

The ABCs of Block Polymers

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Abstract

The *Macromolecules* catalogue is a record of seminal advances in block polymer self-assembly, connecting experiments, theory, and simulations. This editorial highlights three *Macromolecules* articles in one area that reflects the potential of the field: the self-assembly of ABC triblock terpolymers. In this editorial, concepts of frustration and interfacial tension are used to organize the wide design space. Network morphologies and hierarchical X-in-Y morphologies are described to provide examples of the remarkable morphological complexity available to ABC triblock terpolymers.

Block polymers have captured the interest and imagination of scientists and engineers for over sixty years, beginning with the first precise synthesis reported by Szwarc and coworkers in 1956.¹ For over half of the ensuing time, advances across experiments and theory focused almost exclusively on AB diblock and ABA triblock copolymers. In recent decades, however, higher-order multiblock sequences (*e.g.* ABC) and additional architectural complexity (*e.g.* graft, star, cyclic) have greatly expanded the scope of block polymer design.²⁻³ For all block polymers, the formation of equilibrium mesophases reflects a competition between entropic and enthalpic demands.⁴ In order to minimize both chain stretching and interfacial area, a profusion of periodic structures emerges at the nanoscale. The *Macromolecules* catalogue is a record of seminal advances in block polymer self-assembly, connecting experiments, theory, and simulations. In this editorial, we highlight three *Macromolecules* articles in one area that captures the complexity and

potential of the field: the self-assembly of ABC triblock terpolymers. This editorial will use concepts of frustration and interfacial tension – introduced in a 1995 *Macromolecules* article by Zheng and Wang⁵ – to organize the wide design space for ABC triblock terpolymers. We will first describe how ABC triblocks unlock new morphologies compared to AB diblocks, then highlight (1) network morphologies identified by Matsushita and coworkers⁶ and (2) hierarchical X-in-Y morphologies identified by Stadler and coworkers⁷ as examples of the remarkable morphological complexity available to ABC triblock terpolymers.

In the block polymer design space, linear AB diblock polymers represent the simplest possible configuration. Their equilibrium phase behavior can be largely anticipated by three independent parameters: (1) the total degree of polymerization, N ; (2) the block volume fraction, f_A ; and (3) the Flory-Huggins interaction parameter, χ_{AB} .⁸⁻⁹ Despite the ostensible simplicity of AB diblocks, the interplay of N , f_A , and χ_{AB} produces

a wide variety of equilibrium morphologies, including body-centered cubic spheres, the Frank-Kasper σ and A15 phases,¹⁰⁻¹¹ hexagonally packed cylinders, bicontinuous gyroids, orthorhombic (O^{70}) networks,¹² and lamellae.

Adding a third, unique block – forming linear ABC triblock terpolymers – unlocks additional complexity and new opportunities for materials design. Whereas AB diblocks can be specified by

three independent parameters, ABC triblocks require *six*: (1) the total degree of polymerization, N ; (2–3) two independent block volume fractions, f_A and f_B ; and (4–6) three pairwise interaction

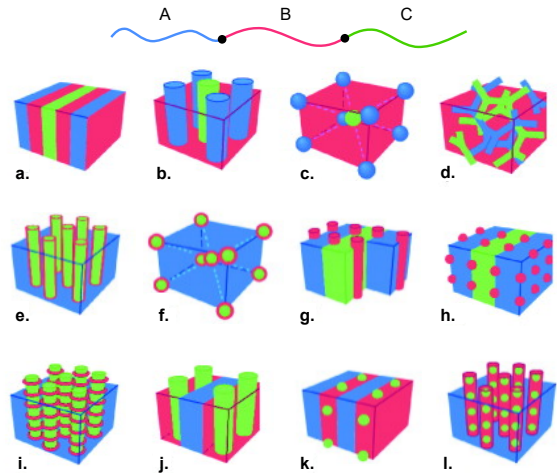


Figure 1. Potential equilibrium morphologies for linear ABC triblock terpolymers. Adapted with permission from Refs. 5–7; note that the arrangement has been changed from the original.

parameters: χ_{AB} , χ_{BC} , and χ_{AC} . In addition, whereas only one unique sequence exists for AB diblock polymers ($AB = BA$), *three* unique sequences exist for triblocks: ABC, ACB, and CAB. Zheng and Wang, in their seminal contribution,⁵ communicated how these parameters can produce new morphologies. Although not the first theoretical treatment of ABC triblock self-assembly, the article provides a particularly insightful platform for both organizing reported morphologies and predicting yet-undiscovered structures. **Figure 1**, adapted from their work,¹ illustrates selected examples. These range from direct analogues of canonical diblock morphologies (*e.g.*, **Fig. 1a–c**) to more exotic network structures (*e.g.* tricontinuous gyroid, **Fig. 1d**), core-shell structures (*e.g.*, core-shell cylinders and spheres, **Fig. 1e–f**), and hierarchical X-in-Y structures (*e.g.*, cylinders-in-lamellae, **Fig. 1g**). We will return to these morphologies and comment on specific systems in which they have been identified and/or predicted, with particular focus on the network morphologies reported by Matushita et al.⁶ and X-in-Y morphologies reported by Stadler et al.⁷ First, however, we consider how two concepts highlighted by Zheng and Wang – frustration and interfacial tension – provide a basis for capturing the tremendous complexity available to ABC triblock terpolymers.

For all block polymers, the equilibrium morphology is determined by minimizing the total free energy subject to the incompressibility of the melt. The free energy of the system has two components: the entropic component captures chain stretching, while the enthalpic component captures interfacial tensions. A derivation by Zheng and Wang – using an approximation for the chain conformational free energy by Nakazawa, Kawasaki, and Ohta¹³⁻¹⁴ – shows that *relative* interfacial tensions play a crucial role in the self-assembly of ABC triblock terpolymers.⁵ In AB diblocks, interfacial curvature can only be induced by asymmetric compositions ($f_A \neq 0.5$); in comparison, in ABC triblocks,

Table 1. Classifying relative interfacial tensions for ABC triblock terpolymers, where $\gamma_1 = \sigma_{BC} / \sigma_{AB}$ and $\gamma_2 = \sigma_{AC} / \sigma_{AB}$, as proposed by Zheng and Wang.⁵

- | | |
|----------------------------------|----------------------------------|
| (1) $\gamma_1 = 1, \gamma_2 < 1$ | (4) $\gamma_1 > 1, \gamma_2 < 1$ |
| (2) $\gamma_1 = 1, \gamma_2 = 1$ | (5) $\gamma_1 > \gamma_2 > 1$ |
| (3) $\gamma_1 = 1, \gamma_2 > 1$ | (6) $\gamma_2 > \gamma_1 > 1$ |

interfaces can be configured not only by asymmetric compositions but also by asymmetric interactions ($\chi_{AB} \neq \chi_{BC} \neq \chi_{AC}$). Zheng and Wang capture the relative interaction strengths through the ratios $\gamma_1 = \sigma_{BC}/\sigma_{AB}$ and $\gamma_2 = \sigma_{AC}/\sigma_{AB}$, where $\sigma_{ij} \sim \chi_{ij}^{1/2}$ is the interfacial tension between i and j

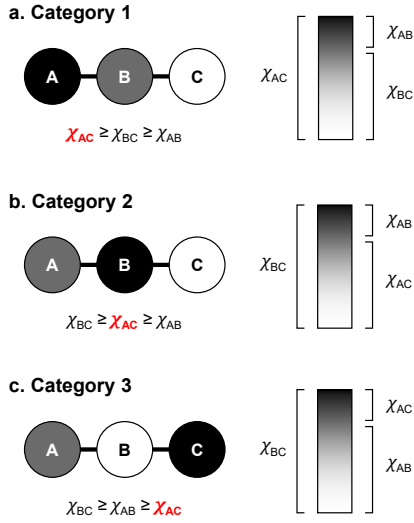


Figure 2. ABC triblock terpolymers can be classified according to the relative magnitude of the penalty to A/C mixing, χ_{AC} .

domains. The magnitudes of γ_1 and γ_2 relative to unity and to each other therefore specify which interfaces are preferred at equilibrium: A/B, B/C, or A/C. In their article, Zheng and Wang proposed six combinations of γ_1 and γ_2 to classify the relative interaction strengths (**Table 1**). The key consideration that emerges from their analysis is the magnitude of χ_{AC} relative to χ_{AB} and χ_{BC} ; A/B and B/C contacts are required by the chain connectivity (ABC), whereas A/C contacts are not. These concepts are illustrated in **Figure 2**, where the equalities in Table 1, Entries 1–3 are subsumed into the inequalities in Entries 4–6 following the approach later suggested by Bailey and coworkers.¹⁵ (For example, Entries 1, 2, and 4 can be combined into the inequalities $\gamma_1 \geq 1$ and $\gamma_2 \leq 1$, suggesting $\chi_{BC} \geq \chi_{AB} \geq \chi_{AC}$, Category 3.) **Figure 2** compares the three possible unique ways to connect three different blocks; here, the letters (A, B, and C) indicate block positions (1, 2, or 3, respectively), while the colors indicate different block chemistries. Swapping any two blocks changes the pattern of relative interfacial tensions. For example, in **Fig. 2a**, χ_{AC} is the largest interaction parameter (represented by the largest contrast, black/white), and therefore A/C interfaces are penalized more severely than B/C and A/B interfaces. Switching the first two blocks (**Fig. 2b**) changes the relative interaction strengths, making A/C interfaces more favorable than B/C interfaces but not A/B interfaces. One final switch (**Fig. 2c**) again alters the relative

interactions, making A/C interfaces the *most* favorable in the system. In the latter two categories (**Fig. 2b–c**), the conflict between the block sequence and the enthalpic preference for A/C interfaces introduces frustration.

Zheng and Wang show that the formation of exotic morphologies in ABC triblock terpolymers (**Figure 1**) can be understood in terms of the concepts of frustration and interfacial tension (**Figure 2**). For example, systems without frustration (Category 1, $\chi_{AC} \geq \chi_{BC} \geq \chi_{AB}$) tend to avoid unnecessary A/C contacts, thereby forming three-domain analogues of typical AB diblock morphologies. A series of publications by Matsushita and coworkers in *Macromolecules* provides illuminating examples of Category 1 phase behavior in polyisoprene-*b*-polystyrene-*b*-poly(2-vinylpyridine) (ISP) triblock terpolymers.^{6,16-18} For ISP, the relative interaction parameters ($\chi_{IP} \gg \chi_{SP} \approx \chi_{IS}$) describe a non-frustrated system. Matsushita and coworkers prepared ISP triblocks with symmetric end blocks ($f_I \approx f_P$) and examined the morphologies upon varying the midblock content, f_S . Direct analogues of AB diblock morphologies were observed, including three-domain lamellae (**Fig. 1a**, $0.10 \leq f_S \leq 0.40$), tricontinuous alternating gyroids (**Fig. 1d**, $0.48 \leq f_S \leq 0.66$), tetragonally packed alternating cylinders (**Fig. 1b**, $0.68 \leq f_S \leq 0.76$), and alternating spheres on a CsCl lattice (**Fig. 1c**, $0.78 \leq f_S \leq 0.89$). We note that the gyroid morphology (**Fig. 1d**) was initially identified as the ordered tricontinuous double diamond (OTDD) phase, having $F\bar{4}3m$ symmetry.^{6,18} Subsequent self-consistent field theory (SCFT) calculations by Matsen suggested reassignment to tricontinuous alternating gyroids ($I4_132$).¹⁹ The reassignment to the gyroid morphology was later experimentally verified by Matsushita and coworkers for one of the reported ISP triblocks ($f_S = 0.48$).²⁰ Other equilibrium network morphologies, including pentacontinuous core-shell gyroids ($Ia\bar{3}d$) and tricontinuous orthorhombic networks (O^{70} , $Fddd$) have been identified in other non-

frustrated triblock terpolymers, including polyisoprene-*b*-polystyrene-*b*-poly(ethylene oxide) (ISO)²¹⁻²³ and poly(1,2-butadiene)-*b*-polystyrene-*b*-poly(methyl methacrylate) (BSM).²⁴⁻²⁵

Introducing frustration (**Figure 2**, Categories 2 and 3) opens opportunities to create and configure A/C interfaces. The competing drives to minimize *both* unfavorable interfaces and chain stretching, subject to the block connectivity, can produce a remarkable variety of morphologies not observed for AB diblocks or non-frustrated ABC triblocks. These new morphologies include but are not limited to core-shell cylinders (**Fig. 1e**), core-shell spheres (**Fig. 1f**), and X-in-Y morphologies (**Fig. 1g–l**). Stadler and coworkers have identified many of these morphologies in two types of triblock terpolymers: polystyrene-*b*-poly(1,2-butadiene)-*b*-poly(methyl methacrylate) (SBM)^{7,26-30} and its partially hydrogenated analogue, polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-poly(methyl methacrylate) (SEM).^{7,28-31} In both systems, the end blocks are significantly more compatible with each other than with the midblock: $\chi_{BM} \geq \chi_{SB} \geq \chi_{SM}$ and $\chi_{EM} \geq \chi_{SE} \geq \chi_{SM}$ (Category 3). We will focus here on one article, published in *Macromolecules* in 1995 by Stadler, Leibler, and coworkers, that combines experimental characterization with theoretical insight.⁷

Stadler and coworkers observed striking new morphologies in SBM and SEM triblocks with symmetric end blocks ($f_S \approx f_M$). For both SBM and SEM, when the volume fraction of the midblock was 0.17 (*i.e.*, $f_B, f_E = 0.17$), an unusual cylinders-in-lamellae morphology (*lc*) was observed (**Fig. 1g**). This morphology features square-packed cylinders of the midblock (B or E) at the interfaces of S/M lamellae. When the volume fraction of the midblock was decreased ($f_B, f_E = 0.06$), new hierarchical morphologies emerged: SBM-0.06 formed spheres-in-lamellae (*ls*, **Fig. 1h**), whereas SEM-0.06 formed rings-on-cylinders (*cr*, **Fig. 1i**). The *ls* morphology comprises spheres of B at the interfaces of S/M lamellae, and the *cr* morphology comprises rings of E

encircling hexagonally packed cylinders of S in a matrix of M. In these frustrated ABC triblocks, the relative interaction strengths favor the formation of A/C interfaces over A/B and B/C contacts, which are required by the chain connectivity. As a result, the B midblocks are *squeezed* into isolated domains (cylinders, spheres, and rings in *lc*, *ls*, and *cr*) along A/C interfaces. The formation of different morphologies in SBM-0.06 and SEM-0.06, which differ only in the partial hydrogenation of the minority block ($f_B, f_E = 0.06$), highlights the exquisite sensitivity of ABC triblock self-assembly to molecular structure.

The publication by Stadler, Leibler, and coworkers⁷ demonstrates how frustration can lead to exotic new morphologies. Complementary theoretical treatment in the same article captures the reported experimental features. Stability analyses on the basis of domain geometries and elastic penalties successfully predict the experimentally observed phase transitions. For example, for SEM triblocks with $f_S \approx f_M$, as f_E decreases, the following sequence of phases is predicted and observed: lamellae (*ll*) $\rightarrow$ cylinders-in-lamellae (*lc*) $\rightarrow$ rings-on-cylinders (*cr*) $\rightarrow$ spheres-in-lamellae (*ls*). The union of experiment and theory provides valuable insight into the subtle factors controlling the formation of A/C interfaces in frustrated ABC triblock terpolymers, involving both interfacial tensions and molecular structure.

The three publications featured in this editorial reflect the important role *Macromolecules* has played in communicating the tremendous morphological complexity available to ABC triblock terpolymers. The 1995 article by Zheng and Wang⁵ organizes the triblock design space in terms of frustration and relative interfacial tensions, described by the three unique interaction parameters, χ_{AB} , χ_{BC} , and χ_{AC} . The 1994 article by Matsushita and coworkers⁶ describes how non-frustrated ABC triblocks ($\chi_{AC} \geq \chi_{BC} \geq \chi_{AB}$) tend to form direct analogues of canonical AB diblock morphologies (**Fig. 1a–d**). Introducing frustration ($\chi_{BC} \geq \chi_{AC} \geq \chi_{AB}$ or $\chi_{BC} \geq \chi_{AB} \geq \chi_{AC}$) creates

opportunities to access new morphologies, such as core-shell cylinders (**Fig. 1e**), core-shell spheres (**1f**), and hierarchical X-in-Y structures (**1g–l**). The 1995 article by Stadler, Leibler, and coworkers⁷ reveals how frustration motivates the formation of unprecedented exotic structures, such as cylinders-in-lamellae (**Fig. 1g**), spheres-in-lamellae (**1h**), and rings-on-cylinders (**1i**).

Zheng and Wang, in their theoretical treatment of ABC triblock self-assembly, provide a basis for both *rationalizing* observed structures (**Fig. 1a–i**) and *predicting* yet-undiscovered structures (**Fig. 1j–l**). The latter structures – featuring either different configurations of lamellae-in-cylinders (**Fig. 1j**) or spheres-in-lamellae (**1k**), or unusual spheres-in-cylinders (**1j**) – are predicted to be stable for certain frustrated triblocks. However, to the best of our knowledge, the morphologies remain undiscovered in experimental systems. This article highlights the rich potential in opening dialogues between experiments and theory. Each motivates the other to new advances, forming a feedback loop that resonates today across many areas of polymer research. What other morphologies are possible? What new complexity remains unexplored? *Macromolecules* has played a key role in motivating these questions, celebrating advances in molecular and materials design.

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