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Hyperbranched polyethers with tunable glass transition temperature: controlled synthesis and mixing rules

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By taking advantage of competing side reactions, controlled synthesis of a series of homo- and co-polymerized hyperbranched polyethers (HBPEs) is demonstrated using a series of AB_2 monomers of different spacer lengths. This reacting system shows good controllability and scalability. More importantly, the degree of branching is found to be insensitive to molecular weight and the spacer length
10 in monomers. Thus, the value and width of T_g can be tuned by varying monomer spacer length, terminal groups, molecular weight, as well as by copolymerization and physical blending. The dependence of T_g in binary homopolymers blends on composition and the dependence of T_g in copolymers on monomer ratio are established and compared for the first time. T_g of copolymers obeys Fox equation, whereas T_g in binary blends only follows Kwei equation. Copolymerization does not increase the width of T_g. In
15 contrast, the width of T_g in binary blends is much broader than that of copolymers, even though the broadening in T_g can be reduce by increasing the polarity of terminal groups.

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Introduction

Hyperbranched polymers (HBPs) have been a hot research area[1]
20 for two decades due to their unique structures, such as highly branched structure, compacted shape, ample and modifiable terminal groups. The special structure imparts unique properties and leads to wide applications in various fields.[2] Properties of HBPs depend on many factors, including backbone structure,
25 terminal group, molecular weight (MW), and degree of branching (DB).[3] However, the random growth nature in one-pot synthesis often lead to poor controllability, which is a big issue not only for industrial applications but also for in-depth scientific studies.[4] Progress has been made to target that issue; however, most efforts
30 have been focused on controlling molecular weight distribution (or polydispersity, PDI) and degree of branching (DB).[8] On one hand, addition of polyfunctional core and slow monomer addition are found to be effective in lowering PDI to as low as 1.3.[5] For certain reacting systems in which the reactivity of formed
35 oligomers is much higher than that of monomers, PDI can be further lowered to 1.13.[6] On the other hand, progress has also been made in controlling DB. High DB values (>90%) have been achieved using Suzuki-Miyaura coupling reaction[7] and click chemistry[8]. Recently, HBP with tunable DB (from 0 to 100%) has
40 been achieved by adjusting catalyst dosage.[9] Min and Cao[10] also showed that the micro-emulsion polymerization technique is beneficial in obtaining HPBs with high DB and low PDI.

The glass transition temperature (T_g) is the most important parameter for polymers and is closely related to mechanical,
45 thermal, and other properties.[11] However, due in large part to the poor controllability, controlled synthesis of HBPs with tunable T_g has not been reported, especially for HBPs with polar terminal groups. T_g of linear polymers depends on the chemical structure of backbone and MW.[12] T_g of HBPs, however, depends on more
50 factors[4], including backbone structure, terminal groups, DB, and MW and thus is more difficult to control. In HBPs, changes in MW are often accompanied by changes in DB, which is also an important factor in determining T_g, making the control of T_g more challenging. In one-pot synthesis of HBPs, the control of MW
55 without changing DB is notoriously difficult. In addition, reproducibility and scalability are also difficult to achieve when the reactor size changes. This paper is organized into three parts. First, one-pot controlled synthesis of a series of hyperbranched polyethers (HBPEs) with almost invariant DB, controllable MW,
60 and good scalability is presented using a series of AB_2 monomers with different spacer lengths. Second, the tuning of T_g was demonstrated using several ways, including varying monomer spacer length, terminal group, and MW, as well as physical blending and copolymerization. Third, the relationship between
65 the T_g of copolymers and monomer ratio and that between T_g of binary homopolymer blends and composition are compared in detail for the first time. Effects of terminal group on miscibility of binary blends were also discussed.

Experimental section

70 **Materials**

All chemicals were analytical pure and used as received unless otherwise stated. Phenol and p-toluenesulfonic acid (PTSA) were purchased from Tianjin Fuguang reagent Co., China. 1,2-dibromoethane (98%), 1,4-dibromobutane (98%), and 1,6-
75 dibromohexane (98%) were purchased from Beijing Ouhe

Technology Co., China. 2-Phenoxyethylbromide (98%), 4-hydroxybenzaldehyde (PHBA, 98%), and benzyl bromide (98%) were obtained from Zhongsheng Huateng Reagent Co., China. 4-bromo-1-butene (98%) was obtained from Energy Chemical Co., China. All other solvents and reagents were purchased from Beijing reagent Co., China. N,N-dimethyl formamide (DMF) were dried before use.

Characterization

Nuclear magnetic resonance (NMR) spectra were collected on a Bruker AV-600 spectrometer (600 MHz), and chemical shifts are reported in ppm. Fourier transform infrared spectroscopy (FTIR) spectra were collected on a Bruker Tensor 37 spectrophotometer using the potassium bromide (KBr) disc technique. Molecular weights of the hyperbranched molecules were determined using a Waters 515-2410 gel permeation chromatography (GPC) system which was calibrated using linear polystyrene calibration standards and with tetrahydrofuran (THF) as the eluent. T_g values of HBPEs were determined on second heating runs (typically 10 K/min) under a dry nitrogen atmosphere (40 ml/min) using a DSC-1 (Mettler-Toledo, Switzerland) differential scanning calorimeter, which is equipped with an intra-cooler. All measurements were performed at 25±3 °C.

Synthesis of AB_2 monomers

All three monomers were synthesized in a two-step procedure (Scheme 1). As an example, the procedure for synthesizing 2C-AB_2 (n=2) is given below. 4C-AB_2 (n=4) and 6C-AB_2 (n=6) were synthesized using similar procedures but with different reactants, and the characterization results are supplied in the supporting information (SI).

The first step is the synthesis of 4-(2-bromine-oxethyl)-benzaldehyde. Under mechanical stirring, PHBA (12.2 g, 0.1 mol), 1, 2-dibromoethane (75.2 g, 0.4 mol), K_2CO_3 (27.6 g, 0.2 mol), and 500 mL ethanol were added into a three-necked flask and refluxed for 10 h. After cooling to room temperature, the mixture was filtered, and ethanol was removed using a rotary evaporator. The crude product was purified using silica gel column chromatography (GPC) with CH_2Cl_2/petroleum ether (1:1) as the eluent. The obtained product is a light green crystal-like solid. Yield: 19.01 g, 83%. Please note that the crude product can be directly used in the next step without purifying, because byproducts can be automatically removed the next step. ^{1}H-NMR (600 MHz, CDCl3, δ): 3.65 (t, 2H, OCH2C*H*2Br), 4.35 (t, 2H, OC*H*2CH2Br), 6.99 (d, 2H, C6H4O), 7.81 (d, 2H, C6H4O), 9.87 (s, 1H, PhCHO). ^{13}C-NMR (600 MHz, CDCl3, δ): 28.56, 67.95, 114.89, 130.45, 132.01, 163.00, 190.70.

In the second step, 4-(2-bromine-oxethyl)-benzaldehyde (11.5 g, 0.05 mol), phenol (0.25 mol, 23.5 g), $ZnCl_2$ (0.7 g, 5 mmol), and PTSA (0.95 g, 5mmol) were added into a three-necked flask under mechanical stirring. After stirring for 1 h, reactants were heated to 45 °C for 24 h and then washed at least twice with hot water (>70 °C) to remove residual salts. After evaporation at 140 °C, most phenol was removed, and the crude product was then purified by silica column chromatography with 1:5 ethyl acetate/petroleum ether as the eluent, and the obtained 2C-AB_2 is a yellow solid. Yield: 8.78 g, 44%. ^{1}H-NMR (600 MHz, acetone-d6, δ): 3.76 (t, 2H, OCH2C*H*2Br), 4.33 (t, 2H, OC*H*2CH2Br), 5.38 (s, 1H, CHPh3), 6.76 (d, 4H, C6H4O), 6.89 (d, 2H, C6H4O), 6.94

(d, 4H, C6H4O), 7.06 (d, 2H, C6H4O), 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.

Typical polymerization procedure

Procedures for homo- and co-polymerizing different monomers are the same (Scheme 2), when describing the detailed procedure, 2C-AB_2 is used as an example. 2C-AB_2 (0.8 g, 2 mmol), K_2CO_3 (0.55 g, 4 mmol), and 20 mL DMF were added into a two-necked flask. Under magnetic stirring, reactants were heated to 80 °C for 24 h under a dry nitrogen atmosphere. After cooling to room temperature, the mixture was acidified with hydrochloric acid and filtered. The filtrate was precipitated into water to remove DMF and residual salts. The crude product was dissolved in THF and added drop wise into 2:1 ethanol/water solution under strong agitation. The precipitate was collected, washed with ethanol, and dried under vacuum at 90 °C to give a brick red solid product. Yield: 0.49 g, 77%.

Typical procedure for terminal group modification

The procedure for terminal group modification is shown in Scheme 4. 1 g HBPE-2C or HBPE-6C, 5.2 g benzyl bromide, and 1.8 g K_2CO_3 were added into 20 mL DMF. Under magnetic stirring, reactants were heated to 80 °C for 24 h under dry nitrogen atmosphere. After cooling to room temperature, the mixture was filtered and precipitated into petroleum ether twice. After the precipitate was dried under vacuum at 90 °C, the obtained benzyl-terminated HBPE-2C (BHBPE-2C) is a light red solid. Yield: 0.90 g, 70%. ^{1}H-NMR (600 MHz, CDCl3, δ): 4.22-4.30 (br, O-CH2CH2-O), 5.00-5.05 (br, Ph3CH2-O), 5.36-5.42 (br, Ph3CH), 6.80-7.44 (br, C6H4O).

Physical blending

Binary blends were prepared by dissolving two homopolymers in THF according to different designed weight ratios. After transparent solution was obtained, THF was removed completely in a vacuum oven at 90 °C.

Results and discussion

Synthesis of AB_2 monomers and HBPEs

The synthesis route for three AB_2 monomers of different spacer lengths (*i.e.*, n=2, 4, and 6) is shown in Scheme 1. In the second step, although both ortho- and para-substituted products are obtained.[13] The para-substituted products are the main products and will be used as monomers in later polymerization processes.

Using the three AB_2 monomers, which have different space length, a variety of homo- and co-polymerized HBPEs were prepared using one-pot polymerization. The synthesis route for homopolymerized HBPEs is shown in Scheme 2. Homopolymerized HBPEs synthesized from monomers of different spacer lengths, (*i.e.*, n=2, 4, and 6 in Scheme 1) are labelled as HBPE-2C, HBPE-4C, and HBPE-6C, respectively; suffixes "-1, -2, and -3" after "HBPE-nC" denotes different MWs. Polymerization reactions were carried out under nitrogen protection using water-free solvents. Two types of terminal groups were found in HBPEs: the double bond and the bromine
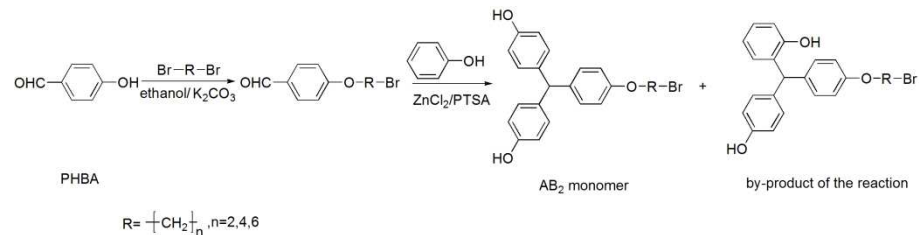
Scheme 1 The synthesis route of AB$_2$ monomer and its byproduct.
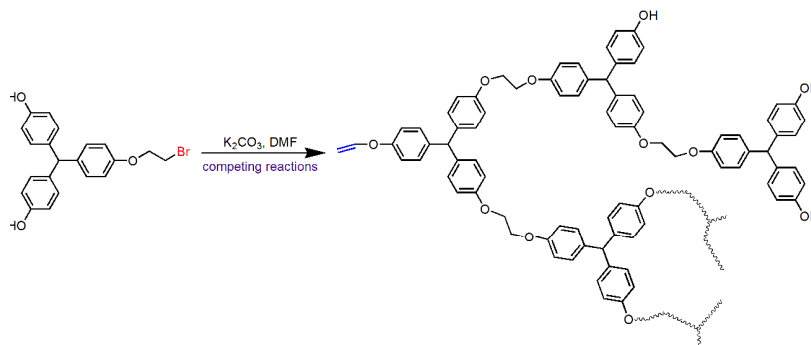
Scheme 2 Typical synthesis route for synthesizing homopolymerized HBPEs.

Table1 Characterization results of phenol-terminated HBPEs obtained at 80 ºC.

Code[a]	Concentration (mol/L)	M_n (kDa)	M_w (kDa)	PDI	T_g (°C)	DB[b]
HBPE–2C-1	0.10	3.8	6.8	1.8	127	0.53
HBPE–2C-2	0.20	6.0	12.6	2.1	129	0.51
HBPE–2C-3	0.40	7.3	18.3	2.5	131	0.50
HBPE–4C-1	0.10	3.5	6.0	1.7	101	0.51
HBPE–4C-2	0.20	4.1	7.8	1.9	109	0.51
HBPE–6C-1	0.10	4.2	8.4	2.0	93	0.53
HBPE–6C-2	0.20	8.9	22.3	2.5	97	0.53
HBPE–6C-3	0.40	10.0	27.0	2.7	99	0.50

[a] The first number in the code represents the number of carbon atoms in alkyl spacer, i.e., n in each structural unit. The second number in the code distinguish HBPEs of different MWs.
[b] Degree of branching is calculated according to Hawker's definition using ^{1}H NMR.

group. As shown in the ^{1}H NMR results (Fig. 1), Ph$_3$CH protons at ~5.3 ppm split into three peaks. For HBPE-2C, three peaks are well separated. As the spacer length increases, three peaks are closer to each other. Chemical shifts of Ph$_3$CH proton are affected differently by the dendritic (D), linear (L), and terminal (T) units and thus spilt into different peaks, which can be used to determine DB[14].

MW control in HBPEs

Effects of reaction condition, including temperature, monomer concentration, and reaction time, on MW were studied. Characterization results of homopolymerized HBPEs, which were all obtained at 80 ^{o}C, are summarized in Table 1. The MW was determined using GPC which was calibrated using linear polystyrene standards in the corresponding MW range. We note that the MW of HBP obtained from GPC may be smaller than

actual values. However, studies also show that for the MW of HBP is close to its actual value when MW is not very high (ca. 10000 g/mol).[13] HPBs show notable deviations only when the MW is high and the backbone structure is stiff. In our HBPEs, the
5 MW is not very high, and the backbone structure is not that stiff. Thus, no notable deviations from actual values are expected.

For easy comparison, normalized GPC curves corresponding to different reaction times (from 4 h to 72 h) are shown in Fig. 2. At 60, 80, and 100 °C, GPC results corresponding to 4 h and 6 h
10 almost overlap, indicating that MW and its distribution stabilize in 6 h. When temperature increases from 40 to 100 °C, number-average molecular weight (M_n) of HBPE-2C goes through a maximum at 80 °C (Fig. 3). The fast stabilization and temperature-dependence in M_n are somewhat unexpected, and
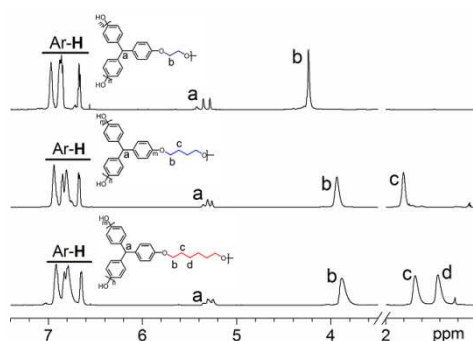15 explanations are offered in the following paragraph.

Fig. 1 ^{1}H NMR spectra of HBPEs obtained from monomers with different spacer length (*i.e.*, n = 2, 4, and 6).

20 Two assumptions were made in Flory's classic treatment of AB$_2$ polymerization[15]: the reactivity between A and B groups remain unchanged during polymerization; side reactions, such as intermolecular cyclization, are absent. Based on those assumptions, MW only stabilizes after long times when steric
25 hindrance become dominate, making MW sensitive to local reaction conditions, such as mixing and heat transfer. We realize that violation of any of the two assumptions can lead to some degree of controllability. Similar fast stabilization has been ascribed to intermolecular cyclization.[16] However, cyclization
30 cannot occur in our system due to the short spacer length in monomers, which has been confirmed by NMR. Rather, the elimination reaction[17], which competes with the main substitution (or propagation) reaction, is responsible. Comparing the corresponding peak areas in ^{1}H NMR spectra of HBPE-4C-2 (Fig.
35 4) to that of a model molecule, 4-bromo-1-butene (see Fig. S9 in SI) reveals that more than 70% Br group was converted to C=C after reacting at 80 °C for 24 h, which essentially terminates the substitution reaction and leads to a fast stabilization in MW. Thus, the relative speed of the elimination to substitution
40 reactions changes with temperature and lead to temperature-dependent MW. We note that fast stabilization is not achieved at 60 °C (Fig. 2A). This can be explained by the low reaction speeds of both elimination and substitution reactions at 60 °C, which lead to incomplete termination even after 4 h reaction. Thus, MW
45 continues to increase with time. In contrast, at the highest temperature of 100 °C, the elimination reaction is favored and leads to a decrease in MW (Fig. 3).
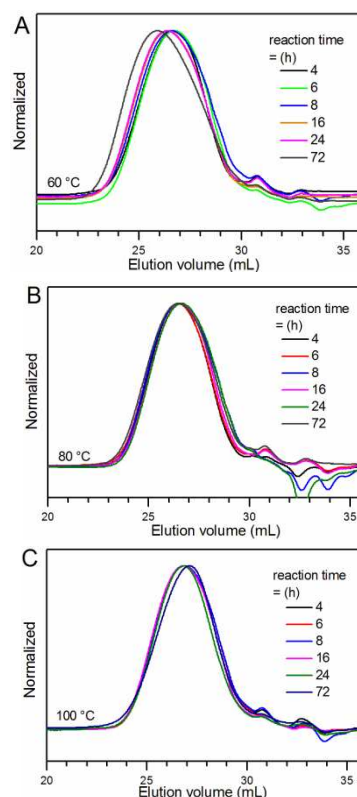

Fig. 2 Normalized GPC results of HBPE-2C as a function of
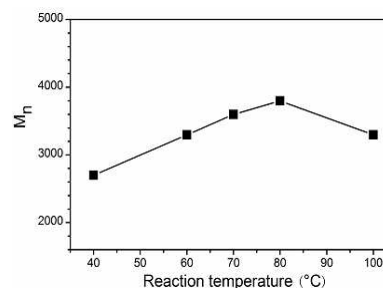50 reaction time for polymerization carried out at (A) 60 °C, (B) 80 °C, and (C) 100 °C.

Fig. 3 The variation of number-average molecular weight (M_n) of HBPE-2C with reaction temperature when polymerized for 24 h
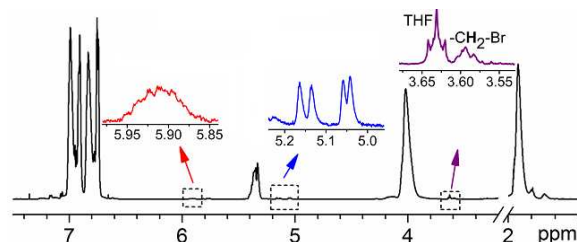55 and at a monomer concentration of 0.1 mol/L.

Fig. 4 The ^{1}H NMR spectrum of HBPE-4C-1 (80 °C, 24 h). Insets show the enlarged views of boxed parts.

60 In the synthesis of HBPs, side reactions can lower MW and are thus often undesirable. In the absence of side reactions, MW and DB are mainly determined by reaction kinetics, making them

sensitive to changes in local variations in temperature, mixing, concentrations of reactants and catalysts. As aforementioned, violation of two assumptions (*i.e.*, constant reactivity or/and absence of side reactions) can lead to better controllability. Yokozawa[7] showed that, for reacting systems with increasing reactivity, HBPs with narrow polydispersity (PDI) can be obtained. In our systems which violate the second assumption, good controllability and reproducibility can also be achieved. As aforementioned, at the right temperature range, the competing side reaction can lead to fast stabilization and allows us to control MW simply by controlling temperature and monomer concentration.
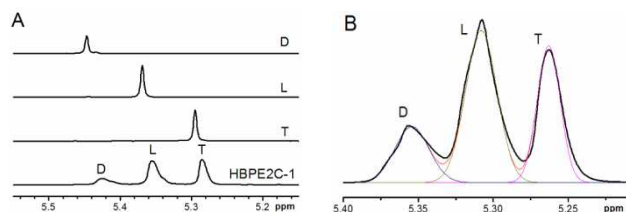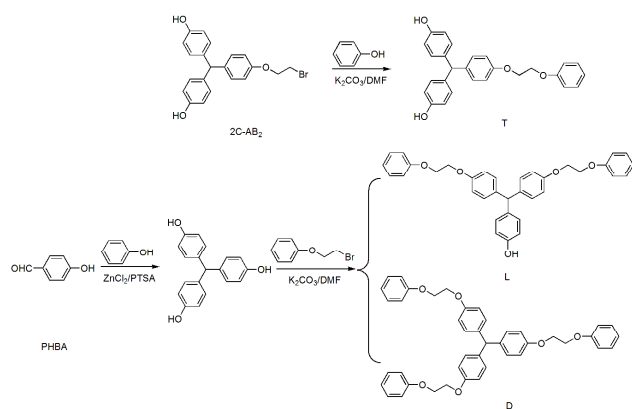

Fig. 5 (A) ^{1}H NMR spectra of three model molecules with well-defined D, L, and T units. Isolated peaks of HBPE-2C-1 at corresponding locations are also shown. (B) The typical curve-fitting result for HBPE-4C-2 showing the deconvolution of each type of structural unit.

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

Insensitivity of DB to MW and monomer spacer length

It is well know that DB in HBPs plays crucial roles in determining physical properties, such as T_g and viscosity.[6] One of the most used definitions of DB is that proposed by Hawker and Fréchet[14]:

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

where D, T, and L represent numbers of dendritic, terminal, and linear units, respectively. In order to assign corresponding chemical shifts to the dendritic, terminal, and linear units, three model compounds that have well defined NMR peaks for D, L, and T units are synthesized (see Scheme 3 and Fig. 5A). For HBPE-2C, three peaks corresponding to Ph₃H protons are well defined and isolated (Fig. 1). However, for HBPE-4C and HBPE-

6C, the three peaks are not well separated and but can be deconvoluted by assuming a Gaussian distribution.[18] A typical convolution result of HBPE-4C-2 is given in Fig. 5B. DB values of other HBPEs (prepared at 80 ºC) are summarized in Table 1. It is clear that although HBPEs samples are prepared from different monomers and monomer concentrations, they all have a DB of ~0.51. The insensitivity of DB to monomer type could be explained by the fact that the reactivity between A and B group is insensitive to spacer length. This important finding implies that DB of copolymerized HBPEs is similar to that of homopolymers.

T_g-Tuning in HBPEs

T_g of HBPs depend on many factors, including MW, DB, and structures of backbone and terminal group.[19] One complication in HBPs is that changes in MW are often accompanied by changes in DB, which also has notable effects on T_g. Thus, the control and tuning of T_g in HBPs is often challenging. For our HBPE systems, the fast stabilization in MW and the insensitivity of DB make them a good model system for making HPBEs with tunable T_g, which is also very useful for other scientific investigations. Several ways of preparing T_g tunable HBPEs are demonstrated below. The reported T_g values were obtained from second heating runs in DSC at 10 K/min unless otherwise stated.

(1) T_g-tuning by varying MW, monomer spacer length, and terminal group. At 0.1 mol/L and 80 ºC, the one-pot approach yields a M_n of ~4000 g/mol in the case of HBPE-2C-1. By increasing monomer concentration, M_n can be further increased to ~7000 g/mol. Alternatively, by adding additional batches of monomers into the already stabilized systems, the propagation reaction can be reinitiated and yield HBPEs with a M_n of more than 10000 g/mol. However, increasing M_n from 4000 to 10000 g/mol only increase T_g by 10 ºC, suggesting changing T_g by varying MW is not very effective for our system. Thus, in later studies concerning the binary blends and copolymerization, effects of M_n on T_g are not shown.

T_g of HBPEs can also be varied by changing backbone structure. As shown in Table 1, at comparable M_n, T_g of HBPE-2C is approximately 30 ºC higher than that of HBPE-6C. Terminal groups in HBPs also have notable effects on T_g. After converting the phenolic terminal groups in HBPE-2C-1 into benzyl groups (Scheme 4), T_g decreases approximately 50 ºC due to the weaker interactions between terminal groups. Thus, changing backbone structure and terminal group are more effective ways of tuning T_g.
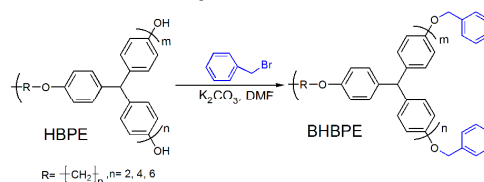

Scheme 4 The reaction route for terminal group modification.

(2) T_g-tuning by varying copolymerization and binary blending. Copolymerization and physical blending have been used to change T_gs of linear polymer systems, and prediction of T_g with composition in those systems (T_g mixing laws) has been well documented. However, mixing laws for hyperbranched

systems have not been systematically studied. Based on our HBPEs, the variation of T_g in binary homopolymerized blends with composition and variation of T_g in copolymers with monomer ratio are demonstrated. Furthermore, the difference in two mixing laws is investigated in detail for the first time.

Random copolymerized HBPEs were obtained using two monomers (*i.e.*, n=2 and 6) at different monomer mole ratios, and the synthetic route is shown in Scheme 5. M_n of copolymerized HBPEs is in the range of 3800~4300 g/mol. Please note that DB of copolymerized HBPEs (80 ºC, 0.1 mol/L) cannot be accurately determined due to the stronger overlaps in ^{1}H NMR peaks. However, as explained before, DBs of copolymers are expected to be close to those of homopolymers. As shown in Fig. 6, both copolymers and binary blends of HBPE-2C and HBPE-6C show only one T_g. In copolymers, T_g increases systematically when the molar fraction of 6C-AB$_2$ monomer (X) decreases; in binary blends, T_g also increases systematically with the weight fraction of HBPE-6C (w).
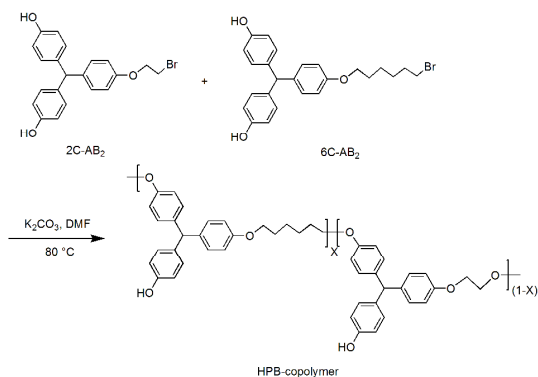
Scheme 5 The route of copolymerized HBPEs using 2C-AB$_2$ and 6C-AB$_2$. X denotes the mole fraction of 6C-AB$_2$.
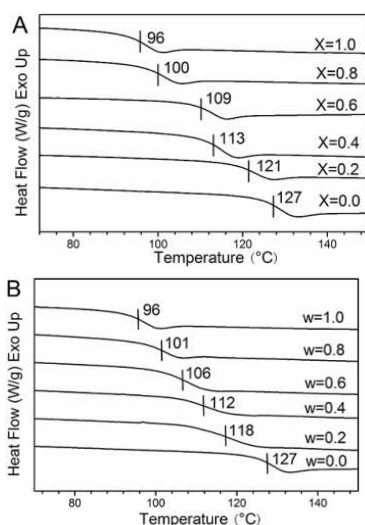

Fig. 6 DSC traces of copolymers and binary blends. (A) T_gs of copolymerized HBPEs (2C-AB$_2$ and 6C-AB$_2$) as a function of molar fraction of 6C monomer (X); (B) T_gs of binary homopolymers of HBPE-2C and HBPE-6C as a function of the weight fraction of HBPE6C (w)

For miscible blends and copolymers without interactions, the variation of T_g with composition can be described by Couchman equation based on entropy continuity[20] or a simplified version of Couchman equation, *i.e.*, the Gordon-Taylor equation that can be derived from volume additivity.[21] Due to its simplicity, Gordon-Taylor equation is often used to predict the composition-dependent T_g of binary blends of linear polymers:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad (1)$$

where T_g, T_{g1} and T_{g2}, are T_g values of the binary blend (or copolymer), homopolymers 1 and 2, respectively; w_1 and w_2 are weight fractions of homopolymers 1 and 2; k is a fitting parameter. Further simplifications ($\rho_1/\rho_2=1$; $\Delta\alpha_1 T_{g1} =\Delta\alpha_2 T_{g2}$) lead to the Fox equation[12, 22]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (2)$$

Theoretically, for systems with strong interactions such as our phenol-terminated HBPEs (BHBPEs), both Gordon-Taylor equation and Fox equation are not adequately; instead, Kwei[23] equation which takes into the strong interactions between different components has to be used:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \qquad (3)$$

where q quantifies the degree of interactions, including effects of both steric hindrance and hydrogen bonding. Generally, hydrogen bonding leads a positive q, and the steric effects lead a negative q.
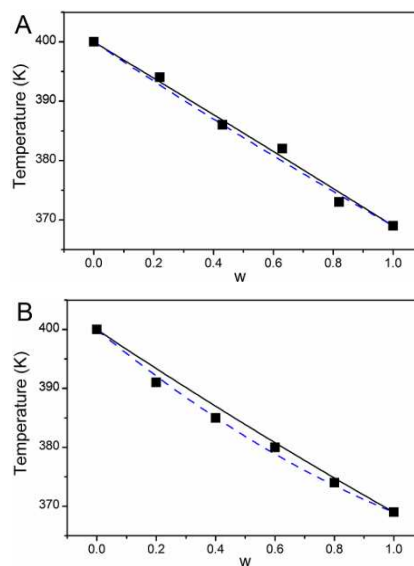

Fig. 7 (A) Variations of T_g in copolymers with weight fraction of 6C-AB$_2$ monomer HBPEs; (B) variation of T_g in binary blends with weight fraction of HBPE-6C. Data are shown in symbols; predictions from Kwei and Fox equations are shown as dashed and solid curves, respectively.

Variations of T_g in both copolymers and binary blends along with fittings from Kwei (dashed curve) and Fox Eq. (solid curve) are shown in Fig. 7. Notable differences between copolymers and blends are clearly shown: T_g values of copolymers follow Fox Eq., whereas T_g values in binary blends show negative deviations from Fox Eq. In both cases, Kwei Eq. can fit data well, with k= 1

and q= 0.6 for copolymers, and k= 1 and q= -10.6 for binary blends. Interestingly, for T_g of copolymers, Fox Eq. which does not take into account of the effects of interactions can also fit data well. Satisfactory fitting using Fox Eq. has also reported for hyperbranched copolymers with nonpolar terminal groups. [24, 25] In our case, the unexpected good fit from Fox Eq. could be explained by two competing effects: on one hand, phenolic terminal groups can form hydrogen bonding and lead to an increase in q; on the other hand, ample terminal groups and the highly branched structure can also lead to steric hindrance and thus decrease q. The two competing factors result in a small q (0.6) and negligible qw_1w_2 term in Kwei Eq., and thus lead to a satisfactory fitting with Fox Eq. In contrast, in binary blends, the steric hindrance effects dominate and lead to a large negative q (-10.6), thus Fox Eq. does not apply. The effects of heating rate on T_g is demonstrated by reducing the DSC heating rate from 10 K/min to 2 K/min. Results show that the T_gs in blends and copolymers obtained at 2 K/min are all *ca.* 2.3 ºC lower than those obtained at 10 K/min. However, the new sets of data can still be fitted by Fox or Kwei Eqs.
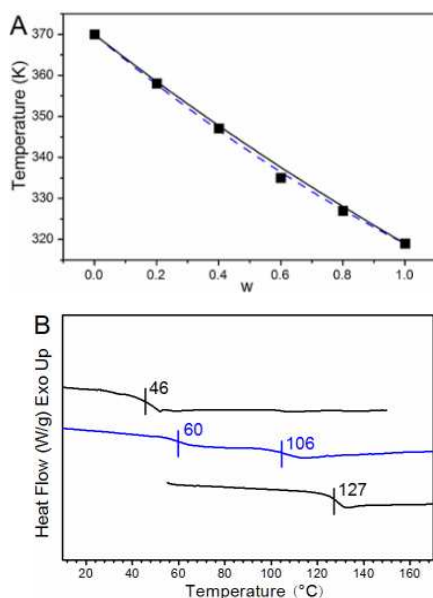

Fig. 8 (A) T_g of benzyl-terminated binary blends as a function of weight fraction of HBPE-6C, and predictions from Kwei equation (solid curve) and Fox equation (dashed curve). (B) DSC traces of binary blends (*w*:*w*= 50:50) of benzyl-terminated BHBPE-2C-1 and phenol-terminated HBPE-2C-1.

In order to investigate the effects of terminal group on the glass transition phenomena in binary blends, HBPE-2C and HBPE-6C, which have phenolic terminal groups, were converted to BHBPE-2C and BHBPE-6C, which have less-polar benzyl terminal groups. For binary blends of BHBPE-2C and BHBPE-6C, dependence of T_g on the weight fraction of BHBPE-6C along with fitting results from Kwei Eq. is shown in Fig. 8A. Again, in the benzyl-terminated binary blends, only one T_g is observed for mixtures at all compositions. Kwei Eq. can fit data well with k= 1 and q= -12.5. Compared with the phenol-terminated blend, the more negative q value in benzyl-terminated blends suggests that

steric hindrance is more pronounced in benzyl-terminated blends, which is reasonable considering the lack of hydrogen bonding and the bigger size of benzyl groups. We note that only one T_g is observed in both the phenol-terminated blends and benzyl-terminated blends. In binary blends of linear polymers, stronger interactions, such as hydrogen bonding, are often necessary to ensure misciblility.[26] However, our results suggest that strong interactions are not necessary to ensure miscibility in binary blends of HBPEs. Thanks to the large numbers of contact sites in HBP blends, the same terminal groups (though not polar) in both components is enough to achieve adequate miscibility. This is further confirmed by dual T_g values found in binary blends of phenol-terminated HBPE-2C-1 and benzyl-terminated BHBPE-2C-1 (Fig. 8B). Please note that although two T_gs are observed, they do move closer to each other compared with T_gs of pure components.
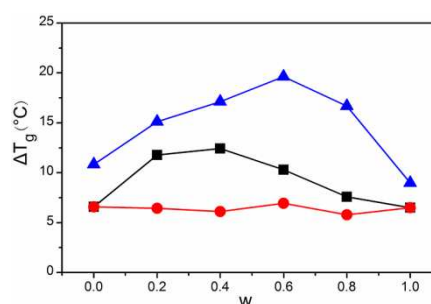

Fig. 9 The width of T_g (ΔT_g) in copolymers (circles) as a function of the weight fraction of the 6C-AB$_2$ monomer, ΔT_g in blends of HBPE-2C and HBPE-6C (squares) as a function of the weight fraction of HBPE-6C, and ΔT_g in blends of BHBPE-2C-1 and BHBPE-6C-1 (triangles) as a function of the weight fraction of BHBPE-6C-1.

Aside from the value of T_g, the width of T_g (ΔT_g), which is reported as the difference between the extrapolated onset and endset temperatures, can provide additional information on miscibility. Although only one T_g is observed in binary blends of both phenol-terminated and benzyl-terminated HBEPs, ΔT_g does vary with composition (Fig. 9). ΔT_g values of both phenol-terminated blends of HBPE-2C-1 and HBPE-6C-1 (squares) and benzyl-terminated blends of BHBPE-2C-1 and BHBPE-6C-1 (triangles) are bigger than that of copolymers (circles). ΔT_g values of both blends go through maxima at intermediate compositions. However, ΔT_g in benzyl-terminated blends is bigger than that in phenol-terminated blends, suggesting that hydrogen bonding between polar terminal groups can enhance miscibility and lead to a narrower T_g. In contrast, for copolymers prepared from 2C-AB$_2$ and 6C-AB$_2$ monomers, ΔT_g is always close to that of homopolymers despite the different monomer ratios. As a result, ΔT_g in copolymers is always smaller than binary blends.

Conclusions

A series of homo- and co-polymers were synthesized via one-step polymerization using AB$_2$ monomers of different spacer lengths. Thanks to the elimination side reaction, fast stabilization in M_n

can be achieved in 6 h with good controllability and scalability. More importantly, the degree of branching is found to be insensitive to molecular weight and monomer type, making it a good model system for producing HBPE with tunable T_g in large scale.

T_g-tuning in HBPEs was demonstrated using several methods, including terminal group modification, copolymerization, and physical blending. Moreover, the dependence of T_g in binary blends on composition and the dependence of T_g in copolymers on monomer ratio are compared in detail for the first time. For copolymers, variation of T_g with monomer ratio can be fitted with both Kwei and Fox equations; and the width of T_g (ΔT_g) in copolymers is similar to that of homo-polymers. For both phenol- and benzyl-terminated binary blends, the relationships between T_g and composition can be fitted with Kwei Eq.; however, they show negative deviations from Fox Eq. In addition, the q value in Kwei equation is found to depend on the nature of the terminal groups, including polarity and steric hindrance. For binary blends, ΔT_g values are always bigger than those of homo-polymers. Unlike linear polymer blends, hydrogen bonding is not necessary to ensure miscibility in blends of hyperbranched polymers as long as both components have the same terminal groups; however, hydrogen bonding can indeed improve miscibility and decreased the width of T_g.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details of synthetic procedures of model molecules,and NMR, GPC and DSC spectra which are not shown in the text. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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