Polydispersity-Induced Macrophase Separation in Diblock Copolymer Melts

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Author: M.W. Matsen

Recommended and a commentary by Randall D. Kamien,

University of Pennsylvania

"Plastics." It has been forty years since Mr. McGuire said that one word to *The Graduate*. Since then, polymer science attracted the interest of the physics community where, thanks to de Gennes and others [1], the techniques of scaling theory, broken symmetry, and the renormalization group have been fruitfully employed. Diblock copolymers, made of two immiscible polymers covalently bound have been a model system, both because of their materials potential and because they may be viewed as giant amphiphiles, the building blocks of the cell. In seminal work, Ludwik Leibler developed the theory of microphase separation in these systems. Based on a Landau-like theory near the order-disorder transition, he predicted the now common lamellar, columnar, and cubic phases found in these systems. These phases have been found, along with the beautiful gyroid phase, in relatively pure, or *monodisperse* systems [3].

It is only through great effort and expense that such pure samples can be produced. Other than through biological methods (which introduce a new host of problems), typical synthetic routes are expensive. Recent work by Matsen, one of the pioneers of the gold-standard, self-consistent field approach to copolymer phases [4], has now studied the effect of polydispersity on the ordered phases – do polymers of different lengths phase separate or can they cooperate to make stable phases? It is certainly the case the suspensions of colloidal particles of different shapes phase separate, even rods of different thicknesses [5]. Just what are the bounds that prevent this in copolymers? Matsen's results shed light on this important issue.

When all the polymers are exactly the same, the chain length and the chain mass are equivalent measures. However, when there is a mixture of varying lengths, one can either calculate the number-averaged molecular weight, N_n, or the weight-averaged molecular weight, N_w. The ratio of these two, $PDI = N_w/N_n \geq 1$ is a measure of polydispersity. To put this into context, living anionic polymerization can be used to produce $PDI \approx 1.1$, while the simpler method of free-radical polymerization results in $PDI \approx 1.2-2.0$. Matsen finds that even at the moderate polydispersity of 1.2, two-phase coexistence occurs, along the phase boundaries of the monodisperse phases, and that the close-packed spherical micelle phase edges out the usual BCC phase. By the time the PDI is 1.5, the phase diagram has been drastically altered and two-phase coexistence spoils a good deal of the monodisperse phase diagram. Why should this be the case? It is notoriously difficult to predict or even explain, *ex post facto*, the stability of the different diblock phases. Matsen conjectures that packing frustration is relieved through polydispersity, in a similar spirit to the way in which a solvent can relieve chain stretching in periodic phases [6]. As with his original work with Schick [4], these results are sure to lead to new theoretical methods and models which will first explain the new phase diagram and then predict new phase behavior. Another important step on the way to rational design.

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