

Effect of Branching Architecture on Glass Transition Behavior of Hyperbranched Copolystyrenes: the Experiment and Simulation Studies*

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Abstract By controlling the feed ratio of CMS/styrene and the polymerization time, a series of hyperbranched copolystyrenes (HBCPS) were synthesized with comparable weight-averaged molecular weights (M_w) but different degree of branching (DB) through atom transfer radical self-condensing vinyl copolymerization (ATR-SCVCP) with CuBr/2,2'-bipyridyl as the catalyst. The resulting HBCPS samples were used to investigate the effect of branching architecture on their glass transition behavior. With the DB increased, the glass transition temperatures (T_g) of HBCPS samples measured by DMA and DSC both decreased. Their spin-lattice relaxation times ($^1\text{H } T_{1\rho}$) of protons displayed the same downtrend with increasing DB. Besides, a correlation between the T_g s and the DB was well established by all-atom molecular dynamics (MD) simulations. The values of MD-determined T_g s are little higher than the corresponding experimental ones. However, the dependence of T_g s on DB is in good agreement with the experimental results, *i.e.*, T_g decreases both in experiments and simulations with increasing DB.

Keywords: All-atom molecular dynamics simulation; Degree of branching; Glass transition temperature; Hyperbranched copolystyrene.

INTRODUCTION

The effects of molecular architecture on polymer properties are always of both theoretical and practical interest. Dendritic polymers, including dendrimers and hyperbranched polymers (HBPs), represent a new class of functional materials with significantly different chemical and physical properties from their linear analogues. Compared to dendrimers, HBPs can be produced by ‘one-pot’ polymerization with relatively low costs and widely used in various fields of drug delivery systems, supramolecular chemistry, coatings, nanotechnology and so on^[1–6]. Although a great number of HBPs have been synthesized and characterized comprehensively, there are still some uncertainties existing in their structure-property relations, *e.g.*, the relationship between the branching topological structure and glass transition temperature.

Being different from dendrimers and linear polymer, HBPs have all three structure units, *i.e.*, linear units, dendritic units, and terminal units. Thus, degree of branching has been defined as a key structure parameter to describe the composition of the above three structure units in HBPs and greatly influences their chemical and

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physical properties^[7–12]. In order to illustrate the relationship between DB and T_g , many experiments were performed on different HBPs with their corresponding linear analogues and some different conclusions were reported. First, the branching structure slightly affected the T_g of highly branched polymers. For example, Frechet *et al.* demonstrated that the T_g of dendritic aromatic polyesters dramatically depended on the nature of terminal groups and internal monomer units but not on the branched architectures^[13]. Similarly, Ramakrishnan *et al.* found the T_g of the PET copolymers with various amounts of branching and kinks was less affected by their branched architecture, as well as Munari *et al.* reported that the linear and branched poly(butylene isophthalate)s possessed the similar T_g ^[14, 15]. Second, Lederer *et al.* summarized that the T_g not only depended on the branching structure but also strongly influenced by the type of end groups when they investigated the aliphatic-aromatic polyesters with a well defined degree of branching^[16]. Third, the T_g of hyperbranched polymers decreased with increasing the degree of branching. For instance, Mai *et al.* synthesized a series of hyperbranched polyether with different degrees of branching (DB) and found their T_g decreased from 64.0 °C to 37.8 °C with the DB increasing from 0.09 to 0.41^[17]. In addition, Peter *et al.* reported that T_g decreased from 266 °C for linear polyimide down to 222 °C and 231 °C for hyperbranched polyimides with amino- and anhydride-terminated groups, respectively^[18]. Recently, we investigated the relationship between DB and T_g of branched polyethylenes. As one kind of polymer being prone to crystallize, the glass transition behavior of branched polyethylenes was additionally influenced by their partially crystalline nature. We observed that both melting temperatures and T_g s decreased with increasing their DB^[19]. Fourth, Zhu *et al.* obtained an interesting conclusion when they investigated the T_g of amorphous hyperbranched polyethers with different DBs, *i.e.*, the T_g first increased and then decreased sharply with DB increased from 0.06 to 0.4. The maximum T_g appeared at the DB of 0.27^[20]. These controversial tendencies may be attributed to the combined effect of various factors, such as different molecular weights, polydispersity or crystallization *etc.* The aim of this work is to explore the effect of branching on T_g .

As a typical amorphous linear polymer, atactic polystyrene has distinct glass transition behavior, which was studied by experiments and molecular simulations for several decades^[21–23]. In recent decade, polystyrenes or copolystyrenes with hyperbranched architecture were synthesized by different approaches and their glass transition behavior was also studied^[24–30]. However, most studies just focused on measuring T_g values of the resulting products and did not discuss the effect of branching on T_g . In this study, a series of HBCPS samples with different DBs but comparable M_w was synthesized by ATR-SCVCP and selected as the model system to study the influence of branching structure on T_g . The DB was controlled by adjusting the feed ratio of *p*-chloromethylstyrene (CMS)/styrene and calculated according to the method reported by Müller *et al.*^[31]. The relationship between DB and T_g was characterized by DMA, DSC and solid-state NMR measurements. Furthermore, a correlation between T_g and DB of HBCPS samples was established by the all-atom molecular dynamics simulation. The results of experiment and simulation were compared with each other.

EXPERIMENTAL

Materials

Chlorobenzene (Sinopharm Chemical Reagent Co. Ltd) was dried over calcium hydride and distilled under vacuum just before use. *p*-Chloromethylstyrene (CMS, Acros) and styrene (Sinopharm Chemical Reagent Co. Ltd) were passed through a column of basic alumina, further purified by vacuum distillation, and stored at –20 °C under argon atmosphere. CuBr (98%) was washed with an order of acetic acid, methanol and ether at room temperature, and then stored under argon atmosphere. 2,2'-Bipyridyl (Bipy, 99%) and other reagents were purchased from domestic market and used as received.

Instruments

Nuclear magnetic resonance (NMR) analyses were processed on a 400 MHz Varian NMR spectrometer with CDCl₃ as solvent. The weight-average molecular weight and polydispersity index (PDI) were measured by a Gel Permeation Chromatography-Multi-Angle Laser Light Scattering (GPC-MALLS) system, which was consisted

of a Waters liquid chromatography system, a Wyatt Optilab DSP differential refractometer detector, and a Wyatt DAWN EOS MALLS detector. THF was used as the mobile phase at a flow rate of 1 mL/min at 30 °C. Dynamic mechanical analyzer (DMA) was performed on PerkinElmer DMA 8000 at a heating rate of 4 K/min from −80 °C to 100 °C under a frequency of 1 Hz. Differential scanning calorimeter (DSC) analysis was performed on a TA Instruments differential scanning calorimeter (TQ 2000) system in nitrogen atmosphere. First, all the samples (about 9.0 mg in weight) were heated from room temperature to 150 °C, and held at this temperature for 2 min to remove the thermal history and then quenched to −30 °C. Then all samples were heated again from −30 °C to 150 °C at a heating rate of 10 K/min. The densities of all HBCPS samples were measured by 3H-2000TD Automatic True Density Analyzer of BeiShiDe Instrument S&T (Beijing) Co. Ltd. Elemental analyses were obtained using Carlo Erba1106 and ST02 apparatus. Solid-state NMR experiments were recorded on a Bruker Avance III 400 spectrometer at a ^1H resonance frequency of 400.13 MHz. All samples were powdered and tightly packed into MAS rotors spinning at the rate of 5 kHz. ^1H $T_{1\rho}$ relaxation time measurements were performed at 20 °C with the ^1H 90° pulse of 3.5 μs . The number of scans was 128 and the contact time was 1.5 ms. The recycle delay time was 5 s and the acquisition time was 34.5 ms. The spin-lock power was 5 dB, and a standard pulse sequence of $T_{1\rho}$ was used.

Polymer Synthesis

The HBCPS samples were synthesized by ATR-SCVCP under argon atmosphere in a glove box with an oxygen content of less than $\delta = 0.4$. A typical example is as follows: Bipy (0.33 g, 2.1 mmol) and CuBr (0.15 g, 1.05 mmol) were added into a 20 mL round-bottomed flask equipped with a magnetic stirrer. Then 1.5 mL (1.62 g, 10 mmol) CMS, 1.2 mL (1.09 g, 10 mmol) styrene and 3 mL of dry chlorobenzene were injected into the flask. The mixture was stirred vigorously at room temperature for 1 min, then the flask was placed into an oil bath at 120 °C for a given time. At last, the mixture was cooled to room temperature, diluted with 5 mL THF, and passed through a neutral alumina column to remove CuBr. The light yellow solution was concentrated by rotated evaporation. Then the residual yellow viscous solution was poured into methanol and some white powder was obtained. After filtration, the white precipitate was collected and dried at 60 °C under vacuum overnight. Other HBCPS samples were prepared by the same procedure.

Model Construction and Simulation Details

The topology of HBCPS, which was characterized by DB, was mainly controlled by the ratio of CMS/styrene. Utilizing α ($\text{I}_2^\circ\text{-BCl/I}_1^\circ\text{-BCl}$)^[24] and DB obtained from experimental analysis, we could roughly speculate the topology of HBCPS samples synthesized under different polymerization conditions.

HBCPS samples with different DB were subjected to a slow stepwise isothermal-isobaric (NPT) cooling process from 600 K to 120 K with an interval of 20 K at 0.1 MPa. The cooling rate could be roughly determined as 7×10^9 K/s, which was much higher than that in experiments. The Berendsen methods were employed for controlling both temperature and pressure^[32].

The COMPASS force field parameters were employed for modeling the HBCPS systems^[33]. The van der Waals interactions were calculated utilizing a cutoff distance of 0.95 nm, with a switch function and long-range dispersion correction. The electrostatic interactions were treated with the particle-particle particle-mesh (P3M) technique. The velocity Verlet algorithm was used to integrate Newton's equations of motion with a time step of 1 fs. The full MD trajectory was recorded every 5 ps for analyzing various properties of interest.

RESULTS AND DISCUSSION

As a typical linear amorphous glassy polymer, atactic polystyrene was often used as a model system to study the glass transition behavior in previous researches^[21, 34, 35]. In order to investigate the nature of branching architecture effect on T_g , we also selected the branched polystyrene copolymer as the research system. Matyjaszewski *et al.* first reported the preparation of hyperbranched polystyrene by ATR-SCVP of CMS and Frechet *et al.* gave a more detailed study in the same system^[24, 36]. In addition, Zhang *et al.* investigated the influence of reaction conditions on the molecular weight and DB of the resulting polystyrene copolymers from

CMS and styrene in detail^[29]. These studies gave us a convenience to prepare HBCPS samples with comparable M_w and various DBs to study the relationship between branching structure and T_g . In this copolymerization system, CMS was used as an inimer to initiate styrene and itself to copolymerize and produce HBCPS samples through ATR-SCVCP with the same catalysis system as that reported for CMS homopolymerization. The DB and comparable M_w of HBCPS samples were controlled by adjusting the feed ratio of CMS to styrene and the polymerization time appropriately at 120 °C. The synthetic route and potential structure of HBCPS are shown in Fig. 1.

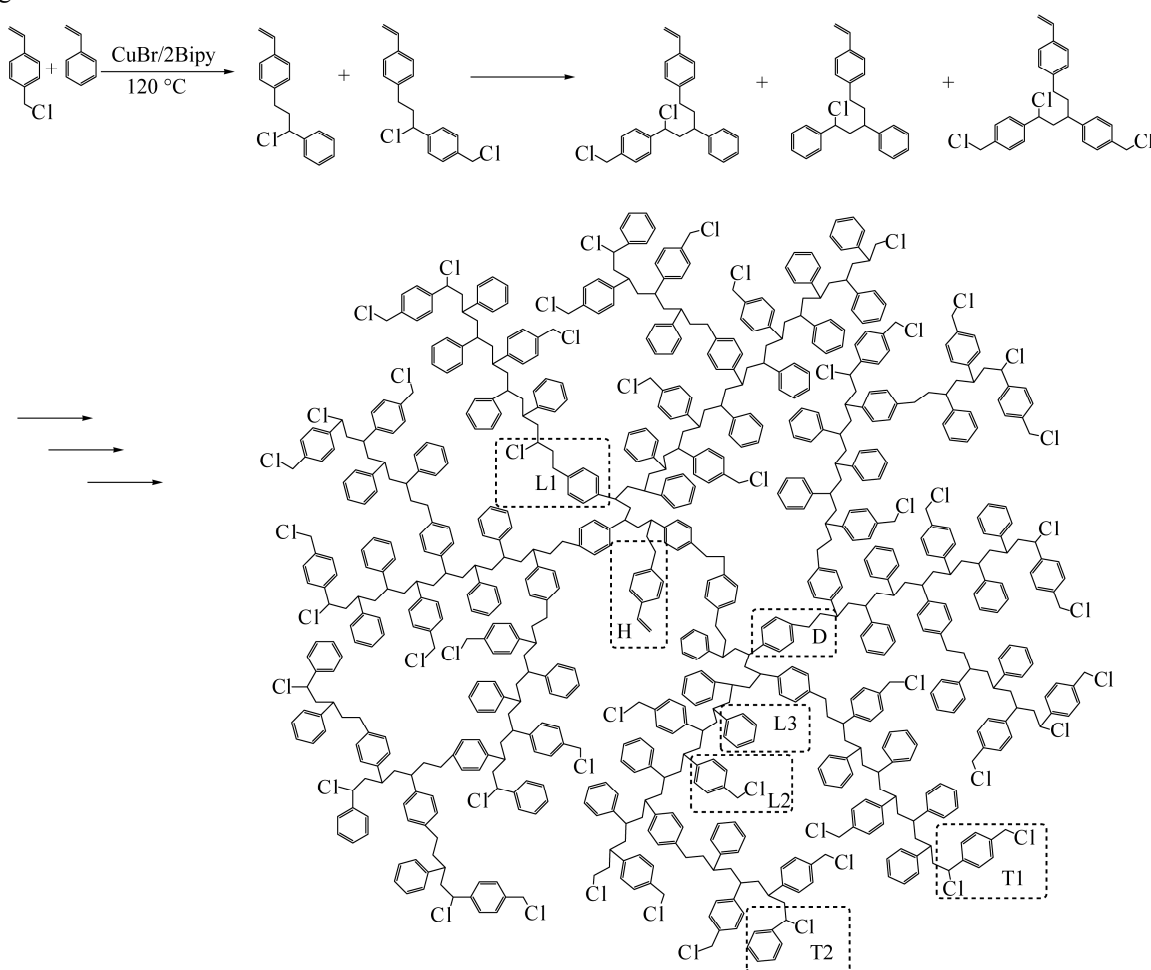


Fig. 1 The synthetic route of HBCPS

As shown in Fig. 1, the resulting HBCPS is composed of various structure units, including a head unit (H), one type of dendritic unit (D), three types of linear units (L1, L2, L3), and two types of terminal units (T1, T2). Among them, the head units H and dendritic units D are all derived from CMS; linear units L1 and L2 are derived from CMS, and L3 is from styrene; terminal units T1 is derived from CMS and T2 is from styrene. Correspondingly, there are three types of reactive sites in the process of ATR-SCVCP, including the PCMS-based primary benzylic chlorine ($\text{CH}_2\text{CHPhCH}_2\text{Cl}$, 1°-BCl), the derived PCMS-based secondary benzylic chlorine ($-\text{CH}_2\text{CHCl(PhCH}_2\text{Cl)}-$, 2°-BCl), and the derived PS-based secondary benzylic chlorine ($-\text{CH}_2\text{CHCl(Ph)}-$, 2°-BCl). 1°-BCl can be formed from L2 linear units and T1 terminal units, whereas 2°-BCl from H head units, D dendritic units, and L1 linear units. In addition, styrene can react with T1 terminal units to produce L1 linear units and T2 terminal units, which changes the ratio of 1°-BCl and 2°-BCl. Each reactive center can facilitate the polymer chain propagation further.

The resulting HBCPS samples were first characterized by element analysis, GPC-MALLS, and $^1\text{H-NMR}$ measurements. According to previous studies concerning the copolymerization of CMS and styrene to prepare linear copolymers, the reactivity ratios of CMS and styrene were not equal^[37, 38]. Therefore, the real composition of CMS and styrene in HBCPS may be different from the ratio of both in feed. Here we calculated the real contents of CMS and styrene in HBCPS on the basis of elemental analysis measurements and the results are shown in Table 1. Obviously, the content of the styrene units in the copolymers was slightly higher than that of styrene in the feed, which indicated the relatively higher conversion of styrene than that of CMS.

Table 1. The element analysis results of HBCPS samples

No	CMS (mol%)	C ^a (%)	H ^a (%)	Cl ^b (%)	CMS ^c (mol%)	St ^c (mol%)	X_M
1	10	90.84	7.12	2.04	6.15	93.85	0.9604
2	20	87.86	6.87	5.27	16.64	83.36	0.9602
3	30	85.38	7.12	7.50	22.28	77.72	0.9914
4	40	83.19	6.93	9.88	32.06	67.94	0.9785
5	50	80.39	6.70	12.91	37.56	62.44	0.9394

^a Determined directly by the elemental analysis measurement; ^b Calculated from the contents of C and H;

^c Calculated from elemental analysis measurement

Table 2 summarized the polymerization conditions and results of the synthesis of HBCPS samples by varying the concentration of CMS. As expected, with increasing concentration of CMS (from 10% to 50%) in the copolymerization system, five samples of HBCPS with comparable M_w s were obtained by prolonging the polymerization time at the same polymerization temperature. The M_w s of resulting HBCPS samples were in the range from 46.35 kg/mol to 90.69 kg/mol with the PDI from 1.73 to 2.06. Noticeably, the M_w s of resulting HBCPS decreased evidently and the molecular weight distribution became slightly wider with the polymerization time increasing when the molar ratio of CMS was larger than 50%. For example, when the molar ratio of CMS was increased to 75%, the M_w of HBCPS decreased to 5.93 kg/mol with PDI of 2.50 even though the polymerization time was increased to 72 h. This can be ascribed to the different monomer reactivity and the steric hindrance. According to the results in Table 1, the real molar content of CMS in the copolymers was slightly lower than that of CMS in the feed, which indicated the reactivity of CMS is relatively lower than that of styrene. On the other hand, the M_w growth of HBCPS was still restricted by the steric hindrance of CMS to form branched structure in the polymerization when the molar content of CMS was larger than 40%.

Table 2. The polymerization condition and characterization data of HBCPS samples

CMS (mol%)	Polymerization Time (h)	M_w (kg/mol)	PDI	Yield (%)	(I _{2°-BCl} /I _{1°-BCl})
10	8	46.35	1.73	92	0.06
20	14	66.20	2.00	92	0.24
30	25	77.31	1.91	90	0.28
40	30	90.69	2.06	88	0.32
50	41	84.52	2.03	86	0.41
75	72	5.93	2.50	52	–

The $^1\text{H-NMR}$ spectra of five resulting HBCPS samples are shown in Fig. 2 and the protons on the two types of benzylic chlorides can be clearly distinguished *i.e.*, at $\delta = 4.8$ and 4.6 for 2°-BCl and 1°-BCl, respectively. In the pure system of hyperbranched polychloromethylstyrene, the ratio of 2°-BCl to 1°-BCl is 0.5 for a perfect branched structure and 0 for a linear one, which can be used as an index of DB^[24]. In this copolymerization system, this ratio can also be calculated on the basis of $^1\text{H-NMR}$ spectra of HBCPS samples in Fig. 2 and changed from 0.06 to 0.41 with the molar content of CMS in feed improved from 10% to 50%.

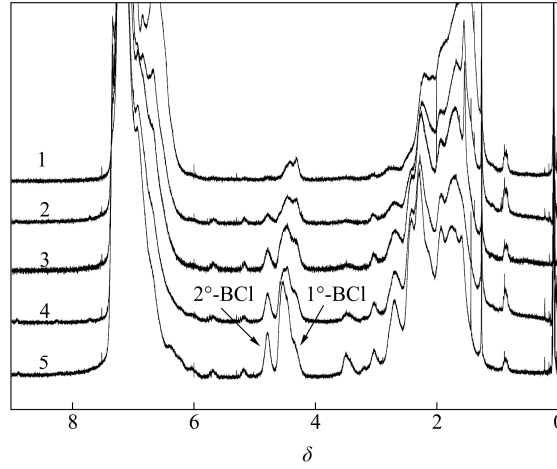


Fig. 2 ^1H -NMR spectra of HBCPS samples with different DB

In general, DB is a key structure parameter of HBPs. According to the kinetic analysis of a self-condensing vinyl copolymerization (SCVCP) system with non-equal reactivity of monomers by Müller *et al.*^[31], the DB values of the hyperbranched copolymers can be calculated via Eq. (1).

$$\text{DB} = \frac{2(1 - Z_B)(X_A - Z_A)}{\gamma X_M + 1 - (1 - X_A)(2 - Z_B)} \quad (1)$$

where X_M represents the conversion of styrene, which can be calculated from yields and elemental analysis; X_A represents the double bond conversion of CMS; $Z_B = B^*/I_0$, $Z_A = A^*/I_0$, B^* is an active center derived from the benzyl chloride of CMS, A^* is an active center derived from the vinyl group of CMS, I_0 is the initial concentration of inimer CMS; γ is the ratio of initial concentrations of styrene and CMS, $\gamma = M_0/I_0$.

On the basis of the analysis of Müller *et al.*, the sum of the fraction of active centers A^* , B^* and M^* is 1 (Eq. 3), M^* is the initial active center of styrene. The ratios of Z_A and Z_M were calculated using the ratios of CMS and styrene as comparable values, and in Eq. (2), it is $1/\gamma$. The ratios of two types of benzylic halides $2^\circ\text{-BCl}/1^\circ\text{-BCl}$ were defined as α in the study by Weimer *et al.*^[24]. From Eqs. (2), (3) and (4), we can calculate the values of Z_A , Z_B and Z_M . The value of X_A can be considered to be 1 at high conversion. Then all above values were substituted into Eq. (1) to calculate the DB values, and the results are displayed in Table 2.

$$\frac{Z_A}{Z_M} \approx \frac{1}{\gamma} \quad (2)$$

$$Z_A + Z_B + Z_M = 1 \quad (3)$$

$$\frac{Z_A + Z_M}{Z_B} = 2\alpha \quad (4)$$

Obviously, the DB of HBCPS samples was slightly smaller than the corresponding value of $I_2^\circ\text{-BCl}/I_1^\circ\text{-BCl}$, but both of them were increased with increasing molar content of CMS in feed. This also confirmed that we had obtained HBCPS samples with comparable M_w s but with various DBs.

The density of HBCPS samples was measured by 3H-2000TD Automatic True Density Analyzer, and the results are shown in Table 3. Interestingly, the density of HBCPS samples increased with the DB increasing, which seems in conflict with the results in our previous study about branched polyethylene, *i.e.* the density of branched polyethylene was reduced with increasing DB due to more inner cavities existing in the samples with higher DB^[19]. But in the system of HBCPS, the density not only depends on the inner cavities in HBCPS

samples, but also relates to the composition of copolymerization. With increasing DB, the number of branch units derived from CMS increased, which leads to much more chlorine atoms in HBCPS (See the data of Cl% in Table 1). Due to the atomic weight of Cl is larger than that of carbon and hydrogen atoms in HBCPS, the density of HBCPS increased with increasing DB. Thus the composition of copolymerization is the overwhelming factor to affect the density of HBCPS.

Table 3. The density and T_g of HBCPS samples

No	CMS (mol%)	DB	Density (g/cm ³)	T_g (DSC)	T_g (DMA)
1	10	0.02	1.117	98.7	114.1
2	20	0.13	1.132	87.6	109.6
3	30	0.21	1.143	85.6	107.2
4	40	0.28	1.159	80.5	102.9
5	50	0.38	1.166	76.3	98.9

Considering that T_g usually relates to the thermal history, all HBCPS samples with different DBs were heated to 150 °C and maintained at this temperature for 5 min to erase any previous thermal history. Then the samples were directly cooled to −30 °C at 10 K/min to perform DSC measurements. All the values of corresponding T_g are shown in Table 3. The DSC curves of all HBCPS samples with different DBs are displayed in Fig. 3. It can be found that T_g gradually decreased with increasing DB. This can be attributed to the following two factors. Firstly, with increasing DB, more and more junction points are created in the backbone of HBCPS that increase the number of inner cavities. Secondly, more and more terminal units are formed with increasing DB, which leads to the increase of free volume. Both of them strengthen the mobility of molecules, therefore the T_g shifts to lower temperatures. According to the previous report^[39], the T_g of a linear polystyrene with the similar molecular weight was about 100.5 °C measured by DSC, which was slightly higher than 98.7 °C of the HBCPS with DB = 0.02 and also confirmed the effect of DB on T_g of HBCPS.

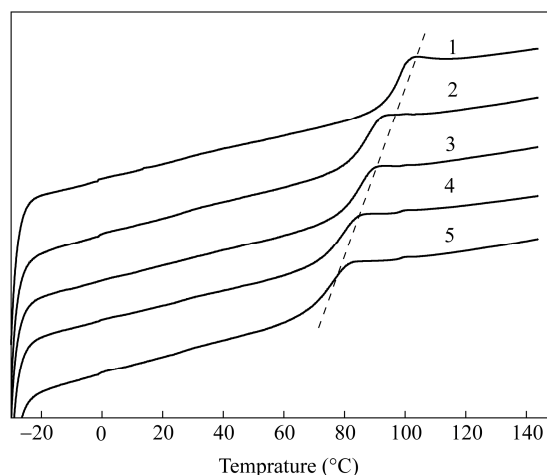


Fig. 3 DSC curves of HBCPS samples with different DBs

Furthermore, we also examined the glass transition dynamics of HBCPS samples with different DBs by DMA measurements and the results are shown in Fig. 4. In all cases, typical α -transition peak due to segmental motion was clearly observed and the peak position systematically shifted to lower temperatures with DB increasing. This can be ascribed to the fact that molecular architecture becomes more incompact and the rigidity decreases gradually for HBCPS samples with increasing DB. These results were entirely consistent with those found by DSC presented in Fig. 3 and Table 3.

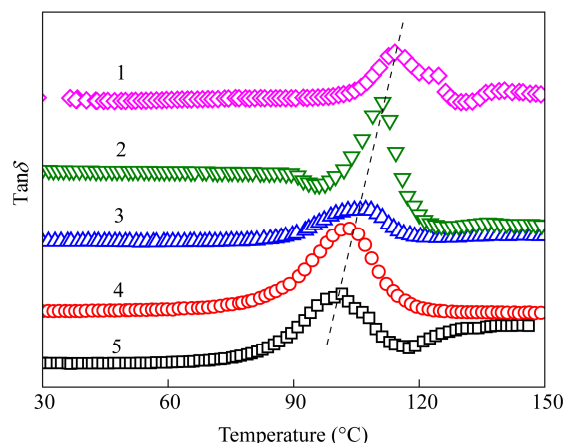


Fig. 4 Plots of $\tan\delta$ versus temperature for HBCPS samples with different DBs

As a powerful tool, nuclear magnetic resonance (NMR) spectroscopy is often used to study the structure and dynamics of polymer chains. The spin-lattice relaxation time of protons in the rotating frame ($^1\text{H } T_{1r}$) is very sensitive to molecular motions in the range of 10^4 Hz in modern spectrometers^[40, 41]. Thus the determination of $^1\text{H } T_{1r}$ would be a perfect way to detect the internal molecular motions for HBPs^[42, 43]. Here $^1\text{H } T_{1r}$ values were measured to validate the aforementioned observations from DSC and DMA. The plot of $^1\text{H } T_{1r}$ versus DB was displayed in Fig. 5. It can be seen that the relaxation time decreases continuously with increasing DB, which indicates that the molecular mobility of HBCPS is enhanced by the successive introduction of branching units. In other words, the higher the molecular mobility, the lower T_g , which demonstrates a close relationship between the mobility of molecular chains and the glass transition temperature. Therefore, Fig. 5 confirms the effect of branching architecture on the T_g of HBCPS samples.

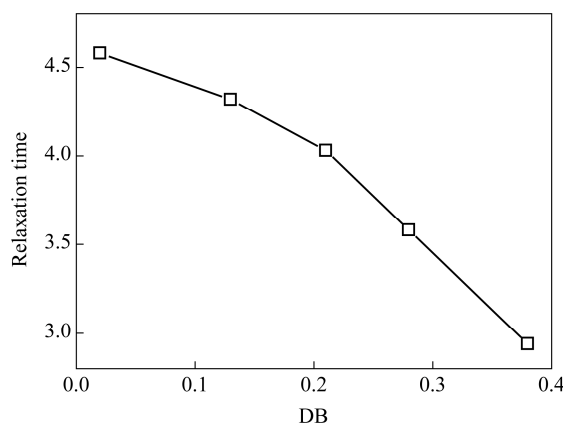


Fig. 5 DB dependence of $^1\text{H } T_{1r}$ values

Besides, all-atom molecular dynamics simulations were also used to study the T_g of HBCPS samples with different DBs. Figure 6 depicts the specific volume of three samples (DB = 0.02, 0.21, 0.28) determined from the last 2 ns trajectories of NPT runs at different chosen temperatures, and the other two samples (DB = 0.13, 0.38) are not shown for clarity. We can easily identify T_g by the temperature at which the slope of specific volume changes.

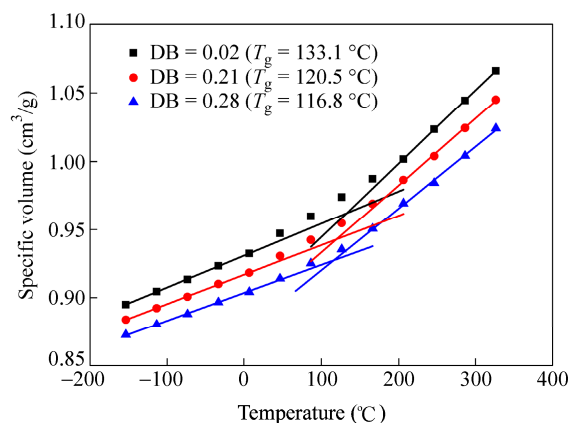


Fig. 6 Specific volume as a function of temperature for systems with different DBs, obtained from NPT simulations

For clarity, we only show three systems with DB = 0.02, 0.21, 0.28, respectively. The lines represent least-square fits to temperatures below and above the glass temperature and the latter is obtained from the line intersection. The error bars are smaller than the symbol size.

The relationship between T_g and DB measured by DSC, DMA and obtained from simulations is shown in Fig. 7. Obviously, with increasing DB, the trend of T_g obtained from DMA and DSC measurements was consistent with each other, but T_g measured from DSC was lower about 20 K than that from DMA for the HBCPS with same DB. This deviated absolute values were attributed to the different measurement methods^[44, 45]. Furthermore, the values of MD-determined T_g s were higher than the corresponding experimental ones too, which were ascribed to the much higher cooling rate used in simulations than that in experiments. However, the dependence of T_g s on DB was in good agreement with experimental results: with increasing DB, T_g was decreasing both in experiments and simulations.

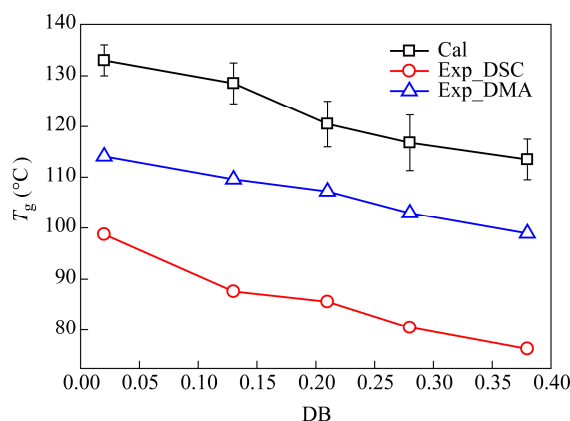


Fig. 7 The T_g from simulations and experiments as a function of DB

CONCLUSIONS

HBCPS samples with comparable M_w s but various DBs were obtained through ATR-SCVCP by adjusting the molar ratio of CMS/styrene in feed and the polymerization time. The effect of DB on T_g of HBCPS samples was studied by DSC, DMA and NMR spectroscopy. Both of DSC and DMA results displayed that T_g decreased monotonically with increasing DB. The NMR result also showed that the ^1H $T_{1\rho}$ decreased continuously with increasing DB, which indicated the molecular mobility of HBCPS was enhanced with increasing DB that led to

the decrease of T_g . Besides, a correlation between DB and T_g of HBCPS samples was well established by all-atom molecular dynamics simulations. The values of MD-determined T_g s were little higher than the corresponding experimental ones, which can be attributed to the much higher cooling rate used in simulations than that in experiments. However, the dependence of T_g on DB was in good agreement with the experimental results: T_g was decreased both in experiments and simulations with increasing DB.

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