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One-Pot Synthesis of Amphiphilic Core−Shell Suprabranched Macromolecules

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Several dendritic architectures have been developed from Flory's theory of highly branched polymers over the past two decades.[1−3] Dendrimers (including dendrons) and hyperbranched polymers (HPs), the most intensely studied subclasses, are among the most interesting ones for their unique structures and properties. Nowadays, synthesis of dendritic polymers with a core−shell structure has attracted much attention because of their potential applications. Chemists have combined linear and dendritic structures together to prepare novel dendritic core−shell polymers, which include dendronized polymers, hypergrafted polymers, and multiarm star polymers.[2,3] Dendronized polymers and hypergrafted polymers have linear macromolecular cores and dendritic side chains, which provide them with rodlike or cylindrical shapes. Multiarm star polymers are mostly prepared by grafting linear polymers to or from dendritic cores.[4] However, core−shell dendritic−dendritic hybrid macromolecules are rarely reported because of the difficulty associated with their synthesis methodology.

The aim of this communication is to develop a novel approach to amphiphilic core−shell polymers with complex hyperbranched−hyprebranched structures. It can be speculated that the targeted hyperbranched−hyperbranched polymers will have much inner space, which is very useful for the encapsulation of small compounds such as noble metal ions and dyes. Furthermore, this novel amphiphilic core−shell structure is a potential candidate for self-assembly research. Because the resulting macromolecules are constructed from hyperbranched macromolecules, the core−shell hybrids are termed suprabranched polymers in this paper.

This work employs the one-pot two-step synthesis approach based on self-condensing (or multibranching) ring-opening polymerization of two monomers in succession to generate the suprabranched macromolecules. Thus, 3-ethyl-3-(hydroxymethyl)oxetane (EHOX, **1**) and glycidol (**2**) are carefully selected as raw monomers,[5] and poly(glycidol) (P2) is highly hydrophilic but poly(EHOX) (P1) is more hydrophobic. Therefore, **1** and **2** are appropriate candidates for the generation of hydrophobic core and hydrophilic branches, respectively.

A typical synthetic procedure for the one-pot cationic copolymerization of **1** and **2** is described below (sample SP1, Table 1): The polymerization of **1** was first carried out (0.025 mol of $BF_3 \cdot Et_2O$ and 0.05 mol of **1** in 100 mL of 1,2-dichloromethane) at −10 to 0 °C[6] until the growth of P1 was exhausted (ca. 24 h in our experiments). Then **2** (0.05 mol) was added dropwise through a nitrogen-filled funnel, whereupon the viscosity rose dramatically. After a further 24 h, the reaction was terminated by addition of methanol. The resulting mixture (dissolved in methanol) was neutralized with solid CaO, filtered, and precipitated by addition of diethyl ether. The crude product was redissolved in methanol and precipitated by addition of a mixture of tetrahydrofuran (THF) and water, three times, to remove the possibility of mixed P1 and P2.[7] Thus, the so-called suprabranched polymer SP1 was obtained with molecular weight (M_n) (GPC with PMMA as calibration and LiBr/DMF (0.01 mol/L) as eluent) of 16 750. If the added amount of **2** in the second step was varied, other samples with a series of P2 content and high yields (>70%) were prepared (Table 1). The synthesis process and structure of the macromolecule are shown in Scheme 1 (see also Supporting Information S1).

Table 1. Block Copolymerization Conditions and Results of 3-Ethyl-3-(hydroxymethyl)oxetane (1) and Glycidol (2)

sample	R_{feed}	R_{unit}	$M_{n,NMR}$	$M_{n,GPC}$	PDI	T_g/°C
SP1	1:1	1:1.3	19 350	16 750	1.38	−50.5, 19.1
SP2	1:2	1:2.8	29 500	20 500	1.45	−51.4, 3.9
SP3	1:5	1:6.9	57 200	22 830	1.62	−47.1
SP4	1:8	1:10.9	84 230	25 240	1.69	−44.3
SP5	1:10	1:14.1	105 850	26 460	1.74	−43.0

The appearance of different samples varies greatly. SP1 is a solid whereas SP2 is a semisolid. Samples with higher P2 content are more viscous liquids. As their polar structure implies, all the products are easily soluble in polar organic solvents such as DMF and DMSO but poorly soluble in chloroform, acetone, and THF (pure P1 is easily soluble in THF). Interestingly, their solubilities in water change regularly with increasing the **2**:**1** feed ratio (R_{feed}): SP1 is rarely soluble; both SP2 and SP3 can be partially dissolved or solubilized to form a microemulsion, while SP3 is easier; and both SP4 and SP5 can be rendered soluble to form a clear solution. But SP5 displays higher solubility. (A photo of samples placed in water is given in the Supporting Information **S2**.) Such a phenomenon proves that the units of **2** have been covalently linked to the P1 cores by the one-pot method, giving rise to core−shell amphiphilic copolymers, and the content of P2 moieties increases as R_{feed} rises. Because P1 is insoluble in water, whereas P2 is very water-soluble, this leads to the higher content of P2 units, the easier the solubilization and the greater the solubility in water of the resultant products. Therefore, the polarity and solubility of the copolymers can be expediently controlled by the feed ratio.

To measure the true M_n of such complex hybrids is a big challenge for us, since to determine accurately the M_n of convenient HPs is still an ever-present problem. We have tried to measure the relative M_ns by GPC (GPC traces of SP1 and SP5 are shown in Supporting Information S3) and NMR. The results are listed in Table 1. The $M_{n,GPC}$ of the core taken from the first step is ca. 10 580 with a polydispersive index (PDI) of 1.25. When the second monomer, **2**, was added, the M_ns of the copolymers rose remarkably and increased with increasing R_{feed}. This strongly suggests again that the in situ formed P1 initiated further ring-opening polymerization of **2**, affording hyperbranched−hyperbranched copolymers, neither homopolymer nor mixed. Nevertheless,

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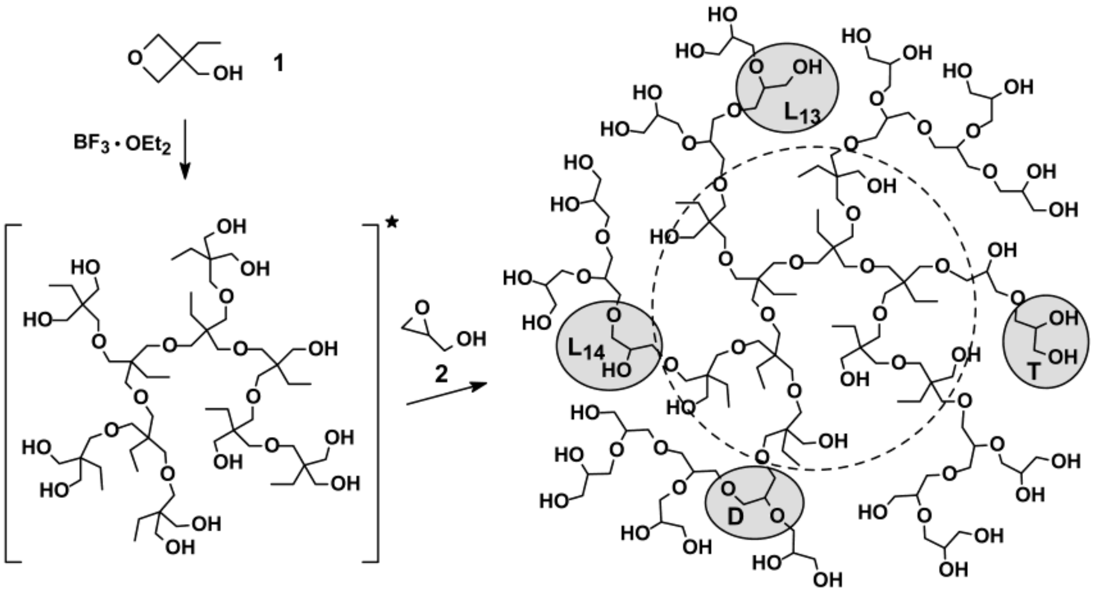
Scheme 1



the increased extent on $M_{n,GPC}$s is not so significant as the variation of solubility in water, which implies shortage of GPC in the M_n measurement of globular macromolecules like HPs due to the calibration of linear polymers: lower M_n than the true molecular weight. Meanwhile, all PDIs are very narrow (<1.75) by comparison with those of general HPs and are also quite close to those of Frey's polymers made from **2** and small molecular cores.[5a] Such narrow PDIs exclude the existence of considerable amounts of homopolymers. According to the kinetic theory, on the other hand, the PDI of HP with a core having so many functional groups should be narrower.[8] The reason for this can be partly attributed to the polydisperse nature of the in situ formed P1 cores or initiators which makes the further amplification of PDIs for resultant copolymers. Besides, only part of the potential initiating sites of P1 cores initiated polymerization of **2,** making PDI higher than the theory's value.

To confirm the $M_{n,GPC}$ listed in Table 1, the $M_{n,GPC}$s of the copolymers end-capped with benzoyl chloride were measured in THF. Both results are in accordance with each other. In addition, M_ns calculated from ^{1}H NMR spectra ($M_{n,NMR}$),[9] with methyl (CH_3-) and $M_{n,GPC}$ of core as the references, also show a similar increasing tendency, although its value is much higher than the corresponding $M_{n,GPC}$. The greater unit ratio of **2**:**1** (R_{unit}), possibly caused by the relatively poor solubility of the compressed P1 core in the NMR measurement, results in the higher $M_{n,NMR}$ value.[10] So we believe that the true M_n for the suprabranched polymer ranges between its $M_{n,GPC}$ and $M_{n,NMR}$.

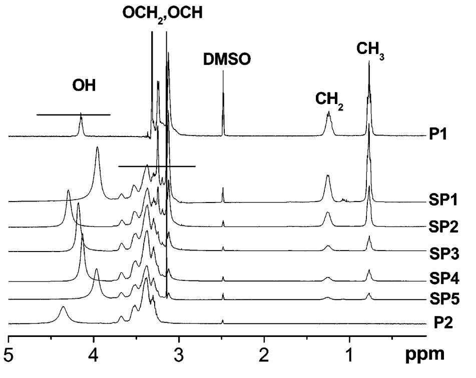


Figure 1. ^{1}H NMR spectra of P1 (core), SP1, SP2, SP3, SP4, SP5, and P2.

The structure of the copolymers is confirmed by ^{1}H NMR and quantitative ^{13}C NMR (see Figure 1 and Supporting Information **S4**), identical with our prediction, the intensity of P1 peaks (ethyl groups) decreases in an orderly fashion as the R_{feed} increases.

To determine the degree of branching (DB) of the complex objects is also difficult. The P1 core removed from the first step has a DB of ~0.38. For the hybrids, the peaks of P1 and P2 units partly overlap (69−74, 60−64 ppm), which hinders the calculation of the copolymers' DB. For SP1, because only very low "generations" of P2 units grow from the P1 cores, the peaks around 80 ppm for dendritic and linear units of P2 are not distinctively observable. Such spectra also provide further evidence for the negligible content of the mixed homo-P2. Otherwise, the peaks assigned to P2 units should be much stronger. For SP5, on the contrary, the proportion of P2 units is so high that we can ignore the interference of the weakened peaks of P1 units (Figure 2). DB of ~0.54 is gained for the shell according to Frey's equation.[5a] Because the M_n of the P2 block increases with R_{feed}, the DB of a HP rises if its M_n becomes higher,[11] so the DBs for other shell moieties should be lower than 0.54.

Because of the overlap, the grafting degree (GD) of the P1 core cannot be deduced from the NMR. Model reactions with ethylene oxide (EO), as the second-step added monomer, showed that the GD of the hyperbranched−linear copolymer (P1-*b*-PEO) was nearly 70−72%.[12] The GDs of the hyperbranched−hyperbranched copolymers would be lower than 70% due to the steric effect of branched molecules.

The specific viscosity (η_{sp}) of SP1 and SP5 as a function of concentration in methanol solution was measured (see Supporting Information S5). Significantly, no linear relationship between η_{sp} and concentration was observed for the core−shell amphiphilic macromolecules in the investigated concentration range. On the contrary, two inverse-inflection points appeared in the curve of SP1 and one for SP5. This implies that

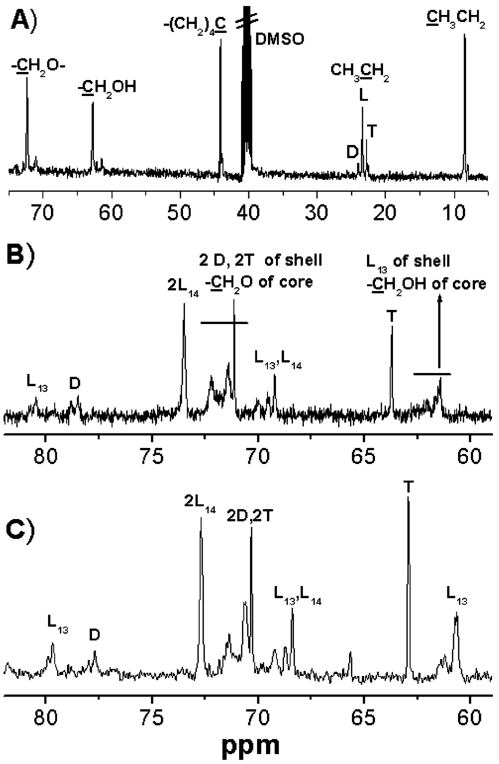


Figure 2. Quantitative ^{13}C NMR spectra (DMSO-d_6) of P1 (A), SP5 (B), and P2 (C). The D, L and T in spectrum A represent the carbon signals of $-CH_2CH_3$ belonging to the dendritic, linear, and terminal units of core macromolecules (P1), respectively. In spectra B and C, carbons belonging to the dendritic, linear 1,3, linear 1,4, and terminal units of suprabranched macromolecular shell and P2 are indicated by D, L_{13}, L_{14}, and T, respectively.

aggregation occurs in methanol solutions of the amphiphilic polymers. As a comparison, a linear relationship between η_{sp} and concentration was detected for the pure P1 or P2, which showed that no aggregation occurred in each of the homopolymer solutions.[5a]

To confirm the aggregation phenomenon, dynamic light scattering (3000Hs, Malvern) was measured for the methanol solution of the resulting copolymers (see Supporting Information S6). Two or three peaks were found for the sample with a lower **2**:**1** feed ratio (e.g., SP1, SP2, and SP3). For the samples SP4 and SP5, only one peak was detected for mean values of 3552 and 3149 nm, respectively. The data further showed that aggregation does exist in the methanol solution of the amphiphilic copolymers.

The thermal properties of the hybrids were characterized by DSC and TGA. When the amount of P2 units is lower (for SP1 and SP2), two T_gs were detected, and the higher one assigned to the P1 moiety becomes lower with the increase of P2 content, which indicated that the flexibility of the core chains strongly depended on that of the shell chains. In other words, the higher flexibility of P2 chains led to higher flexibility of P1 chains because of free energy transfer within one molecule. If the proportion of P2 becomes higher, each sample exhibits only one T_g, which suggests that the relatively independent flexibility of different blocks cannot be detected by the DSC measurements or the whole molecular chains having the same flexibility. In addition, the T_g corresponding to P2 blocks increased with increasing the **2**:**1** feed ratio, which is in agreement with the increasing tendency of molecular weights of the resulting copolymers. The parallel blending experiments showed that the higher T_g of P1 in the mixture became higher and higher if enhancing the ratio of P2, and the lower T_g of P2 is dramatically higher than that of the copolymer when the feed ratio is the same (Supporting Information S7). This showed that the hydrogen bonds between P1 and P2 influence the flexibility of molecular chains. Such comparative measurements and different results indicated that the P1 and P2 blocks covalently graft together in the hybrids.

The TGA results revealed that the main decomposition temperatures (T_ds) for the hybrids are ~380 °C, and T_d of SP5 is ca. 20−40 °C greater than those of other ones (Supporting Information S8), which may result from the higher molecular weight of SP5.

To explore the potentials of the suprabranched macromolecules, host−guest encapsulation[13,14] and other functions such as supramolecular self-assembly compared with the model (P1-*b*-PEO)[12] are in progress and will be reported later. We believe that the realization of the suprabranched polymers opens a door for the wider and deeper application of dendritic polymers and enlightens the exploration of other complex polymeric hybrids such as dendritic−hyperbranched macromolecules and even well-defined megamers.[3b]

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Supporting Information Available: Experimental details (S1); photographs for the samples placed in water (S2); GPC traces of SP5, SP1, and P1 (S3); ^1H NMR and quantitative ^{13}C NMR spectra of the samples (S4); specific viscosity of SP1 and SP5 as a function of concentration in methanol at 25 °C (S5); curves and results of dynamic light scattering measurements for the resulting copolymers in methanol solution (S6); DSC curves of the samples (S7); TGA curves of the samples (S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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