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Effect of long chain branching on rheological properties of metallocene polyethylene

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Abstract

Polyethylenes (PE) with long chain branching (LCB) densities up to 0.44 carbons/10 000 carbons and narrow molecular weight distributions were synthesized using a continuous stirred-tank reactor (CSTR) with the Dow Chemical's constrained geometry catalyst system, CGC-Ti/TPFPB/MMAO, in Isopar E solution at 500 psig and 140–190°C. Rheological properties of these metallocene polyethylenes (mPE) were evaluated and correlated to the LCB density. Measurements included steady-state viscosity, dynamic viscoelasticity, melt flow index and extrudate swell. Compared to their linear counterparts with the same molecular weights, LCB PEs gave higher viscosities at low shear rates and lower viscosities at high shear rates. These shear-thinning properties measured by a melt flow index ratio I_{10}/I_2 strongly depended on the LCB density. PE with an average of fewer than one branch per six polymer molecules exhibited a I_{10}/I_2 value of 25.7 compared to linear PEs $I_{10}/I_2 = 6\sim8$ having similar molecular weights. An increase in the LCB density also significantly reduced the ratio of loss modulus over storage modulus, and yielded longer relaxation lifetime and higher level of extrudate swell. In contrast to the rheological properties, tensile strength, melting temperature, and other physical and mechanical properties were not noticeably affected by LCB. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Metallocene polyethylene; Long chain branching; Shear thinning

1. Introduction

Metallocene polyethylene (mPE) has attracted great attention from both manufacture and processing sectors since the recent development of commercial products in polyolefin markets [1–6]. The single-site type nature of metallocene catalysts allows scientists to design polymer chain structure at a molecular level and thus to tailor product properties. Different from the conventional Ziegler–Natta catalysts, metallocene catalysts produce polymers with narrow molecular weight distributions. While the metallocene polymers give better physical and mechanical properties than their Ziegler–Natta counterparts with the same average molecular weights [6–10], they often have poor processibilities due to high viscosities. However, the polymer processibility can be improved by introducing long chain branching (LCB) [4,7,9,10].

It has been known that the polymer processing behaviour and many end-use properties are influenced not only by molecular weight and molecular weight distribution, but also by long chain branching. The chain structural parameters have interactive effects on polymer properties. Numerous investigations have been carried out in the past few decades for the effects of LCB on rheological properties [11–19]. Many interesting phenomena were observed. Mendelson [11] reported that increasing LCB in low-density polyethylene (LDPE) at constant molecular weight and molecular weight distribution yielded a reduction in both Newtonian viscosity and elasticity. Their fractionated LDPE samples had narrow MWD less than 1.5 and LCB frequencies greater than 2 per polymer molecule. Based on an investigation on LDPE with polydispersities (M_w/M_n) about 7, Bersted and co-workers [12,13] concluded that LDPE generally had lower melt viscosities than HDPE at similar weight-average molecular weights (M_w). However, they also observed a striking enhancement in viscosity for polyethylenes having a low level of LCB and high molecular weight. Similar observations were also reported by Constantin [14], Wild and Ranganath [15], and Jacovic et al. [16]. Constantin [14] found that the enhancement in Newtonian viscosity was molecular weight dependent. Bersted and co-workers [12,13] reported that the effects of LCB on rheological properties also depended on the branching mechanism. Branches introduced in peroxide-initiated

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polymer modification showed stronger effects on viscosities than those by thermal or mechanical initiation.

LCB enhances polymer chain entanglements, provided side chains are sufficiently longer than some critical molecular weight, M_c. It also reduces polymer hydrodynamic volume. These two factors are opposing each other in influencing polymer rheological properties. At low shear rates, LCB polymers would have higher viscosities than linear ones due to the enhanced chain entanglement. However, the former are more prone to be disentangled than the latter due to the small hydrodynamic volume. LCB polymers are therefore expected to have better shear thinning properties. One of the reasons for the discrepancies observed in the previous experiments [11–16] regarding the effects of LCB on polymer viscosities may be due to the characteristic of LDPE chain structure: broad molecular weight distribution and coexistence of long and short chain branches. Branches in LDPE are introduced by chain transfer to polymer and backbiting mechanisms in free-radical polymerization of ethylene monomers. The transfer to polymer mechanism produces long chain branches, while backbiting generates short chain branches in the polymerization system. Both types of branches are usually not distinguishable for side chains having more than six carbons by spectroscopic methods.

The discovery of metallocenes as catalysts for ethylene polymerization in the early 1980s has provided great opportunities for polymer synthesis with tailored chain properties [17–19]. Particularly, the recent development of Dow Chemical constrained geometry catalysts (CGC-catalyst) has offered new synthetic routes and processes for LCB high-density polyethylenes with narrow MWD [20–22]. In metallocene polymerization, polymer chains terminated by β-hydride elimination mechanisms bear terminal double bonds at their chain ends. These chains can act as vinyl macromonomers in further polymerization. The active centre of the CGC-type catalysts is based on Group IV transition metal (e.g. Ti) covalently bonded to a monocyclopentadienyl ring and bridged with a heteroatom unit, forming a constrained cyclic structure. This geometry allows the transition metal centre to be open to addition of high α-olefins and macromonomers at high reactivities. *In situ* copolymerization of ethylene monomers with the macromonomers results in LCB. Branched polymers thus formed have high molecular weight side chains comparative to backbones.

Lai et al. [7] synthesized polyethylene having LCB densities in the range of 0.01–3 carbons/1000 carbons. These LCB PEs were compared to their Ziegler–Natta counterparts. At narrow polydispersities of 1.5–2.5, the shear thinning I_{10}/I_2 of polyethylene could be increased by introducing more LCB. Swogger and Kao [23] synthesized four PE samples with LCB frequencies of 0.20, 0.44, 0.53 and 0.66 per polymer molecule. The syntheses of LCB PEs via copolymerization of ethylene with various linear and branched high-carbon α-olefins using CGC catalysts were also reported [24–26].

Very recently, we have built a high temperature high pressure continuous stirred-tank reactor (CSTR) system for the homogeneous polymerization of olefin monomers using metallocene catalysts. Advantages of the high temperature homogenous CSTR process for LCB include high concentration and low diffusion barrier of macromonomers in the polymerization system. The reactor system was first used for the solution polymerization of ethylene with zirconocene dichloride (Cp_2ZrCl_2)/modified methylaluminoxane (MMAO)/ trimethylaluminium (TMA) [27]. We have also used the reactor system for ethylene polymerization with a CGC catalyst to produce LCB PEs. Branching kinetics and polymer characterization were reported elsewhere [28,29]. The objective of this paper is to present the results of our experimental studies on rheological and mechanical properties of the LCB polyethylenes.

2. Experimental

2.1. Polymer preparation and characterization

LCB polyethylenes were produced using our continuous stirred-tank reactor (CSTR) at 500 psig and 140–190°C. Dow Chemical's constrained geometry catalyst system, titanium [N-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-η)-2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl] silanaminato (2-)-N] dimethyl- (CGC-Ti), and co-catalysts, tri(pentafluorophenyl)boron (TPFPB) and modified methylaluminoxane (MMAO), were used with Isopar E as solvent. Detailed experimental conditions and reaction procedure were published elsewhere [28,29]. Polyethylene samples were collected after polymerization reached a steady state, thoroughly washed with methanol and dried overnight under vacuum at 75°C. Molecular weight (MW) and molecular weight distribution (MWD) of the polymers were measured by a Waters-Millipore 150 C High Temperature SEC equipped with three linear mixed Shodex AT806MS columns, using differential refractive index detector. Calibration was performed against known monodisperse TSK polystyrene (PS) standards from TOYO SODA Mfg.

PE LCB densities were determined using a Bruker AC 300 pulsed n.m.r. spectrometer with broad band decoupling and quadrature detection at 75.4 MHz. The sample concentrations were over 35 wt% in deuterated *o*-dichlorobenzene (d-ODCB) and 1,2,4-trichlorobenzene (TCB) using 10 mm sample tubes. Chemical shifts were referenced internally to TCB and lock was provided by d-ODCB. Spectra required more than 20 h to attain an acceptable signal-to-noise ratio. Fig. 1 gives a typical spectrum of a LCB PE sample, and the assignment of different chemical shifts. In the integration of the resonance peaks close to the peak $\delta\delta^+$, the baseline effect by the 'tree trunk' of peak $\delta\delta^+$ was subtracted from the signals. LCB densities (i.e. the number of branches per 10 000 carbons) were calculated according to

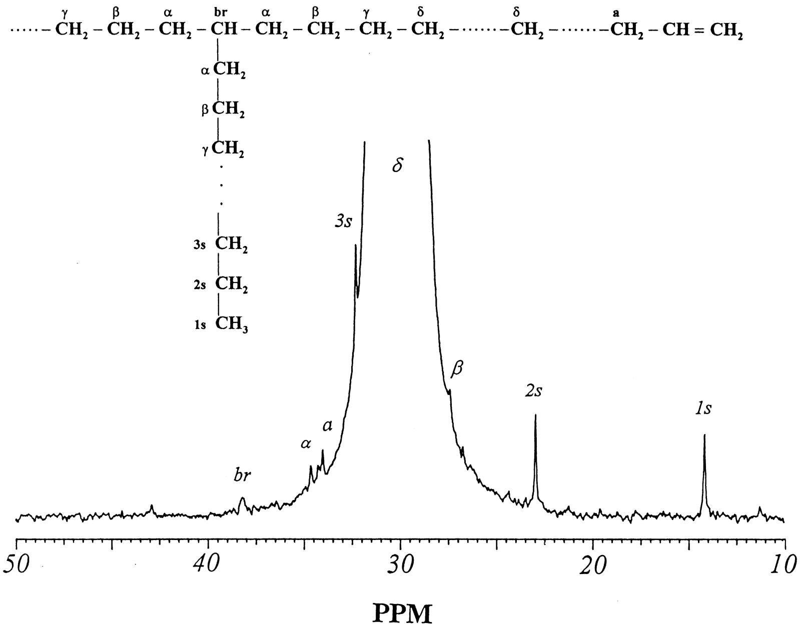

Fig. 1. ^{13}C n.m.r. spectrum of polyethylene with long chain branching measured at 120°C using deuterium *o*-dichlorobenzene and 1,2,4-trichlorobenzene as solvents. The PE sample was produced in our high temperature high pressure continuous stirred-tank reactor using Dow Chemical CGC-Ti/TPFPB/MMAO catalyst system. The experimental conditions were $T = 140°\text{C}$, $P = 500$ psig, $\nu_E = 6$ g/min, $\tau = 4$ min, $[\text{Ti}] = 15\ \mu\text{M}$, $[\text{B}] = 45\ \mu\text{M}$ and $[\text{Al}] = 150\ \mu\text{M}$

LCBD $= \text{IA}_\alpha/3\text{IA}_{\text{tot}}$, where IA_α and IA_{tot} are the integral areas of α-CH_2 resonance and total intensity of carbons, respectively.

2.2. Rheological property measurements

Polyethylene samples were stabilized with 0.6 wt% of Irganox 1010 antioxidant supplied by Ciba-Geigy Canada. Acetone as a solvent for the stabilizer was used to assist mixing with polyethylene powder, and evaporated under vacuum at 75°C overnight. Melt flow index measurements were carried out at Melt Indexer of Kayeness Model D-0053 with standard weights of 2.16 and 10 kg to evaluate ethylene shear thinning behaviour. The measurements were performed at 190 ± 0.2°C according to the ASTM D-1238-79 method.

The steady-state shear viscosity, dynamic viscosity, storage and loss moduli, and other viscoelastic properties, e.g. relaxation modulus and flow activation energy of the polyethylene samples were determined using Bohlin VOR Rheometer in parallel plate configuration. Polyethylene powder was pelletized and moulded into a circular disk, 2 mm thick and 20 mm diameter at 190°C. Three temperatures were used in the oscillation and relaxation measurements: 170, 190 and 210°C. An additional four temperatures (150, 160, 180 and 200°C) were used in the steady-state measurement to estimate the flow activation energies of steady-state low-shear viscosity. The time between runs was set to 4 min to ensure elastic recovery of the polymer sample. The dynamic viscoelastic properties were determined at frequencies from 0.1 to 20 Hz (0.63–125.6 rad/s). An initiation strain of 0.0037 was used in the relaxation modulus measurement. Die swell was measured using an Advanced Capillary Extrusion Rheometer purchased from Rosand Precision at 190 ± 0.2°C. Extrudates were collected at two shear rates (220 and 600 s^{-1}). An orifice was used to minimize the effect of the length over diameter ratio of a die (*L*/*d*).

2.3. Physical and mechanical property measurements

The melting temperature T_m and enthalpy ΔH of the polyethylenes were measured using a DuPont Model 910 Differential Scanning Calorimeter (DSC) calibrated with an Indium standard. A polymer sample of 5.00 ± 0.1 mg was first pre-heated at 10°C/min up to 180°C and kept at 180°C for 10 min before quenching to 50°C with compressed air at a cooling rate of about 90°C/min. A second heating cycle was performed from 50 to 190°C at a heating rate of 10°C/min.

The density data were obtained using a displacement method according to ASTM D792-91. Pure ethanol was used as non-solvent at 24 ± 1°C. The polymer samples were prepared at a pressure of ≤ 30 mbar, and remained under vacuum conditions overnight before heating up to and keeping at 160°C for 5 min followed by cooling to room temperature.

The tensile strength and elongational properties of the polymers were measured using a 30 kN Lloyd Universal Testing machine in accordance with ASTM 638-90. Dumbbell-shaped specimens were cut from compression-moulded plaques of 2 mm thickness prepared at 190°C for 10 min. A constant stretching rate of 0.1 mm/min was applied during the measurements.

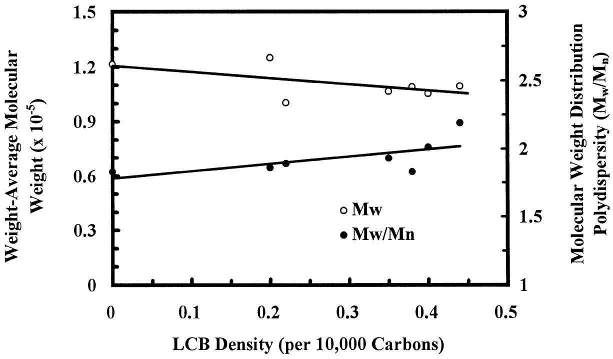

Fig. 2. Weight-average molecular weight (M_w) and molecular weight distribution polydispersity (M_w/M_n) measured by GPC with DRI detector *versus* long-chain branching density. The polyethylenes with different LCB densities have approximately the same MW and MWD

3. Results and discussion

The LCB densities of the polyethylenes produced in this work were measured by ^{13}C n.m.r. giving values in the range of 0~0.44 branch per 10 000 carbons. These numbers are rather small, with the highest density equivalent to a frequency of 0.156 branching points per polymer molecule, i.e. only one branch every 6.39 polymers.

Fig. 2 shows the GPC data of weight-average molecular weight and molecular weight distribution polydispersity. The molecular weights are about 10^5 g/mol. The distributions are narrow with polydispersities close to 2 indicating the single active site type nature of the GCG-Ti catalyst system. MW and MWD are known to have strong effects on polymer properties. The polyethylenes with approximately the same MW and MWD allow us to examine the sole effects of LCB on polymer rheological and mechanical properties.

Fig. 3*a* gives the viscosity data at low shear rates (0.0104~0.065 s^{-1}) for six polyethylene samples with different LCB densities at 190°C. In this range of shear rates, the branched polyethylenes give higher viscosities than their linear counterparts. The higher the LCB density, the higher the viscosity. It is also seen that the viscosity gradually decreases with the shear rate for about 15~40%. The polymers having higher LCB densities experienced more significant reduction in viscosity than those having lower LCB densities with 16 and 37% for the linear and LCBD = 0.44 PE samples, respectively. Fig. 3*b* shows the steady-state viscosities at the shear rate of 0.0104 s^{-1} as a function of the LCB density for three temperatures. LCB with densities lower than 0.2 branch per 10 000 carbons appears to have little influence on the viscosity. However, the viscosity increases greatly with further increase in the LCB density. Double the LCB density from 0.22 to 0.44 branch per 10 000 carbons, the viscosities increased more than six times at all three temperatures (3.68–23.4 × 10^4 Pa.s at 170°C, 2.63–16.1 × 10^4 Pa.s at 190°C, 1.92–12.2 × 10^4 Pa.s at 210°C).

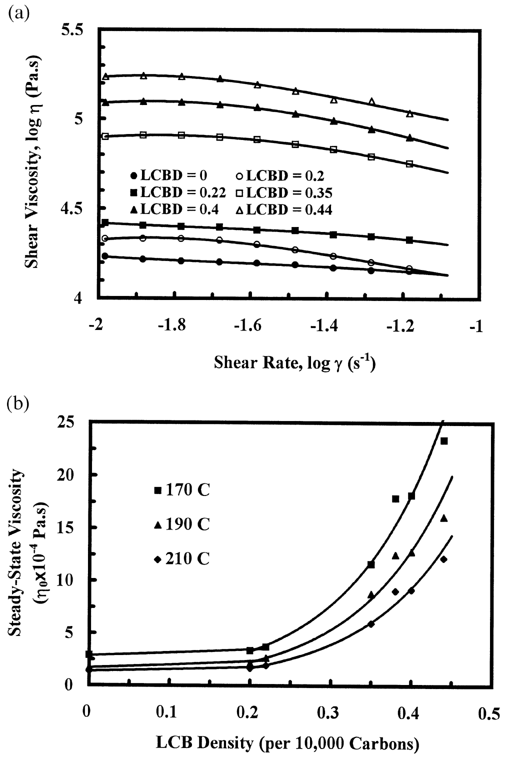

Fig. 3. (a) Viscosity *versus* shear rate for the polyethylenes with different LCB densities. The shear rate range: 0.0104~0.065 s^{-1}; temperature: 190°C. (b) Steady-state viscosity *versus* LCB density at temperatures 170, 190 and 210°C. The values are taken at the shear rate of 0.0104 s^{-1}

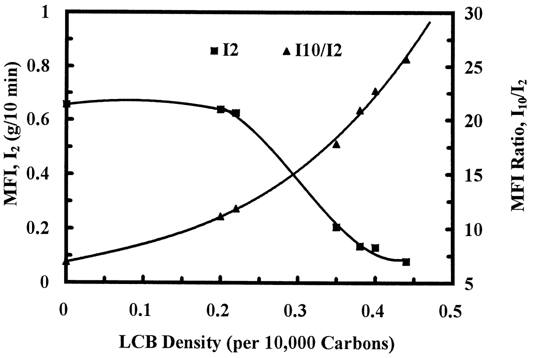

Fig. 4. Melt flow index I_2 and melt flow index ratio I_{10}/I_2 for the polyethylenes measured at 190°C

Fig. 4 shows the melt flow index I_2 *versus* LCB density. The melt flow index and viscosity *versus* shear rate measurements are complementary. Our PE samples have I_2 values in the range of 0.08~0.66 g/10 min, equivalent to the shear rates of about 0.2~1.6 s^{-1}. I_2 decreases with the LCB density. However, little change is experienced for the LCB density lower than 0.2 branch per 10 000 carbons. A great reduction from 0.62 to 0.08 g/10 min is observed with a further increase in the LCB density from 0.22 to 0.44 branch per 10 000 carbons. Fig. 4 also shows the melt flow index ratio of I_{10}/I_2. The I_{10} values of our polyethylene samples are about 2.1~4.5 g/10 min equivalent to the shear

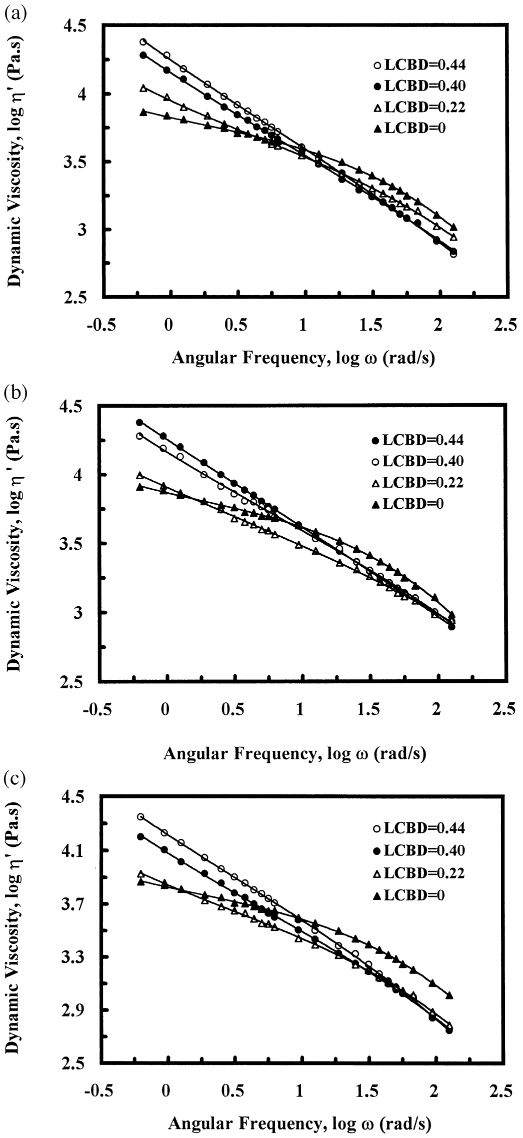

Fig. 5. Dynamic viscosity *versus* shear rate measured by a Bohlin VOR Rheometer for the polyethylenes having LCB densities of 0, 0.22, 0.40 and 0.44 branch per 10 000 carbons. The shear rate range: 0.5~125 rad/s; temperature: (a) 170, (b) 190 and (c) 210°C. LCB polyethylenes give better shear thinning properties

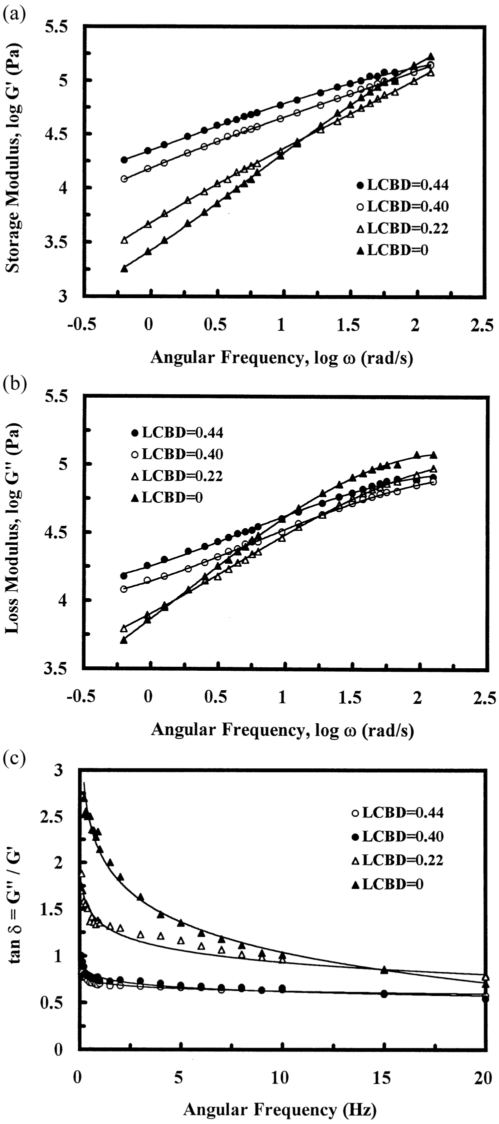

Fig. 6. (a) Storage modulus G', (b) loss modulus G'' and (c) ratio of loss modulus over storage modulus tanδ *versus* shear rate at 0.5~125 rad/s for the PE samples with 0, 0.22, 0.40 and 0.44 branch per 10 000 carbons. The measurement temperature: 190°C

rates of 5~11 s^{-1}. The ratio of I_{10}/I_2 is a convenient measure of the polymer shear-shinning property. Narrow MWD linear PEs often give I_{10}/I_2 in the range of 6~8 with 6.9 for the PE sample produced in this work. The ratio increases greatly with the LCB density. It reaches 25.7 for the sample having 0.44 branch per 10 000 carbons.

Fig. 5*a–c* presents the dynamic viscosities for four polyethylenes having different LCB densities at high shear rates. The angular frequencies are in the range of $\omega = 0.5$~125 rad/s (0.08~20 Hz). These curves show the following features: higher LCB density samples have higher viscosities at low angular frequencies, but lower viscosities at the high angular frequencies; this shear-thinning behaviour becomes more dramatic with increasing LCB density; the viscosity cross-points of branched and linear polyethylenes are in the vicinity of 10 rad/s; similar shear-thinning behaviours are demonstrated at three different temperatures. Take the 170°C measurement as an example. The viscosities decrease 9.8, 12.5, 27.8 and 36.6 times in this shear rate range for the samples having LCB densities of 0, 0.22, 0.40 and 0.44 branch per 10 000 carbons, respectively. Similar levels of shear thinning are observed at the other two temperatures with 8.5, 13.1, 22.4, 30.6 times for 190°C, and 7.1, 13.8, 28.2, 39.7 for 210°C.

It should be emphasized that the polyethylenes in this work have approximately the same MW and MWD. The observed steady-state viscosity increase, melt flow reduction and better shear-thinning performance are therefore solely attributed to the LCB effects. From the view of

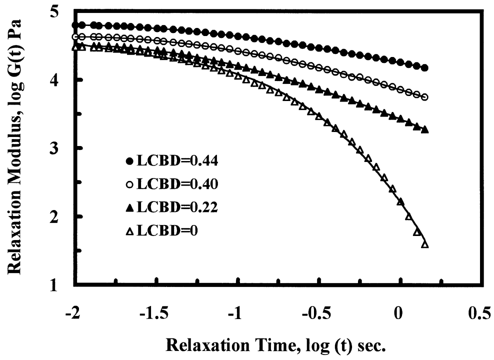

Fig. 7. Relaxation modulus *versus* time at 190°C for the polyethylenes with 0, 0.22, 0.40 and 0.44 branch per 10 000 carbons

polymer chain entanglements, it is rather remarkable for such low LCB densities to exert so strong an influence on polymer rheological properties.

Fig. 6*a* shows the storage modulus in the shear rate range of $\omega = 0.5$~125 rad/s at 190°C. The storage modulus increases with shear rate for all the PE samples with distinctly different slopes. At the low frequency of 0.5 rad/s, the modulus values are 1.8, 3.3, 12.0 and 18.0 kPa for the LCB densities of 0, 0.22, 0.40 and 0.44 branch per 10 000 carbons, respectively. A LCB density of 0.44 gives a 10 times increase in the storage modulus at the frequency of 0.5 rad/s. At the high frequency end of 125 rad/s, the storage moduli for the four samples are 170, 120, 140 and 142 kPa with the linear PE having the highest value. The increases from the frequency of 0.5 rad/s are 94.4, 36.4, 11.7 and 7.86 times, respectively. There appears to be a cross-point for the linear over-branched polymers in the range of 10~100 rad/s. Fig. 6*b* shows the corresponding loss modulus *versus* frequency. The loss modulus increases with the frequency. At the low frequency of 0.5 rad/s, the modulus values are 5.1, 6.2, 12.0 and 15.0 kPa for the LCB densities of 0, 0.22, 0.40 and 0.44 branch per 10 000 carbons, respectively. A LCB density of 0.44 gives a three times increase in the loss modulus at a frequency of 0.5 rad/s. At the high frequency end of 125 rad/s, the loss modulus for the four samples are 120, 95, 76 and 82 kPa, with the linear PE having the highest value. The increases from the frequency of 0.5 rad/s are 23.5, 15.3, 6.3 and 5.4 times, respectively. The cross-points for the linear over-branched samples are at frequencies of 0.1~10 rad/s, which are lower than those for the storage modulus. Fig. 6*c* shows the ratio of loss modulus and storage modulus (tan δ). The ratio decreases with increasing LCB density. At low frequency of 0.5 rad/s, the tan δ values are 2.8, 1.8, 1.0 and 0.83, respectively. The linear polymer is more sensitive to the shear rate than the branched ones with the four samples having 0.71, 0.79, 0.54 and 0.58 at a frequency of 125 rad/s.

Fig. 7 shows the relaxation modulus *versus* time data. The linear sample exhibits the highest rate, giving three orders of magnitude decrease in 1.4 s. In contrast, the branched polyethylenes give much longer relaxation times. In the same time scale, the modulus decreases only 16.3, 7.5 and 4.1 times the samples with 0.22, 0.40 and 0.44 branch per 10 000 carbons, respectively. It again illustrates the strong effect of LCB on polymer viscoelastic properties.

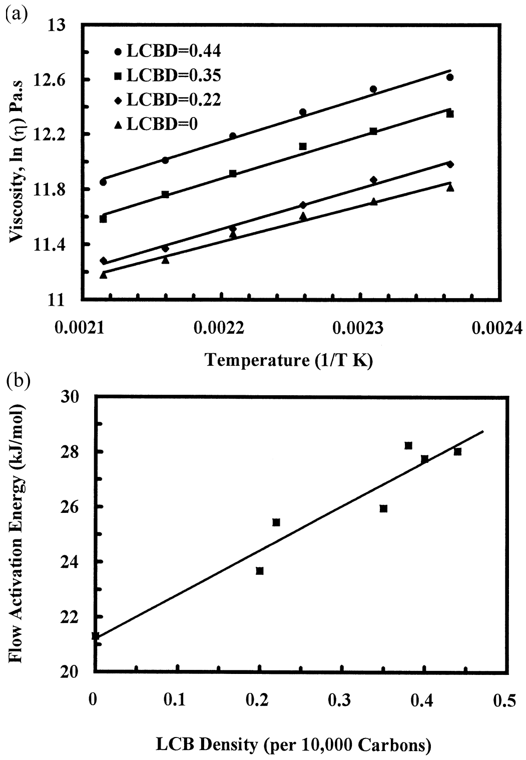

Fig. 8. Effect of temperature on steady-state viscosity (at the shear rate of 0.0104 s^{-1}). (a) Arrhenius plot and (b) flow activation energy as a function of LCB density

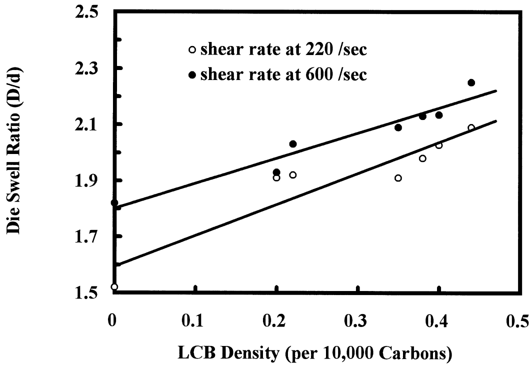

Fig. 9. Die swell *versus* LCB density at the shear rates of 220 and 600 s^{-1}. The measurement temperature: 190°C

The effects of temperature on rheological properties of the polyethylenes were also examined. Fig. 8*a* shows the Arrhenius plots of the steady-state viscosity *versus* temperature for the four PE samples. In the temperature range investigated (150~200°C), the data give a good linear relationship between ln(η) and $1/T$. The flow activation energy, as shown in Fig. 8*b*, is a function of the LCB density with 21.3 and 28.0 kJ/mol for the linear and 0.44 LCB density samples,

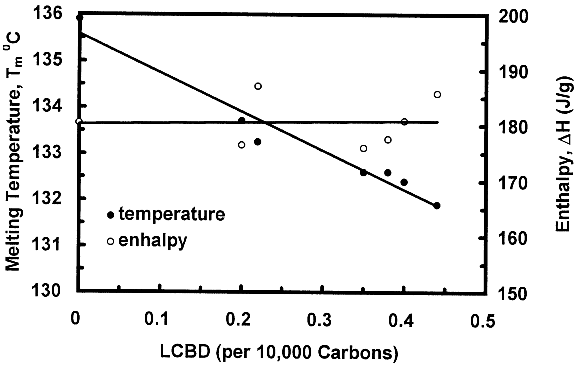

Fig. 10. Melting temperature and enthalpy *versus* LCB density

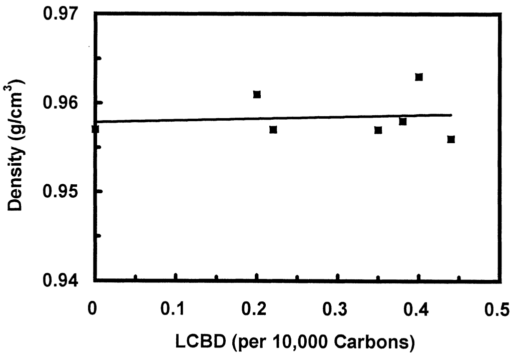

Fig. 11. Polyethylene density *versus* LCB density measured at 24°C using a displacement method according to ASTM D792-91

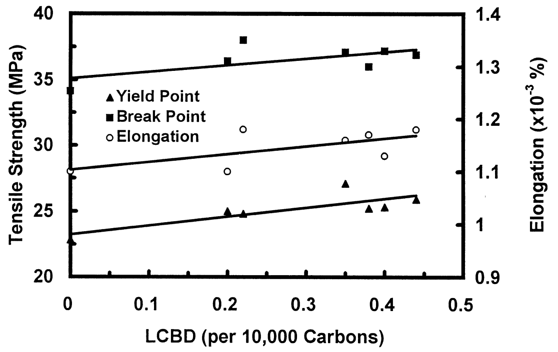

Fig. 12. Tensile strength and elongation *versus* LCB density for the polyethylenes produced in this work

respectively. In addition, we have investigated the die swelling behaviour of the polyethylenes at the shear rates of 220 and 600 s^{-1}. The die swell ratio increases significantly with the LCB density with 37.5% at 220 s^{-1} and 23.6% at 600 s^{-1} Fig. 9.

Similar to the steady-state viscosity, melt flow and shear-thinning measurements, the observed changes in the storage modulus, loss modulus, relaxation modulus and die swell are also remarkable with such low LCB density levels. Since the polyethylene samples have approximately the same MW and MWD, it becomes clear that the LCB exerts very strong effects on the polymer rheological properties. However, the effects of the LCB on polymer mechanical properties are rather minor. Fig. 10 shows the DSC data of melting temperature and enthalpy. The PE samples with different LCB densities have basically the same melt enthalpy about 180 J/g. The melting temperature appears to have a slight decrease with the LCB density. The T_m of the 0.44 LCB density sample is about 4°C lower than the linear PE. Fig. 11 shows little change in density due to the LCB with an average of 0.958 g/cm^3. Fig. 12 shows the tensile strength data for the polyethylenes. The LCB seems to give a small enhancement for the yield and break strength as well as elongation performance.

4. Conclusion

Using our high temperature high pressure CSTR and Dow Chemical GCG-Ti catalyst system, we produced a series of branched polyethylenes having approximately the same MW and narrow MWD. The LCB densities were in the range of 0~0.44 branch per 10 000 carbons. The PE samples were systematically investigated in terms of their rheological and mechanical properties. Remarkable effects of the LCB on the viscoelastic properties of polymer melt were observed. The LCB resulted in steady-state viscosity increase and melt flow reduction. The enhancement of shear-thinning properties was particularly spectacular in the view of such low LCB density levels. The LCB also greatly improved the polymer elasticity, as evident from the increases in storage modulus, relaxation modulus and die swell. However, the effects of LCB on the mechanical and physical properties were small. No noticeable changes in melt enthalpy and density were observed. The melting temperature showed a small decrease with the LCB density, while the tensile strength was slightly enhanced.

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