

Dendronized Block Copolymers

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Synonyms

Block copolymers; Dendronization; Dendritic polymers; Self-assembly

Definition

Dendronized block copolymers (DBC)s refer to the block copolymers which contain at least one dendronized block. A typical DBC can be formed by a linear polymer block together with a dendronized block. The dendronized block can be varied with different dendron generations, thus affording the copolymers with blocks differing not only in lengths but also in thickness. With bulky dendrons surrounded, the dendronized block can adopt cylindrical shape with reduced attainable backbone conformations, depending on the dendron generations. In this sense, DBCs can also be treated as rod-coil block copolymers.

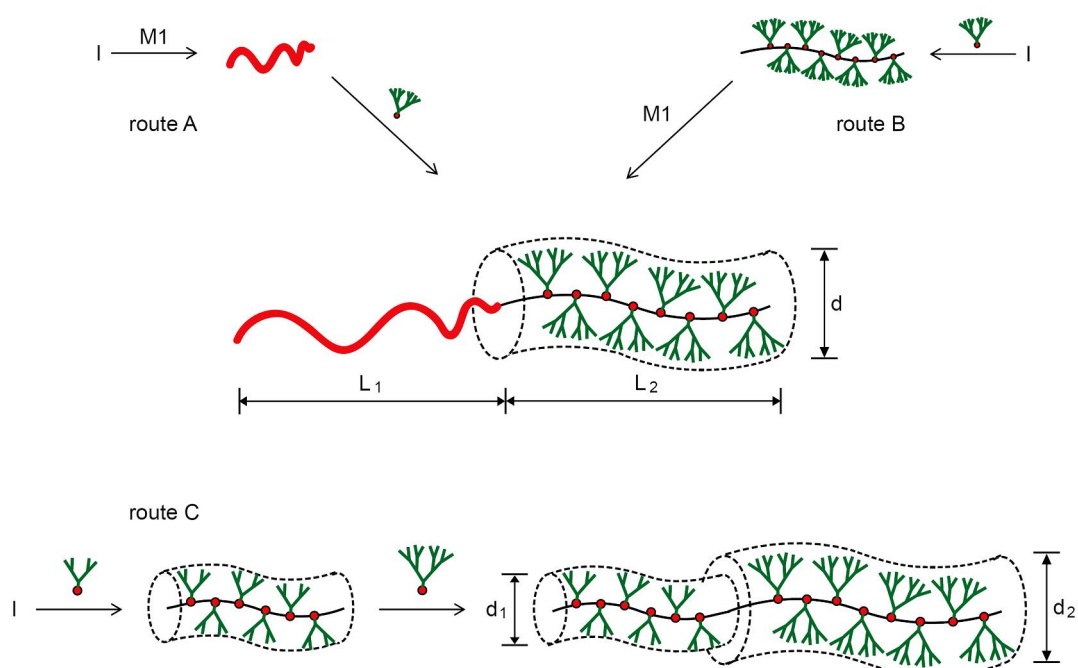
Introduction

Block copolymers can self-assemble in solution, in the bulk, at interfaces, and also in thin films to form ordered supramolecular structures at various length scales [1]. Researches along this line are impelled not only by fascinating applications of these ordered structures

in various areas [2] but also because they can be easily achieved with less synthetic efforts. Block copolymers can be divided into diblock, triblock or multiblock and star block, depending on their constitutions. Traditionally, block copolymers are formed with flexible polymer segments. The incorporation of rigid-rod polymers into the block copolymers will lead to extremely rich self-assembly behavior which differs considerably from these of conventional block copolymers, due to the interplay between microphase separation of the rod and coil components, which results in novel assembled structures. These rod-coil block copolymers [3] contain rod-like blocks with hindered their conformations, which can be aroused by rigid secondary structures, extended π -conjugation, aromatic groups along the polymer backbone, as well as bulky side polymer chains or dendritic wedges.

Dendronized block copolymers (DBC) are constituted with traditional linear polymer block(s) together with dendronized block(s), which combines the structure characteristics of both conventional block copolymers and dendronized polymers. Dendronized polymers are a well-established class of comb polymers in which each repeat unit carries a dendron [4]. This dendronization reduces the attainable backbone conformations and in the extreme case can render a random coil polymer into a cylindrically shaped, rigid molecular object with a more or less stretched backbone in the interior. They are therefore considered unique candidates for a systematic approach to engineer novel ordered assemblies. Based on the structural characteristics of dendronized polymers, DBCs are a class of highly modular macromolecules: the nature of the polymer backbone and the dendritic wedges, as well as the length of the constituent blocks can be independently

varied to afford block copolymers with precisely controlled chemical structures (Fig. 1). They are therefore interesting candidates for supramolecular constructions and for fabricating stimuli-responsive materials. Due to the specific thickness of dendronized polymers, this construction also allows the preparation of copolymers with different shapes and functions that can be directly visualized and manipulated by atomic force microscopy (AFM).



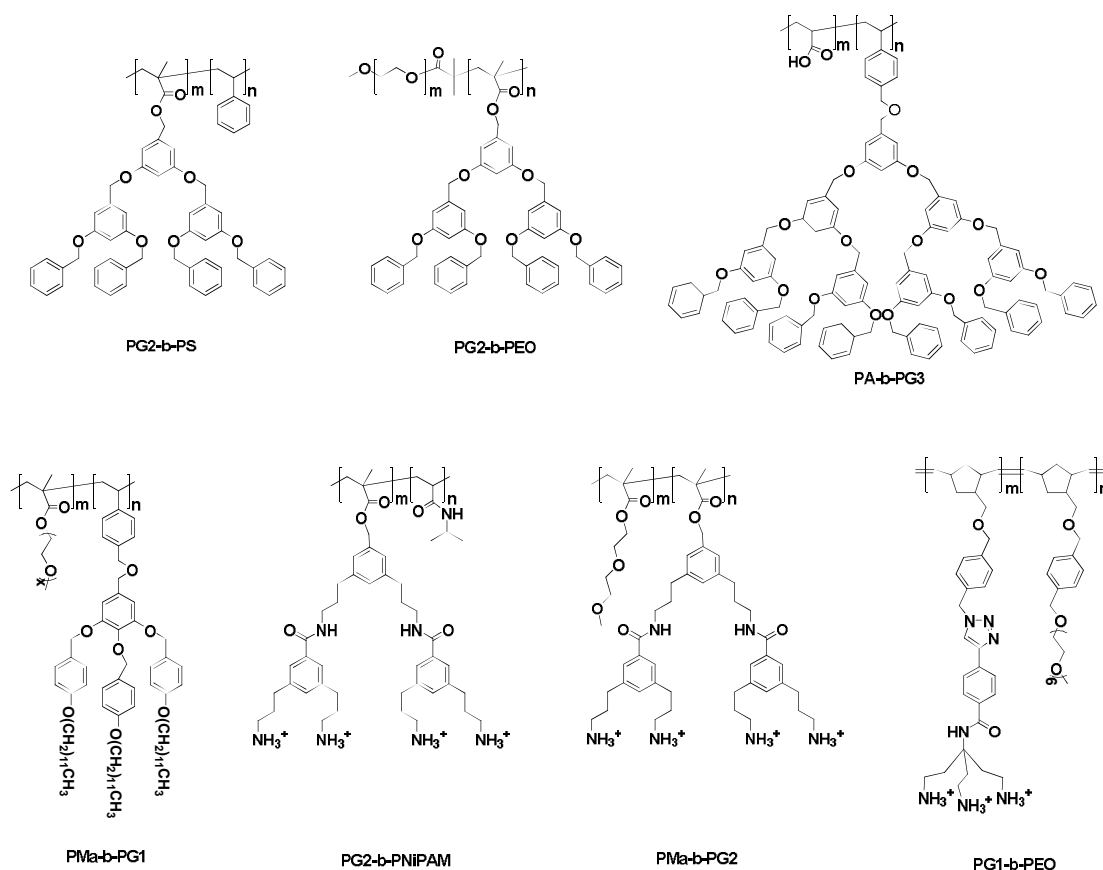
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Fig. 1 Schematic drawing of the synthetic methodologies for dendronized diblock copolymers. Structural characteristics of these copolymers are also elucidated with the structure parameter d which is absent in conventional block copolymers.

Synthesis

The synthesis of DBCs can be preformed through controlled or living polymerization

techniques, including atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and ring-opening metathesis polymerization (ROMP). The overall synthetic methodologies are depicted in Fig. 1, and several representative DBCs are shown in Fig. 2. The first DBC reported in literature was synthesized by ATRP with CuBr as catalyst and pentamethyldiethylenetriamine (PMDETA) as ligand [5]. The dendronized polymethacrylate block carrying Frechet-type dendrons was first prepared and used as macroinitiator to grow the second polystyrene block (route A in Fig. 1). The obtained DBCs showed narrow polydispersities ($PDI < 1.35$). DBCs can also be prepared efficiently with a polymer macroinitiator (route B in Fig. 1). For example, hydrophilic poly(ethylene oxide) (PEO) was used as macroinitiator to grow dendronized block via ATRP [6]. Since the dendronized block carries hydrophobic Frechet-type dendrons, amphiphilic DBCs thus forms, which are expected to show versatile self-assembly behavior. Alternatively, DBCs can also be prepared through ATRP to form a linear polymer block first, which further initiate the dendritic macromonomers to form the dendronized block [7].



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Fig. 2 Chemical structures of covalent DBC representatives. Abbreviations: PS = polystyrene, PA = polyacrylic acid, PMA = polymethacrylate.

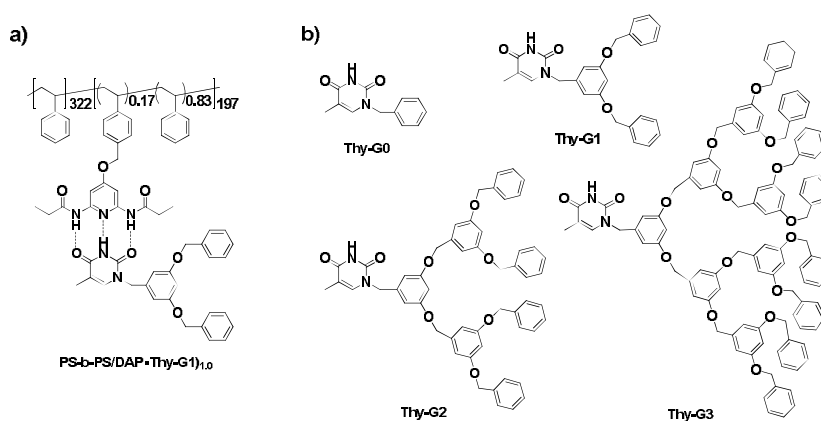
To incorporate a thermoresponsive polymer block into DBCs will not only make these copolymers water-soluble, but also introduce smart environmental responsive properties. This construction makes it possible to tune their self-assembly with temperature. For this purpose, thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) and comb-like polymethacrylates with OEG side chains are ideal candidates. The former is a prominent thermoresponsive polymer [8], which shows a lower critical solution temperature (LCST) around body temperature, is biocompatible, and has therefore been widely used in construction of thermoresponsive block copolymers. The latter are another type of

attractive thermoresponsive polymer [9], which show smaller hystereses than PNIPAM due to their much weak ability to form hydrogen bonds and are also biocompatible. Combination of these two types of thermoresponsive polymers with dendronized architecture, two different types of DBCs were prepared, namely those with a PNIPAM and a dendronized block [10] and those with comb-like OEG or a dendronized block [11]. RAFT polymerization technique was applied for the preparation of the first type of thermoresponsive DBCs, while ATRP was used for the synthesis of the second type of representatives.

DBC's can also be constructed from purely dendronized blocks. By polymerization of one type of dendritic macromonomer to form the first block, DBCs can be obtained with this macroinitiator to further polymerize the second dendritic macromonomer (route C in Fig. 1). For example, DBCs containing a third generation aryl ether dendron in one block and a second generation polyester dendron in another block were prepared [12]. Here, the living polymerization technique, ROMP was used to envisage better structure control. Based on the difference in thickness of these dendronized blocks, they can be directly visualized by AFM on substrates like mica. ROMP technique has also been used for the synthesis of DBCs containing both cationic dendronized block and PEG block [13]. The former was designed to show strong affinity to DNA binding, while the latter is on the purpose to impose an encapsulation of the DNA complex.

Besides the covalent construction for DBCs described above, these block copolymers can

also be formed via combination of covalent linkages and supramolecular interactions. Actually, supramolecular constructions always provide enormous ways to tune their constitutions, thus allowing easily to mediating their assembly behavior of block copolymers. For example, one polystyrene chain is blocked with another polystyrene segment bearing 2,6-diamidopyridine (DAP) anchoring groups to form block copolymers with recognition units [14]. These copolymers interact via strong hydrogen bonding with dendrons guests cored with thymine (Thy) to form the supramolecular DBCs. The main advantages for the construction of supramolecular DBCs are their structure tunability and abundant assembly morphologies.



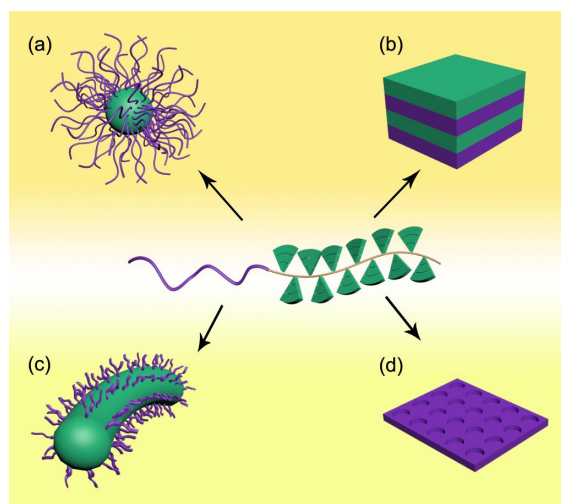
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Fig. 3 Chemical structures of supramolecular DBCs formed from block copolystyrene carrying DAP anchoring groups in one block (a) and Frechet dendrons (G1 to G3) cored with thymine (b). Adapted with permission from reference 14. Copyright 2005 American Chemical Society.

Self-assembly

The main structural characteristic of DBCs differing from conventional block copolymers is

their tunable thickness (d) which is related to dendron generations. This feature affords DBCs a new level of hierarchical structure control (Fig. 4). For example, amphiphilic DBCs consisting of dendronized polymethacrylate-*b*-PEO can assemble in a mixed solvent of THF and water. Due to the rigidity of the dendronized block, spherical aggregates were formed in most cases [6]. However, multiple morphologies, such as rods and fibers can be obtained when the soluble block is longer than the insoluble block. A similar amphiphilic DBCs adopted completely different self-assembly behavior at the interface of water/air [15]. With increase of compression stress, the wormlike surface micelles are compression induced, which, acted as the building blocks, can be arrayed parallel to generate a long-range ordered structure, and bended and twisted upon further compression. Unusual 3D large aggregates of "springs" and "disks" appear when the LB film completely collapses. Such a rich phenomenon of hierarchical nanostructure evolution should be attributed to the coil-semirod architecture of the diblock and the unique assembly ability of the dendronized block. Interestingly, this kind of amphiphilic DBCs can form highly ordered honeycomb films with quasi-horizontally paralleled double-layered structures, fabricated by the on-solid surface spreading method [16-17]. Polypseudorotaxane can be synthesized with moderate yield from dendronized poly(methacrylate)-PEO diblock copolymer [18]. PEO segment was included by α -cyclodextrin (CD) to form the polymer-CD inclusion complex, in which α -CD molecules adopted a symmetrical conformation with a stoichiometry 1:2 of α -CD to EO unit. Furthermore, by threading α -CD onto the PEO segments, the transition of DBCs from rod-coil architecture to rod-rod architecture resulted in a morphological change from spindly aggregates to rods in DMF/water (1:1).



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Fig. 4 Several major morphologies formed from self-assembly of covalent DBC representatives: (a) micelles, (b) lamella, (c) cylinders and (d) honeycomb film.

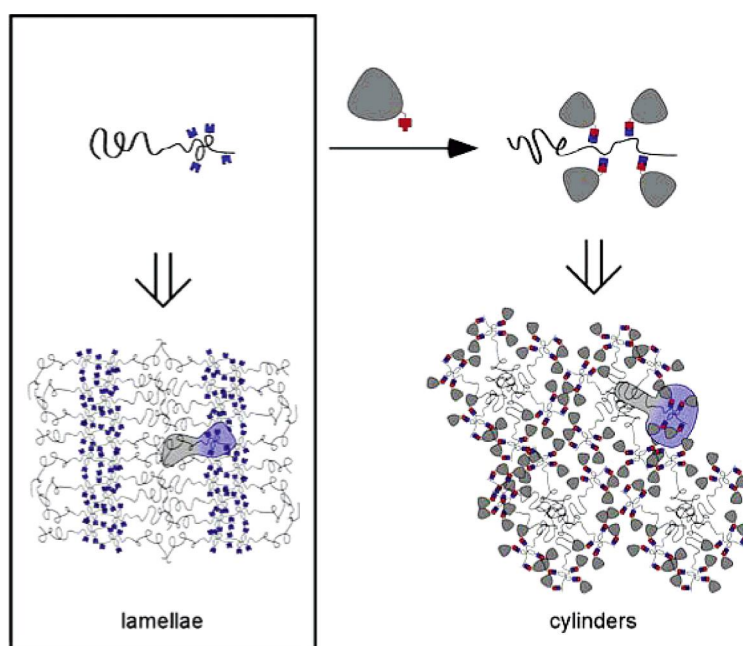
Thermoresponsiveness of DBCs can trigger their self-assembly in aqueous solutions with temperature. For example, DBCs with PNIPAM block prepared by RAFT polymerization technique with varied block lengths are water-soluble at room temperatures, but start aggregating at their lower critical solution temperatures (LCSTs) [10]. The aggregate morphologies were found to not only depend on the block ratios and block lengths, but also on the dendron generations. For DBCs with short first generation (PG1) block uniform spherical objects with sizes in the range of 40 ~ 120 nm were observed. With increasing chain length of the PG1 block, the aggregates become irregular. For DBCs with second generation (PG2) blocks so called "large compound micelles" were observed. The reversibility of DBCs aggregates with PG1 block was investigated to some detail for $\text{PG}_{145}\text{PNiPAM}_{263}$. During three heating and cooling cycles, samples for TEM measurements were taken at 50 °C. In each cycle very similar spherical objects were observed which

indicates that these objects represent a thermodynamic minimum under the applied conditions [19].

Alternatively, DBCs containing the thermoresponsive block from comb-like OEG chains were prepared by ATRP with first and second generation positively charged dendronized blocks [11]. They showed a better phase separation in bulk as compared to the PNiPAM block copolymer system, a property which could be exploited in terms of three-dimensional bulk structure design. For this purpose, the positively charged dendronized blocks were decorated with negatively charged surfactant molecules of different length, and the resulting bulk structures investigated by X-ray diffraction and TEM reveal that 3D hierarchically organized structures with columnar phases at the small length scales can be formed. Dendronized block architecture makes it possible to engineer these approximately nanometer-scaled phases into square, rectangular, and hexagonal lattices.

Supramolecular interactions provide easy structural variations which afford super tunability of assembly morphologies. Based on this conjecture, diblock copolystyrene (PS) with one block bearing DAP anchoring groups interact complementarily with first to third generation (G) Frechet dendrons cored with thymine (Thy) recognition units through three hydrogen bonds to form the supramolecular DBCs. The morphologies of block copolystyrene changed upon addition of thymine dendrons from lamellar (Thy-G0) to cylindrical (Thy-G1 and Thy-G2) to spherical (Thy-G3), which indicate the addition of increasingly larger dendronized thymine derivatives resulted in a progressive increase in

the effective volume fraction of the PS/DAP block, crossing the lamellar/cylindrical phase boundary at G1 and the cylindrical/spherical phase boundary at G3 (Fig. 5).

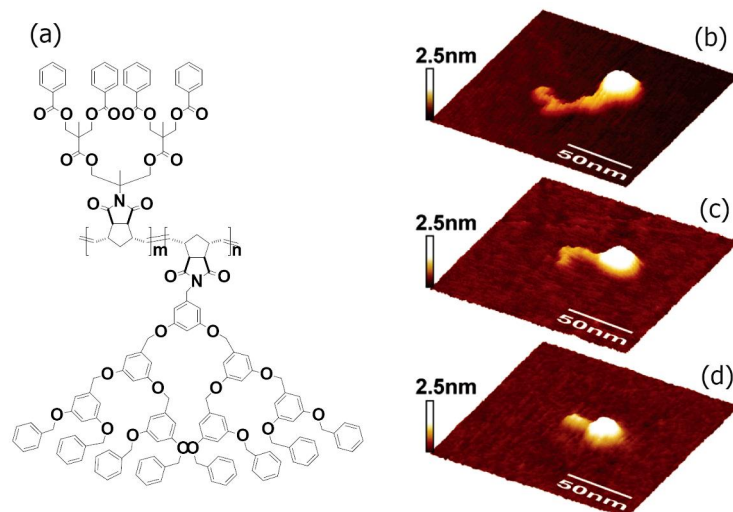


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Fig. 5 Supramolecular block copolymers assemble into different morphologies upon dendronization via complementary interactions between ADA and Thy. Adapted with permission from reference 14. Copyright 2005 American Chemical Society.

Thickness of dendronized polymers makes it easy to visualize and manipulate the individual macromolecules on interface [4]. Thus, it is not surprising to investigate the morphologies of individual DBCs on interface. The idea candidate for this purpose is to have DBCs with all dendronized blocks. By varying the chemical structures and dendron generation, different dendronized blocks will show different thickness. Furthermore, by selecting different polarities, these dendronized blocks should show different affinity to the substrate, which will lead to different morphologies for different dendronized blocks to

adopt on the interface. One example to check these judgments is using a DBC containing a third generation aryl ether dendron in one block and a second generation polyester dendron in another block [12]. Evidence for the nature of the DBC was provided by direct AFM visualization of individual molecules on mica (Fig. 6), which clearly confirmed the presence of distinct blocks. The copolymers synthesized with variable block lengths are shown in decreasing order of dendronized ester block size from Figure 6b to Figure 6d. Although the macromolecules on mica predominantly assume a conformation that resembles a tadpole, it is nevertheless possible to qualitatively correlate between the "tail" length and the number of ester dendron units. Therefore, the contour lengths of the tails were estimated to be 83, 37, and 19 nm for polymers with 200, 100, and 50 ester dendron units, respectively. Despite the uncertainties associated with the AFM technique, the measured variation in the chain length is consistent with the monomer feed ratio and the ^1H NMR data. The "head" of the tadpole has a constant diameter (ca. 20 nm) for the different polymers, which is attributed to the block containing the aryl ether dendron aggregating onto itself to minimize its interaction with the hydrophilic mica. While the more polar polyester dendronized block stretches out to maximize the contact area with the interface. This phenomenon is similar to the morphologies for the hairy dendronized polymers on substrates with different polarities [20].



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Fig. 6 Chemical structure (a) and AFM images on mica (b-d) of DBCs containing a third generation aryl ether dendron in one block and a second generation polyester dendron in another block. The stretched wormlike chain corresponds to the polar polyester dendronized block, while the aggregated in the shape of tadpole corresponds to the hydrophobic block containing the aryl ether dendron. Adapted with permission from reference 12. Copyright 2007 American Chemical Society.

Summary and outlooks

Dendronized block copolymers (DBC) combines the structure characteristics of both conventional block copolymers and dendronized polymers, which makes DBCs a class of highly promising macromolecules for supramolecular constructions and for fabricating smart materials. The characteristic thickness (d) of the dendronized block provides an extra parameter than conventional block copolymers (block length, block ratio, and polarity) to have a higher level of hierarchical control in self-assembly, thus making it possible to organize structures with nanometer-scaled columnar phases into square, rectangular, and

hexagonal lattices. With the multiple functional groups in the periphery, dendronized block architecture makes it possible to engineer biomacromolecules with the synergistical help of non-dendronized block(s). With the structural features of DBCs, further work to utilize them for molecular encapsulation and fabrication of biofunctional nanomaterials will be highly desirable. Future research directions towards functionalizing DBCs with novel stimuli-responsiveness will be attractive to explore characteristics aroused from these unique block copolymers.

Related entries

Dendrimer-like Star polymers

Dendronized Copolymers

Dendronized Homopolymers

Synthesis and Self-assembly of Linear-dendritic Hybrid Polymers

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