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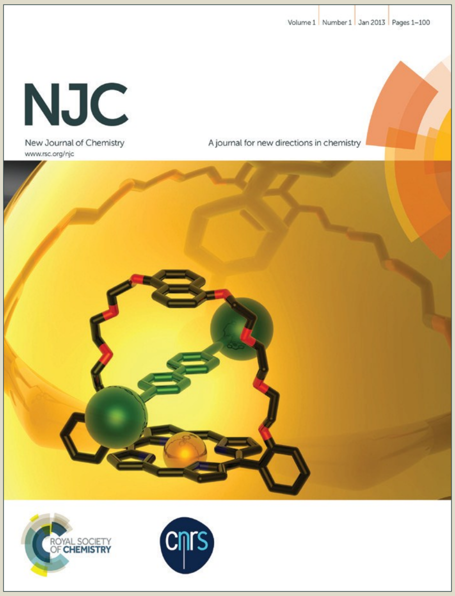

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Control-Synthesized Multilayer Hyperbranched-Hyperbranched Polyethers with Tunable Molecular Weight and Invariant Degree of Branching

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Abstract

A strategy to synthesize multilayer hyperbranched-hyperbranched macromolecules with invariant degree of branching (DB) and controllable molecular weight (MW) is realized by taking advantages of competing reactions. The invariant DB and tunable MW lead to hyperbranched molecules with controlled sub-nano to nano pores, which have potential applications in supramolecular capsulation, gas storage, separation, and catalysts. Hyperbranched molecules with low MW are obtained in one-pot reaction due to the competing reactions between AB_2 monomers. For our systems, hyperbranched molecules with much higher yet controlled MW can be achieved by adding additional batches of the same AB_2 monomers. When different AB_2 monomers with different spacer lengths are fed alternatively, multilayer core-shell hyperbranched macromolecules with controlled layer thickness or MW are obtained. More importantly, the multilayer hyperbranched-hyperbranched macromolecules show not only tunable MW but also invariant DB. In addition, it is found that the T_g of core-shell hyperbranched molecules is mainly determined by the outermost layer.

1. Introduction

Porous organic polymers (POPs) have attracted lots of attention due to their potential applications in catalysis, gas storage, and chemical separations.[1-4] Among the various type of POPs, hyperbranched polymers (HBP) are a new type POPs.[5,6] Depending on the internal structure and molecular weight (MW), HBP show internal cavities ranging from several angstroms to several nanometers, which could be used as sub-nano to nano pores materials without self-assembly.[7-9] In perfect dendrimers, MW and internal cavities cannot grow infinitely due to the overcrowded outmost layers.[10,11] In contrast, the cavities in HBPs, which are also cheaper and easier to produce, do not have upper limits as implied from the monotonic increasing intrinsic viscosity as a function of MW.[12-14] Thus, compared with dendrimers, HBPs afford more inner cavities and are more suitable as candidates for polymers with intrinsic nano-porosity. The internal cavity of HBP depends on many factors, including MW, molecular weight distribution (MWD), degree of branching (DB), and backbone structures; however, when MW of HBPs increases, MWD and DB often change in an uncontrolled way due to the random growth nature during polymerization and render uncontrolled internal pore sizes.[15-17] In addition, when scale-up production is needed, these parameters tend to change with reactor size, mixing condition, and temperature gradient, which further compromise the controllability.[18,19] Thus, the key to produce HBPs with controlled pore size is to control MW, MWD and DB simultaneously. Although progresses have been made in the control-synthesized HBPs,[20-22] controlling all three parameter simultaneously has remained a challenge.

Among the various types of HPBs, hyperbranched-linear type core-shell hyperbranched polymers (HLCSP), which are prepared by attaching linear chains at peripherals of hyperbranched cores, have been reported extensively;[23-25] however, hyperbranched-hyperbranched type core-shell polymers (HHCSPs), in which a hyperbranched shell is built on the top of an existing hyperbranched core, have been explored only by a few research groups due to synthesis difficulties and controllability issues.[26-28] Compared with HLCSP, HHCSP is more effective in producing larger yet controllable inner cavity,[23-25] which is crucial in applications such as small compound encapsulation, catalysts, molecular separation, hydrogen storage, and low κ materials. Gao et al.[29] reported an amphiphilic HHCSP HBP, which could be a potential candidate for self-assembly applications; Xu et. al[30] reported a series of HHCSP with conjugated structures, whose fluorescent emission can be tuned over a wide range of wavelengths by changing the ratio of core to shell. Loontjens[31,32] also reported a three-layer HHCSP; after functionalized by antimicrobials, the hyperbranched polymer shows high efficiency in contact-killing of bacteria. However, those aforementioned systems cannot simultaneously control MW, MWD, and DB, which are the main factors controlling internal cavities of HBPs. Recently, we showed that hyperbranched polyethers (HBPEs) with invariant DB can be achieved by taking advantage of competing reactions between AB_2 monomers[33] (see Scheme 2a). However, in the one-pot reaction, only low MW hyperbranched molecules are obtained, which is good for toughening applications[18] but not for producing nanoporous polymers.

In this paper, for the first time, layer-by-layer hyperbranched-hyperbranched polyethers using the same as well as different AB_2 monomers were demonstrated. The obtained layer-by-layer hyperbranched-hyperbranched polyethers not only have invariant DB, but also show controlled MW, MWD, and tunable backbone structure, which could be used to produce hyperbranched molecules with tunable internal cavities.

2. Experimental

2.1. Materials

1,2-dibromoethane (98%) and 1,6-dibromohexane (98%) were purchased from Beijing Ouhe Technology *Co.* Phenol and *p*-toluenesulfonic acid (PTSA) were purchased from Tianjin Fuguang reagent *Co.*, China. 2-Phenoxyethylbromide (98%) and 4-hydroxylbenzaldehyde (PHBA, 98%) was purchased from Zhongsheng Huateng Reagent Co., China. 4-bromo-1-butene (98%) was purchased from Energy Chemical Co., China. Other solvents and reagents were obtained from Beijing reagent Co. N,N-dimethyl formamide (DMF) were dried before use. All chemical agents were analytical pure and used as received unless otherwise stated.

2.2. Synthesis of 2C-AB$_2$ monomer[14]

2C-AB$_2$ monomer is synthesized following a two-step reaction, and the synthesis route is shown in Scheme 1. In the first step, PHBA (24.4 g, 0.2 mol), 1, 2-dibromoethane (150.4 g, 0.8 mol), K_2CO_3 (55.2 g, 0.4 mol), and 1 L ethanol were added into a three-necked flask. Under mechanical stirring, reactants were refluxed for 10 h. The resultant mixture was filtered, and then ethanol was removed using a rotary evaporator. The obtained crude product was purified by silica gel column using CH_2Cl_2/petroleum ether (1:1) as the eluent. The obtained 4-(2-bromine-oxethyl)-benzaldehyde is a light green crystal-like solid (Yield: 38.02 g, 83%). Note that the crude product can be used directly in the second step without purifying, because byproducts can be automatically removed the second step. ^{1}H-NMR (600 MHz, $CDCl_3$, δ): 3.65 (t, 2H, OCH_2CH_2Br), 4.35 (t, 2H, OCH_2CH_2Br), 6.99 (d, 2H, C_6H_4O), 7.81 (d, 2H, C_6H_4O), 9.87 (s, 1H, PhCHO). ^{13}C-NMR (600 MHz, $CDCl_3$, δ): 28.56, 67.95, 114.89, 130.45, 132.01, 163.00, 190.70.

In the second step, the product (23.0 g, 0.10 mol) from the first step and phenol (47.0 g, 0.5 mol), were added into a three-necked flask and heated to 45 ^{o}C under mechanical stirring. After a clear solution was obtained, PTSA (1.9 g, 10 mmol) and $ZnCl_2$ (1.4 g, 10 mmol) were added, and the mixture was stirring for 24 h at 45 ^{o}C. In post treatment, the mixture was washed with hot water (>70 ^{o}C) twice to remove residual salts, and then distilled at 150 ^{o}C to remove phenol. Finally, the product was purified by silica gel column using 1:5 ethyl acetate/petroleum ether as the eluent. The obtained 2C-AB$_2$ is a yellow solid. Yield: 17.56 g, 44%. ^{1}H-NMR (600 MHz, acetone-d6, δ): 3.76 (t, 2H, OCH_2CH_2Br), 4.33 (t, 2H, OCH_2CH_2Br), 5.38 (s, 1H, $CHPh_3$), 6.76 (d, 4H, C_6H_4O), 6.89 (d, 2H, C_6H_4O), 6.94 (d, 4H, C_6H_4O), 7.06 (d, 2H, C_6H_4O), 8.15 (s, 2H, PhOH). ^{13}C-NMR (600 MHz, acetone-d6, δ): 30.29, 54.30, 67.99, 114.29, 114.87, 130.05, 130.17, 135.64, 138.03, 155.64, 156.65.

2.3. Synthesis of 6C-AB$_2$ monomers[14]

6C-AB$_2$ monomer was synthesized following similar method described in 2C-AB$_2$. NMR results are as follows:

4-(6-bromine-hexyloxy)-benzaldehyde: brown viscous liquid, yield 80%; ^{1}H-NMR (600 MHz, $CDCl_3$, *δ*): 1.48-1.56 (m, 4*H*, $O(CH_2)_2(CH_2)_2(CH_2)_2Br$), 1.81-1.87 (m, 2*H*, $OCH_2CH_2(CH_2)_4Br$), 1.88-1.96 (m, 2*H*, $O(CH_2)_4CH_2CH_2Br$), 3.45 (t, 2*H*, $O(CH_2)_5CH_2Br$), 4.05 (t, 2*H*, $OCH_2(CH_2)_5Br$), 6.99 (d, 2*H*, C_6H_4O), 7.83 (d, 2*H*, C_6H_4O), 9.88 (s, 1*H*, PhCHO); ^{13}C-NMR (600 MHz, $CDCl_3$, δ): 25.19, 27.84, 28.86, 32.59, 33.72, 68.12, 114.73, 129.10, 131.97, 164.13, 190.75.

6C-AB$_2$: pink crytal-like solid; yield 40%; ^{1}H-NMR (600 MHz, acetone-d$_6$, *δ*): 1.48-1.58 (m, 4*H*, $O(CH_2)_2(CH_2)_2(CH_2)_2Br$), 1.75-1.82 (m, 2*H*, $OCH_2CH_2(CH_2)_4Br$), 1.87-1.93 (m, 2*H*, $O(CH_2)_4CH_2CH_2Br$), 3.51 (t, 2*H*, $O(CH_2)_5CH_2Br$), 4.97 (t, 2*H*, $OCH_2(CH_2)_5Br$), 5.36 (s, 1*H*, $CHPh_3$), 6.76 (d, 4*H*, C_6H_4O), 6.85 (d, 2*H*, C_6H_4O), 6.95 (d, 4*H*, C_6H_4O), 7.03 (d, 2*H*, C_6H_4O), 8.14 (s, 2*H*, PhOH). ^{13}C-NMR (600 MHz, (methyl sulfoxide)-d6, δ): 25.19, 27.79, 29.06, 32.66, 35.44, 54.12, 67.66, 114.48, 115.41, 130.22, 130.25, 135.49, 137.37, 155.94, 157.27.

2.4. Synthetic procedures for layer-by-layer HBPE

The synthetic route for layer-by-layer HBPE is given in Scheme 2b. Based on the batch feeding number of 2C-AB_2, the resultant products are labelled as HBPE2C-1, -2, -3, -4, and -5, respectively.

2.4.1 Synthesis of HBPE2C-1

2C-AB_2 (8.0 g, 20 mmol), K_2CO_3 (5.44 g, 40 mmol), and 200 mL DMF were added into a three-necked flask. Under mechanical stirring, the mixture was heated to 80 ^oC for 24 h under a dry nitrogen atmosphere, acidified with hydrochloric acid, and then filtered. The filtrate was precipitated into excessive water to remove residual salts and DMF. The obtained product was dissolved in THF and added dropwise into 2:1 or 3:1 ethanol/water solution under strong agitation. The precipitate was collected, washed with ethanol, and dried under vacuum at 90 ^oC to give a brick red solid product. Yield: 4.9 g, 77%.

2.4.2 Synthesis of HBPE2C-2

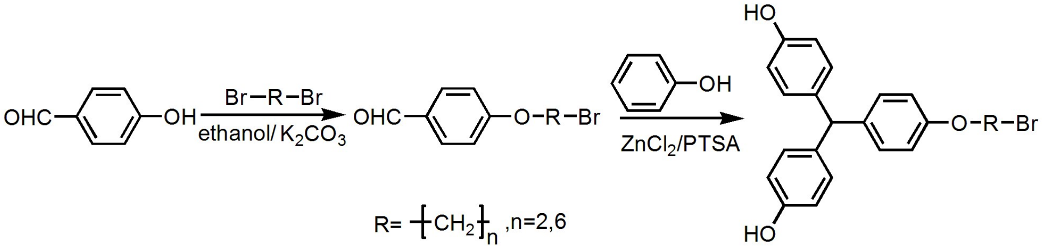
HBPE2C-1 (3.2 g, 0.86 mmol), K_2CO_3 (6.21 g, 45 mmol), and 100 mL DMF were added into a three-necked flask. After HBPE2C-1 was dissolved, 2C-AB_2 (4 g, 10 mmol) was added. Under mechanical stirring, reactants were heated to 80 ^oC and reacted for 24 h under a dry nitrogen atmosphere. The post treatment was similar as in HBPE2C-1. The resultant HBPE2C-2 is a brick red solid with a yield of 81%.

2.4.3 Synthesis of HBPE2C-3, -4, and -5

HBPE2C-3, HBPE2C--4, and HBPE2C--5 were synthesized using similar procedures as described in HBPE2C-2. In each stage, the HBPE2C formed in previous stages was used as a core for the next stage. All products are brick red solid with a yield of at least 80%.

2.5. Synthesis of HBPE with core/shell structures

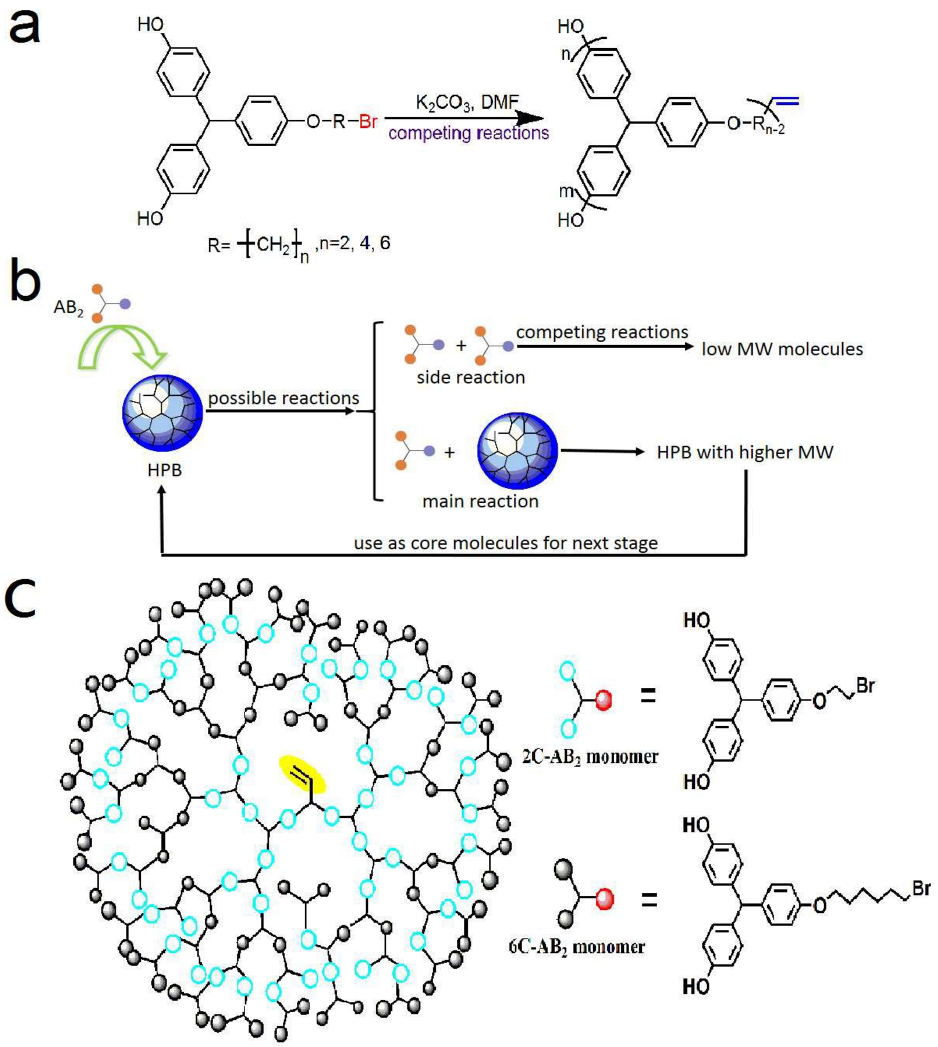
The core/shell HBPEs were obtained using similar method as in the layer-by-layer HBPE, and the synthesis route is shown in Scheme 2c. Core/shell HBPEs with two and four layers are labelled C2-C6, C2-C6-C2 and C2-C6-C2-C6, respectively. Typical procedures for synthesizing C2-C6 are shown below. HBPE2C-1 (3.2 g, 0.86 mmol), K_2CO_3 (6.21 g, 45 mmol), and 100 mL DMF were added into a three-necked flask. After HBPE2C-1 was dissolved, 6C-AB_2 (4.28 g, 10 mmol) was added. Under mechanical stirring, reactants were heated to 80 °C and reacted for 24 h under a dry nitrogen atmosphere. The post treatments were using similar procedures as in the case of HBPE2C-1. The resultant C2-C6 is a brick red solid with a yield of 83%.



Scheme 1. The synthesis route for AB_2 monomer.[14]

2.6. Characterization

Nuclear magnetic resonance (NMR) spectra were collected on a Bruker AV-600 spectrometer (600 MHz). Chemical shifts in NMR are reported in ppm. Molecular weights of HBP were determined using a Waters 515-2410 gel permeation chromatography (GPC), which was calibrated with polystyrene calibration standards and tetrahydrofuran (THF) was used as the eluent. T_g values were determined using a DSC-1 (Mettler-Toledo, Switzerland) differential scanning calorimeter, which is equipped with an intra-cooler. T_gs were obtained on second heating runs (typically 10 K/min) under a dry nitrogen atmosphere (40 ml/min). All measurements were all performed at 25±3 °C unless otherwise stated.



Scheme 2. (a) The synthesis route for one-pot HBPEs; (b) the route for layer-by-layer HBPE; (c) the schematic structure of multilayer hyperbranched-hyperbranched type core/shell HBPEs.

3. Results and Discussion

Our results are divided into two sections: (1) proof of controllability in layer-by-layer HBPE by batch feeding of the same monomers and (2) demonstration of control-synthesized multi-layer HHCSP HBPEs by batch feeding of different AB_2 monomers which have different spacer lengths.

3.1. Control-synthesized layer-by-layer HBPE using the same monomer.

During AB_2 polymerization, the molecular weight distribution (MWD) is wide because reactions between A and B groups often occur in a random fashion.[34] In addition, MW, MWD and DB often change with reactor size, mixing condition, and temperature gradient, which result in poor controllability and scalability. However, as shown previously,[14] when side reactions between A and B groups compete with the propagation reaction (see Scheme 2b), controllability and scalability could be achieved. In particular, for our series of AB_2 monomers, the formed HBPE with invariant DB and controlled MW can be readily achieved. The elimination side reaction converts reactive -Br groups to unreactive C=C in a short time and leads to a steady-state low MW composition (see Figs. S1 and S16). Thus, it is reasonable to believe that adding additional batches of monomers into the already-stabilized systems should reinitiate the reaction and yield HBPEs with controlled higher MW and invariant DB; and the proof is given below.

When new AB_2 monomers are added into the already-stabilized system, they can either react with other monomers or with already-formed hyperbranched molecules. Because the already formed hyperbranched molecules have larger surface area, newly added monomers prefer to react with hyperbranched molecules (which act as core molecules) rather than other monomers. If excessive monomers were added, chances are that more percentage of newly added monomers can react within themselves and compromise controllability. Theoretical prediction has been done by Yan et al for AB_2 polymerization in the absence of side reactions.[36] However, for reacting systems with competing side reactions, theoretical prediction can hardly accurate predictions, and experimental verification is necessary. In order to better controlled MW, pre-calculated amounts of monomer were fed in each additional batch. The pre-calculated amounts in each batch were based on average degree of polymerization (DP) and number-average molecular weight of HBPE formed in the previous stage (M_{np}):

$$m = m_p \div M_{np} \times DP \times M_{AB2}$$

where M_{AB2} is the monomer MW; m and m_{p} are the weights of newly added monomer and HBPE formed in previous stage, respectively. A brief derivation of the above equation is given below. "$\mathrm{m_p \div M_{np}}$" is moles of HBPE formed in previous stage, and multiplying it by DP ($\mathrm{m_p \div M_{np} \times DP}$) amount to moles AB_2 structural unit; further multiplying with $\mathrm{M_{AB2}}$ leads to the weight of newly added monomer.

MW was determined by both GPC and NMR methods. Recent studies showed that GPC-determined MW is very close to true values when M_{n} is less than 10 kDa,[35] and validation will be given when discussing NMR data. The normalized GPC curves of HBPEs after each batch are shown in Fig. 1. For easy comparison, the number-average MW (M_{n}) and the weight-average MW (M_{w}) after each batch are shown in Figs. 2a and 2b, respectively. Both

M_n and M_w increase linearly with the number of batch feeding (or batch number). The GPC-determined M_n and M_w, as well as calculated M_n assuming that all added monomers only react with already-existed HBPE (core molecules), are compared in Table 1. As the batch number or M_n increases, deviation between measured and calculated values increases. In each batch, the amount of added monomers is based on M_n and DP of already-formed HBPE in the previous stage; however, as the HBPE "core" molecules become bigger, mixing efficiency and steric hindrance may become important, which may contribute to the deviation at high batch numbers. In addition, as M_n approaches 10 kDa, the GPC-determined M_n may be somewhat underestimated. When newly added monomers react with other monomers, they can form low MW HBPE, which can be removed in post treatment. Thus, no corresponding peaks for low MW HBPEs are detected (see Fig. 1).

Despite the small deviation (see Table 1), both M_n and M_w vary linearly with batch number. The linear relationship allows us to produce HBPEs with projected M_n and M_w. It is worth mentioning that our post treatment only remove low MW oligomers. Although M_n is sensitive to low MW fraction, M_w is not. The calculated MWD (i.e., M_w,/M_n) is smaller if low MW fraction is removed, which is a reason why MWD is narrower. In addition, it has been shown that adding core molecules with high functionality can lower MWD. In our systems, when batch number increases, the functionality of the already-formed HBPE "core" molecules also increases, which leads to increasingly narrower MWD (see Table 1).[36,37]

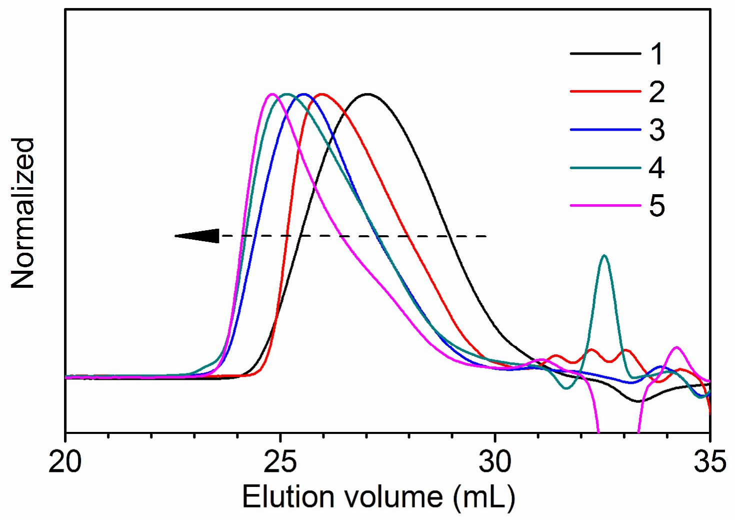


Fig. 1. Normalized GPC curves after each batch feeding. The numbers represent the batch feeding numbers.

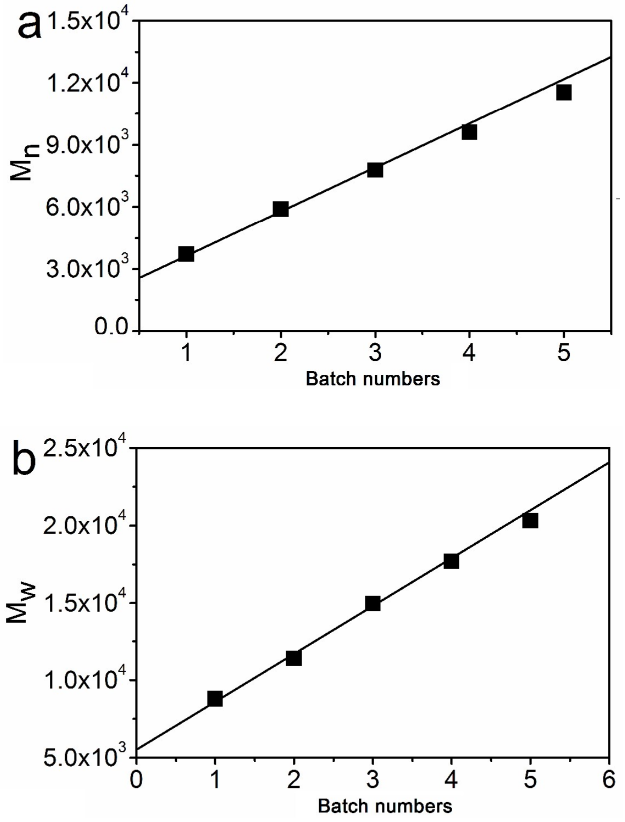


Fig. 2. Variation of (a) M_n and (b) M_w with batch numbers.

Table 1.

Characterization results of layer-by-layer HBPEs.

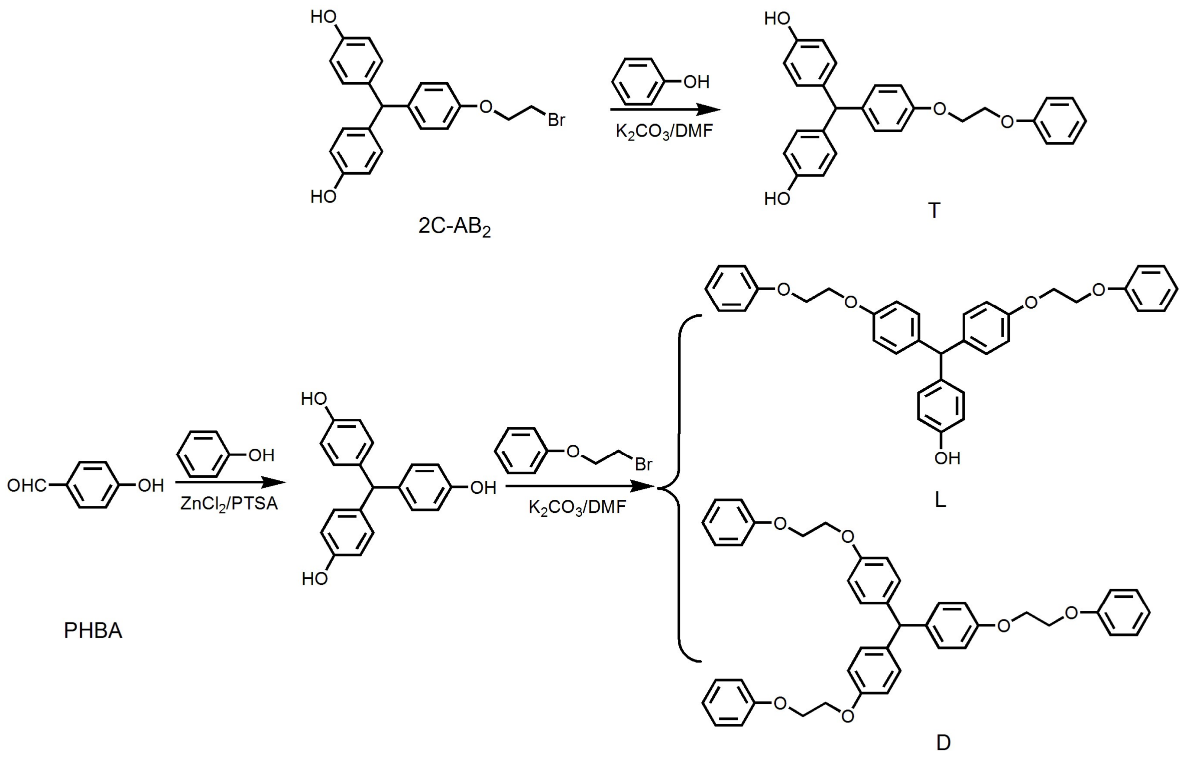
Code[a]	M_n[b] (kDa)	M_w (kDa)	PDI	DB[c]	T_g (°C)	Calculated M_n (kDa)
HBPE2C-1	3.7	7.4	2.0	0.56	123	
HBPE2C-2	5.9	11.4	1.9	0.57	124	7.4
HBPE2C-3	7.8	15.0	1.9	0.57	126	10.8
HBPE2C-4	9.6	17.7	1.8	0.58	133	15.6
HBPE2C-5	12.3	21.0	1.7	0.58	135	19.2

[a] The first numbers represent the number of carbon atoms in spacer. The second numbers corresponds to the batch numbers; [b] M_n obtained from GPC results; [c] DB is calculated according to Hawker's definition using ^{1}H NMR.

Aside from MW and MWD, degree of branching (DB) also plays important roles in determining the controllability and internal cavities of hyperbranched molecules. Based on NMR results, DB as defined by Hawker and Fréchet[38] can be calculated as

$$DB=(D+T)/(D+T+L)$$

where D, T and L are numbers of dendritic, terminal, and linear units, respectively. In order to assign chemical shifts to the dendritic, terminal, and linear units, three model compounds with well defined NMR peaks for D, L, and T units, were synthesized (see Scheme 3). For low MW HBPE2C-1, three types of peaks corresponding to Ph_3H protons are indentified. However, for high MW HBPE, three types of peaks are not fully separated and have to be deconvoluted by assuming Gaussian peaks. For example, the deconvolution of HBPE2C-5 peaks is shown in Fig. 3b. The DB values of HBPE2C are summarized in Table 1. Despite the different MW, all HBPE2C samples show similar DB (~0.57). In typical AB_2 polymerization, when the molecules grow bigger, the steric hindrance effects become more important, which often leads to a lower degree of branching (DB). However, in our reacting systems, DB is not sensitive to MW, which can be related to the following factors: (1) based on probability theory, newly added monomers would prefer to react with the already-formed HBPE that have higher functionalities (“core” molecule), rather than react with other monomers with lower functionalities. Many papers have shown that addition of multifunctional core molecules can help reduce polydispersity and DB; (2) in typical AB_2 polymerization, reactions between different reacting species react in a random fashion, which is dictated by statistics; however, in our case, the competing reactions lead to an inactive reactive “A” group after several hours, making the system a thermodynamically controlled system (i.e., a steady state). The inactive “A” groups can reduce the possible coupling reaction between different HBPE polymers. In addition, post-treatment could remove the unreacted monomers and low MW oligomers, which also contributes to the insensitivity of DB to MW. The invariant DB in HBPEs is favorable for producing HBPs with controlled inner cavity, which has not been reported in other HBPs using the one-pot approach.



Scheme 3. The synthesis route of model molecules which have well defined ^{1}H NMR peaks of terminal (T), linear (L) and dendritic (D) units, respectively.

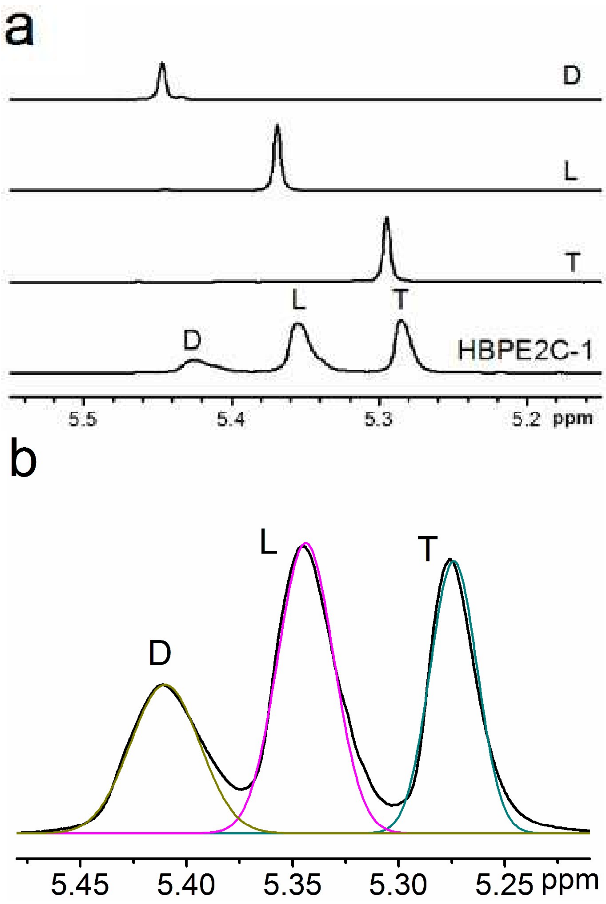


Fig. 3. (a) ^{1}H NMR spectra of three model compounds with well-defined dendritic (D), linear (L), and terminal (T) units. Isolated peaks of HBPE-2C-1 at corresponding locations are also shown. (b) The typical curve-fitting result for HBPE2C-5 showing the deconvolution of each type of structural unit.

3.2 HBPEs with core/shell structures

Following the same methodology used in synthesizing the layer-by-layer HBPE (including reaction condition, amounts of monomers in each batch, and post treatment), core/shell HPBE can be obtained by feeding AB_2 monomers with different spacer lengths (Scheme 2c) alternatively. For AB_2 monomers with longer space length (n>6, Scheme 2a), intermolecular cyclization reactions may occur and thus compromise controllability. Thus, AB_2 monomers with shorter space length (*i.e.*, n=2 and n=6) were used. By alternative feeding of 2C-AB_2 and 6C-AB_2 monomers, HBPEs with core/shell structure were obtained.

The structure of core/shell molecules were confirmed by ^{1}H NMR (Fig. 4). Peak b (~4.2 ppm) corresponds to protons in 2C alkyl chains, and peak c (~3.9 ppm), peak d (~1.7 ppm), and peak e (~1.4 ppm) correspond to protons in 6C alkyl chains. As aforementioned, GPC-determined MW may deviate from actual values when MW is larger than 10 kDa.[35] Because the GPC-determined M_n of HBPE-2C-1 (formed in the 1st batch) is only 3.7 kDa, no appreciable deviation is expected. In order to confirm this, terminal phenol groups in HBPE-2C-1 were fully converted to benzyl groups (Fig. S2), which has been confirmed by NMR (Fig. S3) and FTIR (Fig. S4). In Fig. S3, The peak area ratio between a (~5.4) and b (~5.0) reflects the relationship between the number of terminal groups and that of AB_2 structural units (i.e., the MW is directly related to peak area ratios); thus by evaluating the peak area ratio between peak a and peak b, the absolute MW of HBPE-2C-1 can be calculated. It turns out that the NMR determined M_n is also 3.7 kDa, which agrees perfectly with GPC results. Based on M_n of the first layer, by calculating ratios of corresponding peak areas in NMR, absolute M_n values of additional layers can be calculated based on the peak area of b and c (Fig. 4), and the degree of polymerization (DP) of HBPE formed in the previous stage; the results are shown in Table 2. When M_n is less than 10 kDa, M_n obtained from both NMR and GPC agrees well for the first three layers; however, when M_n exceeds 10 kDa (*i.e.* for the 4th or higher layers) deviation was observed. This may partially explain the negative deviation of M_n in the above-mentioned high MW layer-by-layer HBPE2C. Due to overlapping in NMR peaks, DB of HHCSP HBPE cannot be obtained accurately using NMR data. As shown previously[18-19] and in layer-by-layer HBPEs, DB of HBPEs is insensitive to monomer spacer length (*i.e.*, 2C, 4C, and 6C). Thus, it is not likely that DB of core/shell HBPE should be sensitive to layer number. As a result, multi-layer HHCSP HBPEs with invariant DB, increasingly narrower MWD, and programmable MW could be achieved using our methodology.

It is challenging to synthesize HPBs with well-defined core/shell structure due to the random growth nature in AB_2 polymerization. When another type of AB_2 monomers are added into the already formed HPB reacting system, the newly added monomers also prefer to react with hyperbranched core molecules and yield a core/shell hyperbranched-hyperbranched molecule. Due to the possible steric hindrance at higher MW and side reactions (*i.e.*, self-polymerization of monomers and coupling of HPB core molecules), MWD and DB often change notably as reaction proceeds; however, it is not the case in our systems. Due to competing reactions, the self-polymerized monomers can only form low MW oligomers, which can be easily removed in the post treatment. As a result, narrower MWD, invariant DB and controlled MW of HHCSP HBPE can be obtained.

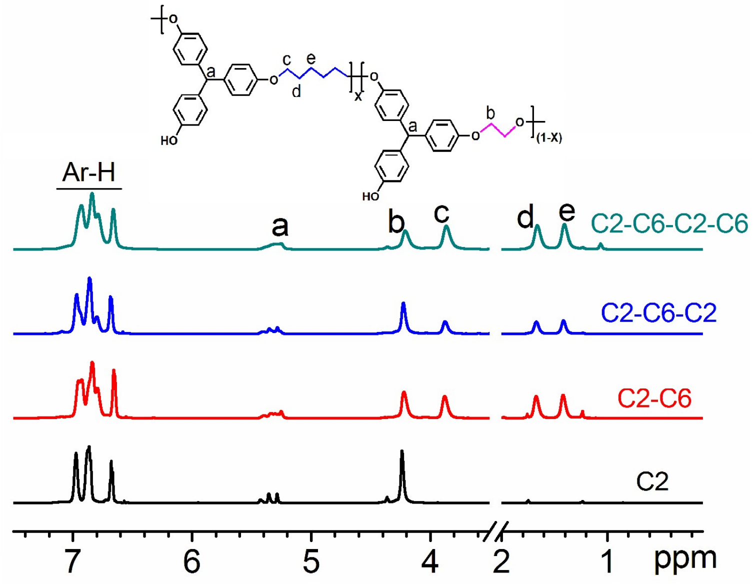


Fig. 4. ^{1}H NMR spectra of HBPEs with core/shell structure.

Table 2

Characterization results of HBPEs with core/shell structure.

Code^a	M_n^{b} (kDa)	M_w (kDa)	MWD	Calculated M_n^{c} (kDa)	T_g (°C)	ΔT_g (°C)
HBPE2C-1 or C2	3.7	7.4	2.0		123	7.7
C2-C6	7.8	15.7	2.0	7.4	111	7.7
C2-C6-C2	10.0	19.1	1.9	10.7	120	7.3
C2-C6-C2-C6	11.9	23.1	1.9	15.5	112	7.5

^{a}Core/shell HBPESs from the first layer to the fourth layer are named C2, C2-C6, C2-C6-C2 and C2-C6-C2-C6 respectively; ^{b}M_ns were determined from GPC measurements; ^{c}Calculated M_n based on ^{1}H NMR results.

For layer-by-layer HBPE using the same monomer, when M_n increases from 3.7 to 12.3 kDa, T_g increases only ~10 ºC (Table 1), showing a weak MW dependence. However, for HHCS HBPEs (see in Fig. 5), the alternative change in T_g with layer number suggests that T_g of HHCS HBPE is mainly determined by the structure of the outermost layer, rather than M_n and internal structure. In addition, the width of T_g (ΔT_g), which is defined as the difference between the extrapolated onset and endset temperatures, could provide additional information on molecular structure. As shown in Table 2, HHCSP HBPEs of different layers show similar ΔT_g despite the different internal backbone structures. This finding is important when HHCS HBPE is used as non-phase-separated tougheners for thermosets,[39-42] because it allows us to design core-shell modifiers with a flexible internal backbone, which could improve toughness, yet still keep a high T_g, which could maintain a high overall T_g.

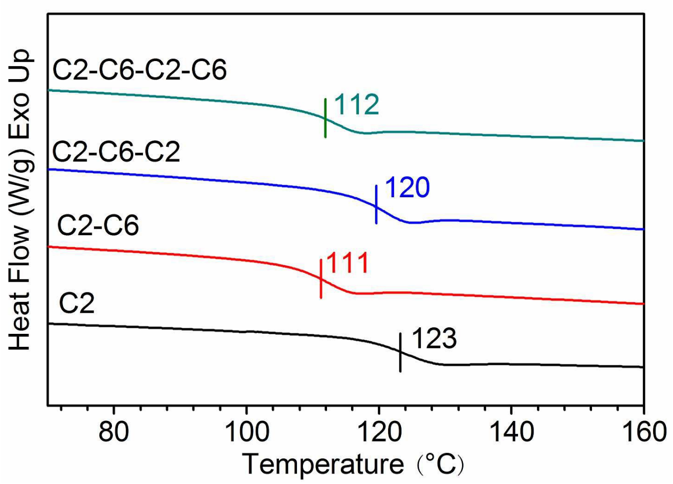


Fig. 5. T_gs of HBPEs with core/shell structure.

4. Conclusions

Layer-by-layer and multi-layer hyperbranched-hyperbranched core-shell type hyperbranched polyethers with tunable M_n, backbone stiffness, and invariant DB and MWD were realized by batch feeding the same or different AB_2 monomers. The invariant DB and good controllability in MW are due to the competing reactions between monomers. The tunable M_n and increasing narrower MWD of multilayer HBPEs are ascribed to the preferential reaction of newly added monomers to the already-formed HBPE core, the pre-calculated batch feeding method, and post treatment. In addition, it is found that T_g of multi-layer HHCS is mainly determined by the chemical structure of outermost layer, rather than internal structure and M_n. Both layer-by-layer HBPE and multilayer HHCS HBPE show tunable M_n, invariant DB and increasing narrower MWD, which can serve as ideal platforms for designing hyperbranched molecules with controlled sub-nano to nano pores.

Acknowledgments

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Supporting information

Details of synthetic procedures of model compounds and relevant characterization results.

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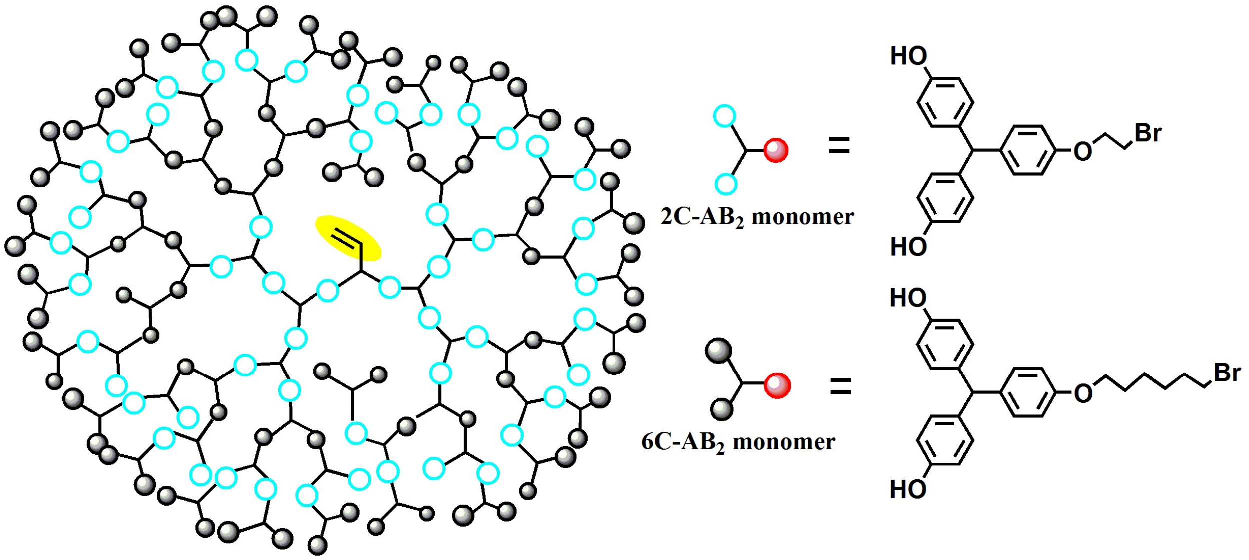
Control-Synthesized Multilayer Hyperbranched-Hyperbranched Polyethers with Tunable Molecular Weight and Invariant Degree of Branching

Tuan Liu[1,2], Xuepei Miao[1,2], Xinxin Geng[1], An Xing[1], Liangdong Zhang[2], Yan Meng[1,*] and Xiaoyu Li[2,*]



Multilayer hyperbranched-hyperbranched polyethers with tunable M_n, invariant DB were reported for the first time.