Discrete Block Copolymers for Self-Assembly

Wei Zhang

Discrete copolymers exhibited a groundbreaking phase diagram with up to one monomer resolution.

In textbooks, polymers are usually described as mixtures of species with varying molecular sizes (usually illustrated by molecular weights), and polymer dispersity ($D, D \geq 1$) is often used to describe the molecular weight distribution of the mixtures. Polymer scientists have continually pursued the precise synthesis of polymers. Over the past three decades, various synthetic methods have been developed to prepare well-defined polymers. Although very low dispersity (e.g., $D < 1.1$) can be obtained nowadays, truly discrete polymers ($D = 1$) are rarely achieved. For instance, a polystyrene with $M_n = 4000$ Da and low dispersity of $D = 1.01$ or $1.02$ (assuming a Gaussian distribution, see Figure 1) only contains about $10\%$ or $7\%$ fraction of species that have the exact molecular weight at the value of $M_n$. In this issue of ACS Central Science, Dong and co-workers reported the synthesis of a library of discrete block copolymers with linear or branched architectures based on oligo dimethylsiloxane (oDMS) and oligo lactic acid (oLA) (Figure 2a).

In this work, the molecular uniformity of the block copolymers is highlighted. All of the polymers have narrow and unimodal traces in size exclusion chromatography (SEC) (Figure 2b). It should be noted that although SEC is the most widely used technique for characterizing the molecular weight and distribution of polymers, inevitable broadening of the curves always exists due to sample diffusion on the column; it may not be sufficient for characterizing polymers with extremely low dispersity (e.g., $D < 1.01$). The authors further adopted matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), which can provide precision at one monomer level, to directly confirm the precise sizes of these polymers. Impressively, all the block copolymers showed single-component peaks in the MALDI-TOF MS spectra (Figure 2c). The precision at one monomer level is not only meaningful from the perspective of polymer synthesis, but could also provide an excellent platform for studying block copolymer self-assembly from the perspective of polymer physics.

Published: July 30, 2020
excellent platform for studying block copolymer self-assembly from the perspective of polymer physics.

Constructing designated hierarchical structures by precisely manipulating the composition of macromolecules has been a fundamental challenge with general implications in the field of material science. Since it is tremendously difficult to synthesize truly monodisperse polymers, there are even fewer systematic studies to tell how such precision in molecular structures can reflect on hierarchical self-assembled structures and properties. The linear discrete block copolymers in this work have clearly shown phase separations owing to the strong chemical incompatibility of DMS and LA blocks. Dong and team further precisely created variations in molecular architectures by using branched junctions between the immiscible blocks of polymers (Figure 2a).

They mapped out a highly accurate phase diagram up to one monomer resolution with versatile phase structures, which is a significant contribution in the field of block copolymer self-assembly.

FK phases, the unconventional phases found in these discrete block copolymers, are a family of ordered structures formed by topologically close-packed spherical motifs,
which originally appeared in metal alloys.\textsuperscript{7} Since the discoveries of FK phases in block copolymers,\textsuperscript{8,9} their formation process remains elusive partially because they were only sporadically identified. Besides, a minor change in composition could lead to different phase behaviors. Furthermore, the polydisperse nature of conventional block copolymers makes theoretical studies more complicated.\textsuperscript{10} The library of precise block copolymers in this work could serve as ideal candidates for future investigations to correlate experimental observations with theoretical calculations. These discrete polymers may also open a nontraditional way to precisely manipulate molecular weight distribution by blending in the future, which could possibly lead to the discovery of other unconventional phases in block copolymers beyond FK phases.

Overall, the discrete polymer system developed in this work is invaluable in block copolymer synthesis and self-assembly. It could provide an excellent platform to bridge experimental observations and theoretical studies on the mechanism of unconventional phase formation and evolution.

Author Information

Corresponding Author

Wei Zhang — Laboratory for Biomaterials and Drug Delivery, The Department of Anesthesiology, Critical Care and Pain Medicine, Boston Children’s Hospital, Harvard Medical School, Boston, Massachusetts 02115, United States; orcid.org/0000-0002-9321-6411; Email: wei.zhang2@childrens.harvard.edu

Complete contact information is available at: https://pubs.acs.org/10.1021/acscentsci.0c00913

Notes

The author declares no competing financial interest.

REFERENCES

(1) Zhang, W.; Zhang, S.; Guo, Q.; Lu, X.; Liu, Y.; Mao, J.; Wesdemiotis, C.; Li, T.; Li, Y.; Cheng, S. Z. D. Multilevel Manipulation of Supramolecular Structures of Giant Molecules via Macromolecular Composition and Sequence. ACS Macro Lett. 2018, 7, 635–640.

(2) Sun, Y.; Tan, R.; Ma, Z.; Gan, Z.; Li, G.; Zhou, D.; Shao, Y.; Zhang, W.-B.; Zhang, R.; Dong, X.-h. Discrete Block Copolymers with Diverse Architectures: Resolving Complex Spherical Phases with One Monomer Resolution. ACS Cent. Sci. 2020, DOI: 10.1021/accentsci0c00798.

(3) Zhang, W.-B.; Yu, X.; Wang, C.-L.; Sun, H.-J.; Hsieh, I. F.; Li, Y.; Dong, X.-H.; Yue, K.; Van Horn, R.; Cheng, S. Z. D. Molecular Nanoparticles Are Unique Elements for Macromolecular Science: From “Nanoatoms” to Giant Molecules. Macromolecules 2014, 47, 1221–1239.

(4) Doncom, K. E. B.; Blackman, L. D.; Wright, D. B.; Gibson, M. I.; O’Reilly, R. K. Dispersion effects in polymer self-assemblies: a matter of hierarchical control. Chem. Soc. Rev. 2017, 46, 4119–4134.

(5) van Genabbeek, B.; de Waal, B. F. M.; Gowsens, M. M. J.; Pitet, L. M.; Palma, N. A. R. A.; Meijer, E. W. Synthesis and Self-Assembly of Discrete Dimethylosiloxane–Lactic Acid Diblock Co-oligomers: The Dononancontamer and Its Shorter Homologues. J. Am. Chem. Soc. 2016, 138, 4210–4218.