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Chain walking copolymerization of ethylene with cyclopentene – Effect of ring incorporation on polymer chain topology

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ABSTRACT

Chain walking ethylene copolymerizations with cyclopentene (CPE) as the ring-forming comonomer were carried out in this study to investigate the tuning of polyethylene chain topology via the unique strategy of ring incorporation. Four sets of polymers containing five-membered rings on the polymer backbone at various low contents (in the range of 0–7.5 mol%) were synthesized by controlling CPE feed concentration at four different ethylene pressure/temperature combinations (1 atm/15 °C, 1 atm/25 °C, 1 atm/35 °C, and 6 atm/25 °C, respectively) using a Pd-diimine catalyst, [(ArN=C(Me)–(Me)C=NAr)Pd(CH_3)(N≡CMe)]$^+SbF_6^-$ (Ar = 2,6-(iPr)$_2$C$_6$H$_3$). The polymers were characterized extensively using ^{13}C nuclear magnetic resonance (NMR) spectroscopy, triple-detection gel permeation chromatography (GPC), and rheometry to elucidate the chain microstructures and study the effect of ring incorporation on polymer chain topology. It was found that CPE was incorporated in the copolymers primarily in the form of isolated cis-1,3 ring units, along with a small fraction in the form of isolated cis-1,2 ring units. Significant linearization of polymer chain topology was achieved with ring incorporation in each of the three sets of polymers synthesized at 1 atm on the basis of the incrementally raised intrinsic viscosity curves in the Mark–Houwink plot and the significantly enhanced zero-shear viscosity of the polymer melts with the increase of ring content despite the decreasing polymer molecular weight. For the set of polymers synthesized at 6 atm/25 °C, the effect of ring incorporation on polymer chain topology was negligible or weaker due to their linear chain topology resulting at this polymerization condition. The results obtained in this study support the proposed blocking effect of backbone-incorporated rings on catalyst chain walking, and demonstrate that effective tuning of polyethylene chain topology from hyperbranched to linear can be conveniently achieved via CPE incorporation while without changing ethylene pressure or polymerization temperature.

1. Introduction

The vast developments in transition metal catalysts in the past decades have provided unprecedented freedom in controlling the chain microstructures of polyolefins. A broad range of microstructures governing the materials properties, including stereoregularity, comonomer incorporation and sequence, molecular weight and distribution, can be flexibly controlled by using catalysts of different structures to tailor design polyolefins for various specific end applications [1]. The discovery of Pd-diimine catalysts by Brookhart et al. in the 1990s is another further major advance in the area [2–4]. Distinctly different from other catalysts, this unique series of late transition metal catalysts is featured with their characteristic chain walking mechanism and allow the unprecedented one-step synthesis of polyethylenes with controllable chain topology [5–7], which is another important structural parameter significantly affecting polymer properties and applications [8,9].

In ethylene polymerization with Pd-diimine catalysts, chain walking of the catalysts is one basic event competing actively with chain propagation. The Pd metal center, at the ethylene-dissociated state, can uniquely "walk" along the growing polymer chains through a serial process composed of β-hydride elimination, bond rotation, and subsequent readdition, rendering branch structures [5–7]. It has been found from mechanistic studies that the catalyst can walk through secondary and tertiary carbons but not quaternary carbons, generating branch-on-branch structures [10]. Adjusting the relative rates of the two competitive events by

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changing polymerization parameters can essentially control the catalyst chain walking distance and subsequently tune polymer chain topology [5–8]. To date, ethylene pressure and polymerization temperature are the two commonly used polymerization parameters that can be changed to render polymers of various chain topology ranging from hyperbranched to linear [5–8].

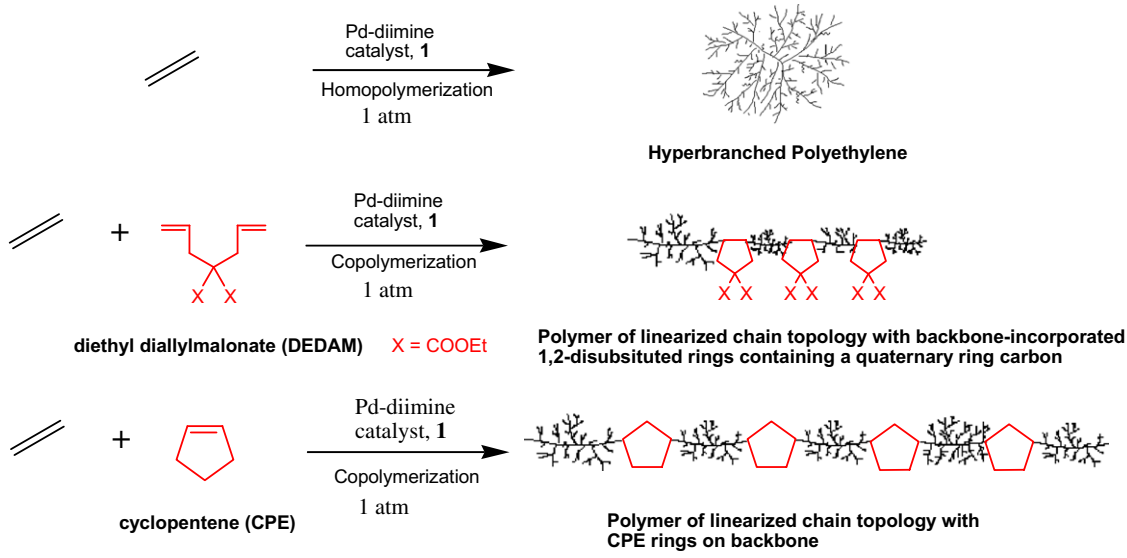
We have been searching for alternative polymerization parameters besides ethylene pressure and temperature that can be used to tune polymer chain topology. Such parameters are expected to offer more freedom and versatility in the control of polymer topology while without changing ethylene pressure and temperature. Recently, we have discovered that the incorporation of aliphatic rings at low contents (below 4%) into polymer backbone (i.e., the chain walking passage) can effectively linearize polymer chain topology and thus, can be used as an alternative strategy for tuning polymer chain topology [11]. In this strategy, 1,2-disubstituted five-membered aliphatic rings containing a quaternary carbon on the 4th position are incorporated into polymer backbone through chain walking ethylene copolymerization with a ring-forming comonomer, diethyl diallylmalonate (DEDAM), which undergoes cyclo-enchainment (Scheme 1). The presence of these backbone-incorporated rings has been shown to effectively linearize polymer chain topology on the basis of the significant enhancement in polymer intrinsic viscosity data upon ring incorporation [11]. This linearization effect was proposed to result from the "blocking" effect of the 1,2-disubstituted rings on catalyst chain walking, in which the rings prevents/minimizes the catalyst from walking past them to prior chain segments and thus restricts chain walking. This proposed "blocking" mechanism is further supported with the evidence that no or negligible change in polymer chain topology occurs if the rings are incorporated in side groups where the catalyst cannot walk to. By controlling the ring content in the polymers via changing the feed concentration of DEDAM as ring-forming comonomer in the polymerization, a convenient tuning of polymer chain topology from hyperbranched to linear can be achieved as effectively as by changing ethylene pressure and temperature [11].

To further investigate this strategy of ring incorporation for tuning polymer chain topology, we report in this study chain walking ethylene copolymerization with another ring-forming comonomer, cyclopentene (CPE). CPE has been extensively used as the cyclic comonomer in olefin polymerization to prepare high-performance cycloolefin copolymers of outstanding thermal, optical, and mechanical properties [12–19]. Pd- and Ni-diimine catalysts have been shown to successfully catalyze the homopolymerization of CPE, yielding high molecular weight polycyclopentene via the exclusive cis-1,3-enchainment of the monomer [20]. Chain walking copolymerization of ethylene with cyclopentene rendering ring-containing polyethylenes, however, has not been reported yet. Herein, we attempt to incorporate CPE at various low contents into the polymer backbone and to study the resulting effects on polymer chain topology. It was envisioned that the ring structure resulting from CPE incorporation would be predominantly 1,3-disubstituted five-membered ring without containing quaternary carbons, which differs from the ring structure achieved by DEDAM incorporation (Scheme 1). This thus enables us to examine the effects of different ring structures on catalyst chain walking and the tuning of polymer chain topology in this strategy.

2. Experimental section

2.1. Materials

The manipulations of moisture- and/or air-sensitive compounds were carried out in a N_2-filled glove box (Innovation Technologies) or using standard Schlenk techniques. The Pd-diimine catalyst, $[(ArN{=}C(Me){-}(Me)C{=}NAr)Pd(CH_3)(N{\equiv}CMe)]^+SbF_6^-$ (Ar = 2,6-(*i*Pr)$_2$ C_6H_3) (**1**), was prepared according to the literature procedure [2]. Ultra-high purity N_2 and polymer-grade ethylene (both from Praxair) were purified by passing through 3 Å/5 Å molecular sieve and Oxiclear columns to remove moisture and oxygen, respectively, before use. Cyclopentene (96%, from Aldrich) was dried over 4 Å molecular sieves. Chlorobenzene (99%, Aldrich) was refluxed over CaH_2 (powder, 90–95%, Aldrich) under N_2 and distilled before use. Silica-bound metal scavengers, triamine tetra-acetic derivatized silica gel (SilicaBond TAAcOH) and thiol-derivatized silica gel (SiliaBond Thiol), were obtained from SiliCycle and used as received. Other chemicals, including anhydrous dichloromethane (99.8%), methanol (≥99.8%), tetrahydrofuran (THF) (>99%), and deuterated chloroform (99.8 atom% D, Aldrich), were obtained from Aldrich and were used as received.



Scheme 1. Schematic effects of ring incorporation on polymer chain topology in chain walking polymerization.

2.2. Chain walking ethylene homopolymerizations and copolymerizations with cyclopentene at 1 atm

Ethylene homopolymerizations (polymers PE1, PE5, and PE9 in Table 1) and copolymerizations with CPE (polymers PE2–PE4, PE6–PE8, PE10 and PE11) with catalyst **1** at an ethylene pressure of 1 atm were all performed in a 500 mL jacketed glass reactor equipped with a magnetic stirrer and a temperature-controlled circulating water bath. The polymerizations were carried out at three different temperatures, 15, 25, and 35 °C, respectively. The polymerization procedure is similar to that used in our previous report [11], and a typical one is described as follows. The glass reactor was first dried overnight at 150 °C in an oven, followed by cooling to room temperature under vacuum, and sealed using a rubber septum. The reactor underwent an ethylene purge-vacuum procedure for at least 3 cycles, and was then pressurized with ethylene at 1 atm. A prescribed volume of anhydrous dichloromethane, along with the applicable amounts of CPE comonomer for copolymerizations, was injected into the reactor. The reactor temperature was then maintained by passing water through the jacket using a circulating bath set at the desired polymerization temperature. After thermal equilibrium for about 10 min, a dichloromethane solution containing the prescribed amount of the Pd-diimine catalyst was injected into the reactor to start the polymerization.

After 24 h, the polymerization was terminated by venting the reactor and the polymerization solution was decanted into a large volume (ca. 300 mL) of acidified methanol to precipitate out the dark-colored oily polymer product. The following purification procedure was used to remove the decomposed catalyst residue in the product. The polymer product was re-dissolved in THF and the silica-bound metal scavenger, triamine tetra-acetic derivatized silica gel or thiol-derivatized silica gel (ca. 0.2 g) was then added into the solution. The solution was stirred overnight and then filtered to remove the silica. For some polymer samples, this purification procedure was repeated until the filtrate became clear. The purified polymer was obtained by precipitating the filtrate in a large amount of methanol. It was dried for ca. 48 h under vacuum at ca. 70 °C and then weighed.

2.3. Chain walking ethylene homopolymerizations and copolymerizations with cyclopentene at 6 atm

Ethylene homopolymerization (polymer PE12 in Table 1) and copolymerizations with CPE (polymers PE13–PE15) at an ethylene pressure of 6 atm were carried out at 25 °C in a 500 mL Autoclave Engineers Zipperclave reactor equipped with a MagneDrive agitator and a removable heating/cooling jacket. The reactor temperature was maintained by passing a water/ethylene glycol mixture through the jacket using a refrigerating/heating circulator set at 25 °C. The typical polymerization procedure is as follows. The reactor was washed with toluene and then acetone. It was heated to ca. 80 °C, subject to a vacuum-nitrogen purge procedure for minimum four cycles, and then cooled down to room temperature under nitrogen protection. Subsequently, prescribed amounts of anhydrous chlorobenzene and cyclopentene were injected into the reactor under nitrogen protection and the reactor was equilibrated at 25 °C. Freshly prepared catalyst solution in dichloromethane (10 mL) was injected into the reactor under nitrogen protection. Nitrogen pressure was released and the reactor was then quickly pressurized to an ethylene pressure of 6 atm (absolute) to start the polymerization. During the polymerization, the temperature and pressure were maintained constant. After 6 h of polymerization, the reactor was vented, and the polymerization solution was taken out from the reactor and decanted into a large volume of acidified methanol. A similar polymer purification procedure as above was subsequently employed, rendering final polymer product.

2.4. Characterizations and measurements

Polymer characterizations with ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy were carried out on a Bruker AV500

Table 1
Polymerization data and polymer characterization results.

Polymer	Temp. (°C)	C_2H_4 pressure (atm)	CPE conc.[a] (M)	Polymer productivity (kg·(mol Pd atm h)$^{-1}$)	CPE content[b] (mol%)	Incorporated CPE[c]		GPC–LS–VIS characterization[d]			Thermal transitions[e]			η_0[f] (Pa s)
						1,3-unit (%)	1,2-unit (%)	$M_{w,LS}$ (kDa)	PDI_{LS}	$[\eta]_w$ (mL/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	
PE1	15	1	0	5.26	0	n.a.[g]	n.a	161	1.32	26.7	−69.7	−36.1	10.8	111
PE2	15	1	0.12	3.97	0.97	77	7.3	123	1.35	27.1	−68.5	−36.7	9.8	130
PE3	15	1	0.24	3.01	1.9	79	7.4	108	1.42	27.9	−64.6	−34.2	6.8	328
PE4	15	1	0.48	1.39	5.3	77	7.7	76	1.41	27.6	−62.8	−32.7	3.6	613
PE5	25	1	0	2.89	0	n.a.	n.a.	114	1.28	16.9	−69.2	−35.0	10.4	53
PE6	25	1	0.12	3.24	0.96	77	7.3	130	1.47	25.4	−68.0	−35.4	7.9	125
PE7	25	1	0.24	3.06	2.9	75	7.2	91	1.47	25.1	−65.2	−34.0	6.4	232
PE8	25	1	0.48	0.74	7.5	77	7.7	56	1.45	22.9	−62.3	−31.8	2.7	478
PE9	35	1	0	2.52	0	n.a.	n.a.	79	1.45	12.0	−68.8	−33.0	9.3	26
PE10	35	1	0.12	1.02	1.5	76	6.8	40	1.55	12.8	−68.5	−34.7	9.6	26
PE11	35	1	0.24	0.27	7.4	78	7.4	21	1.44	13.9	−60.2	−30.0	3.3	69
PE12	25	6	0	5.66	0	n.a.	n.a.	138	1.40	56.0	−66.4	−31.3	15.6	39,200
PE13	25	6	0.75	4.02	0.34	95	5.0	120	1.44	52.8	−65.7	−31.0	15.5	32,020
PE14	25	6	1.50	3.95	2.3	84	5.1	77	1.43	38.9	−62.1	−29.6	13.3	9225
PE15	25	6	4.53	2.40	6.6	82	3.7	38	1.42	28.5	−59.9	−26.8	9.4	2018

[a] Other polymerization conditions: Pd-diimine catalyst amount, 0.2 mmol for PE9–PE11 and 0.1 mmol for all the other polymers; solvent, chlorobenzene for PE12–PE15 and dichloromethane for all the other polymers; total volume, 150 mL for PE12–PE15 and 50 mL for all the other polymers; polymerization time, 6 h for PE12–PE15 and 24 h for all the other polymers.

[b] Cyclopentene (CPE) molar content in the polymers determined with ^{13}C nuclear magnetic resonance (NMR) spectroscopy.

[c] Percentages of isolated cis-1,3 and cis-1,2-enchained CPE units in the incorporated CPE.

[d] The absolute weight-average molecular weight ($M_{w,LS}$) and polydispersity index (PDI_{LS}) were determined with light scattering detector and the weight-average intrinsic viscosity ($[\eta]_w$) was measured with the viscosity detector of the triple-detection GPC.

[e] Thermal properties, including glass-transition temperature (T_g), melting temperature (T_m), and melting enthalpy (ΔH_m), determined with differential scanning calorimetry.

[f] Zero-shear melt viscosity measured at 25 °C.

[g] Not applicable.

spectrometer at ambient temperature with $CDCl_3$ (δ 7.26 for ^1H and δ 77.0 for ^{13}C) as solvent. Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q100 DSC equipped with a refrigerated cooling system (RCS) under N_2 atmosphere. The instrument was operated in the standard DSC mode and was calibrated with an indium standard. A N_2 purging flow of 50 mL/min was used. Polymer samples (~5 mg) were heated from room temperature to 150 °C at 10 °C/min and cooled down to −90 °C at 5 °C/min, and the data were collected on a subsequent heating ramp from −90 °C to 150 °C at 10 °C/min. Glass-transition temperatures (T_g) were read as the middle of the change in heat capacity. The melting temperatures (T_m) were read as the maximum of the endothermic peaks.

Polymer characterizations with triple-detection gel permeation chromatography (GPC) were performed on a Polymer Laboratories PL-GPC220 system equipped with a triple-detection array comprised of a differential refractive index (DRI) detector (from Polymer Laboratories), a three-angle laser light scattering (LS) detector (high-temperature miniDAWN from Wyatt Technology), and a four-bridge capillary viscosity detector (from Polymer Laboratories). This characterization technique has been used in our previous study [11]. The detecting angles of the light scattering detector were 45, 90, and 135°, and the laser wavelength was 687 nm. One guard column (PL# 1110-1120) and three 30 cm columns (PLgel 10 μm MIXED-B 300 × 7.5 mm) were used. The mobile phase was HPLC-grade THF and the flow rate was 1.0 mL/min. The GPC system including the column and detector array was operated at 33.0 °C. The mass of the polymers injected into the columns varied; typically 200 μL of a 3–6 mg/mL solution was injected. Astra™ software from Wyatt Technology was used to collect and analyze the data from all three detectors. Two polystyrene narrow standards (from Pressure Chemicals) with weight-average molecular weight (M_w) of 30,000 and 200,000 kDa were used for the normalization of light scattering signals, and determination of inter-detector delay volume and band broadening, respectively. The two narrow polystyrene standards used were measured to have a typical M_w value of 29,900 and 201,400 g/mol, respectively, with a polydispersity index (PDI) of 1.00 for both, which are in good agreement with the data provided from the supplier.

The DRI increment dn/dc values (in THF) for the ethylene–CPE copolymers of different CPE contents synthesized herein were determined using an off-line method. In this method, the DRI detector was isolated from the above PL-GPC220 system. For each polymer, a range of polymer solutions with defined concentrations (0.20, 0.56, 0.92, 1.28, 1.64, and 2.0 mg/mL, respectively) in THF were prepared. These solutions, along with the solvent THF, were sequentially injected through the DRI detector using a syringe pump. Astra software was used to collect DRI detector signal at these different polymer concentrations, and subsequently calculate the dn/dc value. For polystyrene, the dn/dc value of 0.185 mL/g was used.

Rheological characterization of the polymers was carried out on a TA Instruments AR-G2 rheometer. A peltier plate measurement configuration with a 20 mm parallel plate geometry at a gap size of about 1.0 mm was typically used for the measurements. The measurements were all conducted in the small-amplitude dynamic oscillation mode within the frequency range of 0.001–100 Hz. A strain sweep was performed at 10 Hz before frequency sweeps to establish the linear viscoelastic region for each polymer. The measurements were performed at regular temperature intervals of 10 °C within a temperature range from 15 to 65 °C. Measurement temperature was maintained within ±0.1 °C by using the peltier plate temperature control system. Time–temperature superposition of the rheological data was made with the use of data analysis software provided by TA Instruments.

3. Results and discussion

Chain walking copolymerizations of ethylene with CPE were carried out with the use of the same Pd-diimine complex employed in our previous study [11] on ethylene copolymerization with DEDAM, $[(ArN{=}C(Me){-}(Me)C{=}NAr)Pd(CH_3)(N{\equiv}CMe)]^+SbF_6^-$ (Ar = 2,6–(iPr)$_2$C$_6$H$_3$). The polymerization conditions are summarized in Table 1. Given that chain topology of homopolyethylene by chain walking polymerization changes with ethylene pressure and polymerization temperature [5–8], we synthesized four sets of polymers at various combinations of ethylene pressure and temperature to systematically examine the effects of ring incorporation on polymer chain topology at each condition. For polymers PE1–PE11 (Table 1), the polymerizations were performed at the same ethylene pressure of 1 atm but at three different temperature levels, 15, 25, and 35 °C, respectively. At each temperature, CPE feed concentration was increased incrementally from 0.12 up to 0.48 M to achieve various low ring contents and to subsequently investigate its linearization effect on polymer chain topology. With this CPE feed concentration range, we attempt to control the ring contents in the low range so that CPE is incorporated in the polymers predominantly as isolated rings within ethylene sequences with the negligible formation of CPE sequences. For the set of polymers PE12–PE15, the polymerizations were performed at a higher ethylene pressure of 6 atm and at 25 °C. Given the much higher ethylene concentration, higher CPE feed concentration levels (0.75–4.53 M) were used in this set of copolymerization runs at 6 atm in order to achieve similar levels of ring content in these copolymers as those synthesized at 1 atm. At each pressure/temperature combination, ethylene homopolymerization was also carried out to obtain the control homopolymers (PE1, PE5, PE9, and PE12, respectively, in Table 1), which are used herein as reference samples for investigating the linearization effects of ring incorporation on chain topology. Table 1 also summarizes the polymerization results and polymer characterization data.

Compared to the corresponding ethylene homopolymerization, the presence of CPE in the polymerization system generally reduced the polymerization activity on the basis of the decreasing polymer productivity with the increase of CPE feed concentration at each pressure/temperature combination (Table 1). This is indicative of CPE incorporation in the polymers since the incorporation of comonomers of lower reactivity often leads to reduced polymerization activity. The polymers were characterized using ^{13}C NMR spectroscopy to elucidate the chain microstructures and the incorporation mechanism of CPE in the copolymers. Fig. 1 shows the ^{13}C NMR spectra of two representative copolymers, PE7 and PE8 synthesized at 1 atm/25 °C, along with that of the corresponding control homopolyethylene, PE5, for comparison. Characteristic of Pd-diimine polyethylenes, the homopolymer PE5 exhibits highly branched structures with identified peaks assigned to branches ranging from methyl to hexyl and longer (Fig. 1a). These branching structures are a result of the chain walking mechanism of the catalyst and the assignment of the ^{13}C NMR peaks has been well elucidated in the literature [5,6,21]. The two copolymers PE7 and PE8 are found to possess all the NMR peaks exhibited in the homopolymer (Fig. 1b,c), indicating the presence of highly branched ethylene sequences in the copolymers. Moreover, some new peaks (peaks 1–8, and C–J labeled in Fig. 1c) not seen in the spectrum of the homopolymer are also found in the spectra of both copolymers. These new peaks have been verified to exist in all ethylene–CPE copolymers synthesized herein with enhanced intensities at the increasing CPE feed concentration at each pressure/temperature combination (for example, comparing the spectra of PE7 and PE8 shown in Fig. 1b and c), thus confirming the successful CPE incorporation in the copolymers. These new peaks

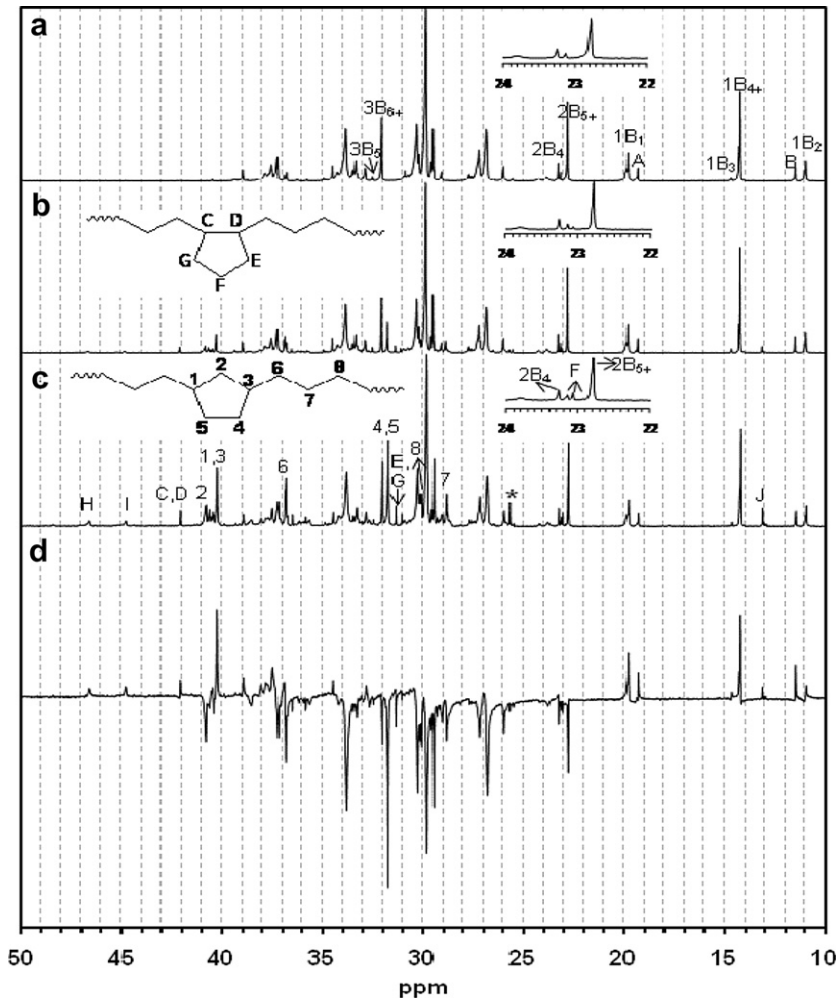


Fig. 1. ^{13}C NMR spectra of (a) PE5, (b) PE7, and (c) PE8; and (d) DEPT (135°) spectrum of PE8. In the label xB_y, y stands for the length of the branch and x stands for the carbon being concerned with methyl end group being numbered as 1. Peaks A and B represent respectively methyls of the methyl and ethyl branches of sec-butyl groups, which are the smallest branch-on-branch structure. In (c), the peak (25.6 ppm) marked with asterisk results from trace THF solvent residue.

should be attributed to the carbons on the incorporated five-membered rings and the carbons of ethylene sequences in the vicinity of the rings. Assignment of these peaks allows the elucidation of CPE incorporation mechanism in the copolymerization.

In vinyl-addition homopolymerization and copolymerization of CPE with ethylene, there are generally two possible CPE incorporation mechanisms, 1,2- and 1,3-enchainment, which have been well demonstrated in a number of polymerization systems employing various metallocene and other early transition metal catalysts [12–19]. In particular, the 1,3-enchainment of CPE is attributed to the isomerization of last-inserted CPE unit through a β-H elimination–reinsertion process and is more likely to occur if the catalyst employed has a higher tendency to undergo β-H elimination [13,17]. In the case of ethylene–CPE copolymers synthesized via metallocene catalysts, the chain microstructures resulting from both incorporation mechanisms have been well elucidated with the use of ^{13}C NMR technique [14–17]. Pd-diimine catalysts have been demonstrated to catalyze homopolymerization of CPE exclusively through cis-1,3-enchainment, with high molecular weight poly(CPE) obtained with a similar Pd-diimine catalyst as catalyst **1** used herein [20]. Considering this and the high tendency of Pd-diimine catalysts to undergo β-H elimination and reinsertion, we hypothesized that CPE was more likely copolymerized herein through cis-1,3-enchainment. Comparison of the ^{13}C NMR peaks resulting from CPE incorporation was made between the Pd-diimine copolymers synthesized herein and metallocene copolymers reported in the literature. Unlike metallocene copolymers, the presence of the highly branched ethylene sequences in the Pd-diimine copolymers adds additional complexity to the assignment of NMR peaks due to significant peak overlap as shown in Fig. 1b and c. Regardless of this, the peaks at 40.8 (peak 2 in Fig. 1c), 40.2 (1,3), 36.8 (6), 31.7 (4,5), 30.0 (8), and 28.8 ppm (7) in Fig. 1c are in good agreement with the corresponding chemical shifts identified for isolated cis-1,3-CPE microstructure (microstructure shown in Fig. 1c) [14,15,16a]. This agreement is further supported with the DEPT (distortionless enhancement by polarization transfer) (135°) spectrum of the polymer (PE8) shown in Fig. 1d, thus verifying the assignment of these peaks to isolated cis-1,3-CPE units. Isolated cis-1,3-CPE units are the predominant CPE microstructure found in the copolymers.

In addition, isolated cis-1,2-CPE units are also present in all the copolymers on the basis of the peaks at 42.0 (C, D), 31.3 (E, G), and 23.0 ppm (F) for ring carbons, which agree well with the chemical shifts found in the literature for this microstructure [14,15,16a]. However, their content is much lower compared to that of isolated cis-1,3-CPE units (comparing peaks C, D, and 4, 5 in Fig. 1). In contrast to the exclusive cis-1,3-enchainment in CPE homopolymerization, the appearance of these isolated cis-1,2-CPE units

in the copolymers suggests that the presence of ethylene in the polymerization can slightly inhibit isomerization of last-inserted CPE unit to form 1,3-enchainment probably due to ethylene coordination right after CPE insertion. As to the other new peaks in the spectra, peak J (13.1 ppm) should be the CH_3 carbon of a new branching structure absent in the homopolyethylenes on the basis of the DEPT spectrum. The new branching structure should be on or close-to the CPE rings. This peak or a similar one was not observed in ethylene–DEDAM copolymers containing 1,2-disubstituted five-membered rings with a quaternary carbon on the 4th position. Given their high chemical shifts, the other weak peaks H (46.6 ppm) and I (44.7 ppm) are tentatively assigned to two CH carbons of rings associated with the new branching structure indicated by peak J. Due to the complex polymer structures and absence of the spectra for model compounds, a conclusive assignment of these three peaks (H–J) is currently not possible.

The CPE content in the four sets of copolymers was calculated from the peaks for CH ring carbons in the ^{13}C NMR spectra. The data are listed in Table 1, along with the percentages of both isolated cis-1,3 and cis-1,2-enchained units. Generally, the CPE content is low, varying in the range of 0.34–7.5 mol%. For all the copolymers synthesized at 1 atm, about 77% of the incorporated CPE units are enchained in the form of isolated cis-1,3 units and about 7% in the form of isolated cis-1,2 units, with the remaining resulting from the peaks H and I in Fig. 1b and c. In the set of copolymers synthesized at 6 atm, the percentage for isolated cis-1,3-enchained units is in the range of 82–95% and that for isolated cis-1,2-enchained units is about 5%. In all copolymers, the presence of CPE blocks should be negligible given the low CPE contents and the ^{13}C NMR spectra as shown in Fig. 1b and c. In each set of polymers synthesized at different pressure/temperature combinations, the CPE molar content in the copolymers increases with CPE feed concentration, along with the concurrent reduction in polymerization activity due to the lower reactivity of CPE compared to ethylene. Comparing polymers synthesized at the same CPE feed concentration and ethylene pressure (1 atm) but at different temperatures, the CPE content increases with the temperature increase from 15 to 35 °C.

The branching density and distribution present in the ethylene sequences of the polymers were analyzed from their ^{13}C NMR spectra. Due to the restriction of ^{13}C NMR technique, only short branches with length below six carbons can be differentiated and details on branch-on-branch structures, i.e., chain topology, thus cannot be obtained [5–7,11]. Table 2 lists the short branch distribution of the polymers. Generally, all polymers show highly branched ethylene sequences with a total branching density in the range of 83–109 per 1000 carbons in ethylene sequences. CPE incorporation slightly reduces the total polymer branching density at each pressure/temperature combination without a distinct effect on the pattern of branch distribution. This reducing effect of ring incorporation on branching density has also been observed in ethylene–DEDAM copolymers [11]. Due to the highly branched ethylene sequences, all the polymers are amorphous at room temperature and are sticky oil-like liquids. DSC characterizations were carried out on the polymers to investigate the ring incorporation on their thermal properties. Representatively, Fig. 2 shows the DSC thermograms for the set of polymers synthesized at 1 atm/25 °C. Two thermal transitions, a glass-transition and a weak but broad melting endotherm, were typically observed with these polymers. The glass-transition temperature (T_g), melting temperature (T_m) and melting enthalpy (ΔH_m) for the polymers are also listed in Table 1. With the increase of CPE content, T_g increases slightly along with the reduction in ΔH_m due to the incorporation of the rigid ring units and the disruption of the formation of polyethylene crystallites [22].

Polymer characterizations with triple-detection GPC incorporating on-line light scattering (LS), differential refractive index (DRI), and viscosity detectors were carried out to determine their molecular weight and, more importantly, to evaluate their differences in chain topology. The characterizations were performed at 33 °C with THF as the elution phase where the polymers show good solubility even at room temperature due to their highly branched ethylene sequences. In this technique, the LS detector, when coupled with DRI concentration detector, measures directly the absolute polymer molecular weight in each GPC elution fraction, and the viscosity detector enables the simultaneous measurement of polymer intrinsic viscosity ($[\eta]$) of the fraction [11]. The dn/dc values of the polymers in THF at the measurement temperature (33 °C) were determined and were found to have a weak dependence on CPE molar content by following: $dn/dc = 0.078 + 0.0011x$ (mL/g), where x is the molar percentage of CPE in the polymers. In particular, the dn/dc value found for the homopolymers, 0.078 mL/g, is identical to that reported in the literature [6]. These measured dn/dc values were used in the calculation of both polymer concentration in each elution fraction from DRI detector signals and polymer molecular weights from LS detector signals. The GPC characterization results, including weight-average molecular weight (M_w), polydispersity index (PDI), and weight-average intrinsic viscosity ($[\eta]_w$), are summarized in Table 1. At each pressure/

Table 2
Short chain branching distribution (in number of branches per 1000 carbons) in ethylene sequences of the polymers determined with ^{13}C NMR spectroscopy.

Polymer	Methyl	Ethyl	Propyl	Butyl	Amyl	Hexyl+	Total	%A[a]
PE1	32.2	23.0	1.8	7.3	2.3	36.6	103.2	23
PE2	34.8	22.9	1.8	7.1	2.5	35.3	104.4	22
PE3	33.5	22.1	1.8	7.0	2.7	34.3	101.4	21
PE4	30.8	20.6	2.1	6.5	3.7	33.9	97.6	20
PE5	36.1	24.0	2.6	7.9	3.0	35.8	109.4	22
PE6	34.4	23.2	1.8	7.3	2.6	35.8	105.1	22
PE7	33.5	22.8	1.9	6.6	2.7	33.3	100.8	22
PE8	26.9	17.2	1.4	5.2	4.0	30.1	84.7	19
PE9	35.0	22.9	2.2	7.5	2.2	35.7	105.5	22
PE10	35.9	22.8	2.5	7.7	2.1	34.7	105.7	22
PE11	28.1	19.0	2.3	5.8	3.6	31.7	90.4	20
PE12	35.5	21.4	2.6	6.8	2.6	31.6	100.5	16
PE13	33.9	20.0	2.2	6.6	2.3	29.7	94.7	14
PE14	33.3	18.8	1.7	5.9	3.1	29.3	92.1	16
PE15	31.2	17.1	1.3	5.1	2.3	26.0	83.0	16

[a] Percentage of methyl from sec-butyl branches in the total methyl.

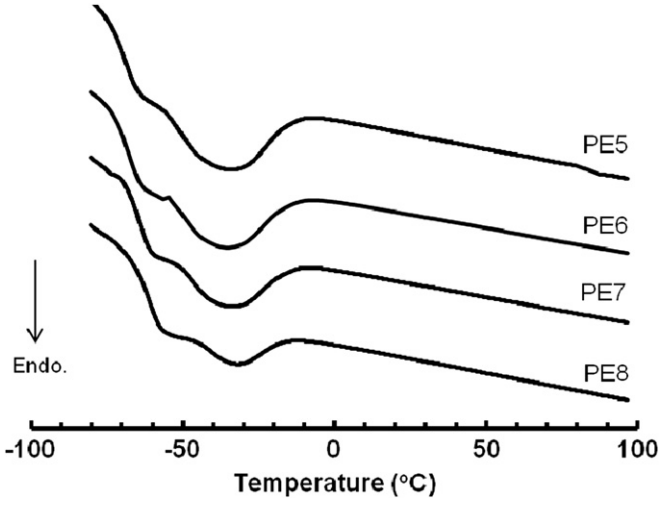


Fig. 2. DSC thermograms for the set of polymers synthesized at ethylene pressure of 1 atm and 25 °C.

temperature combination, a consistent reduction in M_w is observed with the increase of CPE content in the copolymers due to the enhanced chain transfer upon comonomer incorporation. The molecular weight distribution of the polymers is only negligibly affected by CPE incorporation on the basis of marginal changes in PDI data.

To elucidate polymer chain topology and the effect of ring incorporation, Mark–Houwink plots showing the dependence of intrinsic viscosity on polymer molecular weight across the distribution were constructed using the molecular weight and intrinsic viscosity data simultaneously obtained in triple-detection GPC measurements. It has been well demonstrated that intrinsic viscosity is sensitive to polymer chain topology at a given molecular weight, with higher values found with polymers of more linear chain topology. Comparison of the intrinsic viscosity curves in the Mark–Houwink plots thus allows us to examine the change in polymer chain topology after ring incorporation at various contents. Fig. 3a–c shows the Mark–Houwink plots of the four sets of polymers synthesized at the different pressure/temperature combinations. In each plot, ethylene homopolymers synthesized at other pressure/temperature combinations and an ethylene–DEDAM copolymer synthesized in our previous study at the same pressure/temperature combination are included for the purpose of comparison.

In each set of polymers synthesized at 1 atm, a consistent and significant increase of intrinsic viscosity is observed across the whole molecular weight distribution with the increase of CPE ring content. The homopolymers (PE1, PE5, and PE9) synthesized at these conditions should all possess hyperbranched chain topologies with slightly increased chain compactness in the order from PE1 to PE9 given the low ethylene pressure and increasing polymerization temperatures (see Fig. 3a). The elevated intrinsic viscosity curves relative to that of corresponding homopolymer demonstrate the linearization of polymer chain topology upon ring incorporation. Moreover, the extent of linearization is enhanced with the increase of ring content. The linearization effect of CPE incorporation on polymer chain topology is also compared to those of increasing ethylene pressure and decreasing polymerization temperature, which are commonly used methods for linearizing polymer chain topology. For example, a homopolyethylene synthesized at 30 atm/35 °C [11] and PE1 synthesized at 1 atm/15 °C are included in Fig. 3c for the set of polymers synthesized at 1 atm/35 °C. On the basis of the intrinsic viscosity curves, PE10 having a ring content of 1.5 mol% has the similar chain topology as PE1 obtained by reducing temperature to 15 °C, and PE11 with a ring content of 7.4 mol% has more linearized chain topology than the homopolyethylene synthesized at the much elevated pressure (30 atm/25 °C). These comparisons demonstrate that the tuning of polymer chain topology can be achieved by solely controlling CPE ring content while without changing ethylene pressure or polymerization temperature.

The above intrinsic viscosity data are consistent with those found with ethylene–DEDAM copolymers and demonstrate that ring incorporation with CPE as the ring-forming comonomer can also achieve the linearization effect. However, compared to corresponding ethylene–DEDAM copolymers synthesized at the same pressure/temperature combinations and having similar ring contents, the linearization effect of ring incorporation is found to be weaker with the use of CPE. For example, in Fig. 3a for the set of polymers synthesized at 1 atm/15 °C, the ethylene–DEDAM copolymer having a ring content of 1.5 mol% has higher intrinsic viscosity values than PE4 having a ring content of 5.3 mol% across the whole distribution. In Fig. 3b, the ethylene–DEDAM copolymer, synthesized at 1 atm/25 °C and having a ring content of 2.7 mol%, has higher intrinsic viscosity values than PE8 with a ring content of 7.5 mol%. In Fig. 3c,

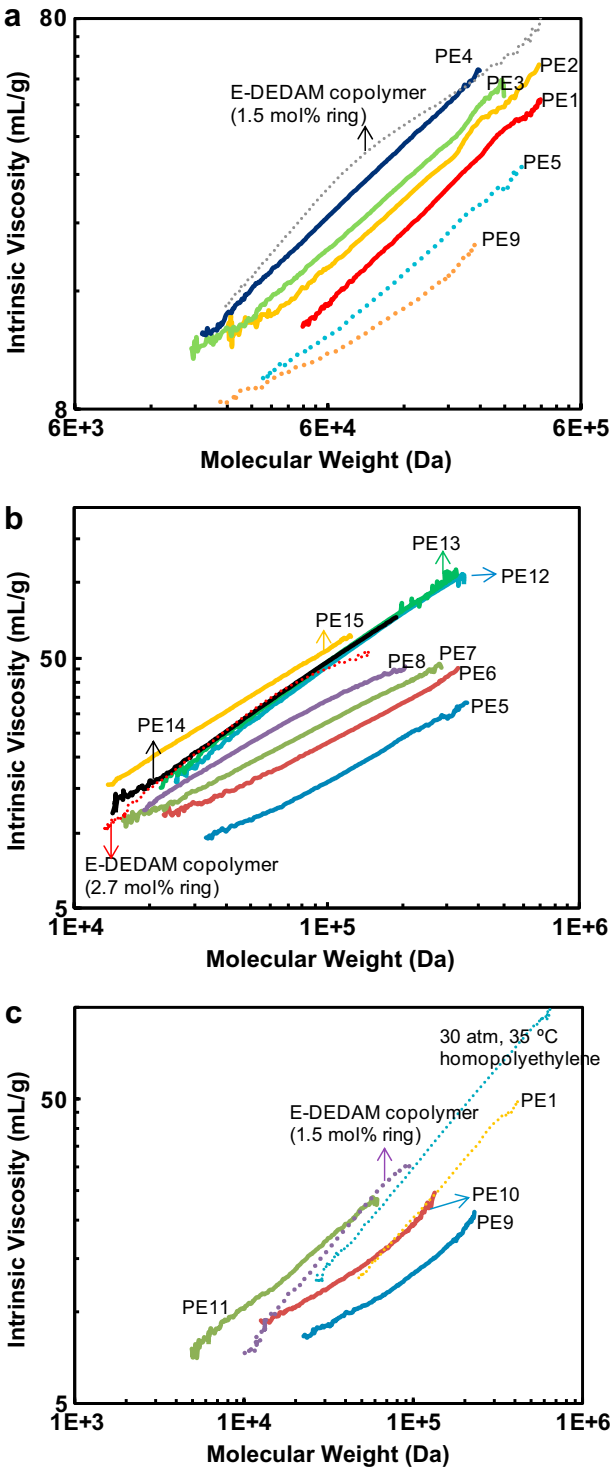


Fig. 3. Mark–Houwink plots of polymers synthesized at (a) ethylene pressure of 1 atm and 15 °C; (b) ethylene pressure of both 1 atm and 6 atm, and 25 °C; (c) ethylene pressure of 1 atm and 35 °C. In each plot, the dotted curves for homopolyethylenes synthesized at other different pressure/temperature combinations or an ethylene–DEDAM copolymer synthesized at the same condition are included for comparison.

PE10 having a ring content of 1.5 mol% has lower intrinsic viscosity values than the ethylene–DEDAM copolymer of the same ring content synthesized at the same condition (1 atm/35 °C).

As proposed in the case of ethylene–DEDAM copolymers, the linearization effect observed here with CPE incorporation is also ascribed to the "blocking" effect of ring incorporation on catalyst

chain walking. These backbone-incorporated isolated five-membered rings (1,3- and 1,2-enchained CPE units) locate in the chain walking passage where the catalyst can potentially walk to. During catalyst chain walking, these ring units can potentially serve as blocking sites as chain walking through them is more difficult compared to through ethylene sequences due to their sterically more encumbered ring structures. The possibility for the catalyst to walk through them to prior chain segments is thus reduced and catalyst chain walking distance is shortened, thereby rendering a more linearized chain topology with shorter polyethylene sequences segregated by CPE rings. Increasing ring content increases the frequency of blocking sites, further reduces chain walking distance, and improves the linearity of polymer chain topology.

Compared to the ethylene–DEDAM copolymers of similar ring contents, the weaker linearization effect observed with ethylene–CPE copolymers is attributed to the different ring structures in the two types of ring-containing polymers. In ethylene–DEDAM copolymers, the rings are all 1,2-disubstituted five-membered rings containing a quaternary carbon on the 4th position (Scheme 1). To walk past the ring to prior chain segments, the catalyst has to walk along the side of the ring composed of two consecutive CH ring carbons as the other side contains the quaternary carbon disallowing the catalyst from walking through. In the case of ethylene–CPE polymers, chain walking through the ring (either 1,3-enchained or 1,2-enchained ring unit) can occur through both sides of the ring given the absence of quaternary carbon on either side. In addition, the 1,3-enchained ring unit predominant in CPE copolymers likely has lower steric resistance for chain walking, due to the presence of a CH_2 carbon between the two CH ring carbons, as opposed to the exclusive 1,2-enchained ring units in ethylene–DEDAM copolymers. These structural features render the higher possibility for the catalyst to walk through the CPE rings than through the rings formed by cyclo-incorporation of DEDAM. The appearance of the new branching structure in ethylene–CPE copolymers as evidenced by peak J in copolymer NMR spectra is suggestive of the chain walking through or to the incorporated CPE ring units. Another evidence supporting the capability of the catalyst to walk through the ring units is the homopolymerization of 4-methylcyclopentene and 4-ethylcyclopentene with Pd-diimine catalysts, which result in methylenecyclopentane and alternating ethylene-cyclopentene polymer, respectively [4].

With the proposed blocking mechanism, the catalyst chain walking distance, at a given pressure/temperature combination, should be sufficiently long in ethylene homopolymerization so that significant effects on polymer chain topology can result upon ring incorporation at low contents in subsequent ethylene–CPE copolymerization. In the three sets of polymers synthesized at 1 atm, the homopolyethylenes are typically hyperbranched with long catalyst chain walking distance and the linearization effect of ring incorporation is significant. If the chain topology of the homopolymer is linear with short chain walking distance in the polymerization, the resulting effect of ring incorporation on chain topology is hypothesized to be negligible or weakened in the copolymers synthesized at the same condition. The set of polymers synthesized at 6 atm and 25 °C was designed specifically to verify this hypothesis. Fig. 3b includes the intrinsic viscosity curves for this set of polymers. Given its much elevated intrinsic viscosity, the homopolymer PE12 synthesized at this condition possesses a much linearized chain topology compared to the homopolymer PE5 synthesized at 1 atm/25 °C due to the much higher ethylene pressure. Compared to the other three sets of polymers synthesized at 1 atm, the effect of CPE ring incorporation on chain topology appears to be much weaker in this set of polymers. From Fig. 3b, negligible changes in intrinsic viscosity curve are observed with PE13 and PE14 having a lower ring content of 0.34 and 2.3 mol%, respectively, relative to PE12 despite their significant ring incorporation. The change with PE15

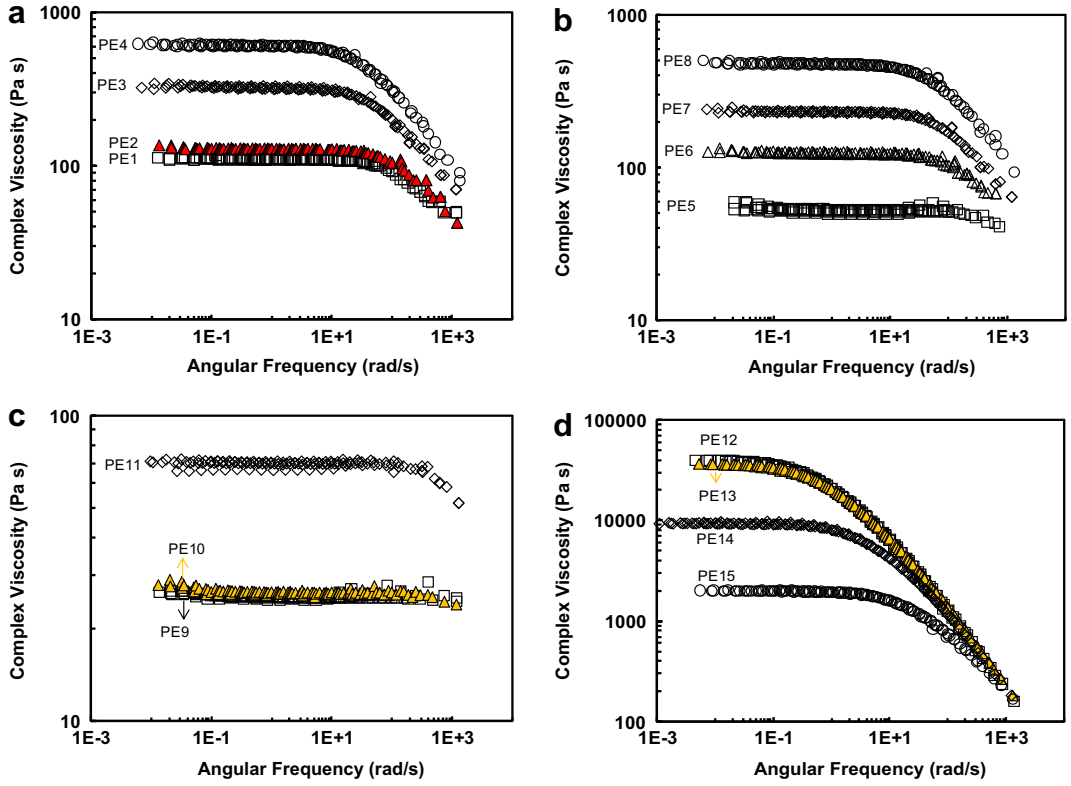


Fig. 4. Complex melt viscosity curves measured at 25 °C for polymers synthesized at (a) 1 atm and 15 °C; (b) 1 atm and 25 °C; (c) 1 atm and 35 °C; and (d) 6 atm and 25 °C.

(ring content of 6.6 mol%) relative to homopolymer control is also much weaker compared to other polymers (e.g., PE4, PE8, and PE11) having a similar ring content in the other sets synthesized at 1 atm. The results with this set of polymers verify the hypothesis and indicate that ring incorporation has negligible or weakened effects on polymer chain topology if the homopolymer contains a linear or close-to linear chain topology.

In addition to the above results from triple-detection GPC characterizations, melt rheological characterization of the polymers were also undertaken to further verify the effect of ring incorporation on polymer chain topology in the four sets of polymers. Fig. 4a–d shows the complex viscosity master curves measured at 25 °C for the four sets of polymers. The corresponding zero-shear viscosity (η_0) data obtained from the Newtonian region of the complex viscosity curves are listed in Table 1. Given their low T_g and T_m values, all the polymers should be in the molten state at this measurement temperature. The zero-shear viscosity of a polymer is a cumulative property governed by polymer chain topology, molecular weight and distribution [8,23]. For the polymers of similar PDI values synthesized herein, zero-shear viscosity is correlated to chain topology and M_w, with the value increasing with the change of chain topology from hyperbranched to linear and/or with the increase of M_w [8]. In each of the three sets of polymers synthesized at 1 atm, one can find a significant increase of zero-shear viscosity with the increase of ring content in the copolymers despite the significant reduction in M_w. For example, for the set of polymers synthesized at 1 atm/25 °C, η_0 increases by nearly one order of magnitude from 53 Pa s for homopolymer PE5 to 478 Pa s for PE8 having a ring content of 7.5 mol% while the M_w value is reduced from 114 kDa to 56 kDa. In consistency with the elevated intrinsic viscosity curves, this trend of change for η_0 further confirms the linearization of polymer chain topology upon ring incorporation by CPE enchainment in these three sets of polymers, which leads to enhanced chain entanglement. For the set of polymers synthesized at 6 atm/25 °C, η_0 changes in the opposite manner upon ring incorporation. The homopolymer PE12 has a η_0 value of 39,200 Pa s. This value is much higher than that of homopolymer PE5 having a similar M_w and synthesized at 1 atm, verifying the much more linear chain topology of PE12 relative to PE5 due to the higher ethylene pressure. With the increase of ring content from 0 to 6.6 mol%, η_0 decreases by nearly twenty folds for this set of polymers from 39,200 Pa s for PE12 to 2,018 Pa s for PE15. This reduction should result primarily from the drop of M_w values in this set of polymers. Meanwhile, it also confirms that the chain topology is negligibly or only weakly affected upon ring incorporation in this set of polymers.

4. Conclusions

Four sets of ethylene–CPE copolymers having various low CPE contents in the range of 0–7.5 mol% were synthesized with the use of a Pd-diimine catalyst, $[(ArN{=}C(Me){-}(Me)C{=}NAr)Pd(CH_3)(N{\equiv}CMe)]^+SbF_6^-$ (Ar = 2,6-(*i*Pr)$_2$C$_6$H$_3$), at four different pressure/temperature combinations. CPE is incorporated in all the copolymers predominantly in the form of isolated cis-1,3 ring units as evidenced from ^{13}C NMR characterization. Triple-detection GPC characterization indicates that significant linearization of polymer chain topology results from ring incorporation for the sets of polymers synthesized at ethylene pressure of 1 atm on the basis of the consistently elevated intrinsic viscosity curves with the increase of CPE ring content in the Mark–Houwink plot. The linearization effect in these polymers is also verified on the basis of the increasing zero-shear viscosity of the polymer melts upon ring incorporation regardless of the reduction in their M_w data. By controlling the ring content through changing the feed concentration of CPE in the polymerization, we can thus effectively tune polymer chain topology from hyperbranched to linear without changing ethylene pressure and temperature. Compared to ethylene–DEDAM copolymers of similar ring contents, the linearization effect with the use of CPE as the ring-forming comonomer is, however, much weaker due to the difference in their ring structures which leads to the different blocking effect of the ring units on catalyst chain walking. Unlike the polymers synthesized at 1 atm, the set of polymers synthesized at 6 atm/25 °C show negligible or only slight changes in chain topology upon ring incorporation at similar contents based on the evidences from triple-detection GPC and melt rheology measurements. This is attributed to the negligible effect of ring units on catalyst chain walking at this condition. The results obtained in this study are in consistency with and provide further support to the proposed blocking mechanism of ring incorporation on catalyst chain walking.

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