

Rheological Behaviors of a Series of Hyperbranched Polyethers^{*}

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Abstract Hyperbranched polyethers with different structures and molecular weights (MW) were synthesized using the A₂+B₃ approach by varying monomer ratio, A₂ structure, and reaction time. Effects of backbone structure and MW on melt rheological behaviors were investigated by both small amplitude oscillatory shear and steady shear measurements. Master curves were constructed using the time-temperature superposition principle and compared. In the reduced frequency range covered, $\lg G'' \sim \lg(\omega \cdot a_T)$ always show a slope of 1.0, suggesting a terminal zone behavior; in contrast, unexpected step changes or plateaus are observed on $\lg G'$ master curves. Effects of backbone structure and MW on master curves were discussed. The Cox-Merz rule was tested at different temperatures and was found to be applicable when flow instability was absent.

Keywords: Hyperbranched polyethers; Rheology; Time-temperature superposition.

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INTRODUCTION

Hyperbranched polymers (HBPs) have attracted lots of attention in the past two decades due to their unique structure and property^[1]. Unlike perfect dendrimers which require laborious multiple-step synthesis, the less branched and polydispersed HBPs can be synthesized easily using one-step or pseudo-one step procedures^[2–4], making them much cheaper to produce in large quantities. The highly branched structure, internal cavities, and ample terminal groups of HBPs lead to minimal entanglements, increased free volume and solubility, and lower viscosity both in solution and in melt state^[1]. The relative low cost and unique properties make them useful in various applications, including biological and medical applications, coatings, and thermosetting applications^[1, 5–7]. During processing, knowledge about rheological behaviors of HBPs is essential in obtaining good end-use products.

Hsieh and Simon^[8] investigated the effects of generation number on rheological properties using aliphatic hyperbranched polyesters (BoltornTM) and found that low generation samples showed shear thinning, whereas high (4th and 5th) generation samples behave Newtonian. Choi and coworkers^[9] studied the effects of end chain length on relaxations and motions. Their results show that the molecular mobility increases when alkyl chain

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ends increase from C_6 to C_{12} ; however, excessively long alkyl chain (C_{18}) retards molecular motions. Magnusson *et al.*^[10] studied the degree of branching (DB) on temperature-dependent complex viscosity using a aliphatic hyperbranched polyether. They found that samples with high DB were amorphous and showed Newtonian behavior; however samples with low DB could crystallize and showed weak step changes in viscosity during cooling. Kannan *et al.*^[11, 12] also studied the effects of branching of hyperbranched polystyrenes (HBPS) and found that the terminal slope of $\lg G'$ was close to 1.1 rather than 2.0, and a plateau in $\lg G'$ appeared in the low frequency zone for very high MW HBPS. In addition, a linear relationship between zero-shear-rate viscosity (η_0) and MW was found for samples with short branching and high DB. Sendijarevic and McHugh^[13] compared rheological behaviors of poly(propylenimine) dendrimers (DAB), BoltornTM hyperbranched polyesters, and poly(ether-imide) HBPs (PEI-HBPs) under steady shear, oscillatory shear, and creep. Both hyperbranched polyesters melt and concentrated solutions of low MW PEI-HBPs show Newtonian behaviors. However, shear thinning and normal stress effects were observed in concentrated solution of high MW PEI-HBPs. Although effects of generation number, end chain length, DB, branch length, and branch density on melt rheological behaviors of HBPs and linear polymers have been reported^[8–14], studies on the effect of backbone structure on melt rheological behaviors of HBPs have not been done.

In this study, a series of epoxide-terminated hyperbranched polyethers (EHBPEs) with different MW and backbone structures were synthesized and characterized. Through small amplitude oscillation shear (SAOS) and steady shear measurements, effects of backbone structure and MW on master curve and the zero-shear-rate viscosity were measured and compared. Cox-Merz rule is also tested at temperatures close to T_g and well above T_g . In addition, the variations of fractional free volume at T_g and η_0 with MW were also reported.

EXPERIMENTAL

Materials

Ether and tetrahydrofuran (THF) were purchased from Beijing Reagent Co. *m*-Dihydroxybenzene was purchased from Tianjin Fuguang Reagent Co. (China). 1,4-Butanediol, bisphenol-A, and tetrabutylammonium bromide (TBAB) were purchased from Tianjin Fuchen Chemical Reagents Factory. 1,1,1-Trihydroxymethylpropane triglycidyl ether (TMPGE) (99%) was purchased from Titanchem Co. Ltd. All solvents and reagents were analytical pure and used as received.

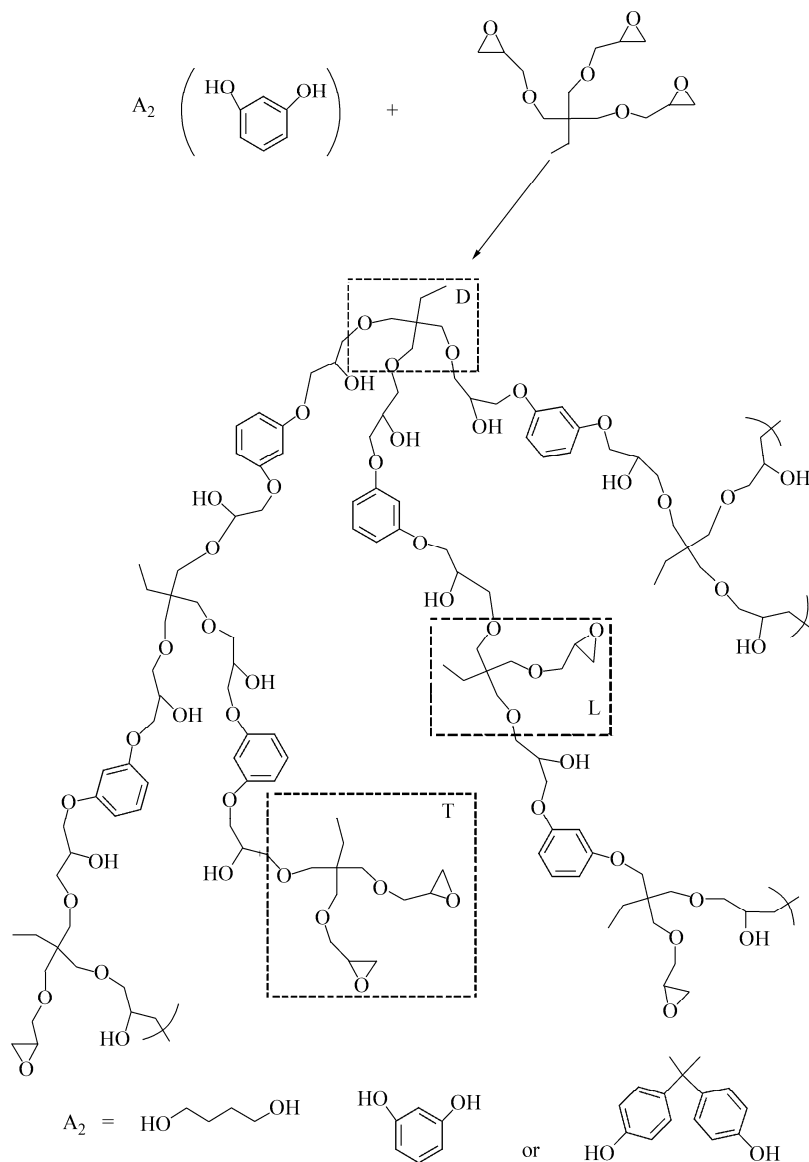
Synthesis of EHBPEs

Epoxide-terminated hyperbranched polyethers (EHBPEs) with different backbone structures and MW were synthesized by reacting TMPGE (B_3) with three different A_2 monomers (see Scheme 1) according to literature^[15, 16]. Detailed information concerning the synthesis and characterization are supplied in Supporting Information (SI). By varying the monomer ratio and reaction time, the MW of three EHBPEs (each corresponds to a different A_2 monomer) can be varied systematically. When TMPGE was reacted with 1,4-butanediol for different lengths of time, EHBPE1 samples with different MW (EHBPE1-1, EHBPE1-2, EHBPE1-3) were obtained; when TMPGE was reacted with *m*-dihydroxybenzene and bisphenol-A using different monomer ratios,

Table 1. Characterization results of EHBPEs

Sample code	$M_n (\times 10^{-3} \text{ g/mol})$	PDI	R_h (nm)	$[\eta] (\times 10^2 \text{ dL/g})$	$10^4 K$	α
EHBPE1-1	1.50	1.88	1.22	5.10	31.93	0.35
EHBPE1-2	2.00	2.78	1.46	5.20		
EHBPE1-3	3.00	2.88	1.99	9.60		
EHBPE2-1	1.40	2.30	1.28	4.90	19.82	0.38
EHBPE2-2	2.10	2.62	1.66	5.60		
EHBPE2-3	2.70	2.74	1.77	6.10		
EHBPE3-1	2.20	1.95	1.50	5.70	14.63	0.44
EHBPE3-2	2.70	2.00	1.60	6.60		
EHBPE3-3	4.40	2.50	2.20	7.80		

EHBPE2 (whose structure is shown in Scheme 1) and EHBPE3 samples of different MW (Table 1) were obtained. Detailed reaction conditions are supplied in Table S1 of SI. All EHBPE samples are soluble in common polar solvents, such as THF, acetone, dichloromethane, and dimethylformamide. The procedures for converting terminal epoxide groups to hydroxyl groups can be found in SI. The hydroxyl values of the EHBPE were determined by acetic anhydride- H_2SO_4 titration for 100 g samples.



Scheme 1 The synthesis routes for three types of EHBPEs. EHBPE1, EHBPE2, and EHBPE3 were obtained by reacting TMPGE (B_3 monomer) with 1,4-butanediol, *m*-dihydroxybenzene, and bisphenol-A, respectively. The schematic hyperbranched structure shown is the structure corresponding to EHBPE2.

Characterizations

^1H Nuclear magnetic resonance (NMR) spectra were collected on a Bruker AV-600 spectrometer (600 MHz) with chloroform- d (CDCl_3) or deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$) as solvents. Fourier transform infrared (FTIR) spectra were collected on a Bruker Tensor-37 spectrophotometer using the KBr disc technique. The

number-average molecular weight (M_n), weight-average molecular weight (M_w), intrinsic viscosity ($[\eta]$), and hydrodynamic radius (R_h) were determined at 40 °C using a Malvern Viscotek GPC max +270 multi-detector GPC/SEC system, in which the SEC column is coupled with a refractive index detector, a multi-angle laser light scattering detector, and an online viscometer. The system was calibrated using linear polystyrene standards in the corresponding MW range. Both calibration and measurements were performed in THF at a flow rate of 1.0 mL/min. The glass transition temperature (T_g) was determined on second heating runs (10 K/min) using a Mettler-Toledo (Switzerland) DSC1 differential scanning calorimeter (DSC) under dry nitrogen purge (40 mL/min).

Small amplitude oscillatory shear (SAOS) measurements were performed on an Anton Paar MCR 702 rheometer (2EC-SMT mode) with 25 mm parallel plates and a gap size of 1.0 mm, covering a frequency range of 0.1 rad/s to 100 rad/s. Steady shear measurements were performed on an MCR301 rheometer (Anton Paar, Austria) with 25 mm parallel plates and a gap size of 1.0 mm, covering a shear rate from 0.01 s⁻¹ to 100 s⁻¹. Zero-shear-rate-viscosities (η_0) were obtained by fitting shear-rate dependent viscosities to the Carreau-Yasuda model. The temperature accuracy is controlled within 0.1 K using a peltier temperature-controlled device. SAOS measurements were repeated after all measurements were done to ensure reproducibility. In order to avoid transient effects, pre-shearing is used before measurements, and samples were given 30 min to achieve equilibrium. In addition, strain sweeps show that all EHBPE samples show wide linear viscoelastic range (> 10%) in the covered temperature and frequency ranges.

RESULTS AND DISCUSSION

Characterization of EHBPEs

NMR and FTIR results of EHBPE and hydroxyl-terminated hyperbranched polyether (HHBPE) samples are supplied in Figs. S1–S8 in Supporting Information (SI), confirming the successful synthesis of the targeted structures. M_n , polydispersity index (PDI), R_h , $[\eta]$, and the Mark-Houwink-Sakurada (MHS) parameters (K and α) are listed in Table 1. The absolute M_w are determined from light scattering.

For simplicity, when discussing effects of MW and backbone structure, comparisons are made in two groups: one group shows effects of MW in the case of EHBPE2 samples (EHBPE2-1, EHBPE2-2, and EHBPE2-3), which have the same backbone; the other shows effects of backbone structure at comparable MW (*i.e.*, EHBPE1-2, EHBPE2-2, and EHBPE3-2). DB as defined by Fréchet^[3] can be estimated from ¹H-NMR spectra. The obtained DB values, T_g , and the hydroxyl values are listed in Table 2. As clearly shown in the case of EHBPE2, DB decreases with increasing MW, which is often observed in other HBPs.

Table 2. Thermal properties, DB, and hydroxyl values of EHBPEs

Sample code	T_g (°C)	DB	Hydroxyl value (mol/100 g)
EHBPE1-2	−24.3	0.54	0.51
EHBPE2-1	−23.1	0.68	0.54
EHBPE2-2	−16.6	0.55	0.43
EHBPE2-3	−15.5	0.50	0.25
EHBPE3-2	−11.9	0.51	0.29
HHBPE3-2	−1.40	0.51	0.82

As shown in Table 1, for EHBPE2 samples, $[\eta]$ which reflects the ratio of effective volume to molecular weight increases with MW, indicating that EHBPE2 samples become more compact with increasing MW. $[\eta]$ of three different types of EHBPEs THF (a good solvent) solutions at 40 °C can all be fitted into the MHS equation:

$$[\eta] = KM_n^\alpha \quad (1)$$

where K and α are constants. As shown in Table 1, α values for EHBPE1, EHBPE2, and EHBPE3 are 0.35, 0.38, and 0.44, respectively. For linear polymers, α is often in the range of 0.5 to 0.8 and may become bigger than 0.8 for stiff molecules; for HBPs, α is smaller than 0.5^[17, 18]. It has been shown that hydrodynamic radius R_h

and the radius of gyration R_g are close to each other^[19, 20], thus the scaling law between R_g and M_w can be approximated by that between R_h and M_w . For EHBPE2, R_h scales with $M_w^{0.41}$; for EHBPE1 and EHBPE3, R_h scale with $M_w^{0.45}$ and $M_w^{0.34}$, respectively. Thus, in dilute solutions, hyperbranched molecules with more flexible backbone tend to have more open structures, which is in agreement with Mansfield's results^[21].

SAOS Measurements

Effects of temperature on complex viscosity (η^*)

The frequency-dependent η^* of different EHBPE samples show similar trends. For simplicity, we only show data of EHBPE3-2. The variation of η^* with frequency at different temperatures are shown in Fig. 1. At 40 °C which is well above T_g , Newtonian behaviors are observed in the covered frequency range. However, shear thinning is observed when temperature becomes close to T_g . Although Newtonian behavior has been reported for a hyperbranched polyether^[22], shear thinning behaviors under dynamic mode were also reported for PAMAM dendrimers and hydroxyl-terminated aliphatic hyperbranched polyesters^[23, 24]. Shear thinning in linear polymers is often related to chain disentanglements and alignment; however, this does not apply to our EHBPEs because no entanglement is expected considering the small M_n (< 4500). Shear thinning in hyperbranched polyester samples has been explained by polar interactions between terminal hydroxyl groups^[8, 24]. In order to test this argument, the epoxide-terminated EHBPE3-2 was converted to its hydroxyl-terminated counterpart, HHBPE3-2, and a comparison is made in Fig. 2. Hydroxyl terminated HHBPE3-2 has stronger interactions, which lead to higher T_g . Thus, when compared at the same temperature, HHBPE3-2 is closer to its T_g than EHBPE3-2 does and exhibits higher viscosities. The physical networks formed by interactions could be destroyed under shear and leads to the observed shear thinning. In addition, computer simulations also suggest that shear thinning may be related to shear-induced stretches or shape change, especially for HBPs with sparse/open structures and low DB^[25, 26].

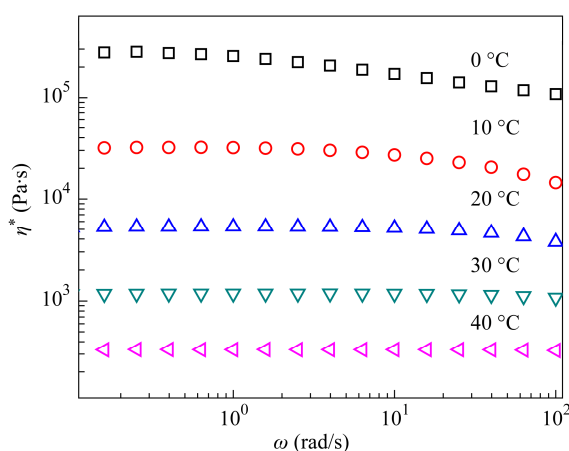


Fig. 1 The frequency-dependent complex viscosities of EHBPE3-2 at different temperatures

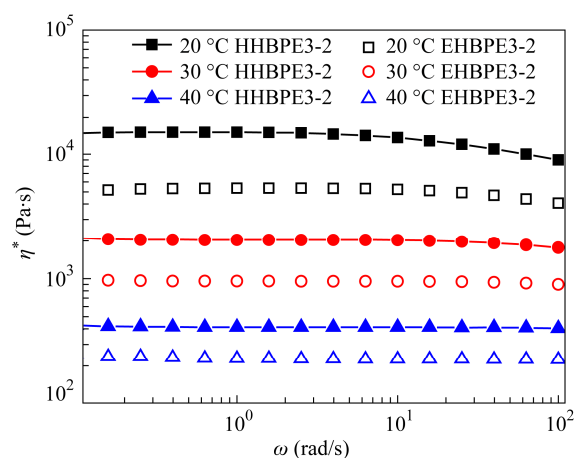


Fig. 2 Comparison of the complex viscosities of epoxide-terminated EHBPE3-2 and hydroxyl-terminated HHBPE3-2 at different temperatures

Effects of MW on η^*

Effects of MW, as illustrated in the case of EHBPE2 on η^* at 20 °C, are shown in Fig. 3. Two characteristics are evident. (1) The limiting low frequency complex viscosity (η_0^*) increases with MW. Unlike linear polymers, MW change in HBPs is accompanied by changes in molecular weight distribution, DB, and density of terminal groups, thus effects of MW are always coupled with those parameters. The higher η_0^* could be explained by the higher MW, lower DB, and more terminal groups which lead to stronger interactions, as well as the difference in $T-T_g$ ^[12]. (2) Samples with lower MW show Newtonian behaviors, whereas those with higher MW show shear thinning. Shear thinning in HBPs could be related to changes in interactions, shape and packing^[10, 27]. When MW

increases, HBPs can pack more effectively and form stronger interactions because of their larger size, shape distributions, and lower DB, which lead to more obvious shear thinning. Moreover, HBPs with higher MW have more open structures, which facilitate shape change under shear and thus show more shear thinning. In addition, when compared at the same temperature, changes in MW also lead to changes in the distance to T_g , ($T - T_g$), which might also contribute to the more obvious shear thinning^[12].

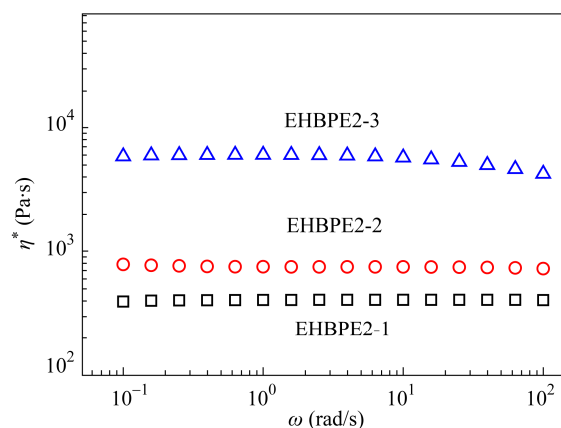


Fig. 3 The complex viscosities of EHBPE2 samples with different molecular weight as a function of angular frequency (ω) at 20 °C

*Effects of backbone structure on η^**

Effects of backbone structure on η^* at 20 °C are shown in Fig. 4. EHBPE3-2, EHBPE2-2, and EHBPE1-2 samples have comparable MW but different backbone structures (Scheme 1). When compared at the same temperature, η^* decrease in the order of EHBPE3-2, EHBPE2-2, and EHBPE1-2. It is known that the viscosity of HBPs is strongly temperature dependent due to the semi-spherical shape. As a result, although they are measured at the same temperature, as shown in Table 2, the distance to their respective T_g , *i.e.*, $20 - T_g$, is different, which greatly affect the viscosity. When compared at the same temperature, samples with lower T_g are more liquid like and show lower viscosity and modulus. Similar arguments have been used to explain the variation of viscosity for dendrimers of different generations^[23]. In addition, other factors that determine the degree of polar interactions, packing and deformability can also affect the viscosity and shear thinning behavior. For examples, the size, shape, and their distributions, as well as number of terminal groups can all affect the degree of polar interactions in a complicated way and thus the viscosity and degree of shear thinning.

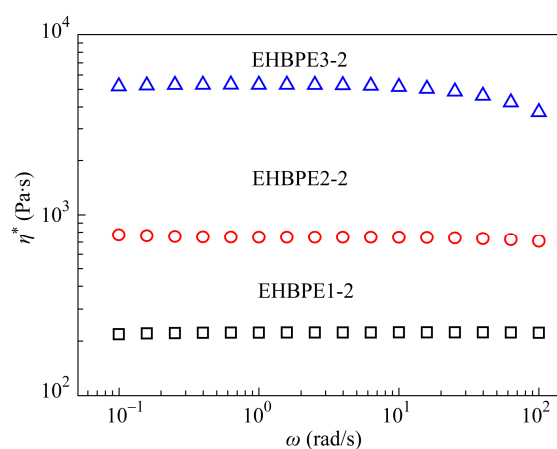


Fig. 4 The variation of complex viscosities of different EHBPEs with angular frequency (ω) at 20 °C

Effects of MW and backbone structure on storage and loss moduli (G' and G'')

Effects of MW on storage and loss moduli (G' and G'') at 20 °C are shown in Figs. S9 and S10. Because T_g of EHBPE samples show strong dependence on MW and structure, in order to minimize the interference due to the difference in T_g , comparisons are made at the same corresponding states (*i.e.*, the same $T - T_g$). Master curves of G' and G'' were constructed based on isothermal frequency sweeps in the range of 0–40 °C. Applicability of time-temperature superposition (tTS) principle can be justified if data collected at different temperatures can collapse on $\lg G'$ versus $\lg G''$ plot or if the collapsing on phase angle δ versus $\lg|G^*|$ plot is satisfied, which is thought a better criterion when no vertical shift is necessary^[28–30]. Satisfactory collapses are observed on both the $\lg G'$ versus $\lg G''$ plot (data not shown) and δ versus $\lg|G^*|$ plot (Fig. 5). In Fig. 5, the van-Gurp-Palmen-plots (δ versus $\lg|G^*|$ plots) show a molecular weight dependency of the phase angle behavior (Fig. 5a), whereas the different backbone structures hardly affect the phase angle (Fig. 5b). In general, both DB and PDI can influence the shape of van-Gurp-Palmen-plots. Thus, for EHBPEs with different molecular weights, the different van-Gurp-Palmen-plots can be explained by the differences in DB and PDI of the three EHBPEs. For EHBPEs with different backbone structures, although PDI of EHBPE3-2 is smaller than that of EHBPE1-2 and EHBPE2-2, the van-Gurp-Palmen-plots of the three EHBPEs show good superposition irrespective of backbone structure, which can be explained by the similar DB values of the three EHBPEs. Although failures of tTS have been reported for long-chain branched polyethylene and hydrogenated 1,2-polybutadiene^[31, 32], tTS holds for all EHBPE samples in the covered range despite the highly branched structure and polar terminal groups. Master curves with reference to ($T_g + 40$ °C) were constructed by applying horizontal shifts. Individual master curves are also supplied in Fig. S11. The horizontal shift factors were fitted into the WLF equation and the Vogel-Fulcher (VF) equation (Fig. S12)^[33]. It is found that the fractional free volume at T_g (f_g) (Table S2) is bigger than the universal value of linear polymers (0.025), and it varies approximately linearly with M_n and f_g , which has been observed for dendrimers with backfoldings and supported by molecular simulations^[13, 20, 21, 34, 35].

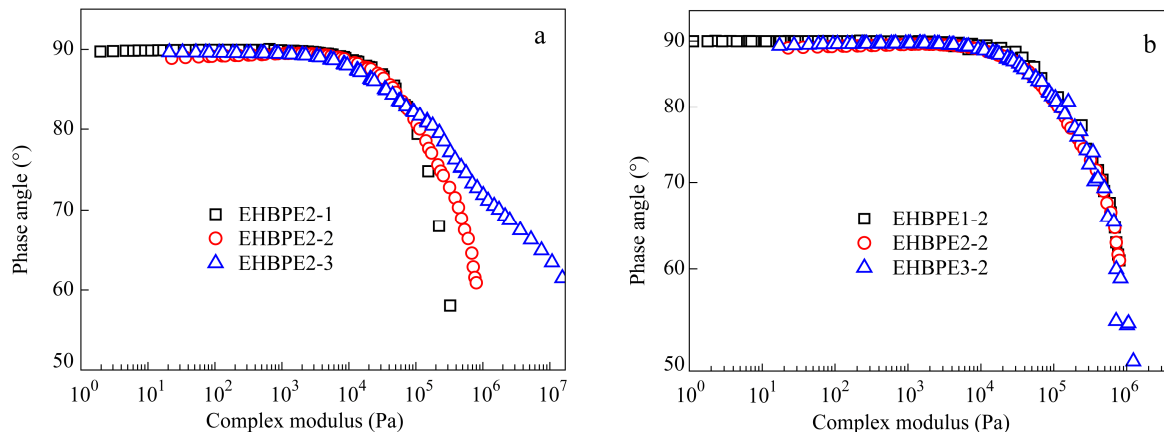


Fig. 5 (a) The phase angle (δ) versus complex modulus ($|G^*|$) plots for EHBPE2 samples of different MW, and (b) for EHBPE samples with different structures

In the covered temperature and frequency ranges, $\lg G''$ master curves are always above $\lg G'$ curves and no crossovers are observed (Fig. S11). In addition, all $\lg G''$ master curves show straight lines with slopes of close to 1.0. Thus, only $\lg G'$ curves deserved further discussion. At the same corresponding state, *i.e.*, $T_g + 40$ °C, Fig. 6(a) shows effects of structure at comparable MW, and Fig. 6(b) shows effects of MW in the case of EHBPE2. For mono-dispersed linear polymers, when the slope of $\lg G''$ master curve reaches 1.0, that of $\lg G'$ often approach the limiting slope of 2.0 at slightly lower frequencies. For polydispersed linear polymers, when the slope of $\lg G''$ reached 1.0, the transition of $\lg G'$ from plateau to terminal zone shows a gradual change and reaches the limiting terminal slope at much lower frequencies. Similar trend was observed for a short branched

polyethylene^[36]. In addition to the smaller limiting slope at low frequencies, $\lg G'$ master curves of EHBPE samples show another unusual features: in the low frequency range (where $\lg G''$ shows a slope of 1.0), when frequency decreases, slopes of $\lg G'$ first increase to ~ 1.7 and then decrease, rather than approaching the limiting slope of 2.0, which could be related to the polydispersed nature and extensive short branching in HBPs. We note that in hyperbranched polystyrenes with lower polydispersity and much higher MW, a terminal slope of 1.1 is observed in $\lg G'$ master curve^[11].

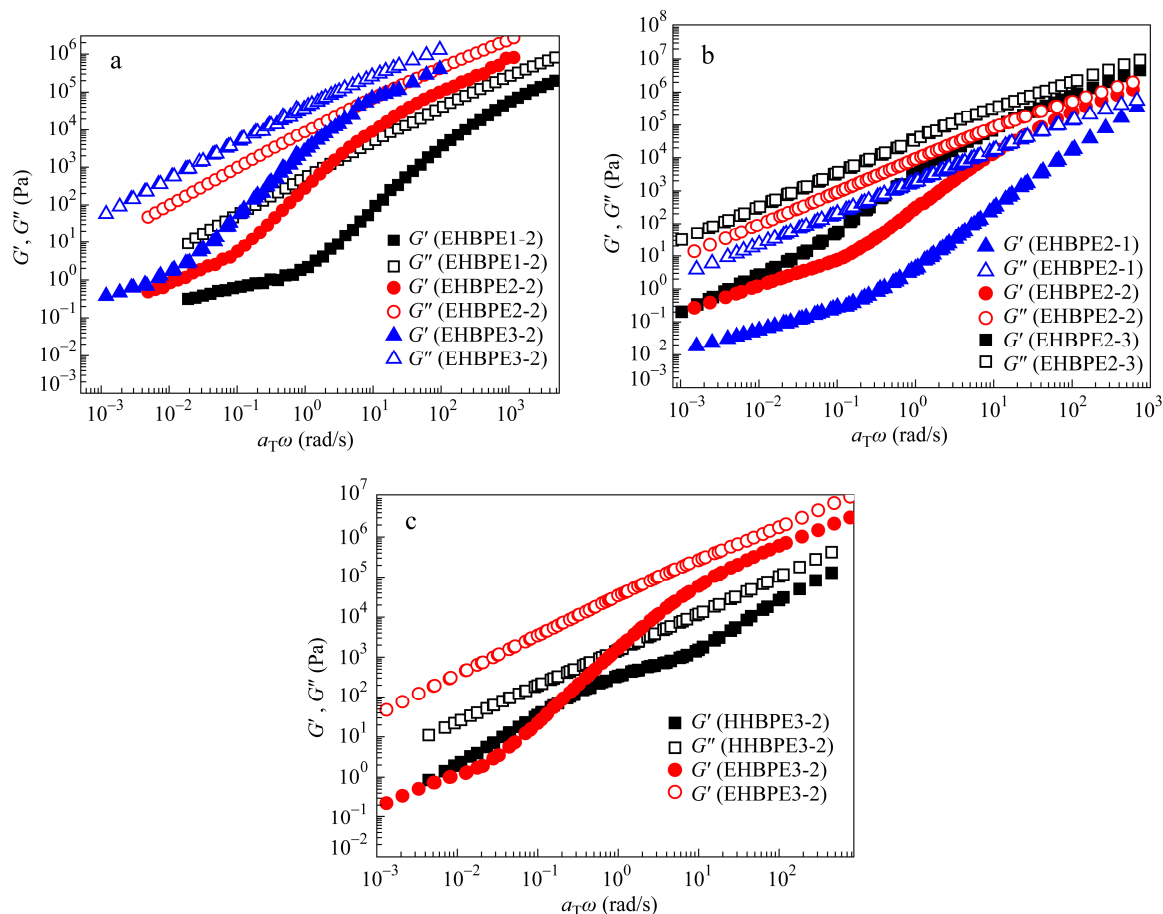


Fig. 6 Effects of (a) molecular weight, (b) backbone structure, and (c) terminal group on master curves when compared at the same corresponding state, *i.e.*, $T_g + 40^\circ\text{C}$

The effects of structure on $\lg G'$ master curve are shown in Fig. 6(a). Master curves of three EHBPEs show similar shape. When backbone stiffness increases, $\lg G'$ master curve shifts upward. For EHBPE1-2 which has the most flexible backbones, $\lg G'$ in the terminal zone becomes flatter than that of EHBPE2-2 and EHBPE3-2 which can be explained by the largest PDI of EHBPE1-2. The effects of MW on $\lg G'$ master curve are shown in Fig. 6(b). It is clear that the storage moduli in the terminal zone become flatter with increasing molecular weight or PDI, which is consistent with the modelling prediction of Winter *et al.*^[37, 38]. For EHBPE2-1 which has the lowest MW, $\lg G'$ can be approximated by two straight lines. When MW increases, $\lg G'$ master curve shifts upward. In addition, the shape of $\lg G'$ changes to a tilted sigmoidal shape (*i.e.*, a step change in shape). The relaxation spectra of all EHBPE were calculated and supplied in Fig. S13 in SI for better comparisons with the work of Winter *et al.* As clearly shown in Fig. S13, the spectrum for the sample with larger PDI has more modes of motions which have longer relaxation times and thus is flatter in shape. We note that in both EHBPE2-1 (Fig. 6b) and EHBPE3-2 (Fig. 6a), step changes might still be possible if $\lg G'$ master curve could be obtained at

much lower frequencies, which is not available due to the high torques at low temperatures. The step change in $\lg G'$ at low frequencies have been reported in bimodal mixtures of linear PBD and PS^[39, 40]; however, in that mixture, a shoulder at slightly higher frequencies is also observed in $\lg G''$ which is not observed in EHBPE samples. We note that, the molecular weight distribution in EHBPE is a continuous distribution rather than a bimodal distribution, which may lead to overlapping in shoulders and make it indistinguishable. Similar step changes have also been reported in compatibilized polymer blends^[39–42], long chain hyperbranched polymers (HyperMacs)^[43], side chain dendritic polymers^[44], and in the complex viscosity of a hyperbranched aliphatic polyether^[10]. In compatibilized polymer blends, observed plateaus have been attributed to the shape relaxation in the dispersed phase and interfacial relaxations^[39–42]. Kannan *et al.* also found a nonterminal response in HBPs^[11], and they believe it may be correlated with the branch density. However, although similar plateaus are observed in η^* versus T curves, due to the complication from crystallization, no explanations were offered^[10]. The sigmoidal shape or step change on $\lg G'$ master curves could be related to the combined effects of polydispersity and highly branched structures, as well as contributions from polar interactions which are in some sense similar to interfaces. Effects of polar interactions on the $\lg G'$ master curves are shown in Fig. 6(c), which compares the master curves of HHBPE3-2 with EHBPE3-2. Both master curves show clear step changes; however, directions of the step changes are different, and a clear plateau is seen in HHBPE3-2. This plateau could be explained by the physical network formed by strong polar interactions between terminal hydroxyl groups. We want to add that the low torque signals at low frequencies could be controversial because it is close to the sensitivity threshold of the instrument. Thus, although the advanced MCR702 rheometer can independently measure torque and strain with great sensitivity, possible uncertainties in the low frequency measurements may still exist.

Steady Shear Behaviors

Temperature dependence

The zero-shear-rate viscosity (η_0) under steady shear at different temperatures was obtained by fitting the shear-rate-dependent viscosities to Carreau-Yasuda model^[45]:

$$\eta = \eta_0 / [1 + (\lambda_n \cdot \dot{\gamma})]^{P_n} \quad (2)$$

where λ_n and P_n are fitting parameters. Effects of structure and MW are shown in Figs. 7(a) and 7(b). As shown in Fig. 7(a), when plot against $T - T_g$, the temperature-dependent η_0 curves of EHBPE2 and EHBPE3 almost collapse with each other, suggesting the similarity in backbone structures. Although η_0 of EHBPE1 also shows similar shape, its value is lower than those of EHBPE2 and EHBPE3 which have stiffer and bulkier backbones. However, the difference in η_0 becomes smaller with increasing $(T - T_g)$ values, showing the insensitivity of η_0 to backbone structures at high $T - T_g$. As shown in Fig. 7(b), the temperature-dependent η_0 curves appear to be parallel and shift upward with increasing MW. However, when a critical MW is reached, curves tend to merge (EHBPE2-2 and EHBPE2-3) and become insensitive to MW.

Test of the Cox-Merz rule

In order to test the applicability of Cox-Merz rule, comparisons of the complex viscosity η^* and steady shear viscosity η for EHBPE2-1 at 60 °C and 20 °C are shown in Figs. 8(a) and 8(b), respectively. All EHBPE samples show similar trends, we only show data of EHBPE2-1 as an example. η^* and η agree well at 60 °C, and the Cox-Merz rule is applicable at this temperature, which is in agreement with results of ester-terminated hyperbranched polyesters and dendrimers^[7, 46]. However, when T_g is approached (*i.e.*, at 20 °C), η^* and η show strong deviation, suggesting a failure of Cox-Merz rule. Similar failures have been observed in entangled polymeric fluids which have strong hydrogen bonding and hyperbranched polyesters^[8, 47–49]. The inconsistency at different temperatures can be resolved by performing a check for wall slip or/and edge fracture. As pointed out by McKenna and co-workers^[50, 51], high elasticity in samples can easily lead to flow instability (wall slip or/and edge fracture) and inaccurate measurements, which leads to an apparent break-down of Cox-Merz rule. In order to test that assertion, isothermal time sweeps at different stress levels were performed, and results are shown in Fig. S14.

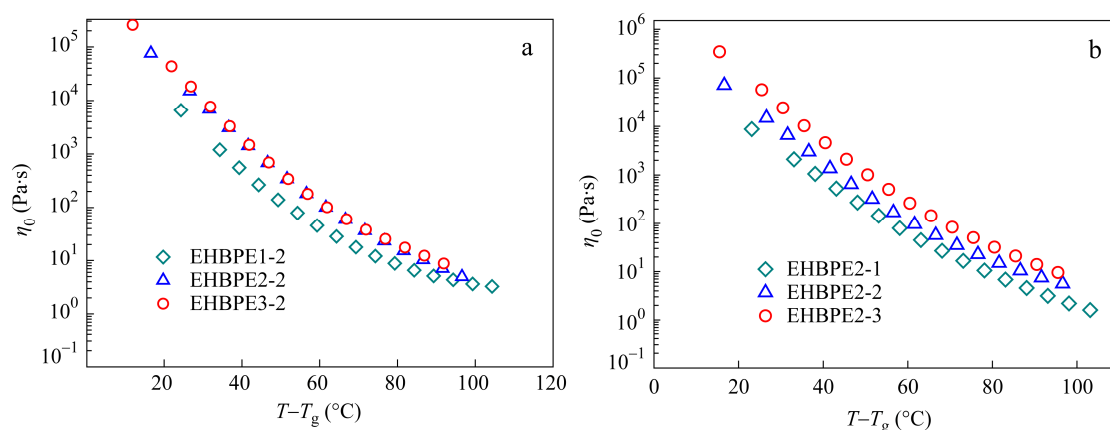


Fig. 7 The temperature-dependent η_0 of EHBPEs with different MW and structure: (a) Effects of structure at comparable MW; (b) Effects of MW in the case of EHBPE2

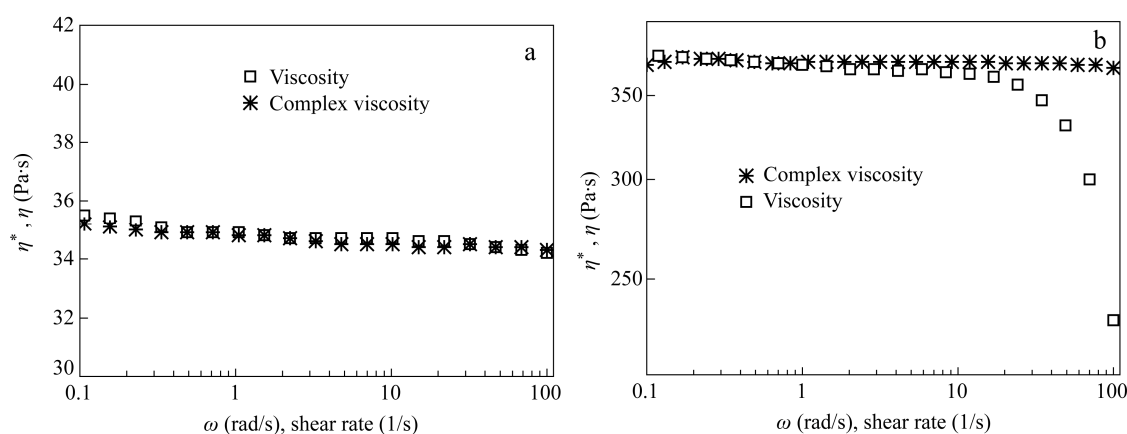


Fig. 8 The complex viscosity η^* and the steady shear viscosity η of EHBPE2-1 at (a) 60 °C and (b) 20 °C

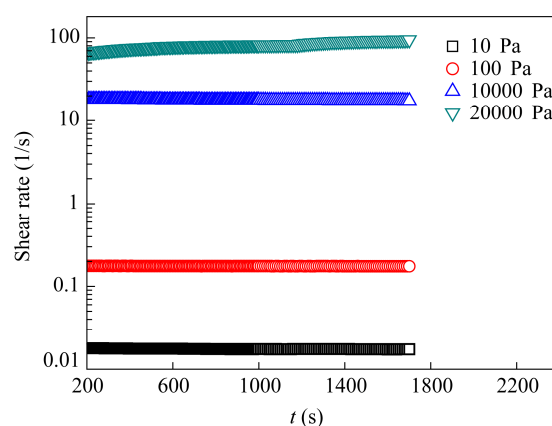


Fig. 9 Time sweep at different constant shear stress of EHBPE2-1 at 20 °C

Both η^* and η show no time effects at 60 °C, (data not shown); however, at 20 °C, although both η^* and η show shear thinning (Fig. 8), they do not agree with each other. Due to the high elasticity at 20 °C, wall slip or edge fracture is observed in time sweeps under constant stress mode (Fig. 9). Clearly, at the highest stress 20000 Pa,

the shear rate show increase from a shear rate of about 60 s^{-1} to 100 s^{-1} , after shearing for some time. In addition, the first and second normal stress differences N_1 and N_2 were measured according to literature^[52, 53]. N_1 and N_2 versus shear rate for EHBPE2-1 in parallel-plate steady shearing flows are shown in Fig. S15 of SI. Generally, both N_1 and N_2 increase with shear rate when flow instability is absent. However, N_1 and N_2 may show sudden drops when the flow instability occurs. As shown in Fig. S15, at 60°C , N_1 and N_2 increase with shear rate when shear rate is below 100 s^{-1} ; at 20°C , N_1 and N_2 first increase then suddenly decrease, suggesting a flow instability. Thus, the apparent discrepancy between η^* and η at 20°C can be explained by flow instability.

CONCLUSIONS

A series of hyperbranched polyethers with different backbones and MW were obtained by varying A_2 structure, the monomer ratio between A_2 and B_3 , and reaction time. Effects of MW and backbone structure on melt rheological behaviors were investigated using SAOS and steady shear measurements. More pronounced shear thinning in complex viscosity can be observed in EHBPE samples with high molecular weight or with stiff backbone structure or when temperature is low. In the covered temperature and frequency ranges, the time-temperature superposition principle is found to be applicable for all samples. $\lg G''$ master curves show slopes of ~ 1.0 in the whole covered range, whereas, $\lg G'$ master curves all show unusual sigmoidal step changes. Increasing MW shows same effects on $\lg G'$ as increasing backbone stiffness, *i.e.*, more obvious step change and higher values in G' . When the epoxide terminal group is replaced with hydroxyl groups, the $\lg G'$ master curves show a step change to the opposite direction and a plateau, which can be explained by the stronger polar interactions between molecules. In addition, in the case of EHBPE2, the fractional free volume at T_g varies linearly with $1/M_n$. Variation of η_0 with $(T-T_g)$ depends on both backbone structure and MW. Increase in MW tends to shift η_0 versus $T-T_g$ curve upward. Increasing backbone stiffness has stronger influence on the low temperature side of η_0 versus $T-T_g$ curves; however, the effects of backbone structure become very weak at higher temperatures. In addition, it was confirmed that the apparent break-down of Cox-Merz rule at low temperatures is due to the flow instability. Cox-Merz rule is found to be applicable for EHBPE samples at temperatures when flow instability does not exist.

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