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Investigation of the effect of branched structure on the performances of the copolymers synthesized from ethylene and α-olefin with *rac*-Et(Ind)$_2$ZrCl$_2$/MMAO catalyst system

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Abstract

The branched copolymers prepared from ethylene and α-olefins using *rac*-Et(Ind)$_2$ZrCl$_2$/MMAO catalyst system were studied. Both the absolute molecular weight ($\bar{M}_w$) and the molecular size (radius of gyration, R_g) of the polymers eluting from gel permeation chromatography (GPC) columns were obtained simultaneously via a high temperature GPC coupled with a two-angle laser light scattering (TALLS) detector. The branched structures and performances of the copolymers display approximate molecular weight and molecular sizes were investigated. Wide angle X-ray diffraction analyses indicate that 16-carbon side branch could co-crystallize effectively with backbone chain at low α-olefin incorporation. The melt behaviors of the copolymers were studied by dynamic rheological measurements. Both branch length and comonomer content affect considerably the loss modulus, storage modulus and complex viscosity of the copolymers. The relationship between the dynamic-mechanical behavior and the comonomer content of the copolymers was also examined by dynamic-mechanical experiments. It is found that the intensity of β-transition raise with comonomer content increasing.

Keywords: Ethylene/α-olefin copolymers; Metallocene polyethylene; Rheology

1. Introduction

The development of catalysts technology has lead to the synthesis of a rich set of new polymers with different structures and performances to feed up the progressive demand of modern industry and life [1–12]. Recently, the branched polyethylenes such as linear low-density polyethylene (LLDPE) have grown in importance because of the specific properties that can be obtained by varying comonomer content and polymerization condition. The recent development of homogeneous single-site catalyst makes it possible to synthesize the copolymers with completely different structures and performances from traditional polyethylenes [13]. The ethylene/α-olefin copolymers obtained by metallocene catalysts show homogeneous comonomer distribution and narrow molecular weight distribution in comparison with those obtained with traditional Ziegler–Natta catalysts [14]. The correlation between the structures of the ethylene/α-olefin copolymers obtained with metallocene and their properties has been extensively studied [15–22]. Quijada reported that the melting temperature (T_m) and melting enthalpy (ΔH_m) of the copolymers decreased with increasing comonomer content [23]. Sun studied the effect of short chain branching on the coil dimensions of the copolymers from ethylene with 1-butene, 1-hexene, or 1-octene in dilute solution [24]. Yoon compared the thermal and mechanical properties of the ethylene/α-olefin copolymers obtained with (2-MeInd)$_2$ZrCl$_2$ and Ziegler–Natta catalyst (Mg(OEt)$_2$/DIBP/TiCl$_4$) [25]. Quinzani [26], Munstedt [27], and Zhu [28] studied the rheological properties of ethylene/α-olefin copolymers, respectively. However, the samples selected by them are not representative. For example, relative molecular weights but not absolute molecular weight were usually used. Furthermore, when the relationship between branched structure and property was investigated, the difference of the molecular weights of some samples is so great that the veracity of research results is suspectable. This prompts us to systematically investigate the effect of branching length and comonomer incorporation on the properties of the ethylene/α-olefin copolymers.

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In this work, the relationship between the performance of ethylene/α-olefin copolymers and branched structure was presented, such as the effect of branch length and comonomer incorporation on the crystallinities, rheological and dynamic mechanical properties of the copolymers.

2. Experimental part

2.1. Materials

Anhydrous toluene was refluxed and distilled from sodium/benzophenone under dry nitrogen. Octadecene, tetradecene, decene and hexene were purchased from Aldrich, and purified by distilling over sodium before use. Modified methylaluminoxane (MMAO, 7% Aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. Catalyst *rac*-Et(Ind)$_2$ZrCl$_2$ was purchased from Aldrich and used as received. All the manipulations of air and/or water-sensitive compounds were performed under a dry nitrogen atmosphere by means of standard Schlenk techniques.

2.2. Typical polymerization procedure

All copolymerizations were carried out under atmospheric pressure in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. Toluene and the required amount of comonomer were introduced into the nitrogen-purged reactor and stirred vigorously (600 rpm). The resultant solution was kept at a prescribed polymerization temperature, and then the ethylene gas feed (100 L/h) was started. After 15 min, polymerization was initiated by the addition of a solution of MMAO and then a toluene solution of *rac*-Et(Ind)$_2$ZrCl$_2$ into the reactor with vigorous stirring (900 rpm). After 30 min, the polymerization was stopped by adding acidic EtOH. The coagulated polymer was recovered by filtration, washed with acetone, and dried at 60 °C for 24 h in a vacuum oven.

2.3. Polymer characterization

The comonomer contents of the resultant copolymers were determined by ^{13}C NMR spectroscopy. The measurements were performed at 120 °C on Varian Unity-400 using *o*-dichlorobenzene as solvent. DSC measurements were performed on a Perkin–Elmer Pyris 1 DSC instrument under N$_2$ atmosphere. The samples were heated from 0 to 150 °C and cooled down to 0 °C at a rate of 10 °C/min. The melting temperature (T_m) and the value of fusion heat (ΔH_f) were taken from the second heating curve. Wide-angle X-ray diffraction patterns were recorded in the reflection mode at room temperature using a D/MAX 2500V, connected to a computer. The samples were pressed into 1 mm thick plates at 30–50 °C above T_ms. The diffraction scans were collected over a period of 20 min from 5 to 40° using a sampling rate of 1 Hz. The crystalline degrees of the copolymers were calculated via Eq. (1) developed by Mo and Zhang [29].

$$W_{c,x} = \frac{I_{110} + 1.42 I_{200}}{I_{110} + 1.42 I_{200} + 0.68 I_a} \tag{1}$$

It has been proved that GPC coupled with a TALLS detector (GPC-TALLS) is a convenient and quick method to study the shape and conformation of polymers in solution [30,32]. When a two-angle laser light scattering (TALLS) detector is connected to a GPC system, radius of gyration (R_g) as a function of the molecular weight of polymer can be obtained [31,32]. Once the concentration C_i, molecular weight M_{wi} and molecular size (R_{gi}) at each retention volume V_i along the entire GPC chromatogram have been determined, their average properties can be calculated as follows:

Weight-average molecular weight

$$\bar{M}_w = \frac{\Sigma C_i M_{wi}}{\Sigma C_i} \tag{2}$$

Weight-average radius of gyration

$$\bar{R}_{gw} = \left(\frac{\Sigma C_i R_{gi}^2}{\Sigma C_i} \right)^{1/2} \tag{3}$$

TALLS and DRI detectors were calibrated by multiple injections of a narrow distribution PS standard with $M_p = 21$ K, $\bar{M}_w/\bar{M}_n = 1.02$. Inter-detector volume between the TALLS detector and the DRI detector was also determined by superimposing the onsets of the TALLS and DRI responses with the PS standard.

Refractive index increment, d*n*/d*c*, a value of 0.053 mL/g for PS and −0.097 mL/g for polyethylene in TCB at 150 °C were used [30]. The value of −0.097 mL/g was also used to evaluate molecular weight of the synthesized copolymers considering the effect of olefin copolymers with longer chain α-olefin comonomers on d*n*/d*c* to be small and can be ignored [24].

Precision Acquirement 32 software from Precision Detectors Inc. was used to acquire data from the TALLS detector and the DRI detector in 1 s intervals. The acquired data were processed with Discovery 32 software (Precision Detectors Inc.) to obtain $M_{wi}(V)$, as well as $R_{gi}(V)$ of polymer at each elution volume V. The obtained M_{wi}, and R_{gi} as functions of retention volume (V_R) were exported to ASCII files and were further analyzed.

In order to discuss how the branched copolymers performed in TCB at 150 °C, several samples were chosen with close absolute molecular weight and distribution, but with different α-olefin incorporated, as shown in Fig. 1. We found that, C14-12 (ethylene-tetradecene, 409 K) and C18-11 (ethylene-octadecene, 412 K), C10-13 (ethylene-decene, 261 K) and C14-13 (ethylene-tetradecene, 262 K) display close R_g values, respectively. The results of incorporation (in mol%) obtained by ^{13}C NMR measurement (Fig. 3(a)) are C14-12, 1.15%; C18-11, 1.03%; C10-13, 4.33%; C14-13, 4.25%.

For the study of rheological properties, the samples were pressed into 1 mm thick plates at 30–50 °C above T_ms. The rheological measurements were carried out on a PHYSICA

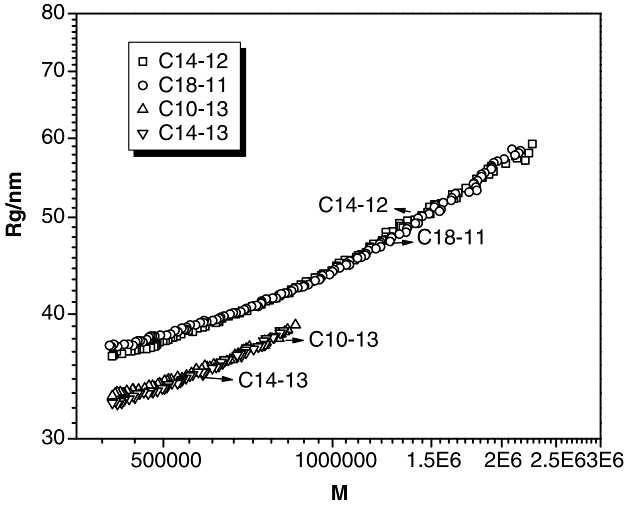

Fig. 1. R_g as a function of M for four copolymers in TCB at 150 °C. Absolute $\bar{M}_w$ for each copolymer: C14-12: 409 K; C18-11: 412 K; C10-13: 261 K; C14-13: 262 K.

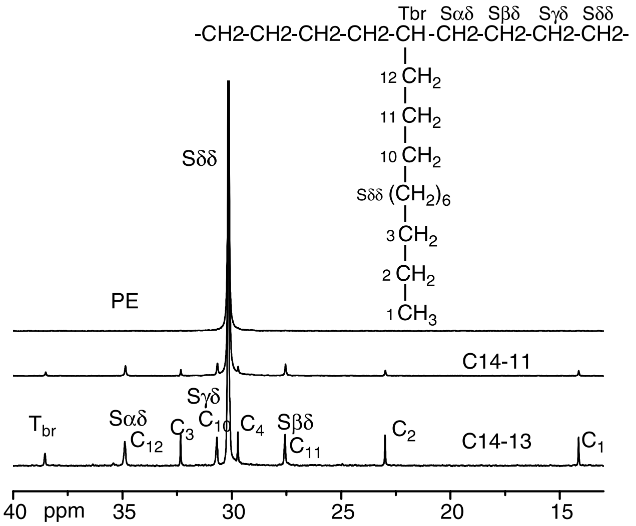

Fig. 2. ^{13}C NMR spectra of PE and ethylene-α-tetradecene copolymers with different percentages of α-tetradecene incorporated: C14-11, 1.31 mol%; C14-15, 5.48 mol%.

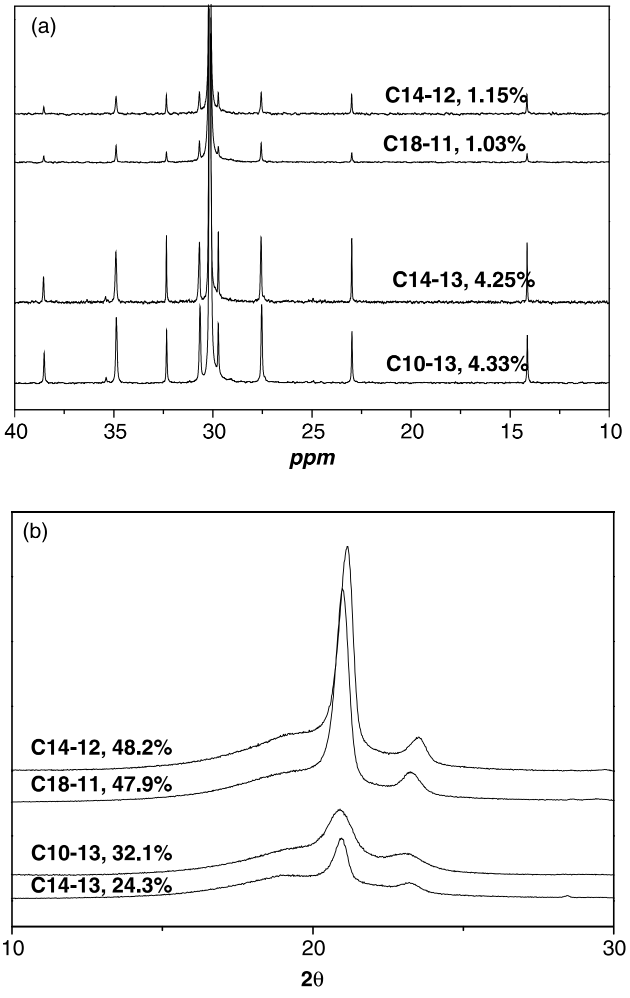

Fig. 3. Influence of branch length on the crystallinity (determined by X-rays) of ethylene/α-olefin copolymers. (a) ^{13}C NMR spectra of the copolymers. (b) X-ray diffractograms of the copolymers.

MCR 300 instrument. Frequency sweep for the polymers were carried out under nitrogen at 200 °C using 25 mm plate–plate geometry. The angular frequency was from 0.05 to 100 rad/s, and the sample gap was 0.5 mm. MCR300 software was used to acquire data.

For DMA measurements, the samples were pressed at 30–50 °C above T_ms to obtain films with homogeneous thickness (0.1 mm) and allowed to cool into room temperature. Rectangular films averaging 5 mm wide, 5 mm long and 1 mm thick were used. The dynamic-mechanical experiments were performed on a polymer dynamic mechanical analyser (DMA) 242C Instrument in tensile mode, and software DMA 242 measurement on 18 was used to acquire data. Measurements were carried out using a frequency of 1 Hz and a heating rate of 3 K/min. The temperature ranged from −150 °C close to the T_m of each copolymer.

3. Result and discussion

3.1. Molecular size and branched structure

The α-olefin incorporations in the copolymers were determined via ^{13}C NMR spectroscopy. The chemical dislocations in the copolymers were calculated according to the rules of Galland and Quijada [16,17]. Fig. 2 shows the typical spectra of the copolymer with different α-olefin incorporation, where the intensity of the peak corresponding to tertiary carbon, T_{br}, increases with comonomer insertion. It is noteworthy that all tetradecene units are isolated by ethylene units, and no sequence of double comonomer units or alternating ethylene/tetradecene units are found. Similar results were also obtained with other α-olefins (Fig. 3).

3.2. Thermal properties and crystallinity

Fig. 4(a) shows the DSC melting curves of the ethylene/tetradecene copolymers with different branching degree. It is

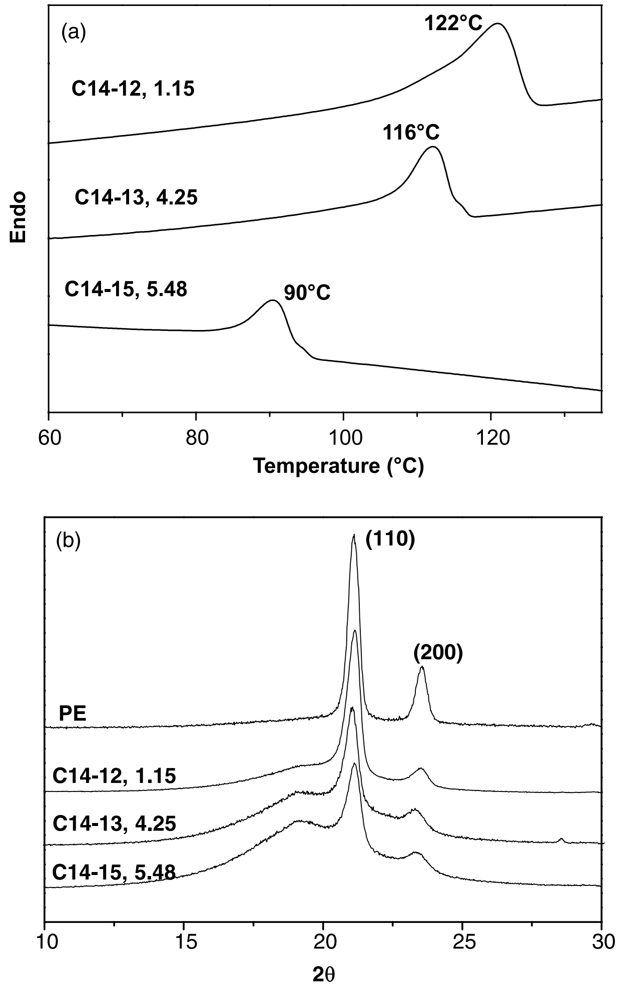

Fig. 4. (a) DSC melting curves of the ethylene/tetradecene copolymers with different branching degree; (b) X-ray diffractograms of the ethylene/tetradecene copolymers with different branching degree, C14-12, 1.15%; C14-13, 4.25%; C14-15, 5.48%.

very interesting that both the melting temperature and the enthalpy of melting decrease with increasing comonomer content, as shown in Fig. 5. Fig. 4(b) shows the X-ray diffractograms of the copolymers and the homopolymer (PE) synthesized under the same polymerization condition. It is observed that all the copolymers exhibit two crystalline peaks at 2θ of 21.1 and 23.5° corresponding to 110 and 200 spacings and one amorphous peak (A) at 2θ of 19.4°. It is evident that the degree of crystallinity decreased with increasing comonomer content.

The degree of crystallinity calculated both by enthalpy and X-ray is shown in Fig. 5 The results are very close to those reported by Koivumäki [20] and Quijada [23], and the values from X-ray determination are higher than those from the DSC.

It is generally accepted that short chain branches affect dramatically the crystallinitiy of polyethylene. Long chain branches, however, have only a little effect on the crystallinity as far as the long chain branches are long enough to co-crystallize with backbone chains, though the rate of the crystallization may be affected [35]. Yoon reported that 16-carbon side chain branches were not long enough to co-crystallize efficiently [25]. However, our research result is different from Yoon's. Fig. 3 shows the influence of branch length on crystallinity (determined by X-rays) of the copolymers synthesized from ethylene and α-olefins. The four curves can be divided into two groups, each of them owning similar $\bar{M}_w$ and comonomer content (shown in Table 1), so the effect of molecular weight and α-olefin incorporation on crystallinity can be ignored, only the branch length can affect the crystallinity. It can be seen that the curves of C18-11 and C14-12 are very close, the two samples display similar $\bar{M}_w$ and comonomer content, and the degree of crystallinity were nearly same (about 48%), indicating that 16-carbon is long enough to co-crystallize effectively with the backbone chains at low α-olefin incorporation. Nevertheless, the curves of C14-13 and C10-13 were different, and the degree of crystallinity were also quite different (about 24% for C14-13 and 32% for C10-13), indicating that compared with 8-carbon side branch, 12-carbon side branch is not long enough to co-crystallize efficiently, so shows more steric effect on the crystallinity. This steric effect works against the crystallinity of the branched copolymer.

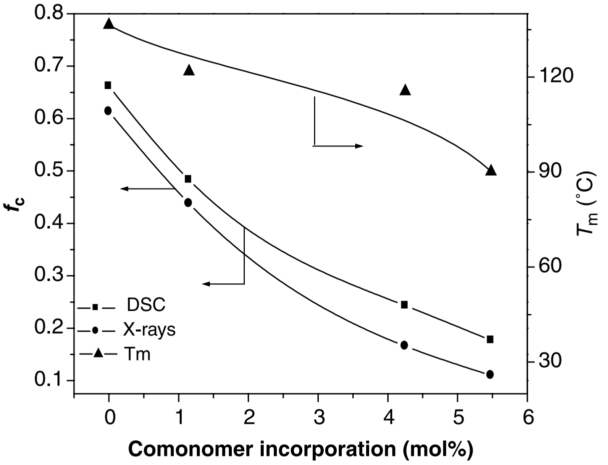

Fig. 5. T_m and crystallinity (*fc*, determined by both DSC and X-rays) of PE and copolymers as functions of branching degree: PE, C14-12, 1.15%; C14-13, 4.25%; C14-15, 5.48%.

3.3. Rheological behavior

Generally, short branches have a little effect on viscosities, while long branches may affect the viscosities markedly. When a branch is not long enough to entangle with other branch, and the chain packing is compact, chain interaction is usually small and the branched samples will display low viscosities. Zhu and colleagues studied the rheological behaviors of some long branched PEs at low shear rate, he found that the higher the long chain branched density is, the higher the viscosity is [28]. However, he did not deal with the effect of branch length. Villar and coworkers investigated the rheological behaviors of the ethylene/α-olefin samples with the variation of the length of the α-olefin. However, they did not find out the fact that the length of the α-olefin affects any of the rheological parameters

Table 1
Results of copolymerization and physical character of the copolymers synthesized from ethylene and α-olefins at 30 °C

Sample	α-olefins	Comonomer incorp. (mol%)	Crystallinity		Melt. Temp. (°C)	ΔH (J/g)	$\bar{M}_\mathrm{w}$ (kg/mol)	$\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$
			X-ray	DSC				
C18-6	Octadecene	5.95			91.4	32.1	113	2.01
C18-11	Octadecene	1.03	47.9		125.9	84.7	412	2.26
C18-12	Octadecene	1.93			114.6	57.1	171	1.95
C14-3	Tetradecene	8.43			67.6	4.6	92	2.11
C14-4	Tetradecene	6.49			86.5	17.5	112	1.97
C14-11	Tetradecene	1.31			116.6	78.2	286	2.34
C14-12	Tetradecene	1.15	48.2	43.8	121.8	80.5	409	2.23
C14-13	Tetradecene	4.25	24.3	16.6	115.5	32.5	262	1.96
C14-15	Tetradecene	5.48	17.7	11.0	90.2	20.2	173	1.80
C10-11	Decene	1.63	47.7		109.5	79.7	218	2.34
C10-13	Decene	4.33	32.1		92.1	30.8	261	1.91
C6-3	Hexane	7.89			68.5	6.1	93	1.93
PE			66.5		136.5	138.3	432	1.73

Reaction conditions: catalyst amount $n(\mathrm{zr}) = 3$ μ mol; $n(\mathrm{al})/n(\mathrm{zr}) = 2500$; temperature = 30 °C; polymerization time = 30 min; ethylene pressure = 1 atm.

studied because the $\bar{M}_\mathrm{w}$s of the samples they used were so wide that their $\bar{M}_\mathrm{w}$s range from 56 to 241 kg/mol [26].

In order to make clear the role of branch length in the effect on the rheological behavior of branched PEs, five batch samples with different branch length were chosen. GPC-TALLS analyses revealed that each batch possesses very close $\bar{M}_\mathrm{w}$s and molecular weight distributions (MWD) (Batch 1: C18-11: $\bar{M}_\mathrm{w} = 412$ K, MWD = 2.26, octadecene incorporation = 1.03%; C14-12: $\bar{M}_\mathrm{w} = 409$ K, MWD = 2.23, tetradecene incorporation = 1.15%, Batch 2: C14-13: $\bar{M}_\mathrm{w} = 262$ K, MWD = 1.96, tetradecene incorporation = 4.25%; C10-13: $\bar{M}_\mathrm{w} = 261$ K, MWD = 1.91, decene incorporation = 4.33%; Batch 3: C14-15: $\bar{M}_\mathrm{w} = 173$ K, MWD = 1.80, tetradecene incorporation = 5.48%; C18-12: $\bar{M}_\mathrm{w} = 171$ K, MWD = 1.95, octadecene incorporation = 1.93%, Batch 4: C18-6: $\bar{M}_\mathrm{w} = 113$ K, MWD = 2.01, octadecene incorporation = 5.95%, C14-4: $\bar{M}_\mathrm{w} = 112$ K, MWD = 1.97, tetradecene incorporation = 6.49%; Batch 5: C14-3: $\bar{M}_\mathrm{w} = 92$ K, MWD = 2.11, tetradecene incorporation = 8.43%; C6-3: $\bar{M}_\mathrm{w} = 93$ K, MWD = 1.93,hexene incorporation = 7.89%). Fig. 6(a) presents the dynamic viscosities of the ethylene/α-olefin copolymers in the shear rate range of 0.5–100 rad/s at 200 °C. Firstly, it is noteworthy that the melting viscosities of ethylene/tetradecene copolymer C14-15 with high comonomer insertion (5.48%) are much higher than those of ethylene/octadecene copolymer C18-12 with low conomoner insertion (1.93%) under the same conditions, which indicates that comonomer incorporation plays an important role in the effect on the dynamic viscosities of ethylene/α-olefin copolymers, higher branched polymer has higher melting viscosities.

It is very interesting that the melting viscosities of ethylene/octadecene copolymer C18-11 are higher than those of ethylene/tetradecene copolymer C14-12 under the same conditions, although the former displays slightly lower branching degree (1.03%) in comparison with the latter (1.15%). The melting viscosities of two samples of batch 2 show alike result. It indicates that branch length has considerable effect on the rheological behavior of

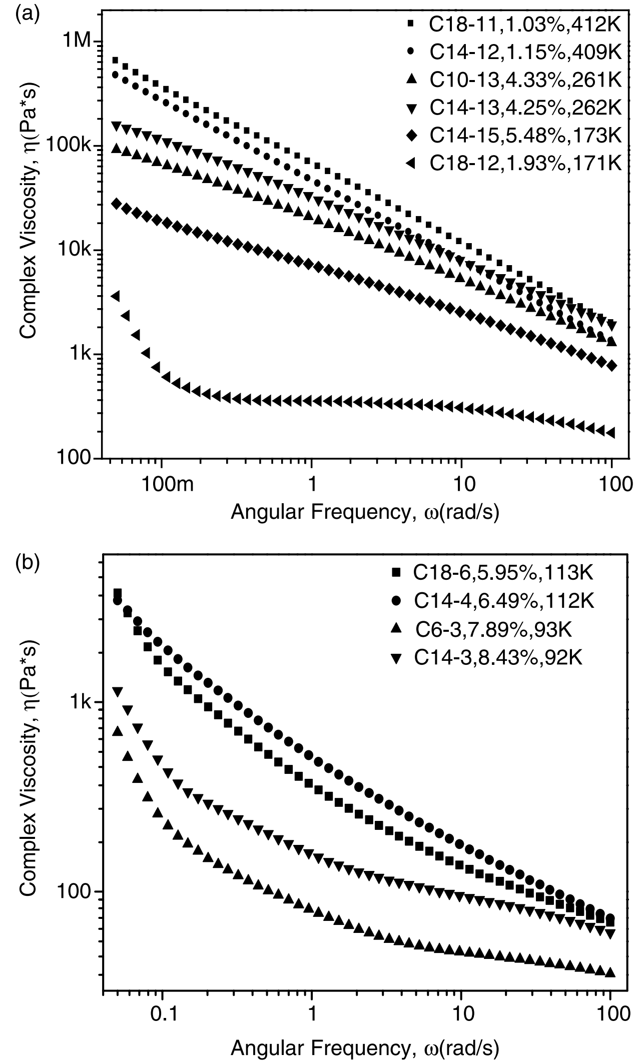

Fig. 6. (a), (b) Dynamic viscosity versus shear rate at 0.05–100 rad/s for ethylene/α-olefins copolymers (1-octadecene, 1-tetradecene, 1-decene and 1-hexene).

ethylene/α-olefin copolymers. To further confirm this argument, two batches of samples with similar distinction (about 0.5% separately) in conomoner incorporation are selected. As shown in Fig. 6(b), when the branch length of C18-6 (16 carbon) is a little longer than that of C14-4 (12 carbon), effect of branch length is much smaller than that of conomoner insertion. Namely, the melting viscosities of C14-4 show little higher than C18-16. Contrarily, when the branch length of C14-3 (12 carbon) is much longer than that of C6-3 (4 carbon), the effect of branch length is more evident than that of conomoner insertion. Exactly, the melting viscosities of C14-3 show much higher than C6-3.

Additionally, it is worthy of noting that the melting viscosities of batch1 and batch 2 are approximate especially in high shear rate area under the same conditions, which indicates that when molecular weight are high enough (for example 260–410 K), effect of molecular weight on the dynamic viscosities of ethylene/α-olefin copolymers is not evident any more.

Fig. 7(a) and (b) shows storage modulus (G') and Fig. 7(c) and (d) show loss modulus (G'') in the shear rate range of 0.5–100 rad/s at 200 °C. Both of them increased with shear rate for all the samples with different slopes. It is interesting to note that when $\bar{M}_w$, MWD and branching degree are very close, branch length of ethylene/α-olefin copolymer also affects storage modulus (G') and loss modulus (G'') considerably like dynamic viscosity, while comonomer incorporations are of evident discrepancy, the branching degree still is the main factor in affecting storage and loss modulus.

3.4. Dynamic mechanical behaviour

Generally, structure and composition have a great influence on thermal dynamic mechanical behaviours of ethylene/α-olefin copolymer [33]. LLDPEs show some transitions or relaxations besides the melting temperature (α-transition) in mechanical relaxation. These transitions are called α-, β- and γ-transition in decreasing order of temperature, and can be observed conveniently from loss tangent (tan δ) curves. Although both α- and β-transition are affected by comonomer structure and incorporation, most information is obtained from the study of β-transition. The β-transition can be determined either from the peak maximum of loss modulus curve E'' or the peak maximum of tan δ (tan $\delta = E''/E'$), and this transition has been shown to originate from the amorphous phase near the branching points [34]. Fig. 8 shows the tan δ versus temperature curves of the copolymers with different comonomer contents. In temperature range from −50 to 10 °C, β-transition can be observed. Although β-transition can hardly be observed for ethylene/octadecene copolymer C18-11 with very low comonomer incorporation (1.03%), the intensity of β-transition increases with the increase of the comonomer incorporation, which indicates that the amorphous phase near

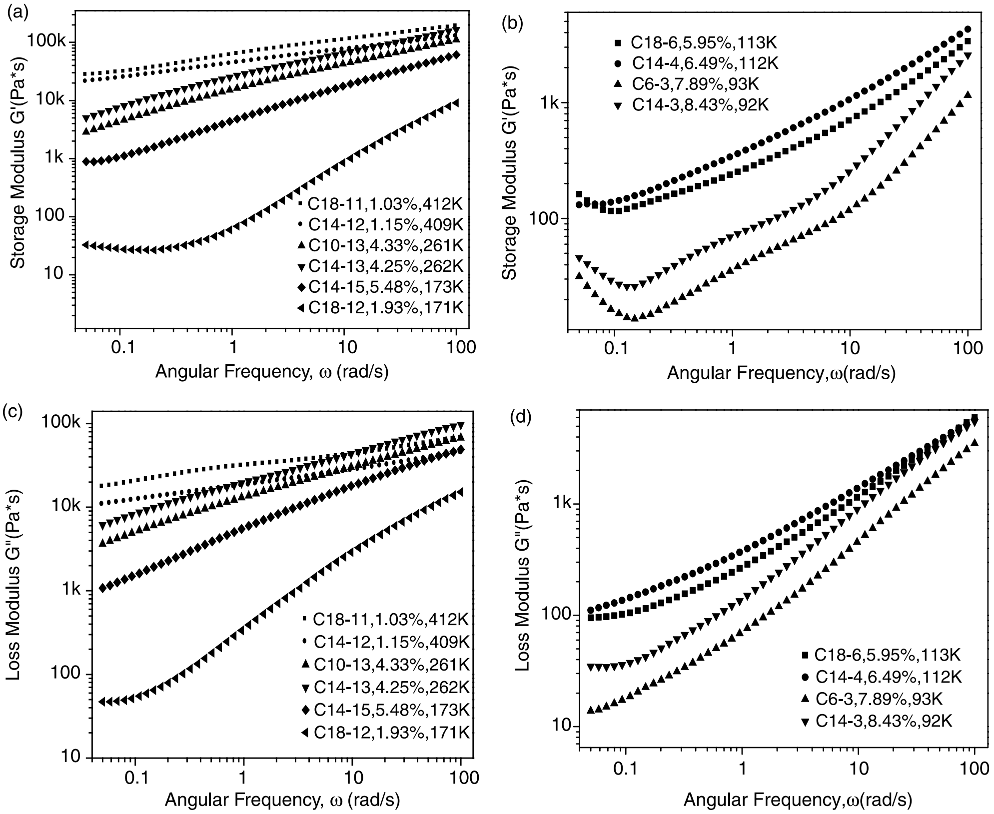

Fig. 7. (a) and (b) Storage modulus G'; (c) and (d) Loss modulus G'' versus shear rate at 0.05–100 rad/s for ethylene/α-olefins copolymers (1-octadecene, 1-tetradecene, 1-decene and 1-hexene).

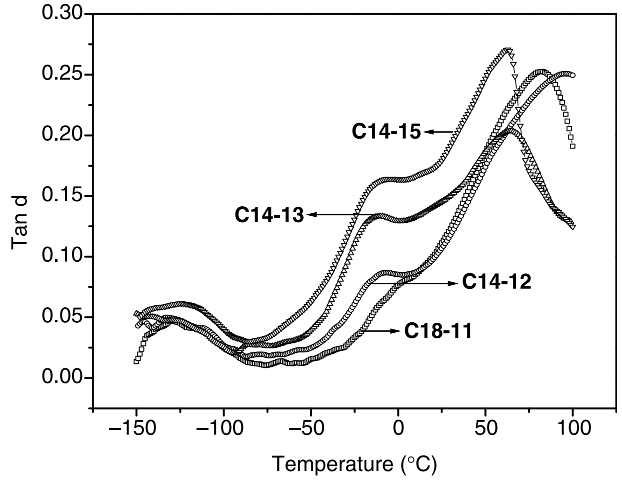

Fig. 8. tan δ curves of the copolymers of ethylene and α-olefins. C18-11: $\bar{M}_w = 412$ K, 1.03%; C14-12: $\bar{M}_w = 409$ K, 1.15%; C14-13: $\bar{M}_w = 262$ K, 4.25%; C14-15, $\bar{M}_w = 173$ K, 5.48%.

the branching points increases with increasing the comonomer content in the copolymers.

In general, the comonomer incorporation in the backbone chain affected considerably the mechanical properties of copolymer. Fig. 9 shows logarithms of the storage modulus (E') versus temperature of the ethylene/tetradecene copolymers with different comonomer contents, at 1 Hz. As shown in Fig. 9, at the temperature above about −50 °C, the storage modulus values (as an indicator of stiffness) lower gradually with increasing comonomer incorporation, indicating that the stiffness of these copolymers decrease with the increase of comonomer content in the copolymers. Of all the five copolymers, ethylene/octadecene copolymer C18-11 with the lowest comonomer content (1.03%) displays the highest level of stiffness, while ethylene/tetradecene copolymer C14-15 with the highest comonomer content exhibits most plasticizing properties. It is noteworthy that although the branch lengths of ethylene/decene copolymer C10-13 and ethylene/tetradecene copolymer C14-13 are different, they exhibit very close stiffness. Analogously, ethylene/octadecene copolymer C18-11 and ethylene/tetradecene copolymer C14-12 possess close comonomer content, and also display the almost same stiffness. This fact indicates that when the branches are of small discrepancy (less than 4 carbons) and the branching degree is very close, the effect of the branch length of copolymer on the stiffness or plasticizing properties can be ignored.

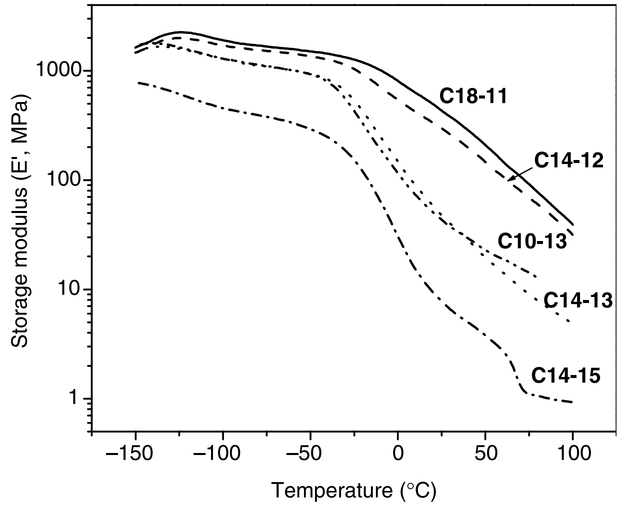

Fig. 9. Logarithms of the storage modulus versus temperature of the ethylene/α-olefins copolymers with different comonomer contents, at 1 Hz.

4. Conclusions

Both absolute molecular weights ($\bar{M}_w$) and molecular sizes (radius of gyration, R_g) of a series of ethylene/α-olefin copolymers were obtained by GPC-TALLS measurement. DSC and WAXD measurements reveal that the melting temperature, the melting enthalpy and the degree of crystallinity of the copolymers decrease with increasing comonomer incorporation. Furthermore, 16-carbon side branch is long enough to co-crystallize effectively with the backbone chain at low comonomer incorporation, although it displays more steric effect compared with short ones. The investigations of the rheological behaviors of the copolymers indicate that comonomer incorporation does affect dramatically the viscoelastic properties of the copolymers. The branch content also greatly improves the copolymer elasticity, as the evidence from the increases in storage modulus with higher comonomer content. Additionally, branch length also affects considerably rheological behaviors of the copolymers. The increase of branch length can improve the processability of ethylene/α-olefin copolymers. DMA measurements show that just comonomer content but not branch length affects significantly on stiffness under the similar conditions. Moreover, the intensity of the β-transition of the copolymer indicates the comonomer content directly, and is not affected by branch length when there is only four-carbon distinction.

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