

Synthesis and Rheological Investigation of Model Symmetric 3-Arm Star Polyethylene

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Abstract A variety of linear and 3-arm star polyethylene (PE) model polymers covering a wide range of molecular weight are synthesized by the living polymerization of butadiene and the subsequent hydrogenation. Several rheological parameters of these model linear and 3-arm star PE samples are analyzed for detecting the long chain branching (LCB) structure. It is found that the analyses based on zero shear viscosity, vGP plot and flow activation energy are very sensitive to the 3-arm star PEs. The information on the presence of LCB can be obtained with these methods even for low molecular weight samples, which can not be determined by GPC-MALLS. However the information about the LCB structure can not be obtained by the rheological methods alone.

Keywords: Long chain branching; Rheology; Star polymers; Polyethylene; Thermorheology.

INTRODUCTION

Molecular structure has been documented to affect both the processing and end-use properties^[1–4]. The introducing of long chain branching (LCB) into polymer chains will affect the rheological behaviors and processing properties, such as enhancements in melt strength and shear thinning, which will finally result in improved processing properties^[5, 6]. The industrial linear low density polyethylene (*m*-LLDPE, metallocene catalyst polymerized LLDPE) has been of great interest due to its outstanding processing properties originated from the sparse LCBs, which were generated during polymerization. The relationship between the LCB structure and the processing behavior has been extensively studied in the past several decades, but it is not yet completely understood due to the absence of model polymers with specific structures and effective characterization of branching structure.

The common methods for characterizing LCB involve NMR, gel permeation chromatography (GPC) coupled with multi-angle laser light scattering (MALLS) and rheological measurements. ¹³C-NMR measurement has long been used to characterize the branching structure of polyethylene^[7–9]. The determinations of the branch length and branch content are based on the characteristic resonances of different methylene carbons and their relative intensities. The sensitivity limitation comes from the low natural abundance of ¹³C, and it is not feasible to count branch-point carbons in concentrations below about 1 in 10⁴^[10]. Owing to the overlapping of methylene resonances in the branch chains longer than 6 carbons and the backbone, the ¹³C-NMR approaches fail to discern branch chain length beyond 6 carbons. Although the application of melt-state ¹³C-NMR exceeds the branch length detection limit up to 16 carbons^[11], it is still difficult to detect LCBs longer than the entanglement length which is defined by rheology (85 carbon atoms for PE when $M_e = 1200$ kg/mol).

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Another LCB detection method is GPC-MALLS, based on a technique that combines GPC with multi-angle laser-light scattering (MALLS), which can determine the absolute molecular weight (M_w) and radius of gyration (R_g) simultaneously. Branched polymers can be characterized with smaller R_g compared to the linear counterparts, which is induced by the shrinkage of branched polymer chains. The detection limit of this method can reach to 0.005LCB/1000C for PE with M_w greater than or equal to 1000000 g/mol^[12], which is more sensitive than NMR detection. But its sensitivity would decrease when the molecular weight of PE decreases.

So far, rheology is admittedly considered to be a sensitive method for probing the LCBs. The presence of LCBs tends to increase entanglements, thereby prolonging the relaxation time of the polymer chains as well as enhancing the shear thinning behavior. The apparent phenomenon can be expressed as a dramatic increase of zero-shear viscosity (η_0) and modulus (G' and G'') at low frequencies, as well as some changes in other rheological properties. However, the rheological behavior of polymer melts depends not only on long chain branching, but also on molecular weight and molecular weight distribution. Thus model polymers with well-defined structure are necessary for the establishment of the relationship between rheological properties and macromolecular structure parameters.

In this work, linear and 3-arm star PEs with well-defined structures, having ethyl branches along the backbone were synthesized, which were analogous to the structure of LLDPE. As the symmetric 3-arm star polymers can be considered as the simplest branched polymers with LCBs, based on the rheological detection of this one-LCB-per-molecule polymer, it is wanted to verify the different characterization methods (GPC-MALLS and rheological measurements) for LCBs and tell how well these detecting methods work for these simplest branched polymers, which will be helpful to reveal and understand the influence of low level LCB on rheological properties of PE.

EXPERIMENTAL

Synthesis

The model PEs were prepared by the hydrogenation of well-defined polybutadienes (PBs). All the linear PB precursors were prepared by anionic polymerization in cyclohexane using the *s*-BuLi as the initiator. The 3-arm star PBs were obtained by coupling the anionic living PB chains with methyltrichlorosilane. Pure star PBs were isolated from excess arms by fractionation using toluene/methanol as the solvent/nonsolvent. The obtained linear and star PBs were saturated with diimine in a method similar to that of Hahn^[13].

GPC-MALLS

The molecular weights and the molecular weight distributions of the hydrogenated PB (PE) samples were determined by a PL-GPC 220 high-temperature gel permeation chromatography coupled with a multiangle laser-light scattering apparatus. 1,2,4-trichlorobenzene (TCB) was employed as the solvent and the temperature was 150 °C.

Rheology

The rheological measurements in shear were performed on a Physica MCR300 rheometer equipped with parallel-plate geometry (25 mm diameter, 0.8 mm gap) under nitrogen atmosphere. The test samples were stabilized with 1 wt% antioxidant Irganox B215 and press-molded into 25 mm × 1 mm discs at 160 °C before testing. Dynamic frequency sweeps were carried out in the range of 0.01 rad/s to 100 rad/s with appropriate strain within the linear region at 150, 170, 190 and 210 °C. Strain sweeps were previously performed to determine the linear viscoelastic region.

RESULTS AND DISCUSSION

The 3-arm star PBs were obtained *via* the coupling reaction of methyltrichlorosilane with living anionic PB chains, which were freshly prepared in cyclohexane using *s*-BuLi as the initiator. The fractionation was used to remove the excess PB arms, and the obtained star PBs were monodisperse as shown in Fig. 1. The PB chains prepared in nonpolar solvent had 7 mol% of 1,2-microstructure and 93 mol% of 1,4-microstructure, hence the

subsequent hydrogenated PB polymers would possess the corresponding small amount of ethyl branches, which are randomly distributed along the arms of the star polymers. The content of short chain branches (SCB) were about 18 ethyl branches per 1000 carbons. The melting temperatures of hydrogenated PBs ranged from 101 °C to 106 °C, and the crystallization temperatures were between 85 °C and 90 °C as shown in Table 1. All these features are similar to those of industrial LLDPE, which make the hydrogenated PBs as a model for a better understanding of the PE structure. Thanks to the narrow distribution of the PB precursors, the resultant PE samples also have a narrow molecular weight distribution (MWD), hence the influence of the broad MWD on rheological behaviors, similar to that of the LCB, can be excluded during the studies on the relationships between rheological parameters and LCB structure of PE.

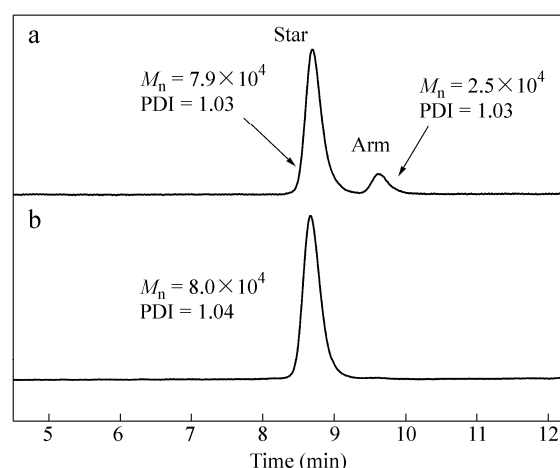


Fig. 1 GPC traces of (a) the coupling reaction mixture and (b) the isolated star PB after fractionation (M_w and PDI were determined from GPC using THF as eluent at 40 °C.)

Table 1. Molecular characteristics and rheological parameters of model linear and 3-arm star PE

Sample ^a	M_w ^b (kg/mol)	M_w/M_n	T_m (°C)	T_c (°C)	LCB/1000C	η_0 ^c (Pa·s)
L4	44	1.22	105.9	89.5	0	2.70×10^3
L8	78	1.04	104.2	86.5	0	5.02×10^3
L10	101	1.10	103.7	87.8	0	1.13×10^4
L20	187	1.11	104.2	86.5	0	5.38×10^4
S6	61	1.02	105.3	88.9	0.34	1.74×10^3
S8	83	1.13	104.3	85.9	0.25	1.49×10^4
S9	90	1.04	102.5	88.1	0.23	5.10×10^5
S11	112	1.07	102.8	85.1	0.19	1.68×10^6
S13	137	1.10	103.2	87.6	0.11	8.09×10^6
S20	206	1.05	101.3	86.3	0.10	9.91×10^6

^a Series L for linear PEs, series S for 3-arm star PEs; ^b by GPC-MALLS; ^c taken at $\omega = 0.01$

GPC-MALLS

The use of GPC coupled with MALLS detector can determine M_w and R_g simultaneously, as a result, the branching information can be obtained^[12, 14, 15]. The identification of LCB relies on the R_g of branched polymers, while it has been found that the R_g could also be affected by SCB^[12]. The SCB content of model PEs in this study is similar, so the influence of SCB could be ignored when comparing these polymers. The results of the molecular characterization of the linear and star PE samples are summarized in Table 1. In Fig. 2, the radius of gyration is plotted as a function of the absolute molecular weights for some linear and star PE samples.

The detection limit for R_g is around 20 nm, which is corresponding to a molecular weight of 100 kg/mol for linear PE^[16, 17]. It was presented by the dashed line shown in Fig. 2. As we know, the broader the molecular weight distribution, the wider the window on R_g is. The R_g data we obtained for all the samples covered relative narrow range of M_w due to their narrow distributions. The data of linear samples L10 and L20 overlapped with

each other. The exponent in $R_g(M_w)$ -relationship ($R_g = KM_w^a$) was 0.52, which was lower than the value reported for PE, around 0.7^[14]. The data points of star samples almost lay on the linear line. It can hardly be found the deviation for S9 and S11, and the deviation of S20 from the linear reference line at high molecular weight was so weak that it might be within the experimental error. The decrease of R_g , which always results from the presence of LCBs, was not found for most of the 3-arm star PEs in this study. The molecular weight dependence of R_g was indeed almost identical to the trend of linear polymer. Hence, it cannot be ascertained the existence of LCB from the $R_g(M_w)$ -relationship qualitatively. For the failure in detecting LCB in 3-arm star PEs, one was due to the low M_w , which resulted in a small coil contraction below the GPC-MALLS detectivity, and the other was due to the low LCB content by the increasing of M_w . It has been reported that the detection level of GPC-MALLS was 0.005 LCB/1000 carbons for PE of M_w equal to or greater than 1000 kg/mol^[12]. When the M_w decreases, the LCB detection level become increasingly poor. For the star PE S20 ($M_w = 200$ kg/mol), though the LCB content was around 0.1 LCB/1000C, it still showed no clear evidence of the presence of LCB. Accordingly, for the one-branched star PEs, of which M_w below 200 kg/mol, the $R_g(M_w)$ -relationship in GPC-MALLS could not serve as a useful tool for detecting LCB.

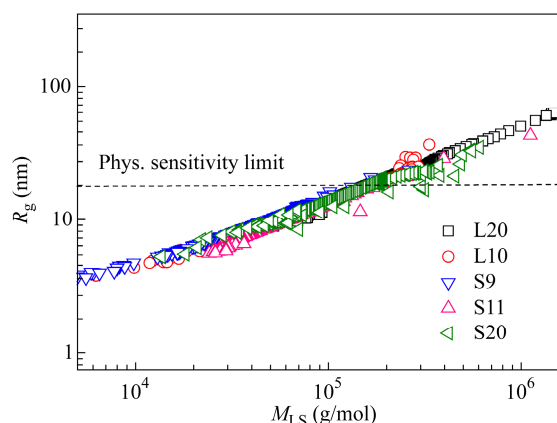


Fig. 2 The R_g versus molecular weight plots of linear and 3-arm star PEs

Melt Viscosity and Modulus Functions

Figure 3(a) shows the complex viscosity (η^*) of the samples as a function of angular frequency (ω) at 150 °C. For the linear samples, the η^* kept constant over the entire testing frequency range, which is approximately the Newtonian liquid character. This is a typical behavior of linear polymers with low M_w and narrow MWD. With increasing molecular weight, the onset of the plateau appeared to shift to lower frequencies. In the case of the star samples with M_w less than 130 kg/mol, the viscosity plateau appeared at lower frequencies than the linear sample with the same M_w , displaying obvious shear-thinning behavior. Even for the star sample S11 ($M_w = 110$ kg/mol), it had higher complex viscosity at low frequencies and more dramatic shear-thinning behavior at high frequencies than linear sample L20, of which the M_w is almost 2 times as that of S11. Moreover, the transition to shear-shinning became broader compared to linear polymers, which resulted from the broadening of relaxation. For the star samples whose molecular weight was higher than 130 kg/mol, the viscosity plateaus cannot be reached within the frequency range (0.01 to 100 rad/s). The η^* at terminal region was increased by more than 2 orders of magnitude in comparison with the linear counterparts of the same molecular weight. Clearly, the characteristics of LCB in viscosity, such as an increase in the zero shear viscosity (η_0 , listed in Table 1) and enhanced shear thinning behavior, can be observed even for the 3-arm star PEs with a M_w below 100 kg/mol. These phenomena were more apparent in the star samples with high molecular weight. Generally, high molecular polymers can mimic behavior of long chain branched polymers, which may lead to confusion in diagnosing the LCB structures. In order to remove the effect of molecular weight on η^* , the data were shifted on both axes by use of the η_0 ^[16, 18] (Fig. 4, the definition of η_0 values will be mentioned below). The straight dash

line with double log slope of -1 at high frequency presented the limiting slope of shear thinning behavior^[16]. The plot of star PE at high frequency clearly deviated from the line, showing a more obvious shear thinning behavior. This will make the estimation of LCB easier.

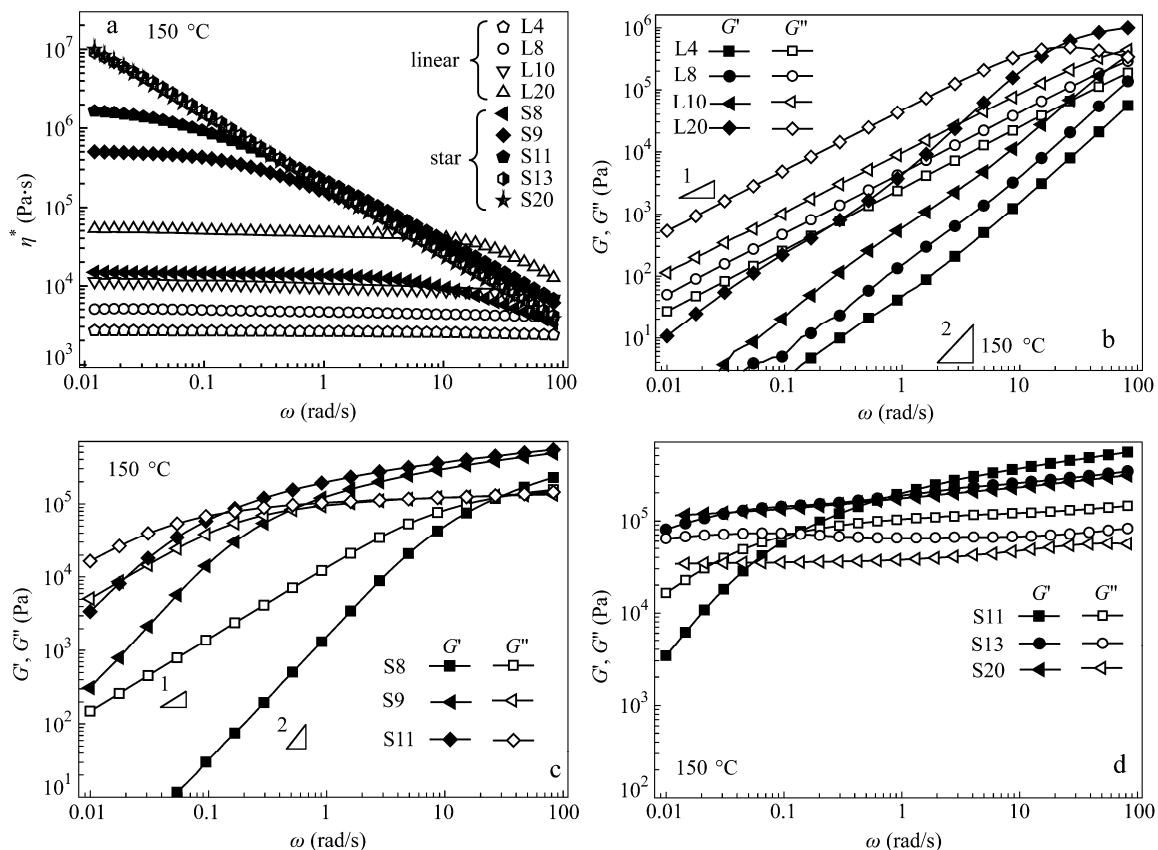


Fig. 3 Plots of complex viscosity (η^*) of all PEs (a) and storage modulus (G') and loss modulus (G'') of linear PEs (b), star PEs with low M_w (c) and star PEs with high M_w (d)

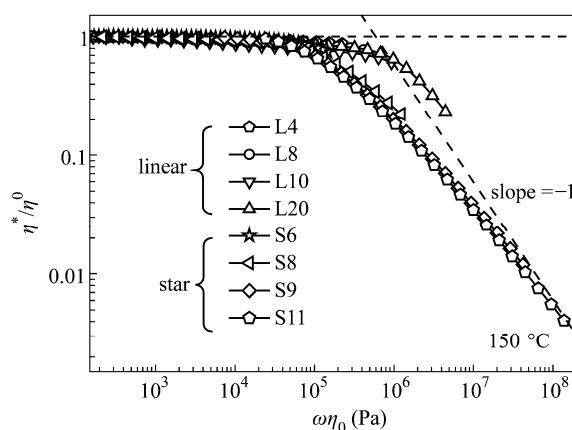


Fig. 4 Normalized viscosity functions of several linear and 3-arm star PEs at 150 °C

The plots of storage modulus (G') and loss modulus (G'') as a function of ω at 150 °C are presented in Fig. 3. Both G' and G'' curves of the linear samples were almost parallel with each other over the whole

frequency region and followed a power law ($G' \propto \omega^2$, $G'' \propto \omega$) in the terminal region (Fig. 3b). There were no crossover points of G' and G'' within the experimental range for the linear samples except L20. As a consequence of large number of entanglements, the G'' curve of L20 attained its maximal value at high frequency region and then decreased, also the G' curve reached a plateau and kept constant at high frequencies.

For the 3-arm star PEs with low molecular weight, G' and G'' had the same slope with linear samples in the terminal region (Fig. 3c). All the G' curves indicated a second relaxation regime which was caused by the presence of LCBs^[19]. The transition from the terminal region to the plateau region broadened, and the onset of transition frequency was decreased with increasing molecular weight of the samples. There were modulus crossovers for all these samples, and they shifted to lower frequencies with the increase of molecular weight. In fact, the inverse of the crossover frequency (ω_c , the corresponding frequency at the crossover point) can be considered as the characteristic time of the long-term relaxation process. Clearly, the time required for the star polymers with high molecular weight to relax was much longer than those with low molecular weight. Figure 5 compares the crossover points of three star PEs. It could be seen that, the crossover modulus (G_c , the crossover point of G' and G'') for the samples with different M_w were extremely close to each other, whereas the crossover frequencies were very different. This result showed the effects of molecular weight and molecular weight distribution on the dynamic modulus, that is, different M_w affected the modulus along the horizontal axis (frequency), and the shifts along the vertical axis (modulus) which was induced by MWD were not observed due to narrow MWD of the samples. Thus the modulus crossover can be an additional method for understanding the molecular structure of narrow MWD polymers.

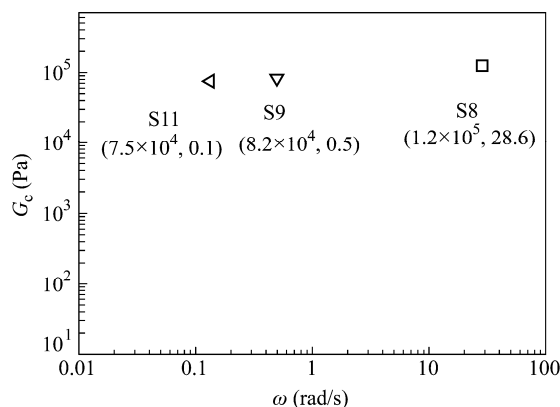


Fig. 5 The modulus crossover points of 3-arm star PEs

The modulus plots of S13 and S20 are shown in Fig. 3(d). Compared to S11, both S13 and S20 did not have modulus crossover points in the accessible range of frequencies. G' and G'' possessed high values over a wide frequency range, and the curves of G' and G'' were even approximately parallel for S20. It is reasonable to speculate that the crossover between G' curve and G'' curve will occur at much lower frequencies owing to the high entanglement of the polymer, and the enhancement of G' and G'' at the terminal region indicated a slow relaxation of the high-molecular weight star polymer. This behavior is in agreement with the calculated results with branch-on-branch (BOB) model in the literature^[20], in which the linear viscoelasticity of symmetric star polymers was independent on the number of side arms and only determined by the length of arms.

In a word, for the star samples with low molecular weight (< 100 kg/mol), the slopes of the modulus plot were very close to those of the linear samples, but the increase of modulus in terminal region and the broadening of the transition zone were clearly observed in comparison with the linear components, from which the presence of LCB can be deduced.

Zero Shear Viscosity (η_0)

As shown in Fig. 3(a), for the linear PEs and star PEs of which molecular weight were below 110 kg/mol, viscosity plateau could be observed in the terminal region, and the ω -independent plateau value was taken as η_0 (at $\omega = 0.01$ rad/s), while for the star PE S13 and S20, the viscosity increased as the frequency decreased and did not reach a distinct plateau even at the lowest frequencies we applied. As the shape of the viscosity plot shows, it is no doubt that η_0 must be distinctly higher than the η^* obtained at $\omega = 0.01$ rad/s, thus it is difficult to directly measure η_0 from the frequency sweeps due to extremely long relaxation time. Figure 6 shows the η_0 of all the samples as a function of M_w , and the η_0 values of S13 and S20 were taken at $\omega = 0.01$ and marked by arrows meaning that the real η_0 was higher than these values. The data of the linear samples fell on a linear reference line (described by $\eta_0 = 9 \times 10^{-15} M_w^{3.6}$)^[16], and the η_0 of the star samples lay above the reference η_0 - M_w -line. Furthermore, it displayed a more notable deviation for the high molecular weight star PEs than the low molecular weight ones. This shows the very high sensitivity of η_0 with respect to long-chain branching, especially for the samples with high molecular weights. The unusual appearance of L4 and S6 may be due to the experimental uncertainty below the detection limit of GPC-MALLS.

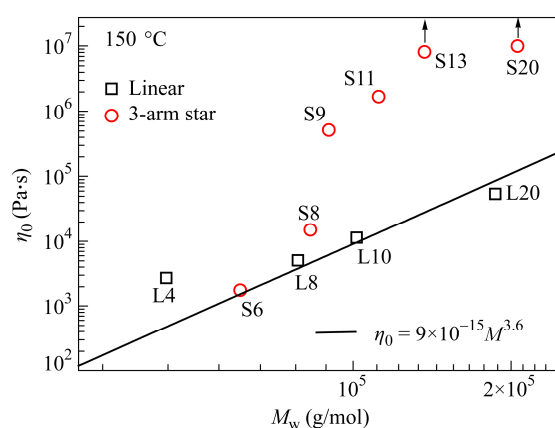


Fig. 6 η_0 - M_w correlation of linear and 3-arm star PEs

Cole-Cole Plot

There are several plotting techniques that have been developed to bring out structure features, for example, η'' versus η' (Cole-Cole plot), and G' versus G'' (Han plot). In these representations, the dependence on frequency is lost and they are useful for qualitative diagnosis. It was first proposed by Cole and Cole regarding the plotting of data for complex dielectric constant^[21], $\epsilon^* = \epsilon' - i\epsilon''$. And then it was found that the temperature shift factors for the dielectric relaxation of several blends were very close to those for the shift of linear viscoelastic data, if a slightly different reference temperature was used for the two types of data. Thus, the plot of the imaginary part (η'') against real part (η') of the complex viscosity was presented and used as criteria for miscibility in polymer blends^[22], or as a tool for the detection of molecular structure^[23]. As described in the literature, for the monodisperse linear polymers which have single relaxation time, Cole-Cole plots yield an arc of a circle, and the arc becomes shallower with the increase of MWD. Figure 7 presents the Cole-Cole plots of the linear and 3-arm star PEs. The differences among the plots can be clearly seen, where the parabolas enlarged with the increased M_w ascribable to the growing η'' derived from the slower relaxation. For S13 and S20, the plots were not a full arc and even did not reach a maximum, which is a sign of extremely long relaxation time and well in accordance with the afore conclusion. The other 3-arm star PEs all presented semicircles as the linear ones, and the deviations resulting from the presence of LCB were not found^[23]. There was no obvious difference between the shape of linear and star samples in Cole-Cole plots, hence it seems not suitable for detecting LCBs in such star branched polymers.

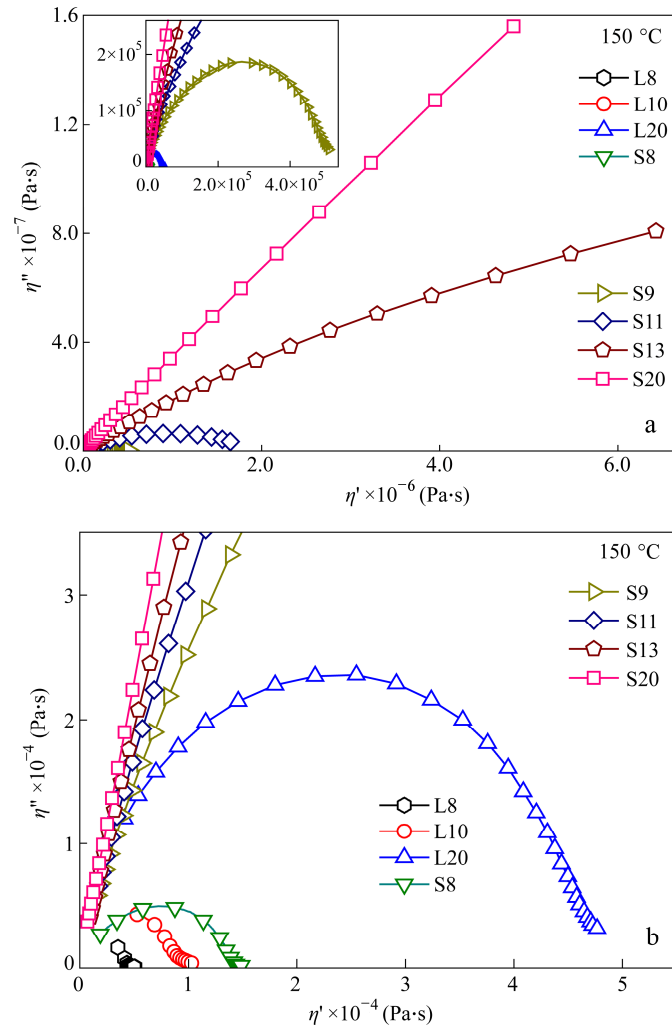


Fig. 7 Cole-Cole plots of linear and 3-arm star PEs

Han Plot

A plot of double-logarithm of G' and G'' was also a useful tool for interpreting the molecular structure. Depending on which modulus is taken as the independent variable, the curve performs a line with a slope of 0.5 or 2. The plot of $\lg G''$ versus $\lg G'$ known as modified Cole-Cole plot was presented by Harrell and Nakajima^[24], which has been widely applied to investigate the effects of LCB^[24–26]. Meanwhile the logarithmic plots of G' versus G'' was used to explore rheological behavior by Han and co-workers^[27]. Figure 8 presents the Han plot of linear and 3-arm star PEs. There was no difference in the shape of the curves for linear PEs with different M_w , and they all lay on a single line with the slope around 2, whereas the plots of star PEs did not superpose and diverged in the region of high modulus, which is different from the reports that divergence appeared in the terminal region for the long chain branched polymers^[23, 25]. The slope of the star PEs increased somewhat with increasing molecular weight. The long solid line in the figure is the locus of equal modulus ($G' = G''$). In the region above this line, the melt behavior is predominantly elastic, whereas under the line, the viscous behavior dominates the sample^[28, 29]. For both the linear and star samples in this study, the most part of the curves were located below the line, indicating a viscous behavior. The plots of polymers with high molecular weight had crossovers with the equi-modulus line, which were G_c as we mentioned before. It could be seen that G_c of the star polymers were slightly decreased with the increase of molecular weight. So the existence of LCB can be judged in contrast to the linear reference.

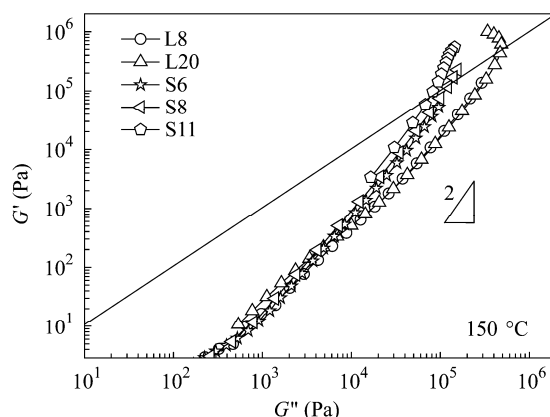


Fig. 8 Han plots of linear and 3-arm star PEs

Thermorheology

Since the rheology of polymer melt depends strongly on temperature, and this temperature dependence is always severely affected by molecular structure (such as molecular weight, molecular weight distribution, and long chain branching). Therefore, thermorheology, as a study of polymer melts at different temperatures, is demonstrated to be an interesting rheological method for understanding the branching structures^[30–33]. For entangled melts of linear chains, the temperature dependence is remarkably simple, but for the branched polymers, it varies at different temperatures due to their sensitivities of relaxation times. Thus it is possible to construct a master curve for the linear polymers by shifting the curves obtained at various temperatures, which is known as thermorheological simplicity, but it is impossible for LCB polymers, indicating a failure of time-temperature superposition (TTS) principle, which is regarded as thermorheological complexity. In general, the thermorheological analysis of polymer structures is mainly focused on whether a polymer melt is thermorheologically simple or complex and the determination of flow activation energy (E_a).

Based on the previous reports, for a thermorheologically simple material, master curves can be obtained from many rheological functions of linear viscoelasticity, *e.g.* $G' \sim \omega$, $G' \sim \eta_0 \omega$, $G' \sim G''$, $\tan \delta \sim \omega$, $\delta \sim |G^*|$ ^[33–35], which have been reported as techniques for detecting thermorheological complexity. Stadler *et al.* has explored the plot of master curve of G' as a function of the shifted frequency ($\alpha_T \times \omega$) for detecting thermorheological complexity^[33, 36], and then the LCB information was inferred. Owing to the different shift factors at different temperatures and different frequencies, master curves cannot be constructed for the polymers with LCBs, and the disagreement of the curves was shown more clearly in linear scaling than in double logarithmic scaling. The plot of the magnitude of the complex modulus versus the product of zero-shear viscosity and frequency ($G^* \sim \eta_0 \omega$), which was proposed by Wood-Adam and Costeux, was another method used to infer thermorheologically complex behavior. Such plots are temperature independent for simple materials and temperature dependent for complex materials^[34]. Robertson has mentioned that a failure of $\tan \delta(\omega)$ superposition was assessed to be a sign of thermorheologically complex polymer^[35]. The Cole-Cole plot and Han plot mentioned above could also be used to detect the thermorheological complexity by the appearance of deviation.

vGP Plot

Besides the aforementioned plots, the plot of the loss angle (δ) as a function of the complex modulus $|G^*|$ (known as van Gorp-Palmen plot) was proved to be very sensitive for detection of thermorheological complexity^[37]. If the effect of b_T (vertical shift factor) on the magnitude of $|G^*|$ is negligible, the data will superpose without shifting as long as the material is thermorheologically simple. Owing to its sensitivity with respect to LCBs and MWDs, the plot would form various shapes according to different structure parameters. Trinkle *et al.* have used this plot to reveal the presence of LCB by the distinctive features of the curves, which are related to different polymer topologies^[38, 39]. There is a transition in the vGP plots for LCB polymers, which

could not be seen for linear ones. Although the physical meaning of such a transition in the vGP plot is not clear from the plot, the frequency of the characteristic transition point can be correlated with the relaxation time of the arm^[20]. Thus, the transition would become obvious with the LCB increased.

For the linear sample L20 (Fig. 9a), the curves measured at different temperatures merged on one single curve, indicating thermorheological simplicity. The $\delta(|G^*|)$ curves of star sample S13 significantly deviated from the linear reference and diverged with increasing $|G^*|$ (Fig. 9b), and master curve could not be constructed by using a single horizontal shift factor. Accordingly, the 3-arm star PE was declared to be thermorheologically complex, which may be induced by the presence of LCB and the microstructure of the polymer chain^[40–42]. Figure 10 shows the vGP-plots of both linear and star samples with different M_w . All the data of linear PEs superimposed on a single curve with good accuracy. The values of δ were close to 90° and reached a plateau at low values of $|G^*|$, meaning that the sample response is almost entirely viscous, and at the region of high $|G^*|$, the δ dropped steeply, implying that the melt is dominated by elastic response. But the vGP plots of star PEs showed a different picture, which shifted to lower $|G^*|$ and showed a bump. The bump transition got more and more obvious and appeared at lower δ as the molecular weight increased, and it finally formed a clear plateau for sample S20 ($M_w = 200$ kg/mol). For the star polymers with molecular weight less than 100 kg/mol, there was only shift but no visible inflection observed.

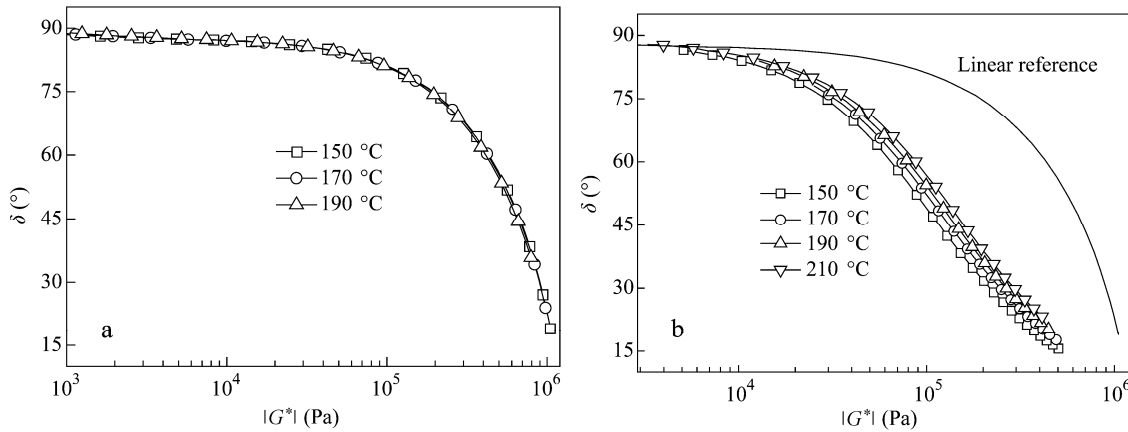


Fig. 9 vGP-plots of linear sample L20 (a) and 3-arm star PE S13 (b) at different temperatures

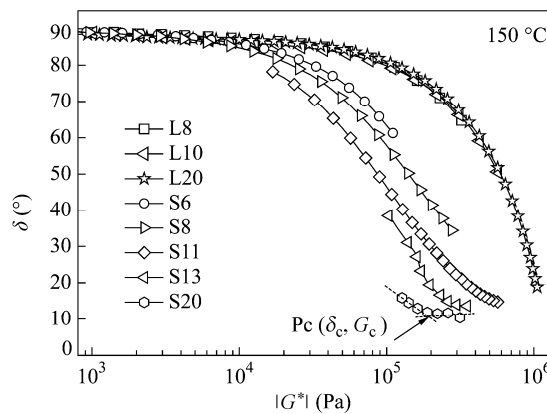


Fig. 10 vGP-plots of linear and 3-arm star PE samples with different molecular weights (at 150°C)

Flow Activation Energy (E_a)

The flow activation energy (E_a) is often discussed as an indicator of the molecular structure, especially the LCBs. In ethylene polymers, the presence of LCB is often associated with an increase of E_a ^[30, 33]. In general,

over temperature ranges far from the glass transition temperature, the temperature dependence of the time scale shift factor (a_T) often follows an Arrhenius-equation:

$$\alpha_T = \exp\left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

Where T is the absolute temperature in K, T_0 is the reference temperature and R is the universal gas constant. E_a can be calculated from the Arrhenius-equation based on different rheological quantities. There have been various approaches proposed for the determination of E_a , e.g., viscosity, modulus and phase angle^[30, 33, 34]. However, the E_a values may not be absolutely equalized from the different ways of defining E_a , so far there is no common method to obtain E_a , thus it is essential to explain in detail how the E_a value is determined.

In this work, the E_a values were calculated by different phase angles (δ) according to the method presented by Keßner *et al.*^[30, 43]. The G' contains the vertical shift factor b_T , thus calculation by G' would lead to a modulus dependent E_a ^[30]. To overcome these difficulties, b_T can generally be excluded by evaluating the temperature dependence using $\tan\delta(\omega, T)$ or $\delta(\omega, T)$, respectively^[30, 43]:

$$\tan\delta(\omega, T_0) = \frac{G''(\omega, T_0)}{G'(\omega, T_0)} = \frac{b_T G''(\alpha_T \omega, T)}{b_T G'(\alpha_T \omega, T)} = \tan\delta(\alpha_T \omega, T)$$

Here we determined E_a from the δ measured as a function of ω at different temperatures. First, plot a_T (derived from ω at distinct δ) semilogarithmically versus reciprocal absolute temperature ($1/T$), then the data would be fitted to a straight line, and E_a can be calculated from the slope of linear fits (Slope = E_a/R). The E_a values are shown in Fig. 11, where E_a is plotted as a function of δ for the linear and star PEs. It clearly showed that, the E_a values were independent of δ for all the samples, and the E_a of linear PEs were all around 28 kJ/mol and independent of the molecular weight. As previously mentioned, the hydrogenated PBs are structurally equivalent to copolymers of ethylene and 1-butene. Thus, the hydrogenated PBs obtained from PB with 7% of 1,2-units, were equivalent to ethylene-butene copolymers with about 4% of 1-butene. It has been reported that the E_a of PE with 4% butene comonomer was 29 kJ/mol^[43], which is consistent with the results of the linear hydrogenated PBs in this study. Although E_a is not only related to the presence of LCB but also the length and content of SCB as reported^[34, 36, 43], all the model PEs obtained from hydrogenated PBs in this study, had the same ethyl branch content, we can neglect the influence of SCB when comparing these samples. The values of E_a for the 3-arm star PEs were higher than those of the linear ones, increasing monotonically with M_w in the range of 48 to 72 kJ/mol. This result revealed that, only one single long chain branch could indeed lead to a higher E_a in comparison with linear PEs, even for low-molecular-weight star samples. Thus the increase of E_a values can be very sensitive to the presence of LCB, which results from the high entanglements. The E_a could attain a very high value when M_w was high to 200 kg/mol, which is approximately equal to the level of comb

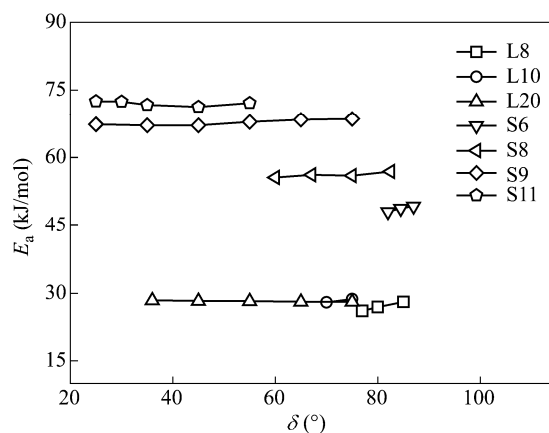


Fig. 11 The activation energy E_a as a function of phase angle δ of linear and 3-arm star PEs

polymer or highly branched LDPE mentioned in the literatures^[44, 45]. So it is impossible to infer the polymer topology just from the value of E_a without knowing the preparation information or without combining with other characterization methods.

Since the industrial LLDPE with sparse LCB, in fact, is often a blend of linear and branched chains, a binary of linear/star blend was also demonstrated for the detection of extremely low levels of long chain branching with the aforementioned techniques. The efficiency was confirmed for the blend in which the content of LCB was low to 0.04/1000C.

CONCLUSIONS

A variety of linear and 3-arm star PE model polymers covering a wide range in molecular weights were synthesized by the living anionic polymerization of butadiene and the subsequent hydrogenation. Analyzing several rheological functions of these model linear and 3-arm star PE samples for detecting the LCB structure, it could be seen that analyses based on zero shear viscosity, vGP plot and flow activation energy were very sensitive to the 3-arm star PEs. The information on the presence of LCB can be obtained with these methods even for low molecular weight samples, which can not be observed by GPC-MALLS, but the information about LCB structure can not be obtained by the rheological methods alone. For the star samples we investigated, the molecular weights of the branch chains were much higher than the entanglement molecular weight of PE, even for the star sample S6, and the molecular weight distributions were approximately monodisperse, thus the sensitivity of the above results may be not applicable to the samples with less entangled branches or high MWD.

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