Double Gyroid Morphologies in Precise Ion-Containing Multiblock Copolymers Synthesized via Step-Growth Polymerization

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ABSTRACT: The double gyroid structure was first reported in diblock copolymers about 30 years ago, and the complexity of this morphology relative to the other ordered morphologies in block copolymers continues to fascinate the soft matter community. The double gyroid microphase-separated morphology has co-continuous domains of both species, and the minority phase is subdivided into two interpenetrating network structures. In addition to diblock copolymers, this structure has been reported in similar systems including diblock copolymers blended with one or two homopolymers and ABA-type triblock copolymers. Given the narrow composition region over which the double gyroid structure is typically observed (∼3 vol%), anionic polymerization has dominated the synthesis of block copolymers to control their composition and molecular weight. This perspective will highlight recent studies that (1) employ an alternative polymerization method to make block copolymers and (2) report double gyroid structures with lattice parameters below 10 nm. Specifically, step-growth polymerization linked precise polyethylene blocks and short sulfonate-containing blocks to form strictly alternating multiblock copolymers, and these copolymers produce the double gyroid structure over a dramatically wider composition range (>14 vol%). These new (AB)n multiblock copolymers self-assemble into the double gyroid structure by having exceptional control over the polymer architecture and large interaction parameters between the blocks. This perspective proposes criteria for a broader and synthetically more accessible range of polymers that self-assemble into double gyroids and other ordered structures, so that these remarkable structures can be employed to solve a variety of technological challenges.

KEYWORDS: double gyroid, self-assembly, ion-containing polymers, multiblock copolymers, block copolymers

DOUBLE GYROID MORPHOLOGIES IN BLOCK COPOLYMERS

The double gyroid (DG) structure is a three-dimensionally periodic bicontinuous structure with Ia3d symmetry that consists of two interpenetrating networks of the minority component and a matrix of the majority component (Figure 1). This ordered structure with Ia3d symmetry was first identified in strontium lipids in 1967.1 The first report of the DG structure in block copolymers was made in 1994.2 Since then, the DG has intrigued the polymer science community due to its structural complexity compared to the more common ordered structures of layers and hexagonally packed cylinders found in linear block copolymers.3 Moreover, the percolating domains of the DG morphology contribute to enhancing mechanical properties such as modulus, toughness, and creep resistance of materials relative to the other morphologies.4−5 The bicontinuous domains of DG can also improve ionic conductivities when the interpenetrating domains contain ionic functionalities.6−9 The triply periodic structure of DG can even control the optical properties and its application into metamaterials.10−13

Followed by the first assignment of DG in the linear polystyrene–polysisoprene diblock copolymers (PS-b-PI),2 comprehensive investigations of polystyrene–polysisoprene block copolymers have advanced the understanding of the structural characteristics of DG in polymeric systems.14−18 Note that the DG structures in star block copolymers and other block copolymer systems were originally reported to be double diamond morphologies with Pn3m symmetry and were later correctly identified as exhibiting the DG.18 Subsequently, various block chemistries including polystyrene-b-poly(2-vinylpyridine),19,20 polyethylene-b-polyethyleneethylenes,21,22 and many others23,24 also identified the DG in diblock copolymers. Building upon the design rules to generate DG structures from linear diblock copolymers, self-consistent field theory (SCFT) was utilized to predict the equilibrium morphologies within the χN−f phase diagram, where χ, N, and f are the Flory–Huggins interaction parameter, degree of polymerization, and the volume fraction of one block component, respectively. The SCFT revealed that the DG structure is thermodynamically stable within a relatively narrow volume fraction range of ∼3.7 vol% at intermediate segregation strength of χN = 20 and ∼1.5 vol% at

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strong segregation of $\chi N = 100$. Note that the DG was originally found to be unstable at high $\chi N$ values due to the increased sharpness at the interface and packing frustration, while experiments and recent SCFT calculations find that the DG exists at high $\chi N$. The narrow composition range of DG in conventional linear diblock copolymers is due to the triply periodic minimal surface and chain packing within the DG. Specifically, polymer chains should minimize the interfacial area and uniformly fill the domains defined for each block species. Linear diblock copolymers that satisfy both conditions are often limited to only a few volume fraction range according to the self-consistent field theory (SCFT) calculation (Figure 2a). Experimentally, PS-b-PI diblock copolymers self-assemble into the DG structures at $f_{\text{PI}} = 0.36-0.39$ and $0.65-0.68$ (Figure 2b). The DG structures have been widely observed in more complicated polymer systems than simple diblock copolymers, such as AB/A diblock copolymer/homopolymer blends,AB/A’/B’ binary diblock copolymer blends, tapered block copolymers, and ABA triblock copolymers. In addition, ABC triblock copolymers exhibit a core-shell-type DG ($Ia\bar{3}d$ symmetry) and alternating gyroid ($I4_132$ symmetry) structures depending on the block species. DG structures exist at a wider volume fraction range in diblock/homopolymer, due to the additional chain ends and increased chain length dispersity that alleviates packing frustration. For example, polystyrene-b-polysisoprene diblock copolymers (10.1 kg/mol PS and 17.3 kg/mol PI) with homopolystyrene (760 g/mol hPS) or homopolyisoprene (650 g/mol hPI) blends demonstrated that the volume fraction window for the DG structure increases up to

Figure 1. Cubic unit cell of a double gyroid morphology with $Ia\bar{3}d$ symmetry, showing the two interpenetrating networks of the minority component (blue) with a volume fraction of 0.30.

Figure 2. (a) Phase diagram for AB diblock copolymers calculated from self-consistent field theory. Reproduced from ref 31. Copyright 2012 American Chemical Society. (b) Experimental phase diagram for PS-b-PI diblock copolymers. Reproduced from ref 17. Copyright 1995 American Chemical Society. (c) Experimental phase diagram of binary blends containing a diblock copolymer (PS-b-PI) and a homopolymer (hEP or hPS). The styrene weight fraction of the pure PS-b-PI diblock copolymer is 37% (arrow). Below and above this point are blends with hPI and hPS, respectively. The shaded region indicates the range of DG morphologies. Reproduced from ref 2. Copyright 1994 American Chemical Society. (d) Phase diagram of PS-polypeptoid diblock copolymers with stiff (top) and flexible (bottom) interfacial linkages. Reproduced from ref 49. Copyright 2021 American Chemical Society.
Figure 3. (a) Precise ion-containing multiblock copolymers synthesized by polycondensation of a sulfosuccinate diester and a diol, and then ion exchange. Reproduced from refs 7, 62, 66, and 67. Copyright 2020, 2021, 2021, and 2019, respectively, American Chemical Society. (b) DSC traces of PES23Li from the second heating and cooling at a ramp rate of 1 °C/min. (c) X-ray scattering of PES23Li at 150 °C identifies the double gyroid morphology (Ia3d symmetry) with a lattice parameter of 7.6 nm. Panels (b) and (c) are reproduced from ref 7. Copyright 2020 American Chemical Society.

~12 vol % after a long time of annealing (Figure 2c). Alternatively, introducing a more flexible linkage between blocks of diblock copolymers expands the accessible DG window (Figure 2d). A comprehensive phase map of PI-b-PS-b-PEO identified core-shell DG structures with PS encapsulating PEO to form both gyroid structures when the PI matrix volume fraction was 0.45–0.50. Note that these block copolymers have been synthesized using predominantly anionic polymerization methods to control the composition range required to produce the DG with a molecular weight dispersity index of 1.01–1.11. While the polydispersity index can significantly impact the self-assembly of block copolymers, dissipative particle dynamics simulations showed that increasing polydispersity index of ABA linear block copolymers results in the destabilization of ordered DG structure into a disordered bicontinuous morphology. Experimental studies on ABA triblock copolymers identified the disordered bicontinuous morphologies in a composition window of ~10 vol %. In contrast, the layered morphologies of ABC triblock copolymers can transform into core-shell DG structures upon increasing the polydispersity of one block species. In summary, the DG morphology has been found in a wide variety of systems containing AB, ABA, and ABC block copolymers, and the composition window within which the DG morphology resides is narrowest for diblock copolymers and broadens for more complex systems.

■ DOUBLE GYROID MORPHOLOGIES IN ALTERNATING MULTIBLOCK COPOLYMERS

Linear \((AB)_n\) alternating multiblock copolymers have the potential for designing ordered nanostructures as they can self-assemble into various nanostructures. For example, SCFT calculations predict that the equilibrium morphologies of \((AB)_n\) multiblock copolymers are identical to the conventional diblock copolymer morphologies with layers, DG, cylinders, and spheres. The number of repeating units \((n)\) impacts various characteristics of \((AB)_n\) alternating multiblock copolymers. First, the microphase separation of multiblocks requires ~50% higher segregation strength \((\chi N_{crit} \approx 15.1\) at \(n > 20)\) than the diblock copolymers \((\chi N_{crit} \approx 10.5\) at \(n = 1)\). Also, the domain spacings of ordered structures of \((AB)_n\) alternating multiblock copolymers decrease with increasing \(n\), particularly at \(n < 10\). Therefore, theory predicts that \((AB)_n\) multiblock copolymers at sufficiently high segregation strength will produce ordered structures, as well as the desired DG structures. Nevertheless, experimental studies showing ordered structures in linear \((AB)_n\) multiblock copolymers are far fewer as compared to studies of AB diblock copolymers, presumably due to the (1) synthetic challenges to produce alternating and monodisperse blocks and (2) insufficient block segregation strength upon increasing the number of repeating blocks. Producing \((AB)_n\) alternating multiblock copolymers using anionic polymerization requires \(2n\) polymerization steps and the polydispersity of each block length impedes the ordering of microphase separated structures. In linear \((PS-b-PI)_n\) multiblock copolymers, an increase of \(n\) resulted in the decrease of the grain size of the layers, i.e., less ordering with increasing \(n\). For these reasons relative to diblock copolymers, accessing ordered morphologies including the DG in linear \((AB)_n\) multiblock copolymers has been quite limited.

Recent studies of precise ion-containing copolymers highlight the phase behavior and formation of DG structures in alternating multiblock architectures. Figure 3a presents the step-growth synthesis of polyester sulfonate multiblock copolymers (PES\(xM\)) using a sulfosuccinate diester with a counterion \((M)\) and an alkyl diol of a fixed length with \(x\) carbons. These PES\(xM\) polymers are linear \((AB)_n\) multiblock copolymers with strictly alternating polar ionic and nonpolar blocks. The polydispersity index for the length of AB repeating subunit \((N)\) is exactly 1.00 because the polar and nonpolar block lengths are fixed by the
monomers. Note that we define \( N \) as the number of backbone atoms in the AB repeat unit, \( N = x + 6 \). In these \((AB)_{n}\) multiblock copolymers, the number of AB repeating units \( (n) \) becomes trivial with increasing \( n \) as the chain-end effects become negligible. In PES23Li, the hydrocarbon blocks crystallize below the melting temperature \( T_{m} \) of \( \sim 123 \, ^{\circ}C \), and the short polar blocks self-assemble into a layered \((LAY)\) morphology as indicated by the differential scanning calorimetry (DSC) traces (Figure 3b). Upon heating above the \( T_{m} \) X-ray scattering with peaks at \( \sqrt{6}, \sqrt{8}, \sqrt{14}, \sqrt{16}, \sqrt{20}, \sqrt{22}, \sqrt{24}, \) and \( \sqrt{26} \) indicate that PES23Li \( (n = 11) \) forms a well-defined DG morphology at \( 150 \, ^{\circ}C \) (Figure 3C). These peak locations unambiguously indicate the DG structure of the \( 1a3d \) space group with a cubic lattice parameter of 7.6 nm. This DG further transitions upon heating into the hexagonally packed cylinder \((HEX)\) morphology with an order-to-order transition \((OOT)\) temperature \( T_{OOT} \) of \( \sim 176 \, ^{\circ}C \). Upon being cooled at \( 1 \, ^{\circ}C/\min \), the phase transitions are reversible at \( T_{OOT} \sim 168 \, ^{\circ}C \) and the DG to LAY crystallization transition \( T_{c} \) at \( \sim 90 \, ^{\circ}C \) (Figure 3b).

The phase transitions found in PES23Li are altered by the choice of counterion. Figure 4 illustrates the ionic aggregate and hydrocarbon chain structures of PES23M as a function of temperature and cation species \( (M = Li^{+}, Na^{+}, Cs^{+}, \) and \( NBu^{+}) \). PES23NBu\(_{4} \) is an intermediate product that includes bulky quaternary ammonium cations prior to the cation exchange with Li, Na, or Cs. For all PES23M polymers, the hydrocarbon blocks form hexagonally packed crystals below the \( T_{m} \). For PES23NBu\(_{4} \) with a bulky quaternary ammonium cation and weak electrostatic interaction, the melting transition is relatively low, \( T_{m} \sim 32 \, ^{\circ}C \), and the polymer transitions directly from layered to disordered ionic aggregates upon heating. In contrast, PESxM polymers with metal cations show melting transition temperatures higher than \( 100 \, ^{\circ}C \) and produce DG structures above the \( T_{m} \). The GYR-HEX order-to-order transition temperatures \( T_{OOT} \) as measured by DSC increase with the increase of cation size \( (Li < Na < Cs) \). PES23Li and PES23Na show GYR→HEX transitions upon heating, while the HEX morphology is inaccessible in PES23Cs below \( 210 \, ^{\circ}C \). When polar ionic diblocks strongly interact via Coulombic cohesion, OOT phase boundaries shift to lower values of \( \chi N \). Since \( \chi \sim 1/T \), this implies that the \( T_{OOT} \) increases with increased Coulombic interaction between ionically charged blocks. For PES23M, the GYR to HEX \( T_{OOT} \) increases from Li to Na to Cs, indicating stronger electrostatic cohesion with increasing cation size.

### EFFECT OF VOLUME FRACTION ON THE PHASE BEHAVIOR OF PESxM

The volume fraction of the polar block in these \((AB)_{n}\) alternating multiblock copolymers is readily controlled by the selection of the alkyl chain length of \( x \) carbons. Figure 5 shows the temperature-dependent phase diagram of PESxNa \( (x = 48–10) \) as a function of polar volume fraction \( (f_{p} = 0.16–0.45) \) and highlights the effect of hydrocarbon chain lengths on the phase behavior.166,167 In all polymers, layered ionic aggregates coexist with a crystalline hydrocarbon block, and the \( T_{m} \) increases with alkyl block length: PES10Na at \( T_{m} = 91.7 \, ^{\circ}C \) and PES48Na at \( T_{m} = 140 \, ^{\circ}C \). The increase of \( T_{m} \) with \( x \) indicates that longer hydrocarbon blocks crystallize into large crystals with fewer defects. Upon heating above \( T_{m} \) DG morphologies are accessible at an unexpectedly wide range of volume fractions of at least \( 14 \, \text{vol}\% \) \((0.27 < f_{p} < 0.41)\) for PES23Na, PES18Na, and PES12Na (Figure 5a). This result demonstrates greater accessibility to the DG in \((AB)_{n}\) multiblock copolymers. These DG morphologies transition into HEX morphologies upon further heating. In contrast, LAY morphologies of PES48Na and PES10Na directly transition into the HEX morphology above the \( T_{m} \). For DG-forming PESxNa polymers \((x = 23, 18, 12)\), HEX→DG transitions are reversible and rapid (a few minutes) upon cooling, whereas the DG morphologies slowly crystallize into layered ionic aggregates upon further cooling below \( T_{m} \) (Figure 5b). The slow crystallization kinetics are associated with the restricted chain mobility imposed by the strong ionic interactions. In PES12Na with a short 12-carbon block, DG morphologies persist during the \textit{in situ} X-ray scattering experiments with an average cooling rate of \( \sim 0.3 \, ^{\circ}C/\text{min} \) and then gradually crystallize at room temperature into a layered ionic aggregate morphology in about a week. Therefore, we observe kinetically trapped DG morphologies with amorphous hydrocarbon blocks upon cooling below \( T_{m} \).

This kinetic competition between the self-assembly of the polar blocks and the crystallization of the hydrocarbon blocks is also evident by comparing PES48Na and PES10Na upon cooling below \( T_{m} \). For PES48Na, the 48-carbon alkyl block crystallizes to form layered ionic aggregates during the \textit{in situ} X-ray experiment, while the 10-carbon alkyl block of PES10Na

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**Figure 4.** Morphology summary of PES23M with varying counterion species \( (M = Li^{+}, Na^{+}, Cs^{+}, \) and \( NBu^{+}) \) as a function of temperature. Hydrocarbon chain structure (symbol) and ionic aggregate morphologies (shading) were determined from \textit{in situ} X-ray scattering upon heating. The table summarizes the melting temperature \( T_{m} \) and order-to-order transition temperature \( T_{OOT} \) as determined by differential scanning calorimetry traces. The cation size is the effective radius of ions coordinated with six oxygens. Reproduced from ref 7. Copyright 2020 American Chemical Society.
The physical properties of PESxNa, such as the non-Gaussian chain statistics of the short alternating blocks and conformational asymmetry of blocks, may further skew the phase diagram. While PESxM systems have charges covalently tethered to the backbone, extensive research on diblock copolymers (e.g., PS-b-PEO) with added salt have found that the salt content significantly impacts the equilibrium morphologies. 71–76 Specifically, a substantial shift of the phase boundaries of salt-doped block copolymers is often explained by factors including ion solvation energy and ion–ion correlations. Clearly, the thermodynamics of equilibrium morphologies in ion-containing block copolymer systems are not yet fully understood. To the best of our knowledge, theoretical studies are lacking to describe the wide range of DG structures and the phase behavior of these ion-containing (AB)$_n$ multiblock copolymers.

Figure 6 shows the isothermal lattice parameters ($a$) of the three ordered morphologies observed in PESxNa polymers along with their scaling relationships to the number of backbone atoms ($N = n + 6$). The lattice parameters are small (<10 nm) and exceptionally well-controlled by selecting the length of the aliphatic diol monomers. The effect of $n$ on the lattice parameter appears to be negligible for the PESxNa polymers, because the value of $n$ spans from $\sim10$ for PES23Na to $\sim37$ for PES12Na. The SCFT for (AB)$_n$ multiblock copolymers predicts the domain spacings of layers when $n = 10$ is only slightly larger (≤2%) than that of $n = 37$. The scaling relationship of $a \sim N^{0.92}$ for LAY is attributed to the crystallization of hydrocarbon, and therefore the distance between the layered ionic aggregates is proportional to the number of carbons in the hydrocarbon block. The relationships for DG ($a \sim N^{0.85}$) and HEX ($a \sim N^{0.52}$) morphologies with amorphous hydrocarbon chains coincide with the scaling relationship of strongly and weakly segregated neutral diblock copolymers, respectively. By comparison, experimental results for diblock copolymers observed exponents of $\sim0.8–1.0$. The $a$–$N$ relationships and morphology map of PESxNa reveal that the nanoscale ordered structures and their length scales in PESxNa multiblock copolymers can be finely tuned within the length scale of 2–8 nm.
Figure 7 shows the morphology diagram of PESxLi ($x = 12, 18, 23$) as a function of temperature upon heating. Both PES23Li and PES18Li form DG above the $T_m$ similar to PES23Na and PES18Na, while PES12Li exhibits disordered morphologies above $T_m$. Consistent with the discussion about the cation effect on the $T_{DGT}$ for PES23M (Figure 4), the $T_{DGT}$ of GYR–HEX transition for PES18Li is 9.2 °C lower than that of PES18Na as determined from DSC. Notably, PES12Li transitions into a disordered morphology at $T_m$ whereas PES12Na transitions into the ordered morphologies of DG and HEX above $T_m$. While cation effects shown in Figure 4 were limited to fixed $x = 23$, the more comprehensive effect of $f_p$ presented in Figure 5a and Figure 7 highlights the cation effects on the phase boundaries in both $f_p$ and $1/T$.

### DETERMINATION OF ULTRAHIGH $\chi$ AND $\chi N - f$

**PHASE DIAGRAM IN PESxLi**

Further development of (AB)$_n$ multiblock copolymer thermodynamics requires knowledge of block interactions. The Flory–Huggins interaction parameter ($\chi$) is obtained from the disordered morphology of PES12Li using the random phase approximation for (AB)$_n$ multiblock copolymers (Figure 8a). The quality of the fit of the random phase approximation theory to the experimental scattering data is high even though the alternating block lengths in PES12Li are short. In Figure 8b, the temperature dependence of $\chi = 77.4/T + 2.95$ (in Kelvin) with a reference volume of 0.118 nm$^3$ indicates a high enthalpic contribution from ion–ion interactions and a high entropic contribution from short block lengths. The value of $\chi$ at 25 °C is 3.21, identifying the PESxLi ion-containing multiblock copolymers as ultrahigh-$\chi$ and low-$N$ block copolymers. This is consistent with the formation of ordered nanostructures with sub-3 nm domain spacings. For comparison, the value of $\chi$ at 25 °C for polystyrene-b-poly(methyl methacrylate) is 0.043. Although the $\chi$ value was inaccessible for PESxNa, the presence of ordered morphologies at $T > T_m$ for PES12Na and PES10Na suggests $\chi$ values even higher than PESxLi. The ultrahigh $\chi$ and ordered morphologies with sub-3 nm domain spacings suggest a new direction for template-assisted nanofabrication technologies (AB)$_n$ multiblock copolymers.

Figure 9 compares the experimentally observed phase transitions of PESxLi polymers and the phase boundaries determined from self-consistent field theory (SCFT) for (AB)$_n$ multiblock copolymers. The experimentally observed morphologies of PESxLi polymers are offset from the SCFT predictions: GYR–HEX transitions for PES23Li and PES18Li and LAY–DIS transition for PES12Li are shifted to a lower $f_p$ relative to the theoretical boundaries. The discrepancies between the phase behavior of PESxLi and the SCFT phase boundaries can be attributed to the short block lengths and the electrostatic interactions between the polar blocks. Theoretically, mean-field approximations including the self-consistent field theory (SCFT) used to describe the uncharged polymer systems are insufficient for predicting phase behavior in electrostatically charged systems because of the field fluctuations. More recently, a polarizable field-theoretic model explored the electrostatically stabilized microphase separation in a blend of oppositely charged polymer systems, which showed a drastic shift of phase boundaries. A hybrid self-consistent field theory and liquid state integral equation theory (SCFT-LS) demonstrates that the ionically
charged blocks of diblock copolymers significantly skew the phase boundaries toward a lower volume fraction of charged blocks. The extent of boundary shift increases as a function of charge fraction and Coulombic interaction strengths. Similarly, dissipative particle dynamics (DPD) simulations show this shift of phase boundaries with an increasing charge fraction. Further development of these theoretical approaches incorporating polarized field effects are needed to improve the understanding of phase behavior in precise ion-containing (AB)\textsubscript{n} multiblock copolymers.

### DOUBLE GYROID MORPHOLOGIES IN THIN FILMS OF PES18Li

To provide a deeper understanding of morphology characteristics of precise ion-containing multiblock copolymers in confined geometries, PES\textsubscript{x}Li thin films were prepared and examined with in situ grazing-incidence X-ray scattering (Figure 10). At 40 °C, distinct in-plane scattering peaks at \( q_z \sim 1.5 \text{ Å}^{-1} \) indicate that the crystalline hydrocarbon blocks pack with an interchain distance of 0.4 nm and the chain axis vertically aligned relative to the substrate (Figure 10a). The out-of-plane scattering peaks along the \( q_z \)-axis indicate well-defined ionic layers parallel to the substrate, where the layer spacing is 3.1 nm (Figure 10d). Upon heating above \( T_m \), the layered morphology spontaneously transitions into highly oriented DG with an epitaxial transition from the (100) plane of LAY to the (211) plane of DG parallel to the substrate (Figure 10e). The domain spacing calculated from the primary (211) peak of the DG structure is \( \sim 2.5 \text{ nm} \). Further heating to 180 °C allows an epitaxial transition of DG into HEX morphology, where the cylinders are parallel to the substrate (Figure 10f). The transitions between the DG and HEX are reversible, and the DG to LAY transition is kinetically trapped due to slow crystallization consistent with bulk behavior. The film thickness in Figure 10 is 44 nm and corresponds to \( \sim 7 \text{ cubic lattices of the DG structure, } \sim 7a_{DG} \). The DG morphology also forms in 26 nm films (\( \sim a_{DG} \)), although a thinner film of 17 nm (\( \sim 2.5a_{DG} \)) leads to coexisting DG and HEX morphologies due to greater confinement. This thin-film study demonstrates the exceptional fidelity of precise ion-containing (AB)\textsubscript{n} multiblock copolymers for designing DG structures and other ordered morphologies in thin films, which could develop into a versatile platform of ion transport membranes, filtration membranes, and templates for pattern transfer.

### CRITERIA FOR DESIGNING DOUBLE GYROID IN (AB)\textsubscript{n} MULTIBLOCK COPOLYMERS

So far, this perspective has highlighted the DG morphology in one class of (AB)\textsubscript{n} multiblock copolymers composed of alternating polyester sulfonate with a metal counterion and hydrocarbon blocks. After inspecting results from other classes of (AB)\textsubscript{n} polymers, we will propose criteria for achieving the DG morphology. First, the removal of ionic groups from PES23M results in the absence of ordered morphologies above \( T_m \), and we attribute this to a significant reduction in \( \chi \). The domain spacing calculated from the primary (211) peak of the DG structure is \( \sim 2.5 \text{ nm} \). Further heating to 180 °C allows an epitaxial transition of DG into HEX morphology, where the cylinders are parallel to the substrate (Figure 10f). The transitions between the DG and HEX are reversible, and the DG to LAY transition is kinetically trapped due to slow crystallization consistent with bulk behavior. The film thickness in Figure 10 is 44 nm and corresponds to \( \sim 7 \text{ cubic lattices of the DG structure, } \sim 7a_{DG} \). The DG morphology also forms in 26 nm films (\( \sim a_{DG} \)), although a thinner film of 17 nm (\( \sim 2.5a_{DG} \)) leads to coexisting DG and HEX morphologies due to greater confinement. This thin-film study demonstrates the exceptional fidelity of precise ion-containing (AB)\textsubscript{n} multiblock copolymers for designing DG structures and other ordered morphologies in thin films, which could develop into a versatile platform of ion transport membranes, filtration membranes, and templates for pattern transfer.
Figure 11 shows a poly(ethylene oxide) (PEO)-based multiblock copolymer synthesized by the A_2 + B_2 melt polycondensation of a hydroxy-terminated oligo(ethylene glycol) monomer and a 5-sulfoisophthalate salt. In these ionomers, PEO lengths of \( m \sim 9 \) and 13 with Li^+ , Na^+ , and Cs^+ exhibit disordered ionic aggregate morphologies with an amorphous PEO backbone. When the length of PEO is long enough at \( m \sim 25 \) and 75, the PEO blocks crystallize and the ionic aggregates form layers. Upon heating above the \( T_m \), these PEO-based multiblock copolymers do not form ordered morphologies such as DG or HEX. The absence of ordered morphologies in these PEO-based ionomers can be attributed to the absence of precision in block lengths and the lack of chain flexibility in the polar block. First, the PEO block lengths are polydisperse as compared to the precise hydrocarbon lengths of the PES_xM polymers. It is well-established that randomly distributed spacer lengths give rise to poorly defined ionic aggregate morphologies compared to precise spacer lengths. Second, the polar blocks with rigid phenyl ring in the backbone are less flexible and impede the chain packing necessary to form DG or HEX morphologies. In addition, the segregation strength of these PEO-based ionomers will be weaker than polyethylene-based PES_xM multiblock copolymers, pushing them toward the disordered state. The lack of precision in block length, a rigid polar block, and a smaller \( \chi \) combine to impede the self-assembly of these PEO-based sodium sulfonated polyesters into ordered nanostructures.

Figure 12a shows the precise acid-containing polymers synthesized via acyclic diene metathesis (ADMET) polymerization of diene monomers containing a symmetric pendant functionality. All-atom molecular dynamics simulations at \( T > T_m \) show that the precise polymer containing COO^-Li^+ on every 21st carbon (p21AA-Li, \( f_p = 0.15 \)) exhibits disordered, stringy, and percolated ionic aggregates (Figure 12b). Similar stringy ionic aggregates are formed above \( T_m \) when the periodicity between the ionic groups is shorter (p9AA-Li and p15AA-Li), indicating that the nonperiodic packing of ionic aggregates is preferred relative to ordered morphologies in these ADMET polymers with pendant acid or ionic groups. One exception to this generalization is the precise ADMET polymer containing geminal phosphonic acids on exactly every 21st carbon (p21gPA, \( f_p = 0.25 \)) that exhibits low symmetry diffraction peaks assigned to spherical aggregates on a face-centered cubic (fcc) lattice symmetry (Figure 12c). In comparison with the PES_xM polymers that contain ester linkages and short polar blocks, the ADMET polymers have all-carbon polymer backbones and the pendant groups on just one carbon. These features of the acid- and ion-containing ADMET polymers provide fewer chain conformations to accommodate microphase separation of the functional groups and prevent self-assembly into ordered morphologies, including the DG morphology. Given the chemical similarities between these...
ADMET polymers and the ionic lipids that originally displayed the DG morphology, the absence of the DG in these polymers is unexpected. The physicochemical properties of the ionic groups, chain flexibility, and block incompatibility of the PESxM polymers provide insight into designing DG-forming multiblock copolymers. Below we propose four criteria for (AB)$_n$ multiblock copolymers to produce the DG and other ordered morphologies at sub-10 nm length scales.

- The A and B blocks are highly incompatible, for example, pairing ionic and nonionic blocks.
- Both the A and B blocks are comprised of flexible chains to accommodate the surface curvature of the double gyroid structure and other ordered morphologies.
- The lengths of the A and B blocks are precise so that the polydispersity index of the AB unit is exactly 1.00.
- The volume fraction of the minority block is 0.27–0.41 to form double gyroid structures. Lower and higher volume fractions can form hexagonally packed cylinders or layers, respectively.

**CONCLUSION**

This Perspective summarizes the recent developments of precise ion-containing multiblock copolymers that self-assemble into double gyroid structures at an unusually wide composition range of >14 vol %. Step-growth polymerization methods could be developed to synthesize an even wider variety of precise ion-containing multiblock copolymers, and greatly expand the investigation of self-assembly in (AB)$_n$ copolymers. Current self-consistent field theories fail to capture the phase behavior of these precise ion-containing polymers, and this is primarily attributed to the presence of charges that induce electrostatic interactions and significant density fluctuations. A combination of experimental, theoretical, and simulation studies are required to fully establish a foundation for designing ordered nanostructures including DG with precise ion-containing multiblock copolymers.

Numerous applications can be envisioned for new (AB)$_n$ multiblock copolymer synthesized by step-growth polymerization. First, precise multiblock copolymers could be used for nanopatterning templates to achieve sub-3 nm domain spacings by having ultrahigh $\chi$ and low $N$. Key next steps include exploring multiblock copolymer kinetics, directed self-assembly of ultrahigh $\chi$ polymers, and sequential infiltration synthesis within sub-3 nm domains to improve etching contrast. In addition, porous materials templated from the precise multiblock copolymers could be explored for filtration membranes. Another set of potential applications involves selective ion transport, including single-ion conductors having covalently bonded ionic functionalities to the polymer backbone as in the PESxM polymers. The ordered morphologies in thin films of these ion-containing polymers create well-aligned ion transport channels, which can be further optimized for high ionic conductivity by selecting optimal block chemistries from step-growth polymerization and by the selective solvation with additives to swell the polar domains and dissociate the ion pairs. Precise ion-containing multiblock copolymers have great potential to expand understanding of block copolymer physics and address a variety of technological challenges.

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Notes

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