

Macromolecular Hybrids with Dendritic-Linear Architecture

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Abstract

Molecular hybrid systems based on dendritic-linear architectures are reviewed. This article describes their macromolecular features mainly focused on the synthesis, physical and self-assembly properties.

Introduction

Dendrimers/dendrons are monodisperse tree-like macromolecules with a regular and highly branched architecture, which consists of dendritic core and peripheral sites. The systematic branching starts from a central core to the outward, leading to materials with swellable core regions and dense end functional groups at the exterior with increasing generation. The peculiar structural feature provides a variety of possible applications in the field of host–guest, medicinal, catalytic chemistries [1]. In addition, the dendrimers/dendrons have been used as a fascinating macromolecular building block. The compartment of chemically distinct peripheries and dendritic core affords microphase-separated structures. In most cases, the dendrimers/dendrons have shown self-assembled micelles and cylinders in the bulk because of their typical cone or taper molecular shape [2–4].

These aesthetic dendrimers/dendrons have been combined with other molecular building blocks such as rods [5], discs [6], linear coils into hybrid macromolecules in order to create novel functional materials. In particular, linear coil has been frequently compared with dendrimer because of their extremely different molecular shapes. As a consequence of the shape difference, they show many different physical properties. For instance, linear coil has larger viscosity and hydrodynamic volume than those of the corresponding dendrimer at constant molecular weight and molecular composition [7].

Since about 10 years ago, the effort to combine these two molecular extremes has been made. In the early stage, the aim was focused on the construction of dendritic-linear hybrid macromolecular structures by using a variety of synthetic strategies. However, the recent

interest is being shifted to material aspects, e.g. self-assembling systems in the bulk or solution, conducting, thin-film applications, etc. Thus, it is meaningful to review what has been done in this field.

In this review paper, we address the synthesis, physical and self-assembly properties of dendritic-linear hybrid macromolecules. For convenience, we describe the paper by classifying the type of dendrons.

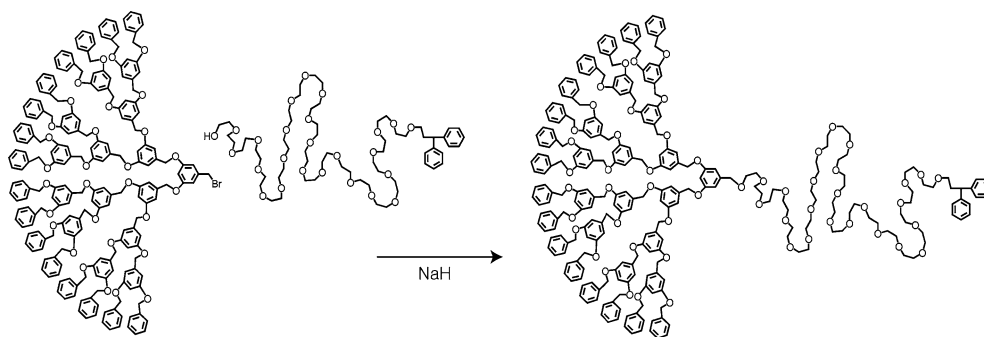
Hybrid macromolecules containing polyether type dendrons

As remarked, the early aim was to construct new macromolecular architectures comprising dendron and linear coil. Overall synthetic scheme is dependent upon the dendron synthesis, classified into convergent or divergent approach [8].

Hybrid macromolecules containing polyether type dendrons (e.g., benzyl or aliphatic ether dendrons), have been mostly synthesized by a sequential synthetic route of (i) a convergent dendron synthesis and (ii) a linear coil introduction by either coupling reactions or coil polymerizations at focal point of the dendrons.

The simplest way is to use coupling reactions of a coil with a dendron. Fréchet and coworkers reported the synthesis of hybrid copolymers consisting of benzyl ether dendrons [9]. As shown in Scheme 1, they employed the Williamson etherification as a coupling reaction. Bromine terminated dendrons at their focal point were reacted with mono-ol or diol type PEO under NaH base, yielding AB diblock or ABA triblock copolymer, respectively. A homologous hybrid structure was also gained by a Tin-catalyzed esterification reaction. As one of the physical natures of the hybrid copolymers, the authors investigated the thermal property. By analysis of the glass transition temperatures, they found that the hybrid copolymers showed a single glass–liquid transition. And they concluded that the two

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Scheme 1.

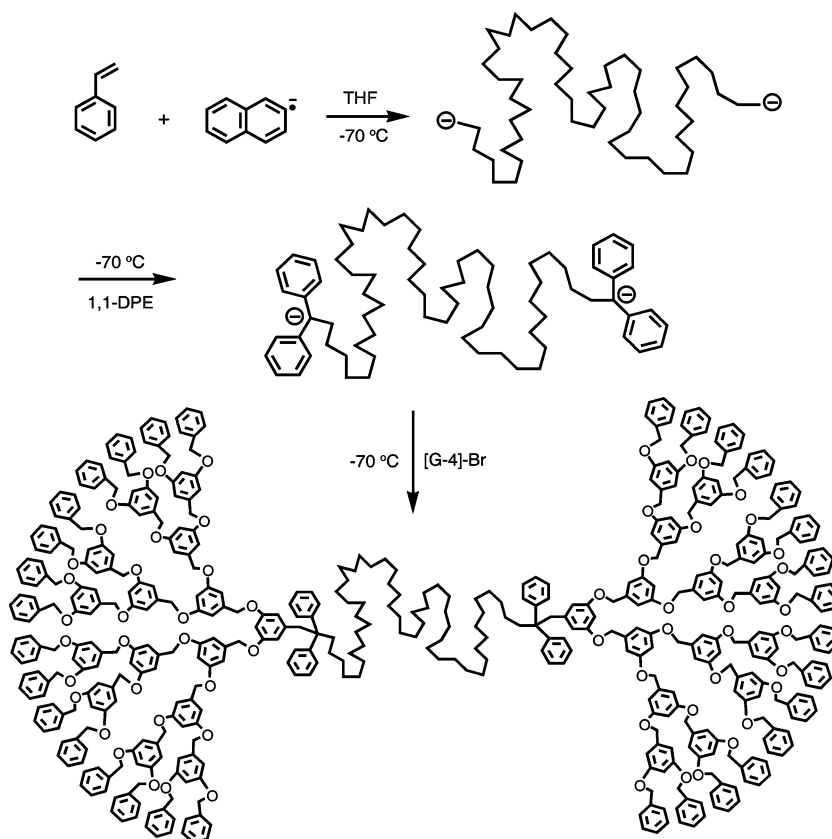
blocks (dendron and linear coil) can mix and plasticize each other without occurrence of phase separation of their blocks on the molecular level.

The next year, Fréchet and coworkers reported another type of ABA type triblock copolymers where the central coil is polystyrenes (PS) instead of PEOs [10]. The reaction scheme is illustrated in Scheme 2. The PS coil with two living anionic ends was made by anionic polymerization of styrene initiated by naphthalene radical anion. Then, the authors functionalized the PS coil ends with 1,1-diphenylethylene (1,1-DPE) to avoid undesirable side reactions.

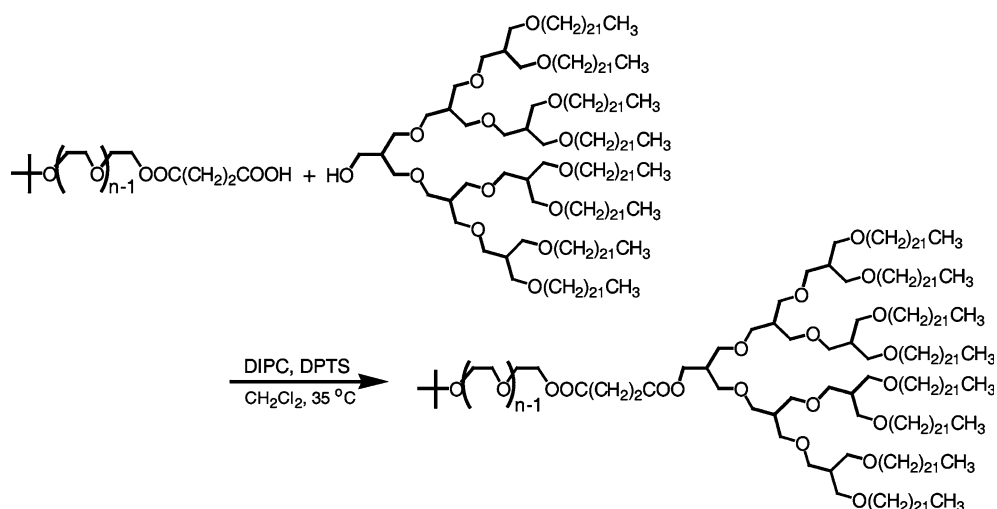
Another polyether dendron is an aliphatic polyether dendron. The synthesis of the aliphatic polyether dendron was devised by Fréchet *et al.* [11, 12]. The synthesis was performed by the Williamson etherification as a

generation growth step and hydroboration/oxidation as an activation step. By iteration of the reactions, the aliphatic ether dendritic structure can be grown.

Recently, Cho and Wiesner reported amphiphilic hybrid copolymers based on the aliphatic ether dendrons [13–15]. The amphiphilic hybrid copolymers are composed of a hydrophilic body (the dendritic core plus PEO linear coil) and hydrophobic docosyl peripheries (Scheme 3). Since the repeating unit of the aliphatic ether dendritic core is nearly identical to that of PEO, the hydrophilicity of the dendritic core would be comparable to that of PEO. The authors suggested that the dendritic cores are miscible with the PEO coils, thus microphase separation occurs at the interface between the docosyl peripheries and the dendritic core. This was confirmed by thermal analysis of PEO melting temper-



Scheme 2.



Scheme 3.

atures. In the synthesis, the prepared dendrons were coupled with carboxylic acid terminated PEO coils by diisopropylcarbodiimide (DIPC)/4-(dimethylamino) pyridinium-*p*-toluene sulfonate (DPTS) mediated esterification to yield the amphiphilic hybrid copolymers (Scheme 3). Besides the synthesis, the authors investigated the self-assembly behavior as a function of PEO coil length in the liquid crystalline phase. The hybrid copolymer with the shorter PEO chain (DP of PEO = 31) showed a micellar phase with Pm3n symmetry, which has been observed in cone shaped dendrons (Figure 1a). On the other hand, the hybrid copolymer with the longer PEO chain (DP of PEO = 96) exhibited three different liquid crystalline phases, i.e. hexagonal columnar, continuous cubic and lamellar mesophases upon heating (Figure 1b). It is quite remarkable that the continuous cubic mesophase with Ia3d symmetry has never been observed in dendrimer/dendron systems, but commonly shown in linear block copolymer systems. In addition, the authors emphasized that the phase sequence upon heating is quite unusual compared to those of conventional coil-coil block copolymers where the phase sequence is the opposite. From these observations, the authors concluded that the amphiphilic hybrid copolymer system shares the self-assembly features of coil-coil linear block copolymer and dendrimer/dendron systems.

On a material functional side, Cho and Wiesner studied the ion transportation behavior in the order liquid crystalline phases developed from the amphiphilic

hybrid copolymers [13]. They prepared ion-doped materials by complexation of above mentioned hybrid copolymers with lithium ions and investigated the charge transport behavior as a function of structural dimensionality. The conductivity analysis revealed that the movement of ions is retarded in the micellar mesophase, but promoted in the mesophases with higher dimensionalities (Figure 2). The authors proposed that the modulation of liquid crystalline structure can be applicable for a supramolecular on-off switch, an ion conductor, etc.

Besides coupling reactions, polymerization methods have been utilized to construct dendritic-linear hybrid copolymers. In particular, nitroxide mediated polymerization (NMP) and atom transfer radical polymerization (ATRP) have been employed as a versatile method because their living character affords well-defined coil segments in hybrid structures.

Hawker and Fréchet made use of benzyl ether dendrons as a macromolecular initiator for NMP and ATRP methods [16]. In the NMP approach, benzyl ether dendrons were converted into macroinitiators by reacting bromine terminated dendrons at their focal point with hydroxyl-containing 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO) derivative under NaH base. On the other hand, in the ATRP bromine terminated benzyl ether dendrons themselves were used as macroinitiators. In the next step, styrene was polymerized from the dendritic focal point in the bulk state under inert atmosphere to give dendritic-linear hybrid polymers

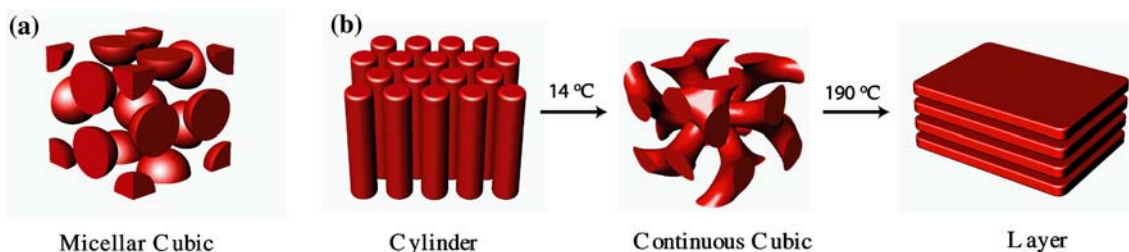


Figure 1. Schematic sketch of (a) the A15 micellar phase with Pm3n symmetry of the hybrid copolymer (DP of PEO = 31); (b) the unusual phase transformation of the hybrid copolymer (DP of PEO = 96) from cylinder, continuous cubic and lamellar liquid crystalline phases on heating.

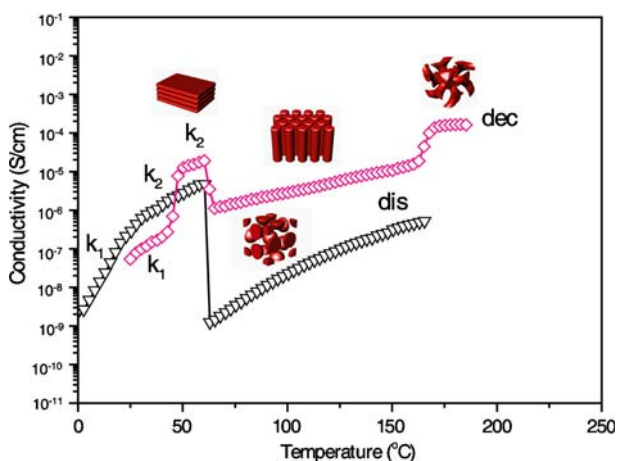


Figure 2. Ion conductivity curves as a function of temperature of lithium doped hybrid copolymers.

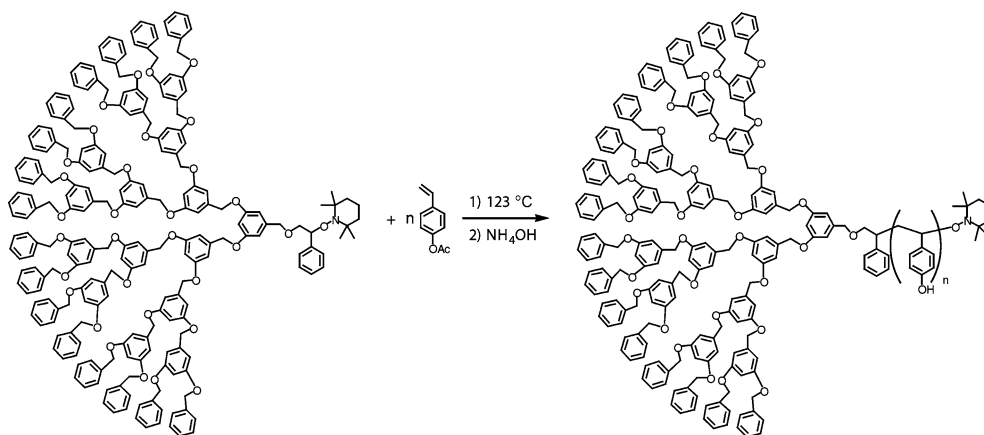
(Scheme 4). In the polymerization step, the ATRP was performed in the presence of CuCl/4,4'-(bis-*n*-heptyl)-2,2'-bipyridyl complex as a catalyst system (Scheme 5). Most polymers obtained from both NMP and ATRP showed low polydispersity (M_w/M_n) indexes less than 1.25, indicating that the lengths of linear PS coils were controlled in a regular size.

Mackay and Hawker studied the self-assembly behavior of a homologous series of benzyl ether dendron-linear polystyrene copolymers [17]. In this

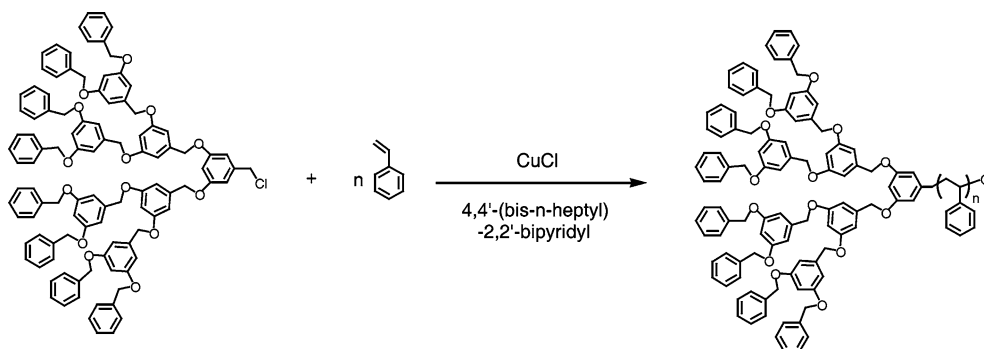
study, the authors chose the large sixth generation benzyl ether dendron as a dendritic part and linear polystyrene coils with different lengths (Scheme 6). They investigated self-assembled structures as a function of PS coil length. They observed that a lamellar structure was changed into a hexagonal columnar structure with increasing PS coil length. The authors suggested that despite the similar solubility parameters between the benzyl ether dendron and the PS coil, the fundamental driving force for the microphase-separation is the difference of conformational entropy.

Zhu and coworkers implemented CuBr/2,2'-bipyridine mediated ATRP to prepare amphiphilic linear-dendritic block copolymers [18]. The macromolecular amphiphiles have linear poly(acrylic acid) coils as a hydrophilic block and dendritic benzyl ether dendrons as a hydrophobic block. The overall reaction scheme consisted of two steps; (i) the ATRP of methyl acrylate initiated by a benzyl ether macrominitiator and (ii) the hydrolysis of linear poly(methyl acrylate) into the hydrophilic conjugate base of poly(acrylic acid) (Scheme 7). The authors examined the solution properties of the polymers (e.g. viscosity, hydrodynamic volume). They found that the dendritic block also plays a significant role in the increase of the hydrodynamic volume in aqueous solution.

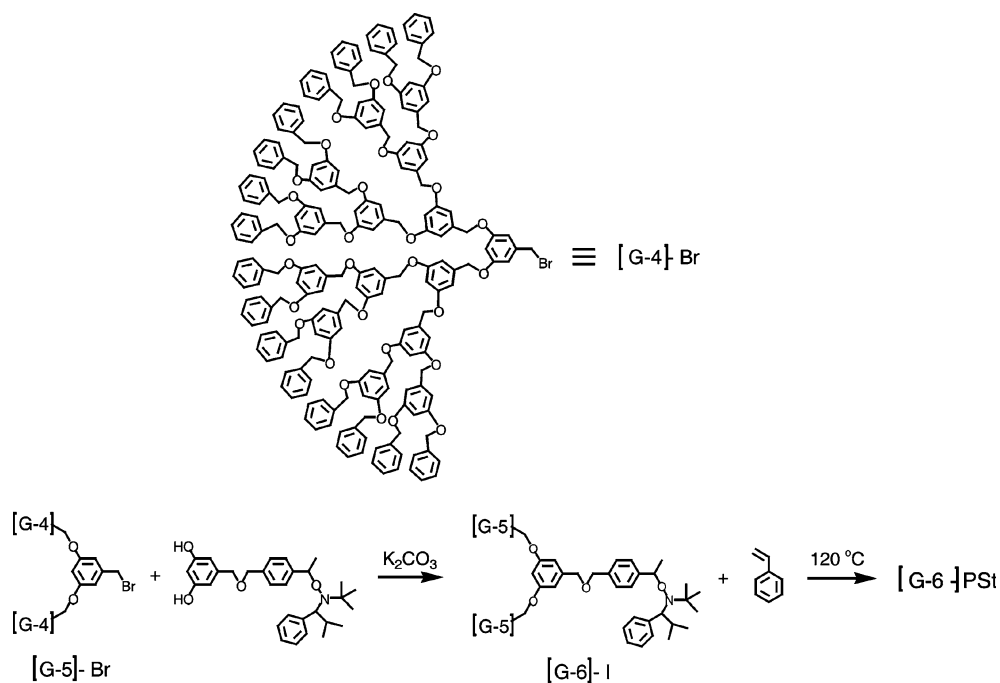
Xi and coworkers carried out the copolymerization of *N*-phenylmaleimide (PhMI) and styrene by ATRP



Scheme 4.



Scheme 5.

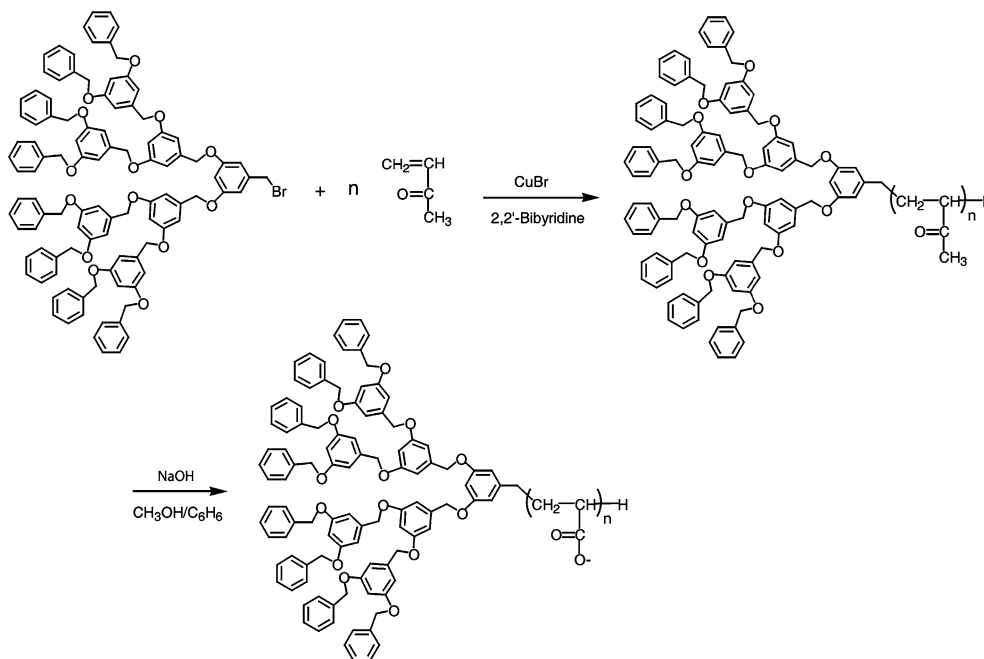


Scheme 6.

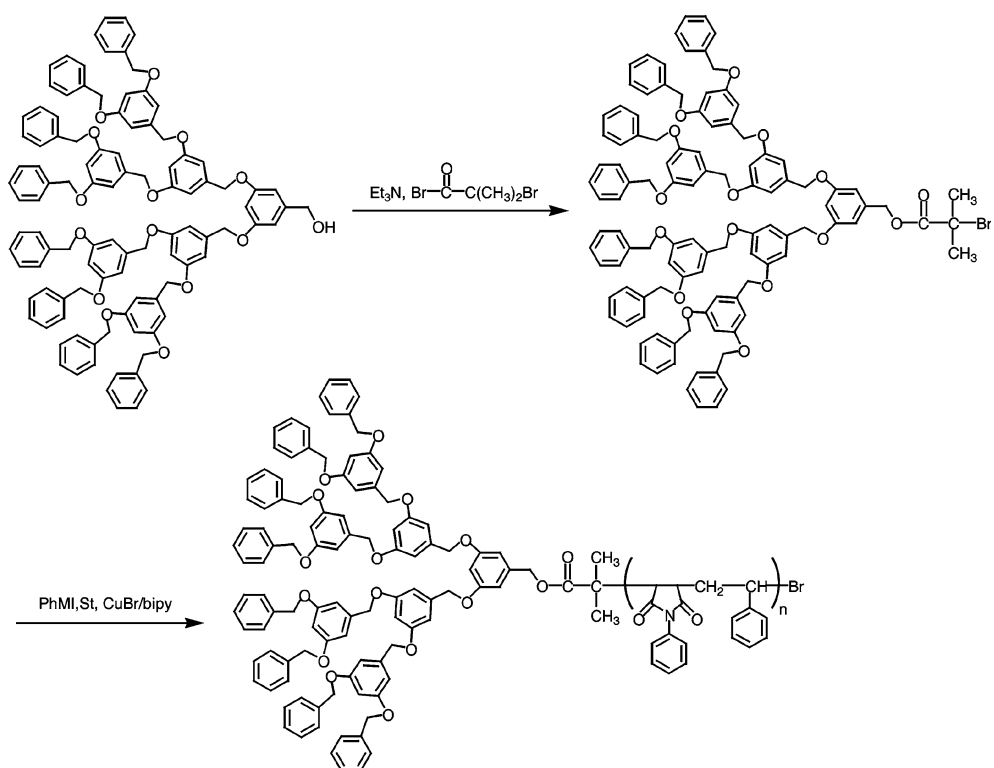
starting from bromine terminated benzyl ether dendrons (Scheme 8) [19]. As Zhu *et al.* did, the authors also utilized CuBr/bipyridine complex as an ATRP catalysis system. By studying the copolymerization kinetics, the authors demonstrated that PhMI and styrene constituting the linear part were polymerized alternately.

The living character of a coordinative ring opening polymerization (ROP), which involves a coordination-insertion mechanism, has been applied for the synthesis

of linear coils in dendritic-linear hybrid copolymers. In particular, the versatility of this method is to introduce nonvinyl linear polymers such as polyesters in a regular size. Dubois and coworkers prepared hybrid copolymers by a coordinative ROP of caprolactones using benzyl ether dendrons with aluminum alkoxide at the focal point as a macroinitiator (Scheme 9) [20]. Most of the polymers exhibited very narrow molecular weight distributions less than 1.15, confirming the living character of the ROP. Also, even after ROP, the prepared



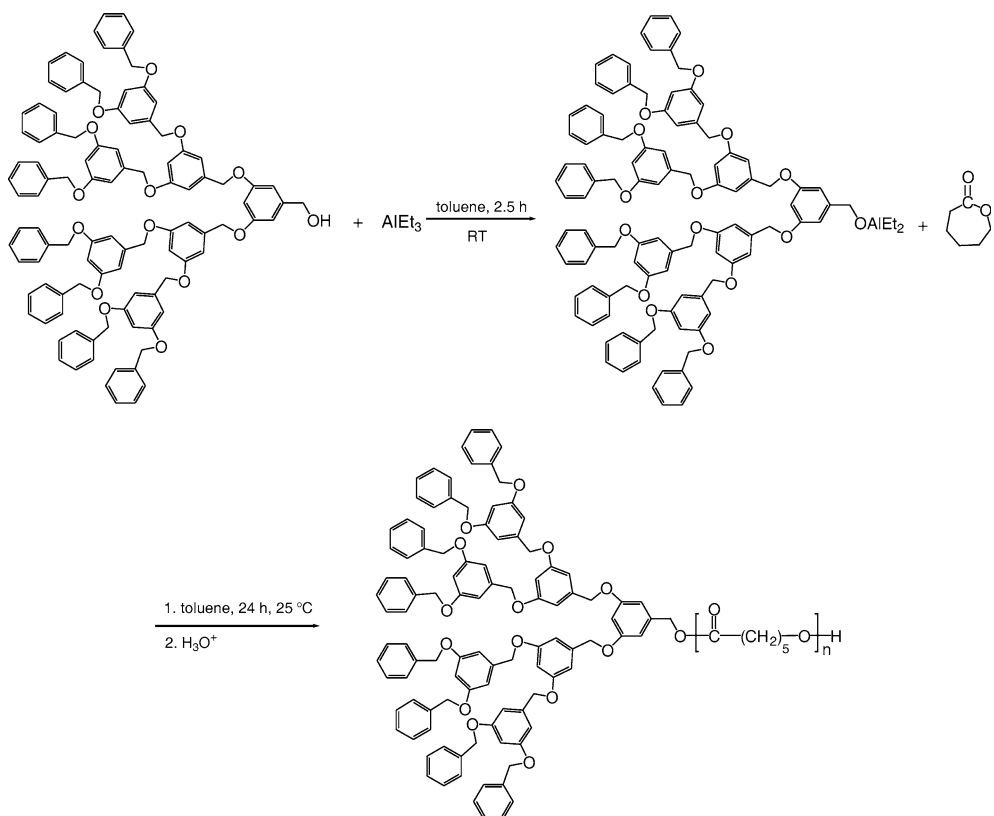
Scheme 7.



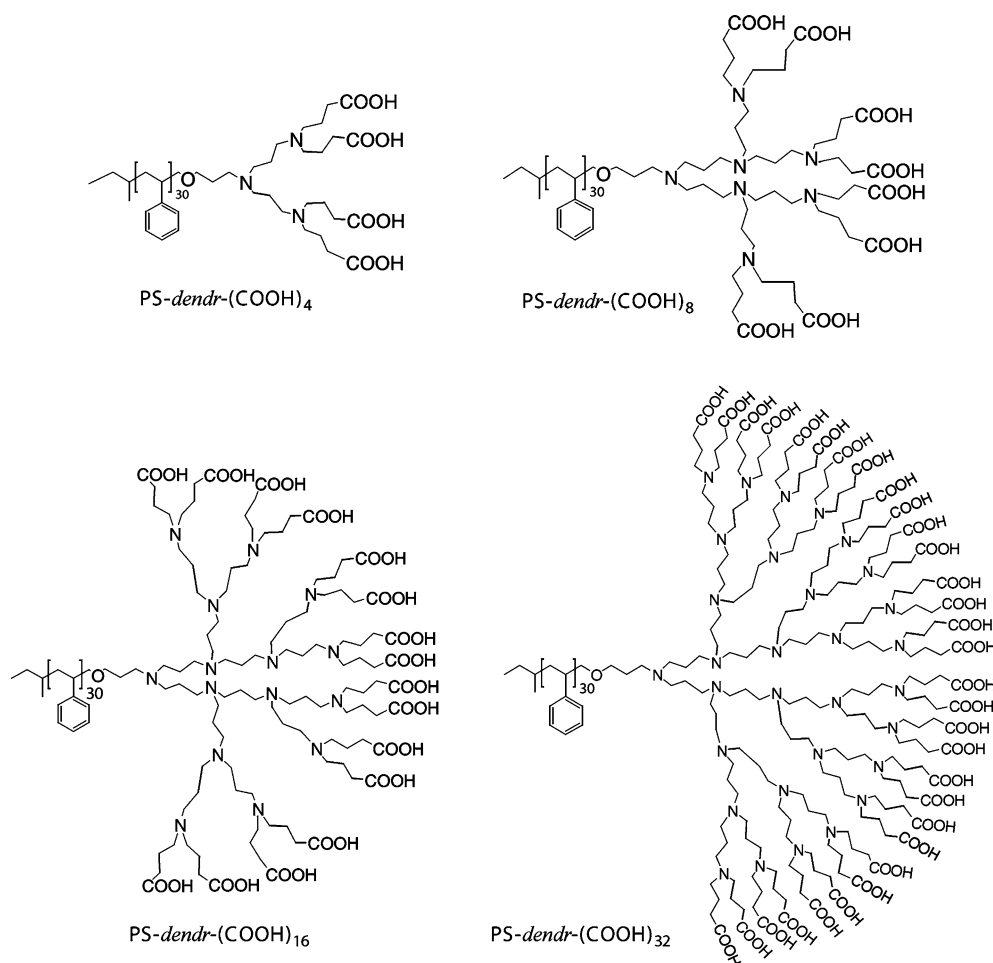
Scheme 8.

polymers bore a reactive hydroxyl group at the polycaprolactone end. Thus, the authors proposed that the combination synthetic method of ROP and NMP/or

ATRP would be a powerful strategy for the synthesis of more complex hybrid copolymers, e.g. dendritic-linear-linear triblock copolymers.



Scheme 9.



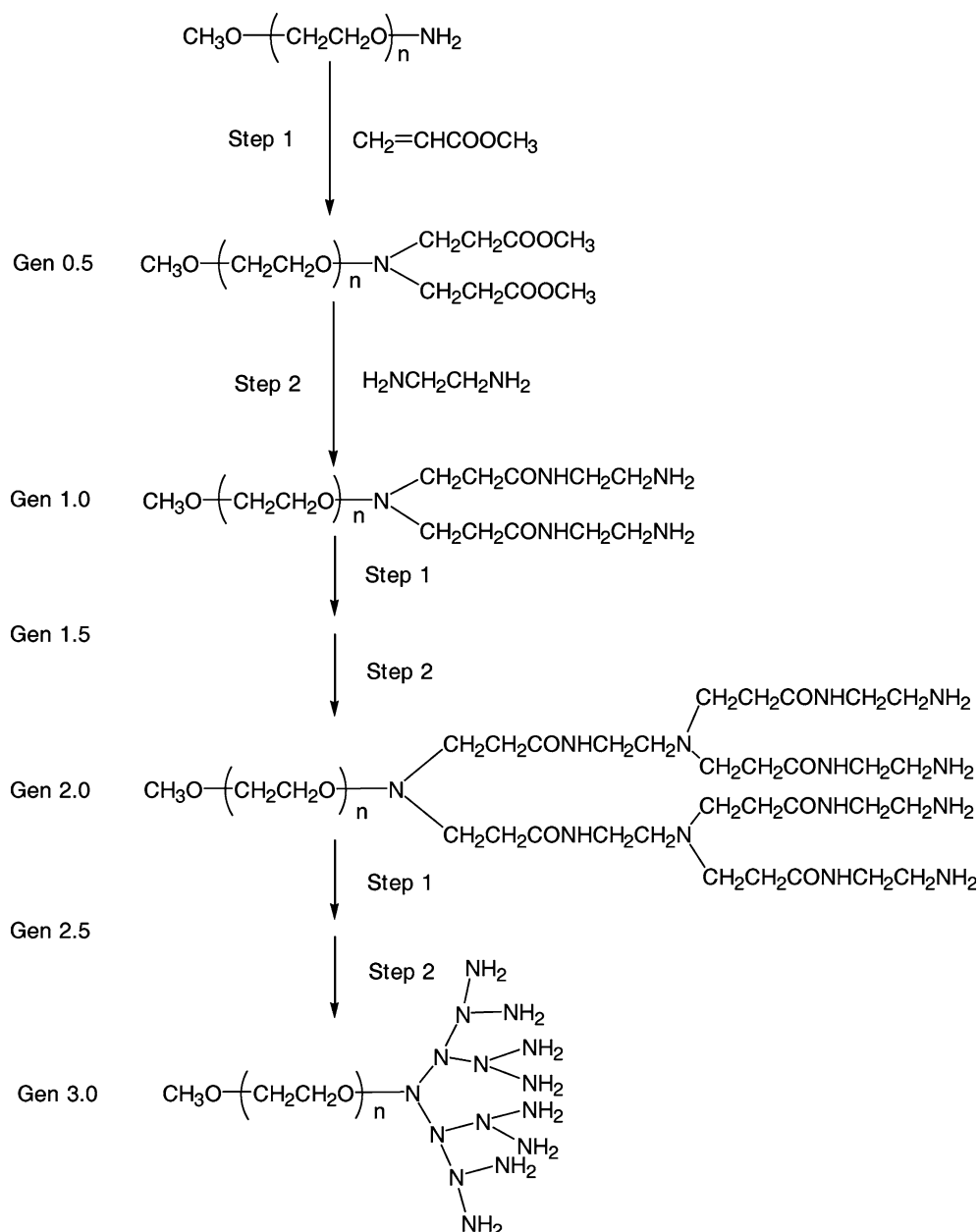
Scheme 12.

different number of branches to the PS coil. The self-assembly behavior in the aqueous solution was investigated as a function of PPI generation. The authors observed that the block copolymers aggregated from vesicles through micellar rods to spherical micelles as dendron generation increased.

The amphiphilic PPI-PS copolymers showed well-defined assembled structures in the aqueous solution, nevertheless they do not have enough amphiphilicity to microphase-separate in the bulk. Thus, in order to obtain ordered nanostructures, structural variation was required to increase immiscibility between PPI and PS. Meijer and coworkers have modified the termini of the PPI dendrons into carboxylic acid groups to reinforce the segregation of the PPI dendrons from the PS phase in the solid state [23, 24]. The carboxylic acid groups were introduced by the acid hydrolysis of the corresponding nitrile-functionalized structures. The self-assembly behavior in the solid state was examined as a function of PPI dendron size. The authors prepared four block copolymers [PS-dendr-(COOH) $_n$ ($n = 4, 8, 16, 32$)] with an identical PS coil (Scheme 12). PS-dendr-(COOH) $_4$ with the smallest PPI dendron showed a hexagonal columnar structure where the PPI dendrons constitute cylinders surrounded by the PS coils. In contrast, the block copolymers with larger PPI dendrons

self-assembled into lamellar structures. The authors also pointed out that chain architecture significantly influences polymer self-assembly. Compared to linear diblock copolymers, the hybrid block copolymers exhibited lamellar structures at relatively small PPI volume fraction [e.g. 0.25 for PS-dendr-(COOH) $_8$], which is attributed to the curvature of the PPI dendritic structure.

Hammond and coworkers have chosen amphiphilic block copolymers with a different molecular design concept from what Meijer and coworkers did. They used poly(amidoamine) (PAMAM) dendrons as a hydrophobic head and PEO coils as a linear hydrophilic tail [25]. In this case the linear PEO tail selectively tends to be compatible with hydrophilic media, thus the block copolymer can be applicable for the formation of ultrathin film membranes. The synthesis was accomplished by alternate two steps, (i) Michael addition of methyl acrylate to primary amine terminal groups and (ii) reaction of methyl ester with ethylenediamine to regenerate primary amines at dendron termini (Scheme 13). The authors investigated the thermal properties of the prepared block copolymers, and demonstrated that the copolymers exhibit some degree of microphase segregation regardless of the composition of the diblock. Also, it was proved that the glass transition



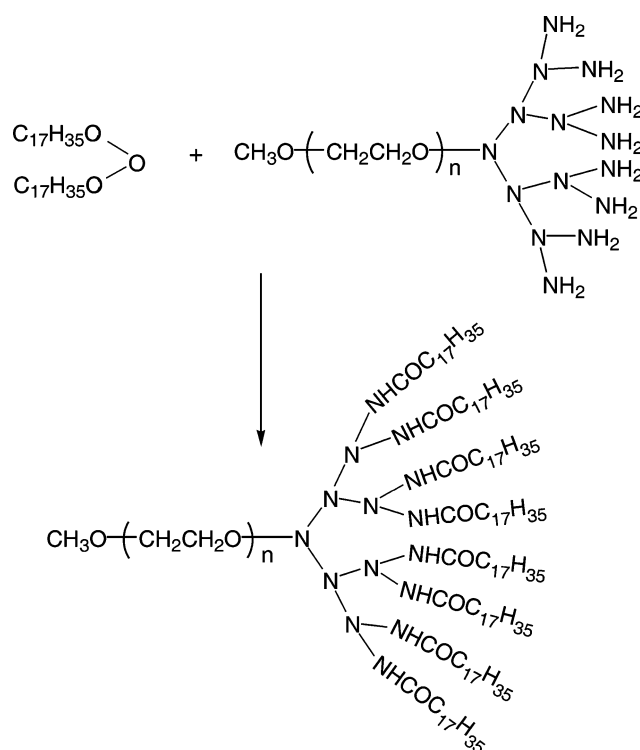
Scheme 13.

temperatures are strongly influenced by the end group functionality of the dendron.

To enhance the amphiphilicity of the hybrid copolymers, Hammond and coworkers attached hydrophobic stearate groups at the dendron ends of the PEO-PAMAM copolymers (Scheme 14) [26]. They studied the amphiphilic character of the modified diblock copolymers by spreading monolayers of the polymers at the air-water interface. They found that the stearate-terminated diblock copolymers gave stable monolayers that formed condensed phases on compression. These monolayers were able to be transferred onto hydrophobically functionalized surface by physisorption. Smoothly transferred monolayer films at high surface pressures were found to be continuous, free of holes. In addition, the authors investigated microphase

segregation in the bulk state [27]. The stearate-functionalized diblock copolymers with generation 1.0–4.0 exhibited segregated structures in the melt at high temperature although structural assignments were not clear. However, all the stearate-functionalized copolymers were observed to be crystallized into lamellar structures at room temperature.

Hyperbranched polymers are homologous to dendrons, but the synthesis has long been known to produce polydisperse materials. Thus, it has not been considered suitable for the synthesis of well-defined blocks. Recently, Müller and Frey demonstrated that slow addition of monomers to suitable core molecules leads to pseudo chain growth condition, which makes it possible to prepare well-defined hyperbranched polymers. Frey and coworkers took advantage of this synthetic

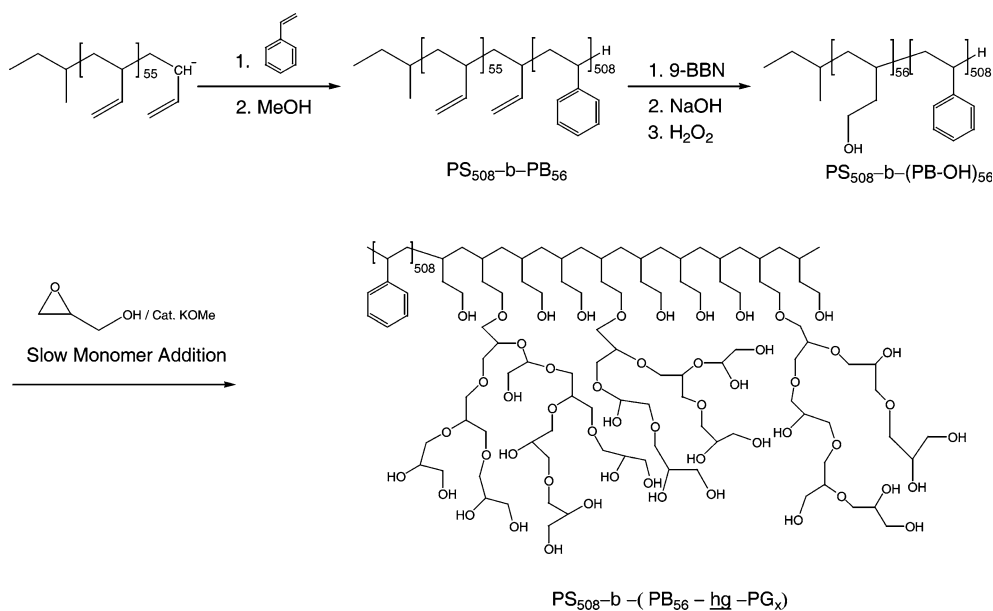


Scheme 14.

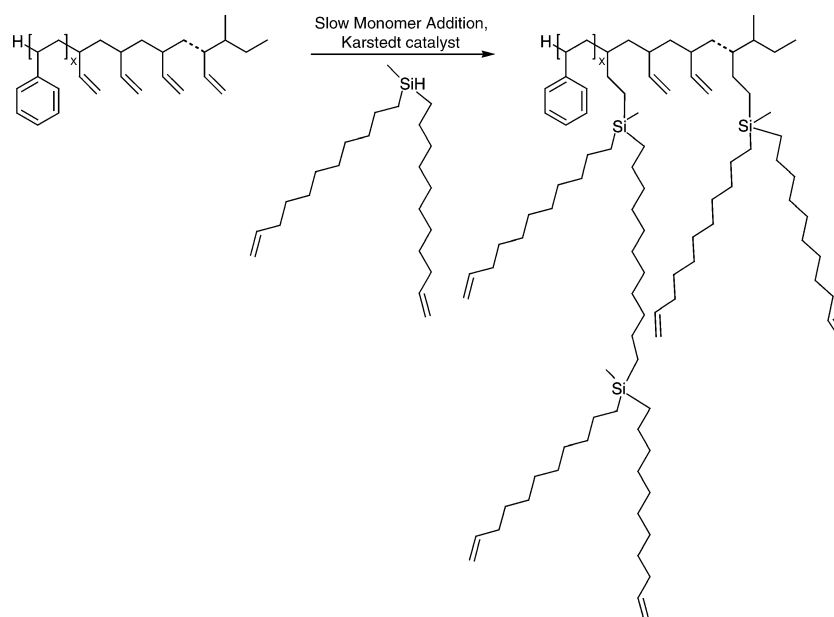
concept for preparing linear-hyperbranched amphiphilic diblock copolymers [28]. The synthetic procedure was performed by a combination of anionic polymerization, hydroboration/oxidation and controlled ring opening branching polymerization (Scheme 15). Polybutadiene-*b*-polystyrene (PB-*b*-PS) diblock copolymers were synthesized via conventional anionic polymerization, then double bonds of the PB block were converted into hydroxyl groups by hydroboration/oxidation reaction. The hydroxylated PB acted as the macroinitiator for the

post polymerization grafting step. In the grafting step, glycidol was used as the monomer, and turned into hyperbranched polyglycerols. The obtained amphiphilic copolymers with small hyperbranched brushes showed very narrow molecular distributions less than 1.02.

Frey and coworkers also prepared another class of linear-hyperbranched block copolymers with a grafted poly(carbosilane) block (Scheme 16) [29]. The synthetic concept to yield well-defined hyperbranched block is the same as the previous example. The grafting step of



Scheme 15.



Scheme 16.

hyperbranched carborasilane was performed by a hydrosilylation reaction in the presence of platinum–divinyltetramethyldisiloxane complex (i.e. Karstedt catalyst). The obtained block copolymers showed classical microphase-separated morphologies such as lamellar and cylindrical structures as a function of weight fraction of hyperbranched component. Also, the constructed phase diagram is relatively asymmetric compared to that of conventional linear type block copolymers.

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