soc.*, 1996, 118, 3168-3181

Building nanostructures using RAFT polymerization
C. Boyer, M. H. Stenzel and T. P. Davis, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49, 551-595

Self-assembly of block copolymers
Y. Mai and A. Eisenberg, *Chem. Soc. Rev.*, 2012, 41, 5969-5985

Comparison of methods for the fabrication and the characterization of polymer self-assemblies: what are the important parameters?
M. Dionzou, A. Morere, C. Roux, B. Lonetti, J. D. Marty, C. Mingotaud, P. Joseph, D. Goudouneche, B. Payre, M. Leonetti and A. F. Mingotaud, *Soft Matter*, 2016, DOI: 10.1039/C5SM01863C

Polymer Compositional Dispersity

Copolymerization. I. A Basis for Comparing the Behavior of Monomers in Copolymerization; The Copolymerization of Styrene and Methyl Methacrylate
F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, 1944, **66**, 1594-1601.

Nonlinear least squares fitting applied to copolymerization modeling
A. M. Van Herk and T. Dröge, *Macromol. Theory Simul.*, 1997, **6**, 1263-1276.

Dynamic Light Scattering (DLS)

Cumulants analysis for DLS

Revisiting the method of cumulants for the analysis of dynamic light-scattering data
B. J. Frisken, *Appl. Opt.*, 2001, 40, 4087-4091

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
B. Zimm, *J. Chem. Phys*., 1948, 16, 1099-1116

Accuracy in Multiangle Light Scattering Measurements for Molar Mass and Radius Estimations. Model Calculations and Experiments
M. Andersson, B. Wittgren and K.-G. Wahlund, *Anal. Chem*. 2003, 75, 4279 - 4291

Guinier analysis

A. Guinier and G. Fournet, *Small angle scattering of X-rays*, 1955, New York, Wiley

Approximations Leading to a Unified Exponential/Power-Law Approach to Small-Angle Scattering
G. Beaucage, *J. Appl. Cryst*., 1995, 28, 717

Berry Method of analysis

Thermodynamic and Conformational Properties of Polystyrene. I. Light-scattering Studies on Dilute Solutions of Linear Polystyrenes
G. C. Berry, J. Chem. Phys, 1966, 44, 4550 - 4564

Transmission Electron Microscopy (TEM)

Automatic particle counting

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

Gerd H. Woehrle, James E. Hutchinson, Saim Özkar, Richard G. Finke, Turk J Chem, **2006**, *30*, 1-13

Reviews on drug delivery systems

Smart polymers in drug delivery: a biological perspective.
A. C. Hunter and S. M. Moghimi, *Polym. Chem.*, 2016, DOI: 10.1039/C6PY00676K.

Polymeric Nanostructures for Imaging and Therapy.
M. Elsabahy, G. S. Heo, S.-M. Lim, G. Sun and K. L. Wooley, *Chem. Rev.*, 2015, 115, 10967-11011

Micellar Nanocarriers: Pharmaceutical Perspectives.
V. P. Torchilin, *Pharm. Res.*, 2006, 24, 1-16.

Nano-engineering block copolymer aggregates for drug delivery.
C. Allen, D. Maysinger and A. Eisenberg, *Colloids and Surfaces B: Biointerfaces*, 1999, 16, 3-27.

EPR Effect

Exploiting the enhanced permeability and retention effect for tumor targeting
A. K. Iyer, G. Khaled, J. Fang and H. Maeda, *Drug Discovery Today*, 2006, 11, 812-818

A New Concept for Macromolecular Therapeutics in Cancer Chemotherapy: Mechanism of Tumoritropic Accumulation of Proteins and the Antitumor Agent Smancs[1]
Y. Matsumura and H. Maeda, *Cancer Research*, 1986, 46, 6387-6392

The EPR effect: Unique features of tumor blood vessels for drug delivery, factors involved, and limitations and augmentation of the effect
J. Fang, H. Nakamura and H. Maeda, *Adv. Drug Deliver. Rev.*, 2011, 63, 136-151

Tumor delivery of macromolecular drugs based on the EPR effect
V. Torchilin, *Adv. Drug Deliver. Rev.*, 2011, 63, 131-135

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.
A. Nagayasu, K. Uchiyama and H. Kiwada, *Adv. Drug Deliver. Rev.*, 1999, 40, 75-87

The adhesive strength of non-spherical particles mediated by specific interactions
P. Decuzzi and M. Ferrari, *Biomaterials*, 2006, 27, 5307-5314

Shaping nano-/micro-particles for enhanced vascular interaction in laminar flows
L. Sei-Young, F. Mauro and D. Paolo, *Nanotechnology*, 2009, 20, 495101

Polymer particle shape independently influences binding and internalization by macrophages.
G. Sharma, D. T. Valenta, Y. Altman, S. Harvey, H. Xie, S. Mitragotri and J. W. Smith, *J. Controlled Release*, 2010, 147, 408-412

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

1. O. Terreau, L. Luo and A. Eisenberg, *Langmuir*, 2003, **19**, 5601-5607.