



Review

Self-Assembly of Block Copolymers to Prepare Advanced Materials with Hierarchical Functional Nanostructures

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Abstract

Block copolymers with diverse compositions and topologies can self-assemble into multi-hierarchical structures, yielding materials with a wide range of functional properties. By adjusting external stimuli such as temperature, solvent polarity, mechanical force, and light exposure, these polymers form various nanostructures—including nanocrystals, micelles, and vesicles in solution; spherical, cylindrical, and lamellar microphases in bulk; and even “fractal” morphologies at interfaces. These hierarchical materials exhibit tailored functionality based on molecular design, enabling broad applications in nanomedicine, electronic devices, optical elements, and catalytic systems. In this review, we first summarize synthetic strategies for block copolymers with varying compositions and architectures. We then discuss their self-assembly behaviors and resulting nanoscale morphologies in bulk, solution, and interfacial environments. Several representative examples of assembled block copolymer systems and their practical applications are highlighted. Finally, we offer perspectives on future developments in the fabrication and application of block copolymer-based nanomaterials. This review provides an overview of strategies and examples for constructing precision nanostructures via block copolymer self-assembly, aiming to inspire further advances in nanomanufacturing technologies.



Academic Editor: Candido Fabrizio Pirri

Received: 26 September 2025

Revised: 3 November 2025

Accepted: 17 November 2025

Published: 20 November 2025

Citation: Liu, Y.; Liu, Y.; Feng, F.; Wang, W. Self-Assembly of Block Copolymers to Prepare Advanced Materials with Hierarchical Functional Nanostructures. *Nanomanufacturing* **2025**, *5*, 18. <https://doi.org/10.3390/nanomanufacturing5040018>

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Keywords: block copolymer; self-assembly; nanostructure; nanomaterials

1. Introduction

Advanced functional materials often exhibit diverse microstructural characteristics. Hierarchical architectures spanning multiple length scales are ubiquitous in biological tissues, conferring them with different dynamic functionalities via microstructural reorganization. Animal tissues present multi-hierarchical fibrous nanostructures, and different fibrous tissues coordinate with each other to promote the development of life processes. Natural biomaterials, in particular, display exceptional physical properties attributable to their coordinated multi-level hierarchical structures [1,2]. A representative example is the skeletal muscle of animals, which comprises hundreds to thousands of bundled muscle fibers. Each fiber contains myofibrils as the functional contractile units, which are in turn composed of myofilaments [3]. These myofilaments are organized into highly ordered arrays of thick filaments (primarily composed of myosin) and thin filaments (mainly consisting of actin) [4,5]. Through regulation by calcium ions, the relative sliding of myosin against actin enables muscle contraction and mechanical work. For instance, human skeletal

muscle can achieve a work density of up to 40 kJ/m^3 and an energy density of 284 W/kg [6]. Such performance remains challenging to replicate with synthetic materials. The integrated cooperation of multi-scale hierarchical microstructures endows natural materials with optimal functionality [7]. Therefore, materials constructed with multi-layered structures will enhance their multi-functional properties. However, the design of hierarchical architectures within synthetic material to concurrently achieve functional integration remains challenging [8]. Although various strategies—including functional molecular synthesis and advanced material processing—have been developed to fabricate smart materials, it remains difficult to produce multifunctional integrated materials with well-defined periodic and hierarchical microstructures [9,10].

The preparation of precise nanostructured materials primarily follows two strategic approaches: top-down and bottom-up. The top-down method involves sculpting bulk materials into nanostructures through techniques such as lithography. This approach demands high-precision equipment and is generally constrained to micro- or nanoscale fabrication. For instance, state-of-the-art semiconductor chips are produced at the 2-nanometer node using advanced photolithography, yet further scaling down necessitates even higher equipment accuracy and incurs significantly greater costs. In contrast, the bottom-up strategy assembles macroscopic materials from smaller building units, as seen in additive manufacturing. Such techniques enable the integration of diverse functional components into multifunctional composites, thereby facilitating the construction of hierarchically structured materials [11,12]. For example, by alternately stacking stimuli-responsive units that react to temperature or light, it is possible to create hierarchical architectures capable of programmable bending, deformation, or actuation under corresponding stimuli [7,13]. Nevertheless, these artificially engineered intelligent materials typically require layer-by-layer deposition, which is not only time consuming and labor intensive but also limited in achieving precise nanoscale structural control.

Block copolymers incorporate distinct block molecules with varied functionalities and compositions into a single macromolecular chain. Driven by thermodynamic incompatibility between different blocks, these polymers spontaneously self-assemble into well-defined microphase-separated structures [14]. In either melt or solution states—where polymers exhibit viscoelastic behavior—similar blocks tend to aggregate, whereas dissimilar blocks segregate to form periodic nanoscale domains [15]. By precisely controlling the composition and topology of block copolymers, it is therefore possible to efficiently fabricate advanced functional materials with precise nanostructures (Figure 1).

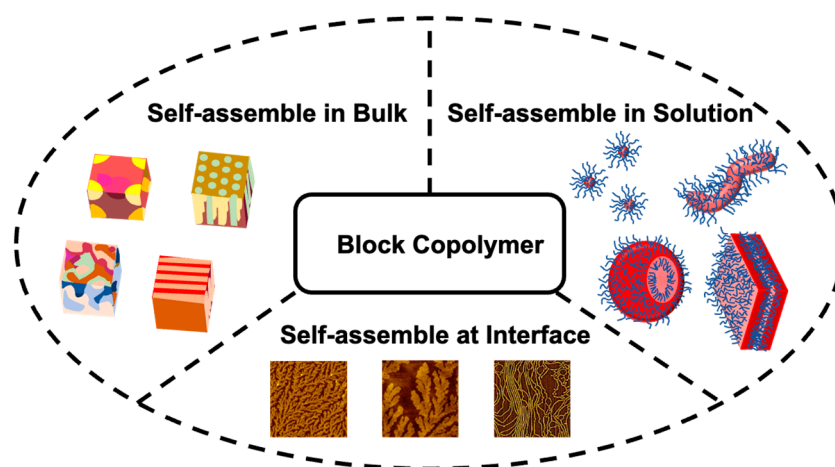


Figure 1. Scheme shows the self-assembled structures of block copolymers and their potential applications.

In this review, we summarize the most common self-assembled structures of block copolymers in bulks, solutions, and interfaces. First, the molecular topological structures, functional molecular units, and synthesis methods of block copolymers are introduced. Then, the self-assembled structures and applications of block copolymers in the bulk, solution, and interface are listed. Finally, conclusion and perspective about the assembly and application of block copolymers are presented. This review will provide references for the synthesis of block copolymers and the preparation of advanced materials with hierarchical functional nanostructures that can mimic natural materials. For further related information on block copolymer assembly and applications, readers are referred to existing literature [16–18].

2. Topologies and Synthetic Methods of Block Copolymers

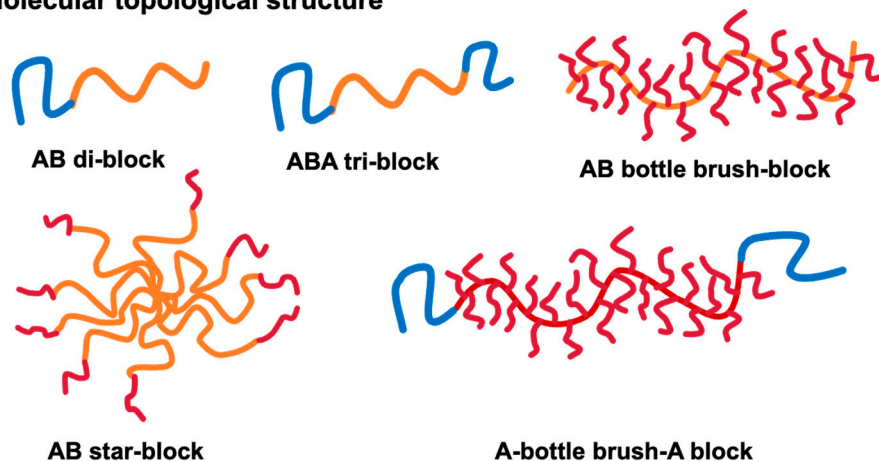
The molecular topology and composition of block copolymers are pivotal in dictating the nanoscale architecture of materials, which in turn governs their macroscopic physical properties. Advances in synthetic methodologies, including living polymerization and click chemistry, have enabled the precise design of block copolymers with diverse molecular compositions and topological configurations. Through these chemical strategies, functionally distinct small-molecule motifs can be efficiently incorporated into macromolecular systems.

2.1. Topologies and Compositions of Block Copolymers

The common topological architectures of block copolymers include diblock, triblock, bottlebrush, star, and triblock bottlebrush shapes (Figure 2). Among these, diblock and triblock copolymers represent the most fundamental molecular topologies. Bottlebrush polymers consist of a long backbone serving as the main chain, with shorter polymer grafts as side chains. The length and grafting density of these side chains are key factors influencing the phase behavior and material properties of the block copolymers. Star-shaped polymers (or dendrimers) are constructed from multiple identical arms radiating from a central core, often surrounded by an outer shell formed by another polymeric segment [19,20]. The liner-bottle brush-liner (A-bottlebrush-A) topology, analogous to a triblock architecture, can be conceptualized as attaching additional block segments at both ends of a bottlebrush polymer. The central bottlebrush segment contributes to extremely low chain entanglement, imparting high flexibility to the material. For instance, Sheiko et al. have utilized this molecular design to engineer various elastic materials exhibiting tissue-like mechanical properties [21].

The complexity of macromolecular topology can be further improved by varying the chemical composition of the block molecules. The incorporation of functionalized molecular units (Figure 2) endows the expansion of accessible topological architectures. For instance, Stephen Z. D. Cheng and coworkers have utilized polyhedral oligomeric silsesquioxane (POSS), fullerene (C₆₀), proteins, and polyoxometalates (POMs) to construct so-called “giant molecules” [22,23]. These functional units, characterized by well-defined sizes and shapes, are often referred to as “molecular nanoparticles” or “nanoatoms” [24]. The giant molecules assembled from such nanoatoms exhibit diverse topological classes, including giant surfactants (nanoatoms conjugated with polymer chains), giant amphiphiles (two chemically distinct nanoatoms), and giant polyhedra (multiple nanoatoms arranged into polyhedral frameworks) [24]. Furthermore, Dong et al. achieved a continuous covalent tandem architecture by linking POSS nanoatoms into a main-chain polymer structure [25]. Similarly, Liu et al. demonstrated the conversion of a main-chain configuration into a side-chain topology using POSS-based building blocks [26].

Molecular topological structure



Functionalized molecular unit

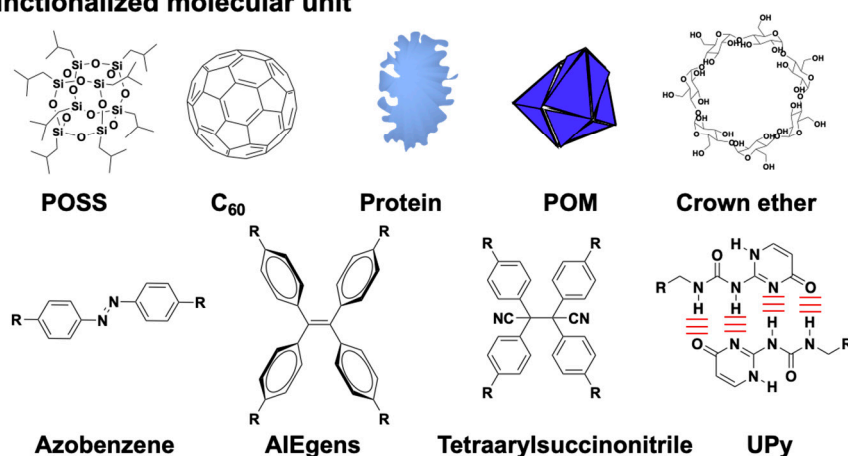


Figure 2. The common topology and composition of block copolymers.

In addition, functional units such as crown ethers [27], azobenzene [28], aggregation-induced emission luminogens (AIEgens) [29,30], tetraarylsuccinonitrile, and ureidopyrimidinone (UPy) can be incorporated to construct intelligent responsive materials (Figure 2) [31–34]. Crown ethers exhibit amphiphilic characteristics, featuring a hydrophobic interior and a hydrophilic exterior [35]. By embedding hydrophobic molecular motifs within the crown ether ring, host–guest interactions can be established [36]. This structural motif has been utilized in the design of supramolecular materials and to enhance elastic and energy dissipation properties [37,38]. Azobenzene is a photo-responsive liquid crystal unit that undergoes cis–trans isomerization upon irradiation at specific wavelengths [39]. Incorporation of azobenzene into polymer main chains or side chains, combined with appropriate alignment treatments, enables the fabrication of light-driven smart materials [40]. Aggregation-induced emission (AIE), a concept introduced by Professor Benzhong Tang [41] has led to the development of numerous AIE-active materials, which have found broad applications in drug delivery, bioimaging, and tumor therapy [30]. Tetraarylsuccinonitrile functions as a mechanoresponsive unit that undergoes cleavage under mechanical stress to generate red radical species, making it suitable for stress-sensing applications via mechanochromism [42]. UPy forms stable dimers through quadruple hydrogen bonds, exhibiting dynamic reversibility—dissociating at temperatures above 90 °C and reassociating upon cooling below this threshold [31]. Owing to this reversible behavior, UPy has been widely employed to engineer materials with superior mechanical properties. Moreover, a wide variety of functional molecular building blocks with diverse properties are avail-

able. These functional units play a crucial role in the molecular design of multifunctional block polymers.

2.2. Common Chemical Synthesis Methods for Block Copolymers

The fabrication of precisely nanostructured assemblies with periodic regularity requires block copolymers possessing well-defined and uniform molecular architectures. Advanced synthetic methodologies are essential for designing such polymers. Living polymerization techniques—including ionic polymerization, coordination polymerization [43,44], living free-radical polymerization such as reversible addition–fragmentation chain-transfer (RAFT) and atom transfer radical polymerization (ATRP) [28,45], and ring-opening polymerization—enable the preparation of block polymers with narrow molecular weight distributions (typically $\bar{D} < 1.1$) [46,47]. Among these, ionic and coordination polymerizations offer precise monomer conversion efficiencies and extremely low polymer dispersion. These methods allow for the precise design of block polymers with desired numbers of repeating units in the polymer chain. However, ionic and coordination polymerizations generally require anhydrous and oxygen-free conditions. Their stringent reaction requirements limit operational flexibility in the lab. In contrast, living radical polymerizations such as RAFT and ATRP, along with ring-opening polymerization, are widely employed in laboratory settings due to their ease of handling and milder reaction conditions.

RAFT polymerization employs thioesters as active initiators to drive the growth of polymer chains. The kinetics and behavior of the polymerization are strongly influenced by the molecular composition and structure of the thioester used. Therefore, to optimize the block polymers synthesized via RAFT, a series of RAFT agents with varying structures were designed based on the characteristics of the monomers. RAFT polymerization is relatively straightforward to carry out; with simple deoxygenation, it enables the polymerization of a wide range of monomers. However, the dispersity of the resulting block polymers is generally higher (typically $1.1 < \bar{D} < 1.2$) compared to other living polymerization techniques [24].

ATRP represents another widely used method in living radical polymerization, presenting several advantages with RAFT. Polymers synthesized by ATRP exhibit lower molecular weight dispersity ($\bar{D} < 1.1$) than those from RAFT. Nonetheless, ATRP is not suitable for polymerizing charged monomers, such as acrylic acid or 2-(dimethylamino)ethyl acrylate, and its polymerization activity can be adversely affected by the presence of charged matter [45].

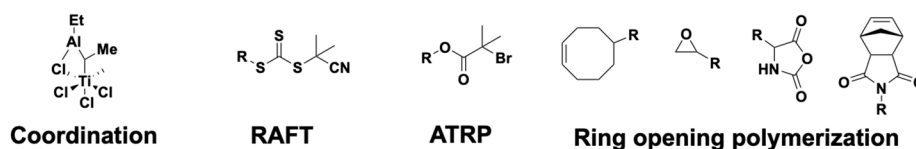
Ring-opening polymerization (ROP) enables the polymerization of small cyclic molecules like ethylene oxide, caprolactam, lactide, and octamethylcyclotetrasiloxane. ROP offers benefits such as mild reaction conditions, low dispersity, absence of small-molecule byproducts, and a broad range of polymerizable monomers. However, ROP monomers are often structurally complex, leading to higher costs, stringent purification requirements, and a dependence on specific initiators or catalysts [46].

Living polymerization is a chain polymerization reaction. Monomers gradually grow along active sites to form molecular chains. The topology of block polymers obtained by living polymerization is highly dependent on the molecular structure of the initiator. Therefore, living polymerization cannot polymerize modular molecules.

However, the synthesis of block copolymers with complex architectures, particularly those incorporating functional units illustrated in Figure 2, demands advanced synthetic methodologies. Click chemistry has emerged as a powerful and versatile tool for constructing block copolymers with precise topological structures (Figure 3) [48–50]. Originally centered on azide–alkyne cycloadditions, the click chemistry toolbox has since expanded

to include thiol-based reactions, oxime ligation, and Diels–Alder cycloadditions [49,50]. These highly efficient reactions overcome limitations associated with steric hindrance in macromolecular systems, thereby addressing challenges such as low reactivity and insufficient conversion [43,51]. As a result, click chemistry is now extensively employed in the synthesis of functional polymers and drug design.

Living polymerization



Click chemistry

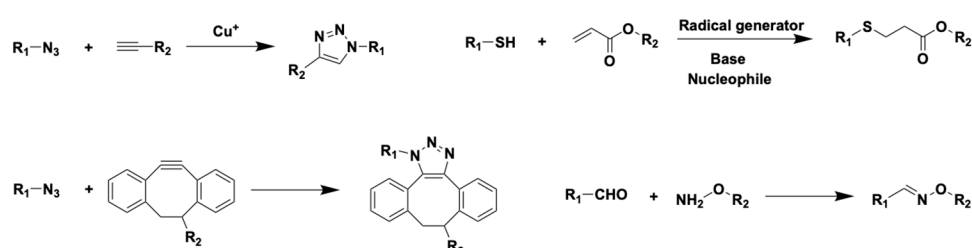


Figure 3. Methods for synthesizing virous topologies of block copolymers.

3. Block Copolymer Self-Assembly in Melt Bulk

The self-assembly of block copolymers requires sufficient molecular chain mobility to facilitate rapid attainment of thermodynamic equilibrium [52]. Driven by the inherent incompatibility between different blocks, the chains undergo microphase separation and spontaneously organize into ordered structures, as described by self-consistent mean-field theory [53,54]. This section introduces the common microphase-separated morphologies of block copolymers and provides representative examples of their use in constructing advanced materials.

3.1. Theory of Self-Assembly of Block Polymer Molecules

The self-assembly of diblock copolymers is well described by self-consistent mean-field theory, as illustrated in the phase diagram in Figure 4A. In the diagram, χ represents the Flory–Huggins parameter, N denotes the total degree of polymerization, and f is the volume fraction of one block [18,53,55]. Microphase separation occurs when the product χN exceeds a critical value of approximately 10.5 ($\chi N > 10.5$) [55]. Therefore, increasing the degree of polymerization or enhancing the polarity difference between blocks promotes microphase separation. Furthermore, varying the volume fraction f of the blocks enables the formation of different ordered morphologies [47,56]. As f increases gradually, the structure transitions from spherical micelles to cylindrical phases, followed by bicontinuous gyroid structures, and finally to lamellar phases [18].

Furthermore, more complex phase structures can be achieved through the blending of different block copolymers [57]. For instance, when A-B and A-C type diblock copolymers are mixed, the thermodynamically incompatible A, B, and C blocks drive microphase separation. However, the chemically identical A blocks from different polymers can co-assemble into shared domains, leading to the formation of intricate morphologies that are unattainable with single-component systems (Figure 4B) [58,59]. By varying the blend ratio,

a rich diversity of microphase-separated structures can be readily accessed (Figure 4B) [60]. It should be noted that achieving a homogeneous, periodic nanostructure through simple physical blending can be challenging. Ineffective mixing often results in macroscopic phase separation rather than the desired nanoscale ordering.

In contrast to well-defined spherical phases, the Frank–Kasper phases represent a family of complex spherical packing structures, including the σ , A15, C14, and C15 types (Figure 4C) [61–63]. The formation of the Frank–Kasper phase requires distinctive size and shape asymmetry between the assembled molecular units, while this asymmetry needs to incorporate a delicate design of the topological structure of the block copolymers [64]. Such hierarchical assemblies can be obtained by carefully designing the molecular topology or selecting blends of different block molecules.

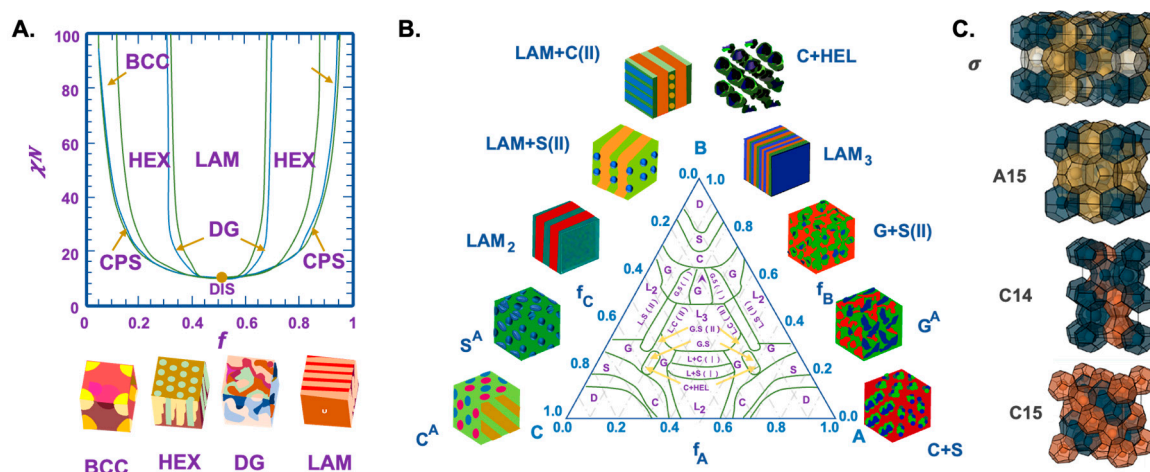


Figure 4. Phase structure and phase diagram of block polymers. (A) Self-consistent mean field theory phase diagram of diblock copolymers. Body-centered cubic sphere phase (BCC), hexagonally packed cylinder phase (HEX), bicontinuous double gyroid phase (gyroid), lamellar phase (LAM). Reproduced with permission from Ref. [18]; Copyright (2020) Elsevier. (B) Phase diagram of blend assembly of different block polymers. Reproduced with permission from Ref. [18]; Copyright (2020) Elsevier. (C) Several familiar Frank–Kasper phases. Reproduced with permission from Ref. [63]; Copyright (2021) American Chemical Society.

3.2. Examples Show the Assembly Structures of Block Copolymers with Different Topologies

With the advancement of organic synthesis techniques, block polymers with diverse topological structures and compositions have been synthesized, and their self-assembly behaviors have been extensively investigated [65,66]. The microphase-separated morphologies of diblock and triblock copolymers can be readily predicted and show strong agreement with self-consistent mean-field theory. By tailoring the volume fractions of the blocks, structures such as spheres, cylinders, and lamellae can be systematically obtained. In contrast, achieving bicontinuous phase structures requires careful consideration of the block polymer composition and architecture, owing to their narrow phase separation windows (Figure 4A) [59].

However, predicting complex microphase-separated structures remains challenging, as it is often difficult to establish clear correlations between the topology and composition of block polymers and the resulting morphologies. Zhong et al. obtained a series of hierarchically structured nanocomposites by changing the composition of bottle brush polymers (Figure 5A) [67]. By adding inorganic fillers of different particle sizes, the composite materials exhibited unprecedented nanostructures. However, rational design of molecular architecture can enable the formation of sophisticated phases such as Frank–

Kasper phases. For instance, Dong et al. synthesized cyclic block copolymers with tailored structures and successfully obtained Frank–Kasper and quasicrystalline phases via self-assembly (Figure 5B) [68]. Unlike linear diblock or triblock copolymers, cyclic polymers exhibit enhanced conformational flexibility and altered steric constraints due to the absence of chain ends. This increased conformational asymmetry helps stabilize nonclassical spherical phases and leads to an overall expansion of the domain size.

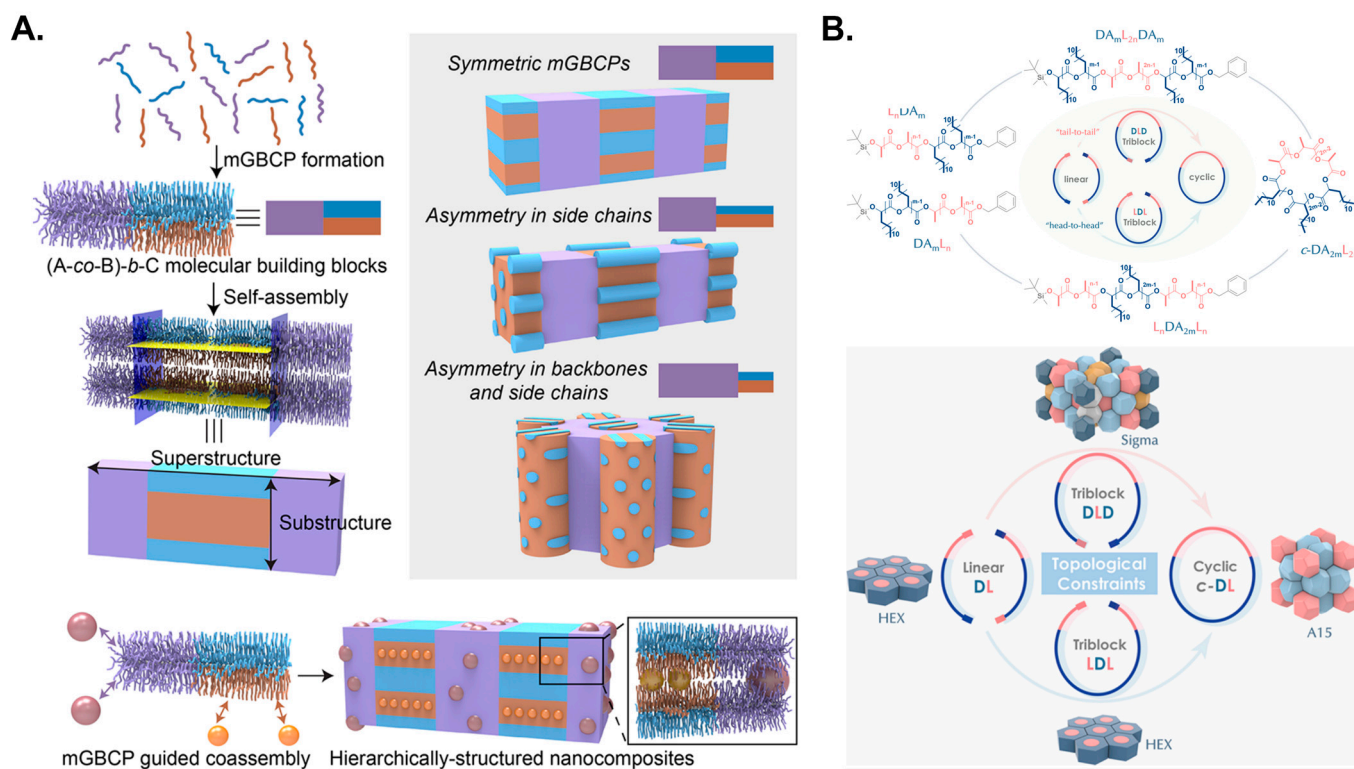


Figure 5. Microphase structures of block polymer assemblies. **(A)** Complex phases assembled by block copolymer blending. Reproduced with permission from Ref. [67]; Copyright (2024) American Chemical Society. **(B)** Frank–Kasper phases assembled by changing the molecular topologies. Reproduced with permission from Ref. [68]; Copyright (2025) American Chemical Society.

3.3. Examples Show the Applications of Materials with Different Microphase Structure

Block copolymers incorporating functionally distinct segments can microphase-separate into well-defined domains, enabling the integration of multiple properties within a single material [68]. For instance, polymer complexes based on hydrogen bonding or electrostatic interactions (e.g., polyelectrolyte complexes) exhibit high sensitivity to environmental stimuli such as pH, ionic strength, and temperature [69,70]. By rationally designing a triblock polymer architecture, a lamellar morphology can be achieved through combined hydrogen-bonding complexation and microphase separation of two constituent blocks (Figure 6A) [71]. Changes in pH dynamically disrupt and reform the interblock hydrogen bonds, leading to reversible expansion and contraction of the layered structure. This actuation mechanism closely mimics the contractile motion of sarcomeres in skeletal muscle (Figure 6A) [71].

In addition, spider silk exhibits exceptional strength and modulus, which are primarily attributed to its inherent hierarchical microstructure [72]. Within silk fibers, hydrophobic β -sheet nanocrystals form a three-dimensional network by cross-linking the surrounding flexible molecular chains, significantly contributing to the material's mechanical robustness [73]. Inspired by this structural motif, researchers have successfully constructed a range of high-performance materials. For instance, by precisely regulating the hydrophobic

domains in a microphase-separated system, the strength and elasticity of an elastomer were effectively tailored (Figure 6B) [74]. This elastomer further demonstrated adaptive self-regulation in response to temperature and humidity variations, showing a distinct mechanical flexibility transition at 25 °C and 55% relative humidity (Figure 6B) [74]. Such smart materials hold promising potential for developing environmentally adaptive textiles.

Animal bones are layered structures composed of alternating layers of hard hydroxyapatite and flexible proteins. Protein is mainly collagen, which can increase the toughness and elasticity of bones. During training, the collagen molecules will orientate along the tension direction, which would further increase the stiffness and strength of the bone (Figure 6D). Based on this, You et al. used covalently cross-linked polyurethane as the mesophase domain and reversible oxime-urethane bonds as dynamic molecular units to strengthen the material in a “dynamic molecular lock” manner to mimic bone (Figure 6D) [75]. After orientation training, the strength and toughness of the material are significantly improved (Figure 6D) [75].

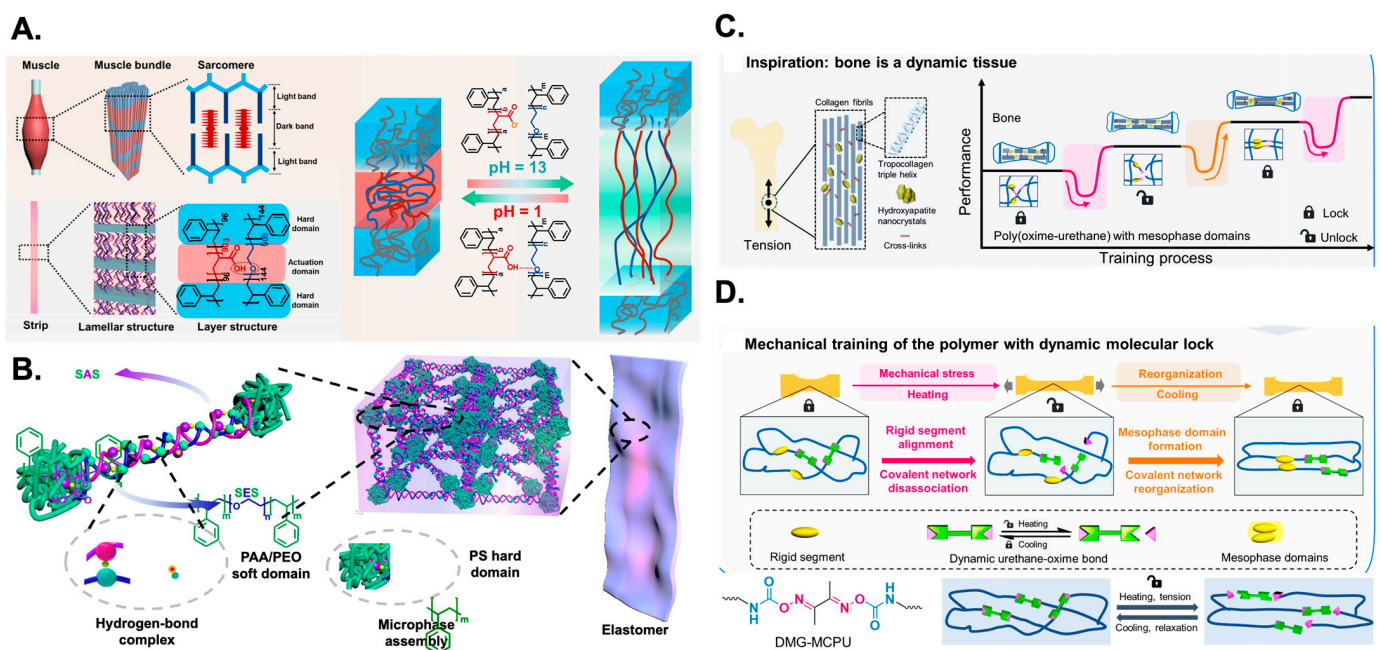


Figure 6. Multi-hierarchical structure of biomimetic materials based on block polymer microphase separation. (A) Microphase separation and hydrogen-bonding complex of block polymers to construct the actuator that mimics the sarcomere movement of skeletal muscle. Reproduced with permission from Ref. [71]; Copyright (2022) Wiley. (B) Microphase separation and hydrophobic interactions optimize the mechanical elastic properties of elastomers. Reproduced with permission from Ref. [74]; Copyright (2023) American Chemical Society. (C) Scheme shows the bone training process. Reproduced with permission from Ref. [75]; Copyright (2024) American Association for the Advancement of Science. (D) The mesophase domain training of poly(oxime-urethane) to mimic bone structure. Reproduced with permission from Ref. [75]; Copyright (2024) American Association for the Advancement of Science.

The high level of matching between materials and tissues, especially the mechanical properties, is one of the key elements to the biomedical application of artificial materials. The mechanical properties of tissues have weak strength and modulus at low strains (<50%), while the strength and modulus increase rapidly at high strains (>100%) to avoid the risk of tissue tearing [76]. However, it is difficult for artificial materials to match the unique mechanical properties of tissues. The high degree of entanglement of polymer chains makes it difficult to achieve extremely low modulus and strength at low elongation [77,78].

Polymer elastomer materials usually have a yield strength before which the modulus of the material is usually higher than several MPa [79]. Sheiko et al. applied liner-bottle brush-liner triblock-shaped block copolymer to construct elastomers with tissue-like mechanical properties (Figure 7A) [80]. Bottlebrush polymers can reduce self-entanglement of molecular chains, when combined with polymers with low glass transition temperatures, low-modulus and low-strain strength materials will be produced [76]. Furthermore, a second block with a high glass transition temperature, capable of microphase separation, is introduced at both ends of the bottlebrush, forming a physically cross-linked three-dimensional network structure. This limits the transitional slip of the bottlebrush molecules under large deformation changes, thereby improving their strength and modulus [81]. Therefore, by this ingenious molecular topology design, simply changing the length of the bottlebrush molecule's side chain can obtain flexible materials that match the mechanical properties of different tissues [21].

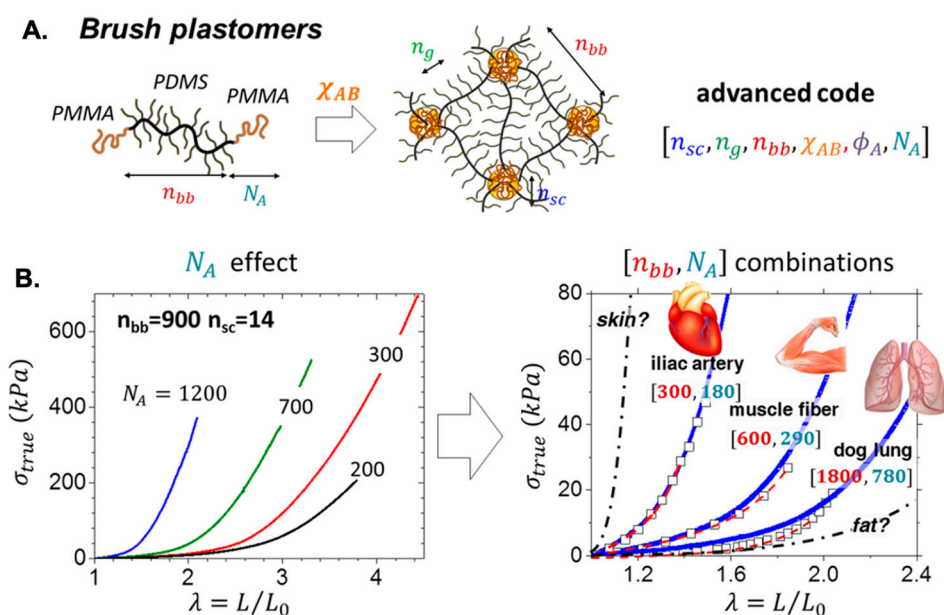


Figure 7. A-bottle brush-A structure of block copolymer for mimicking tissue mechanical behavior. (A) Molecular topology of block copolymer. Reproduced with permission from Ref. [80]; Copyright (2019) American Chemical Society. (B) Relationship between molecular composition changes and mechanical behavior. Reproduced with permission from Ref. [80]; Copyright (2019) American Chemical Society.

4. Block Copolymer Self-Assembly in Solution

Compared to bulk self-assembly, solution self-assembly provides molecules with more freedom of movement, allowing them to quickly reach a thermodynamically stable state. In addition, solvent molecules affect the dissolution behavior of polymers. Therefore, the interaction between solvents and polymers is the main driving force for the self-assembly of block molecules.

4.1. Theory of Block Copolymer Solution Assembly

The amphiphilic nature of segmented polymers is the key factor governing their assembly in solution [82]. The hydrophobic effect serves as the primary driving force for the molecular self-assembly of block polymers [83]. Typically, amphiphilic block polymers can form various nanostructures in solution, such as spherical micelles, worm-like/cylindrical nanofibers, polymersomes (vesicles), and bilayer sheets, as illustrated in Figure 8 [84,85]. The morphology of the assembled block copolymer can be predicted based on the packing

parameter $p = v/al$, where v is the volume of the hydrophobic block, l is the effective length of the hydrophobic segment, and a represents the optimal interfacial area per molecule between the hydrophobic and hydrophilic blocks. Specifically, when $p < 1/3$, spherical micelles are favored; when $1/3 < p < 1/2$, cylindrical or nanofiber structures form; when $1/2 < p < 1$, vesicles (polymersomes) are obtained; and when $p = 1$, planar bilayers are observed [86,87]. Thus, by tuning the relative sizes of the hydrophobic and hydrophilic segments, a range of nanostructures with tailored morphologies can be achieved [82].

Additionally, the solvent and environmental conditions significantly influence the assembled morphologies of block copolymers. However, the effects of solvents and other environmental factors vary across different polymer systems and are often challenging to predict theoretically. Temperature plays a critical role by regulating molecular mobility, thereby affecting the assembly process and resulting nanostructures. In temperature-responsive block copolymers, variations in temperature can lead to distinct morphological transitions. For example, upon heating, a triblock copolymer initially assembled into micelles can reorganize into a hydrogel network [88]. This transformation is attributed to the melting of hydrophobic domains, which promotes chain rearrangement and entanglement. In such systems, the hydrophilic blocks act as bridge chains connecting the hydrophobic regions, ultimately forming a three-dimensional network structure. This principle has been utilized in the design of smart, temperature-responsive polymeric materials. Moreover, solvent polarity markedly influences the self-assembly behavior by altering polymer–solvent interactions. A good solvent enhances polymer solubility and chain dispersion, whereas a selective solvent may induce phase separation and precipitation. Therefore, tuning solvent properties provides an effective route to manipulate assembly morphologies. Importantly, controlling environmental conditions such as temperature and solvent composition offers a versatile strategy to access diverse nanostructures without the need for complex molecular redesign or synthesis, thereby simplifying the pathway to tailored polymeric materials.

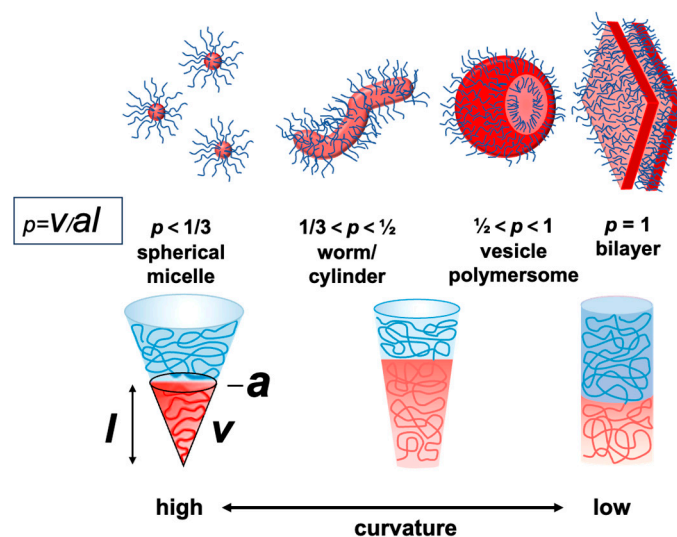


Figure 8. Theory of self-assembly of block copolymers in solution. Reproduced with permission from Ref. [87]; Copyright (2016) American Chemical Society.

4.2. Examples Demonstrate Different Morphological Assembly of Block Copolymers in Solution

Different assembly structures of block polymers in solution can be achieved by designing the hydrophobic composition of block molecules or precisely controlling the solution environment [89–92]. For example, Wang et al. used living anionic polymerization to synthesize polyisoprene-*b*-polystyrene, polyisoprene-*b*-poly (methyl methacrylate), and polyisoprene-*b*-poly (4-vinylpyridine) diblock copolymers with hydrophobic blocks of

different molecular weights [44]. The authors found that the block copolymers can self-assemble into micelle, fiber, vesicle, and even precipitate morphologies in solution by increasing the molecular weight of polystyrene block (Figure 9A) [44]. Moreover, the assembled structures show temperature-responsive properties [44]. By increasing or decreasing temperature, the block copolymer can alter between micelle, fiber, and vesicle morphologies (Figure 9A) [44].

Among the several forms of solution assembly, fibrous structure exhibits different functional properties. The fibrous structure has a certain length, which allows it to form an entangled structure like a polymer chain [92,93]. Through methods such as high-speed centrifugation, the fibrous assemblies can be collected to form a hydrogel with defined volume [93]. This nanofibrous hydrogel material has certain injectable properties [94]. This hydrogel can be loaded with different drugs and injected precisely at the local of disease. Peptide-constructed peptide-drug amphiphiles are used to fabricate such nanofibrous hydrogels (Figure 9B) [93]. This composition of hydrogel has the advantages of high drug loading and stable and precise drug release [93].

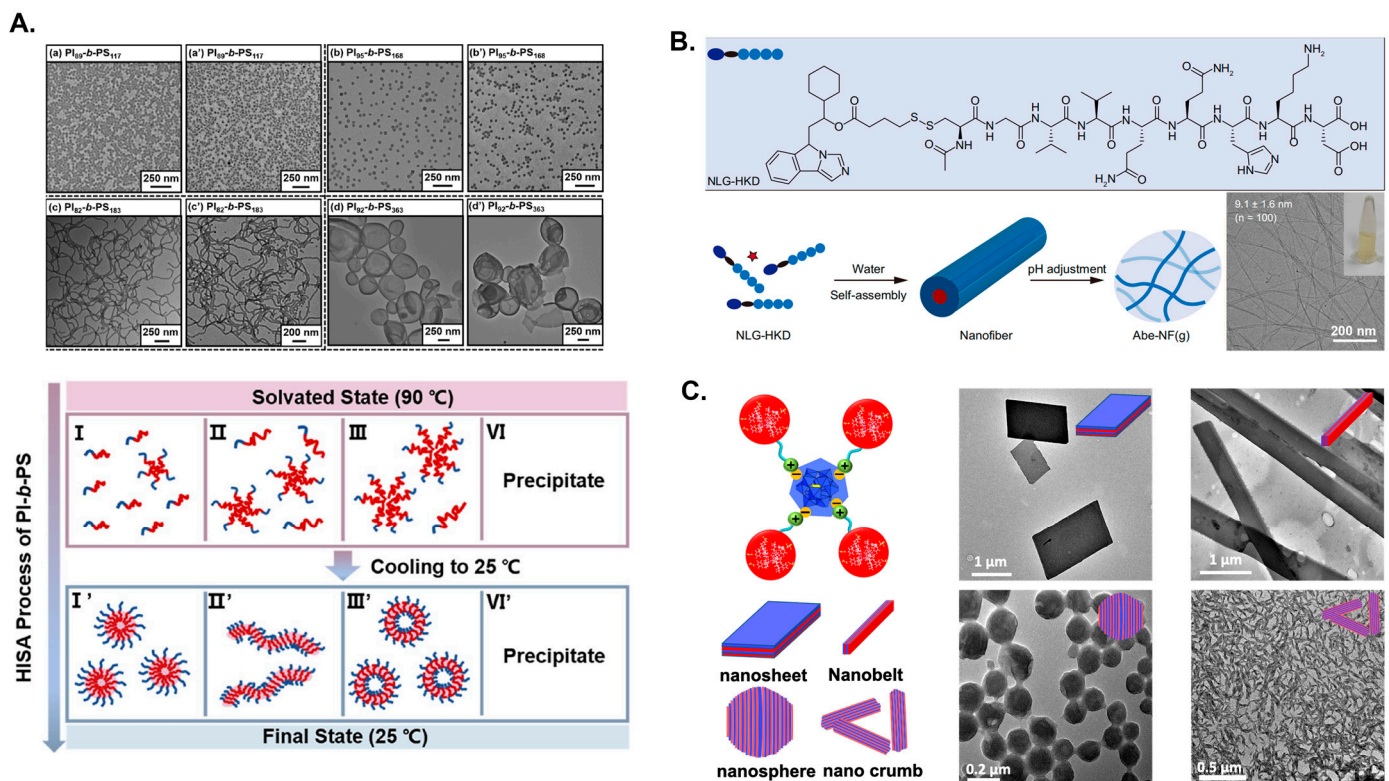


Figure 9. Examples show the various assembled structure by block copolymers. (A) Assembly structure of polymers affected by hydrophobic blocks and temperature. Reproduced with permission from Ref. [44]; Copyright (2025) American Chemical Society. (B) Nanofiber structure fabricated injectable hydrogel. Reproduced with permission from Ref. [93]; Copyright (2025) Elsevier. (C) The solvent polarity induced different assembly structure. Reproduced with permission from Ref. [95]; Copyright (2025) American Chemical Society.

The polarity of the solvent can affect the solubility of the block molecules. Wang et al. applied giant amphiphilic molecules, in which hydrophobic isobutyl BPOSS and hydrophilic POM are combined with electrostatic interactions, to prepare different assembly structures (Figure 9C) [95]. By manipulating the polarity parameters of the solution, the giant amphiphilic assembled into nanosheet, nanobelt, nanosphere, and nanocrumb structures (Figure 9C) [95]. Interestingly, the molecular composition of these assembled

structures is the same, with four hydrophobic POSS and one hydrophilic POM bound by non-covalent interaction [95]. Moreover, transmission electron microscopy results showed that the microstructures of different assemblies all exhibited a layered microstructure, with a layer of BPOSS and a layer of POM alternately assembling [95]. However, the detailed molecular assembly dynamics have not been revealed.

A distinct class of assembly systems differs from the conventional solution-phase self-assembly of block copolymers—namely, polymer complexes or coacervates formed by oppositely charged polyelectrolytes. These charged polymers can undergo liquid–liquid or liquid–solid phase separation in solution due to strong intermolecular electrostatic interactions [96]. Such polyelectrolyte complexes exhibit high sensitivity to environmental changes, including temperature, salt ion concentration, and polymer concentration [97,98]. When oppositely charged polymers are incorporated into block copolymer architectures, they can form a variety of microstructures in aqueous solution [99]. For instance, Tirrell and colleagues designed triblock copolymers containing a neutral poly(ethylene oxide) (PEO) mid-block flanked by oppositely charged polyelectrolyte segments (Figure 10A) [100–102]. The oppositely charged polyelectrolyte segments will associate to form a hydrophobic domain, while PEO is a neutral hydrophilic block segment. As a result, the associated hydrophobic domain and PEO are incompatible and will microphase separate just as block copolymer self-assemble in the bulk state. However, the self-assembly of such oppositely charged polyelectrolyte block copolymers is influenced not only by the segment volume fraction and the interaction parameters between different blocks but also by additional factors including polymer concentration, salt type and concentration, as well as temperature, all of which can significantly affect the resulting microstructures [103,104].

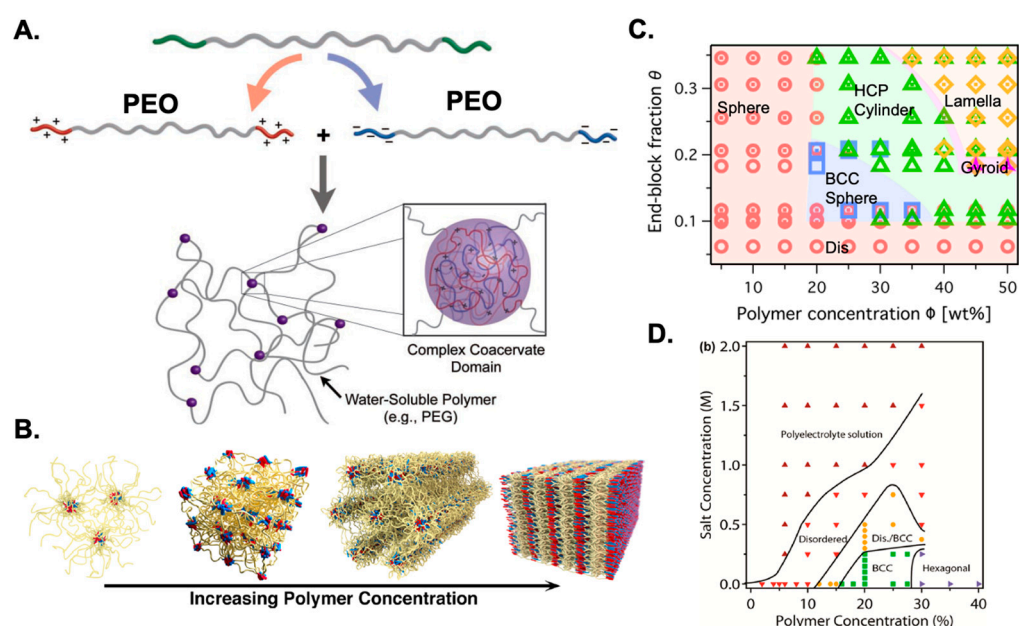


Figure 10. The assembly structure of oppositely charged triblock copolymers. (A) Molecular structure and composition of oppositely charged triblock copolymers. Reproduced with permission from Ref. [102]; Copyright (2011) Wiley. (B) Structural evolution with increasing concentration of oppositely charged triblock copolymers. Reproduced with permission from Ref. [103]; Copyright (2020) American Chemical Society. (C) Phase diagram correlating polymer concentration and block molecule volume fraction. Reproduced with permission from Ref. [103]; Copyright (2020) American Chemical Society. (D) Phase diagram correlating polymer concentration and salt concentration. Reproduced with permission from Ref. [104]; Copyright (2014) American Chemical Society.

By increasing polyelectrolyte block copolymer concentration, these charged complexes are self-assembled into micellar, spherical, cylindrical, gyroidal, and lamellar phases—morphologies typically observed in bulk block copolymer systems (Figure 10B) [103]. As in melt assembly, the resulting microstructure is influenced by the volume fraction of each block (Figure 10C) [103]. As can be seen from the phase diagram (Figure 10C), by increasing the volume fraction of charged blocks, it can transform from a disordered state (Dis) to a spherical phase (BCC Sphere), cylinder phase (HCP Cylinder), Gyroid phase, and lamella phase. Significantly, the polymer concentration is the main factor controlling the self-assembled structure.

Additionally, salt ion concentration would modulate the electrostatic interactions within the polymer complex [104]. Thus, the morphology of oppositely charged triblock copolymers can be tuned by varying the ionic strength of the solution (Figure 10D) [104]. In phase diagram, as the salt concentration increases, the ordered phase structure will gradually become disordered until it turns into a homogeneous solution (Figure 10D). High concentrations of salt ions can disassociate polyelectrolyte complexes, making them easier to dissolve.

4.3. Examples Show the Application of Block Copolymers in Solution Assembly

Block polymers can be assembled in solution to create nanomaterials with precise structures and uniform dimensions. These nanostructured materials have broad applications in drug delivery, energy, biomimetics, catalysis, and other fields [105].

Nanoparticles, ranging in size from a few nanometers to hundreds of nanometers, show the greatest advantage in drug delivery. Spherical micelles can load hydrophobic drugs, while vesicles can load both hydrophobic and hydrophilic drugs. The drug-loaded nanoparticles improve the accuracy of drug delivery and therapeutic efficacy. Moreover, the development of synthetic chemistry can design small molecules with various functions and integrate them into the main chain of block molecules, which exhibit special self-responsive properties after being assembled into nanostructures. Xu et al. designed a glutathione-responsive block copolymer and assembled it into nanoparticles for loading the photosensitizer chloride e6 to treat tumors (Figure 11A) [106]. When the nanoparticles enter the tumor cells, they respond and consume glutathione, quickly release photosensitizers and generate reactive oxygen species under light to effectively kill tumor cells (Figure 11A) [106]. The functionalized nanoparticles enhance the efficacy of drug therapy. In addition, many nanoparticles such as nanofibers, vesicles, and hydrogels with nanostructure that are sensitive to reactive oxygen species, pH, enzymes, temperature, and light have been developed for the treatment of different diseases and have achieved higher efficiency. De et al. developed a photo-responsive nanoparticle that can generate reactive oxygen species and reactive nitrogen species upon visible light irradiation (Figure 11B) [107]. The assembly structure of block polymers in solution present significance applications in the field of advanced drug delivery.

The assembly of block polymers in solution is dynamically reversible. Under the action of external forces, the aggregates and molecular units can be dynamically dissociated and reassembled. If applying this structural property to design hydrogel materials, they will exhibit specific mechanical properties. Nanofibers have a continuous assembly structure, and they can entangle and interweave with each other to form a physical cross-linked network. Therefore, by rationally designing the microstructure, materials with multi-level structures and composite functions can be obtained. Li et al. dispersed the assembled nanofibers into a monomer solution, followed by polymerization and cross-linking to obtain a mechanically strong hydrogel (Figure 11C) [108]. The dynamic assembly structure of nanofibers provides good energy dissipation for the hydrogel [108].

The precise hierarchical structure of fibrillar assemblies provides excellent ion channels. This special structure has potential applications in battery energy storage. Ortony et al. designed a block copolymer applying conductive poly(p-phenylene terephthalamide) as a hydrophobic block while using polyethylene oxide as a hydrophilic block to assemble nanofibers [109]. Due to the conductivity of poly(p-phenylene terephthalamide), electrons can be transported along the fibers, which allows this assembly to be used in the solid-state electrolyte of batteries [109]. Nanobodies assembled from block polymers undergo a series of treatments to create nanopores within the nanobody. These pores can effectively adsorb metal ions or metal complex catalysts. This structure improves the efficiency, stability, and lifespan of the catalyst, making it an excellent catalyst support. Pandey et al. grafted polymer molecules onto nano-silicon spheres as a stable skeleton and assembled them together with a complex copper ion catalyst (Figure 11D) [110], and the author investigated the catalytic efficacy of copper by changing the molecular complexation parameters [110].

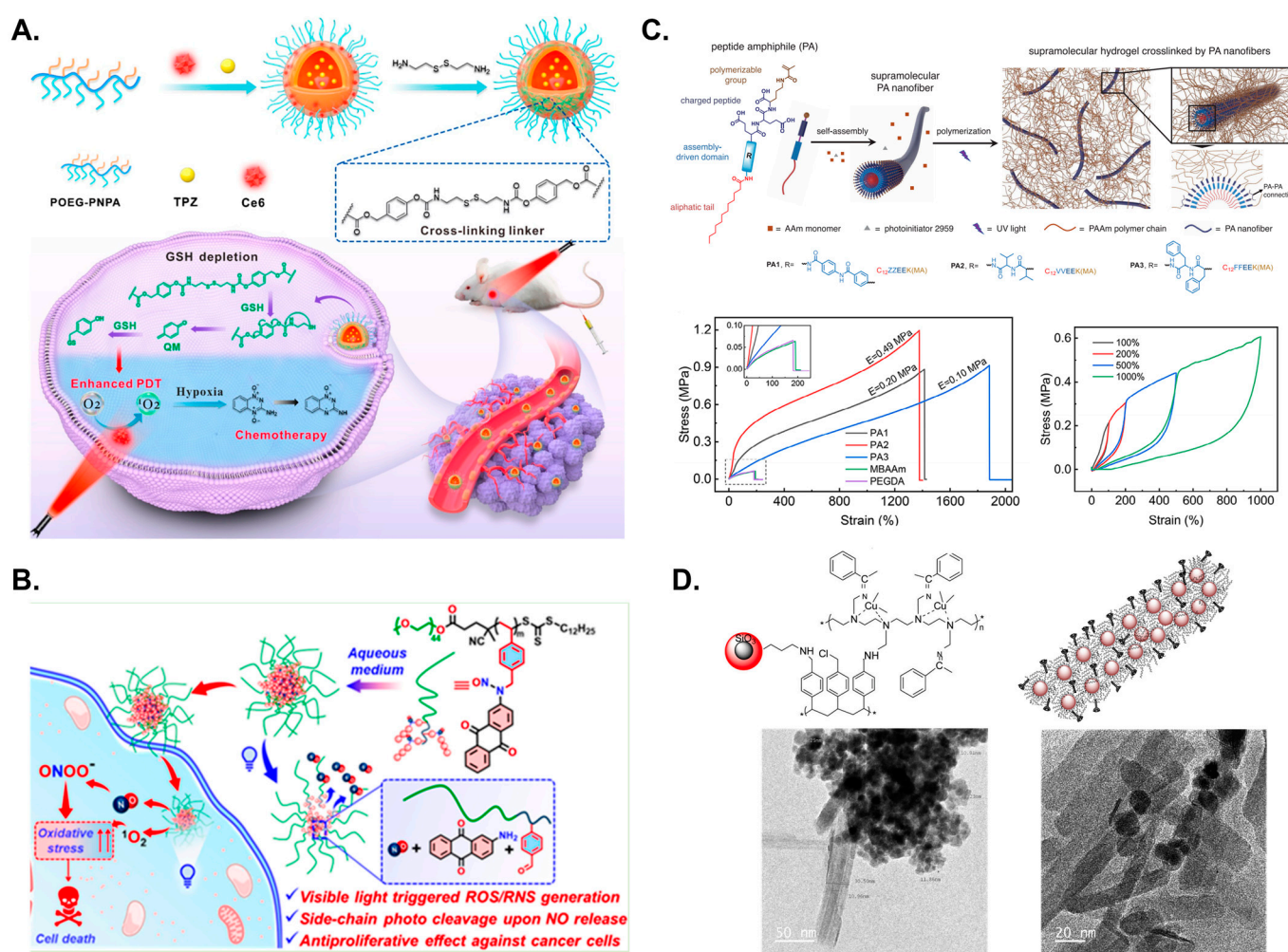


Figure 11. The applications of different assembly of block copolymer in solution. (A,B) Reproduced with permission from Refs. [106,107]; Copyright (2024) American Chemical Society. Functional nanoparticles used on drug delivery. (C) Functional nanofibers used in hydrogel. Reproduced with permission from Ref. [108]; Copyright (2025) Wiley. (D) Conductive nanofibers applied in battery energy storage. Reproduced with permission from Ref. [110]; Copyright (2021) Elsevier.

5. Block Copolymer Self-Assembly at Interface

Block copolymers can be dispersed on the surface of liquid to form a thin molecular film. The block copolymers are self-assembled within a two-dimensional confined area.

Therefore, the assembly pattern of block copolymers will be different from their assembly in the melt and solution states.

The surface tension, molecular topology, and molecular composition will affect the assembly behaviors of block polymers at the interface. When the amphiphilic block copolymer spreads on the water surface, both the hydrophobic and hydrophilic blocks will float on the surface. If the system environment remains unchanged, the hydrophilic block cannot be embedded below the water surface. However, when the surface monolayer is compressed, the intermolecular distance decreases, and the molecules squeeze each other in the two-dimensional plane, which increases the surface tension of the water [111]. At this time, the hydrophilic blocks of the block polymer will immerse themselves in the water surface. Investigation has shown that as surface molecules are compressed, the molecular layer undergoes a transformation from a gaseous phase to a liquid phase and then to a solid phase [111].

The topological structure of a molecule is another important parameter that determines its assembly at the interface. For example, when the molecules are dispersed on the water surface and compressed, the side chain polymer molecules will exhibit the “cusp” phenomenon, while the main chain giant molecules do not exhibit this phenomenon (Figure 12A) [111]. Moreover, by increasing the number of hydrophobic BPOSS, this phenomenon can be found at lower surface pressure (Figure 12A) [111]. The number of hydrophobic BPOSS also can influence the thermal stability and reversibility of monolayer film.

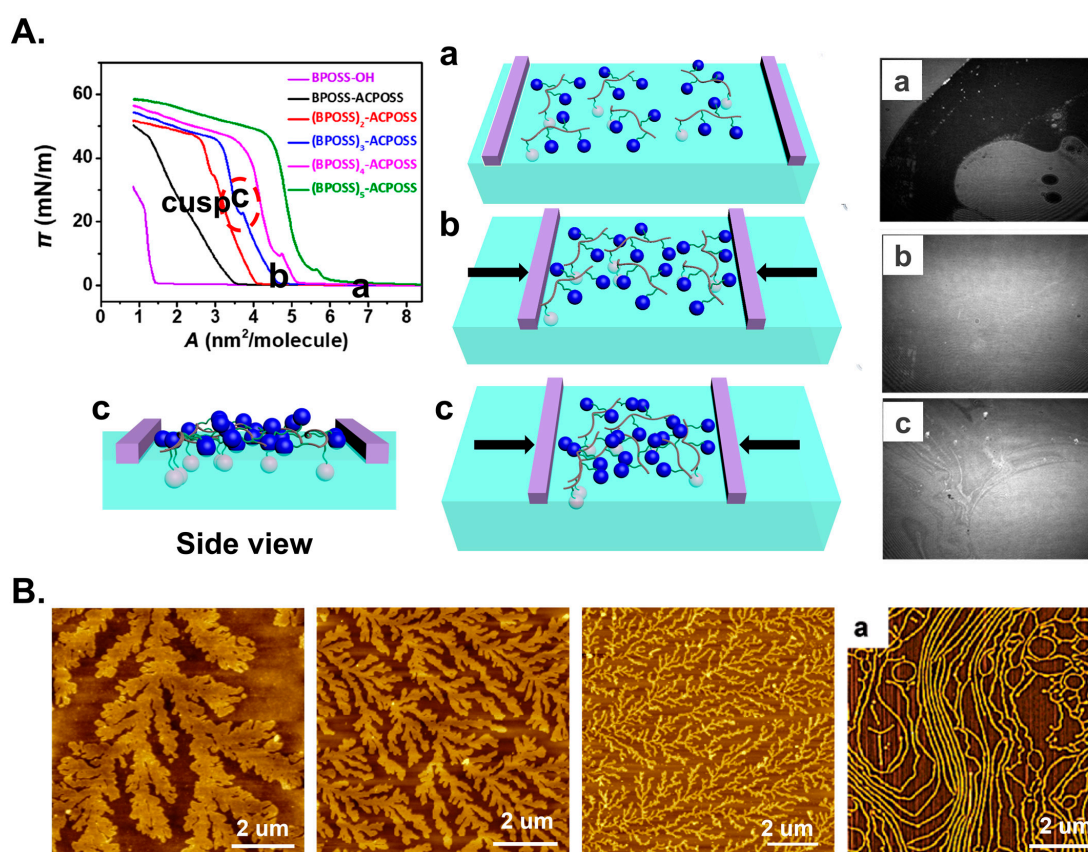


Figure 12. The assembly structures of block copolymers at surface. (A) Assembly behavior of giant molecules with different molecular topologies. Reproduced with permission from Ref. [112]; Copyright (2023) American Chemical Society. (B) Assembly behavior of giant amphiphilic with different composition. Reproduced with permission from Ref. [113]; Copyright (2006) American Chemical Society; 115, Copyright (2020) Elsevier; 116, Copyright (2021) American Chemical Society.

In addition, if a crystalline amphiphilic polymer is dispersed on the surface of water, and then the molecular layers are scooped using a silicon wafer, a seaweed-like assembly pattern emerges [112]. The seaweed's leaves can be regulated by the length of the crystalline chains and the density of the molecular layers (Figure 12B). If the crystalline amphiphilic polymer is replaced with a non-crystalline one, its assembly morphology will be presented as noodle-like (Figure 12B) [113–116]. Although block polymers can assemble into different morphological structures at interfaces, the applications of these assembled nanostructures remain to be further explored.

6. Conclusions and Perspective

Block copolymers possess the ability to self-assemble into diverse microstructures with hierarchical ordering at the nanoscale. By tailoring the topology, composition, and self-assembly conditions of the block molecules, nanostructures with periodicity, well-defined geometry, and uniform dimensions can be achieved. Such hierarchical nanoarchitectures resemble those found in natural systems, making microphase-separated block polymers become a promising platform for constructing advanced functional materials with complex structures. To date, various self-assembled structures of block copolymers have been extensively utilized in applications such as drug delivery, flexible electronics, and soft robotics. Moreover, the dynamics and thermodynamic behaviors associated with their self-assembly have been increasingly elucidated, providing a solid theoretical foundation for the rational design of materials with tailored microphase-separated morphologies. However, further exploration of the types of microphase separation structures and the correlation between molecular composition and phase structure is necessary. The diversity of microphase separation is often directly related to the structure of block molecules. But obtaining block molecules with complex molecular structures through synthetic methods is extremely challenging. Fortunately, with the development of artificial intelligence and computer technology, using machine learning to predict the self-assembled microstructure of block molecules has become an emerging research direction. For example, Weihua Li et al. has used computational methods to predict the self-assembly structures of a series of block molecules, and these structures were subsequently confirmed experimentally. However, predicting the self-assembly structure of block polymers using AI technology has significant limitations. For example, small changes in the external environment can increase the computational complexity and reduce the accuracy of structure prediction.

Simply increasing molecular topological complexity is a limited strategy for diversifying assembly structures. Firstly, synthesizing such intricate architectures of molecules demands more rigorous synthesis technology, which can hinder practical application. Furthermore, the complexity of the structure may lead to uncertainty in the assembly structure of block molecules, making it difficult to obtain a certain correlation between molecular structure and performance. Blending distinct block polymers presents a promising alternative route to achieve complex hierarchical microstructures. However, the miscibility differences between the blocks often make it challenging to establish clear composition–structure relationships. Therefore, investigating the underlying principles and potential applications of mixed block polymer assemblies represents a significant and promising research frontier. Controlling the assembly environment presents an alternative pathway for manufacturing the microstructures of block polymers. While the self-assembly behavior in bulk and in solution has been extensively investigated, the phenomena under two-dimensional nanoconfinement remain comparatively less explored. This environmental control strategy relies on processing conditions rather than intricate molecular design, thereby mitigating synthesis complexity and cost—a significant advantage for practical applications.

Therefore, by mixing block polymers with different compositions and studying their self-assembly behavior under different environments, the functional materials with multi-level structures can be constructed, avoiding the high costs caused by complex synthesis techniques. This may be an important breakthrough for realizing the industrial application of block polymers.

Furthermore, when considering issues of sustainable resource development and environmental protection, the application of block polymers has long demonstrated their advantages. For example, thermoplastic elastomers and ABS plastics have shown a strong market presence in fields such as automobiles. The physical cross-linked network formed by the microphase separation of block polymers avoids the disadvantages of difficult recycling and reuse caused by chemical cross-linking. Moreover, natural materials can also be chemically modified to achieve multi-component molecular structures, thereby constructing bio-based materials with multi-level microstructures. In conclusion, the self-assembly of block polymers would be a powerful tool for preparing materials with nanoscale microstructures.

Author Contributions: Y.L. (Yanzhen Liu) and Y.L. (Yang Liu): Drawing, Writing, and Reference; F.F.: Reviewing and Supervision; W.W.: Writing, Reviewing, Funding acquisition, and Supervision. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by [State key laboratory of advanced fiber materials (Donghua University)] grant number [KF2516], and [the research start-up fund project from the University of Health and Rehabilitation Sciences] grant number [0300901031].

Data Availability Statement: No new data were created or analyzed in this study.

Conflicts of Interest: The authors declare no conflicts of interest.

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