Characterization of Polyethylenes Produced in Supercritical Carbon Dioxide by a Late-Transition-Metal Catalyst

Tjerk J. de Vries, Maartje F. Kemmere,* and Jos T. F. Keurentjes

Process Development Group and Dutch Polymer Institute, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received September 10, 2003; Revised Manuscript Received March 2, 2004

ABSTRACT: The coordination polymerization of ethylene with a palladium-based catalyst is studied using supercritical carbon dioxide ($scCO_2$) as a reaction medium at different temperatures, pressures, and ethylene concentrations. Additionally, the polymerization is performed in dichloromethane as a reference. The polymers are analyzed with gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and hydrogen and carbon nuclear magnetic resonance (^1H and ^{13}C NMR). The polymerizations in $scCO_2$ and dichloromethane result in highly branched amorphous polymers of high molecular weight and narrow molecular weight distributions. Although the polymerization in $scCO_2$ is a precipitation polymerization, the obtained results are similar to the polymerization in dichloromethane, which is a solution polymerization. Moreover, the polymers produced in $scCO_2$ show a higher degree of short chain branching (SCB), which likely originates from the nonpolar environment compared to the polar dichloromethane. Within the range investigated, temperature and ethylene concentration have an effect on the molecular weight of the polymer, however, not on the SCB of the polymers. Furthermore, analysis of the ^{13}C NMR spectra of the polyethylenes gives a strong indication of a new branch-on-branch structure, which has not been assigned before.

Introduction

Supercritical carbon dioxide ($scCO_2$) possesses unique properties as a reaction medium since it is an environmentally benign, nontoxic, nonflammable, and inexpensive compound. The relatively low critical temperature (31.1 °C) and pressure (73.8 bar) permit the use of CO_2 above the critical temperature, which has the advantage that the behavior of CO_2 can be varied from liquidlike to gaslike. Consequently, the physical properties of the reaction medium can easily be tuned by changing pressure and/or temperature,[1] which in principle allows for an efficient process design. The low viscosity of $scCO_2$ permits strong agitation, thus enabling high heat and mass transfer rates during reactions. Furthermore, purification of the polymer is simple as compared to traditional solvents used in polymerization processes. Especially residual traces of solvent can effectively be removed by a combination of plasticization of the polymer and extraction.[2] On the other hand, the application of $scCO_2$ requires elevated pressures, which inherently bring along the associated compression costs. However, techniques that allow for CO_2 recovery at high pressure can reduce these costs substantially.[3]

Most polymers are insoluble in $scCO_2$, whereas nonpolar or slightly polar monomers have a very high solubility. Consequently, most polymerizations in $scCO_2$ initially start homogeneous and become heterogeneous very rapidly. Many polymerizations that have been performed in traditional solvents have also been performed in $scCO_2$.[1] These include radical,[4] carbocationic,[5] and transition-metal-catalyzed[6,7] polymerizations. Although CO_2 is in many reactions an inert solvent, some polymerizations cannot be performed in $scCO_2$. Traditional catalysts for olefin polymerization are incompatible with $scCO_2$, as the early-transition metals are highly oxophilic and will react with CO_2. However, late-transition-metal catalysts for olefin polymerization are less oxophilic[8] and can therefore be used in $scCO_2$.

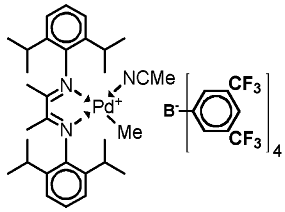

Figure 1. Palladium-based catalyst for polymerizations in $scCO_2$ and dichloromethane.

On the basis of earlier work on olefin polymerizations in high-pressure CO_2 using nickle diimine complexes,[9] a palladium-based catalyst has been successfully applied to polymerize olefins in $scCO_2$.[10] Carbon dioxide as a reaction medium does not influence the molecular weight of the produced polymers, indicating that no complexes with the catalyst are formed. The palladium-based catalyst, however, produces unique polymers when in contact with ethylene, as the polyethylenes produced by this catalyst are highly branched due to chain-walking. Branches ranging from methyl to hexyl and longer as well as so-called *sec*-butyl-ended branches (branch structures on branches) are reported in the literature.[11] This eliminates the necessity to use α-olefins to introduce short-chain branching (SCB) in polyethylenes. SCB is used to modify the chemical and physical properties of the polymer, such as glass transition temperature (T_g) and crystallinity. In this paper, the influence of CO_2 on the produced polymer is investigated by quantitative ^1H and ^{13}C NMR spectroscopy, GPC, and DSC on a number of polyethylenes produced at different reaction conditions in CO_2 and in dichloromethane as a reference.

Experimental Section

Polymer Synthesis. Figure 1 shows the palladium-based catalyst used for the polymerizations.[10] Batch polymerizations

---

* Corresponding author: e-mail M.F.Kemmere@tue.nl.

10.1021/ma035347b CCC: $27.50

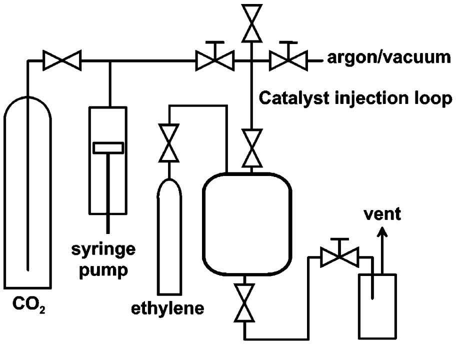

Figure 2. High-pressure setup for ethylene polymerizations in $scCO_2$.

Table 1. Polymerization Conditions of the Synthesized Polyethylenes

polymer sample	1	2	3	4	5	6
solvent	CO_2	CO_2	CO_2	CO_2	CO_2	CH_2Cl_2
initial press. [bar]	207	107	206	108	221	6.9
temp [T]	40	40	50	50	40	40
catalyst [10^{-6} mol/L]	40	39	40	38	41	120
ethylene [g/L]	84	84	75	75	38	35[a]

[a] Polymerization in dichloromethane was carried out using a constant head pressure of 6.9 bar of ethylene, which corresponds to an ethylene concentration of about 35 g/L.[8]

were performed in a 536 mL high-pressure reactor, equipped with two sapphire windows, a magnetically coupled stirrer, a Pt-100, a pressure sensor, a rupture disk, and a heating jacket. The setup is schematically shown in Figure 2. The polymerization procedure was as follows:[12] the air in the reactor was removed by applying vacuum and filling with 2 bar of argon (three times). Second, vacuum was applied, and approximately 50 bar of ethylene (Hoek Loos B.V., grade 3.5) was added directly from the cylinder into the reactor. Subsequently, CO_2 (Hoek Loos B.V., grade 4.5) was added to the reactor up to 10 bar below the final polymerization pressure. The catalyst was put in the catalyst injection loop, which was placed under vacuum to remove air. Subsequently, the catalyst was flushed into the reactor with 300 bar of CO_2 until the desired polymerization pressure was obtained. During the polymerization the pressure and temperature were recorded. After the reaction, the pressure was relieved through a polymer trap, and the polymer was collected by rinsing the reactor several times with heptane. Finally, the heptane was removed from the polymer in a rotary evaporator.

Polymerization in dichloromethane (AR grade, Aldrich, dried over 3 Å molecular sieves) was carried out in a glass reactor equipped with a magnetically coupled stirrer. The reactor was filled with 50 mL of dichloromethane and was gas washed with ethylene by applying vacuum and filling with ethylene (three times). The catalyst was flushed in the reactor with a head pressure of ethylene, and subsequently the polymerization started. After the reaction, the solvent was removed from the polymer in a rotary evaporator. The various polymerization conditions used are summarized in Table 1.

GPC Measurements. GPC relative to polystyrene standards (Polymer Laboratories, $M = 580$ to $M = 7.1 \times 10^6$) was carried out at 40 °C using a Waters model 510 pump and a Waters model 410 refractive index detector. Prior to injection, samples (1.5 mg of polymer per mL of tetrahydrofuran) were filtered over a 0.2 μm PTFE filter. Injections (50 μL) were done by a Waters model WISP 712 autoinjector. The applied columns were a PLgel guard column (5 μm particles, 50 × 7.5 mm), followed by 2 PLgel mixed-C columns (5 μm particles, 300 × 7.5 mm) in series. Tetrahydrofuran (Biosolve, stabilized with BHT) was used as an eluent at a flow rate of 1.0 mL/min. Data acquisition and processing were performed using Waters Millennium32 software.

To determine the absolute molecular weight, SEC analyses were also performed on a system with four columns: a PLgel Mixed-B (10μ Polymer Laboratories), a PLgel Mixed-C (5μ Polymer Laboratories), two PLgel Mixed-D (5μ Polymer Laboratories), and a guard column (PLgel 5μ Polymer Laboratories). This system consisted of an isocratic pump (Gyncotek P580, Separations, flow rate of 1.0 mL/min), UV detector (Spectra Physics Linear UV–vis 200, 254 nm), a differential refractive index and viscosity detector (dual detector 250, Viscotek), and a light scattering detector (RALLS, Viscotek). THF was used as a solvent. All samples were dissolved in the typical range of 10–15 mg/mL, and a dn/dc of 0.078 was used, a value in agreement with literature data.[11]

DSC Measurements. DSC measurements were performed on a Perkin-Elmer Pyris 1 apparatus. The experiments were performed at 10 °C/min using 11–17 mg polymer samples, which were vacuum-dried in an oven at 60 °C for 24 h. The calorimetric glass transition temperature T_g was determined from the second heating cycle, using the midpoint of the heat capacity change as a criterion. DSC temperature calibration was done using indium, gallium, and *n*-dodecane as standards.

^{1}H and ^{13}C NMR Characterization. Standard proton spectra of 5 wt % polymer in $CDCl_3$ were obtained on a 300 MHz Varian spectrometer at 25 °C and referenced to tetramethylsilane. The spectra were zero-filled up to 64K data points. Baseline correction was applied to the NMR spectra before integration.

Quantitative 125 MHz ^{13}C NMR experiments and standard attached proton test (APT) experiments were performed on a Varian Unity Inova 500 MHz spectrometer. Measurements were performed on 10 wt % solutions of polymer in 1,2,4-trichlorobenzene and 0.05 M $Cr(acac)_3$ using a 10 mm probe with a 3 mm insert. The insert contained *o*-dichlorobenzene-d_4 as a lock solvent. Quantitative spectra were obtained at 120 °C using a 90° pulse (approximately 13 μs), a relaxation delay of 5 s, an acquisition time of 0.64 s, inverse gated decoupling, and spectral width of 35 kHz. Under the selected conditions, the T_1 values of all carbons are less than 0.9 s.[11] About 5000–10 000 scans were obtained per spectrum. The spectra were zero-filled up to 256K data points. Carbon shifts were referenced to the main-chain carbon peak at 29.98 ppm. Baseline correction was applied to the NMR spectra before integration.

Modeling the Pressure Decay during Polymerization. We have developed a model to calculate the pressure as a function of conversion, for which it is assumed that the reaction mixture consists of a polymer phase swollen with ethylene and CO_2 and a supercritical ethylene–CO_2 phase. For a similar polymer it has previously been confirmed that no polymer dissolves in the ethylene–CO_2 phase within the experimental conditions used.[13] The swollen polymer phase, i.e., the polymer–ethylene–CO_2 system, is modeled using the statistical associating fluid theory (SAFT) equation of state.[14] The use of SAFT for describing both phases results in physically inconsistent behavior, as SAFT is known to overpredict the critical properties. The supercritical phase, i.e., the ethylene–CO_2 system, has therefore been modeled using the Lee–Kessler–Plöcker equation of state.[15]

SAFT requires three parameters for each pure component: a segment volume, v^{00}, the number of segments per molecule, m, the segment–segment interaction energy, u^0/k, and a parameter e/k to describe the temperature dependency of the interaction energy u.[14] LKP uses three parameters for the description of pure components: the critical temperature, T_c, the critical pressure, P_c, and an acentric factor, ω. To describe multicomponent systems, a binary interaction parameter, k_{ij}, is used in both models for each pair of components. The data used in the calculations are summarized in Table 2.

Results

Polymer Synthesis. Polymerizations of olefins in $scCO_2$ start homogeneous and rapidly become heterogeneous when the polymer precipitates. The polymers resulting from all polymerizations are clear and transparent rubbery materials. Contrary to the experiments performed in $scCO_2$, the polymerization in dichlo-

Table 2. Pure-Component Parameters and Binary Interaction Parameters Used for the SAFT and LKP Equations of State

	pure-component parameters				
SAFT	u^0/k (K)	v^{00} (mL/mol)	m	e/k	ref
CO_2	216.08	13.578	1.417	40	14
C_2H_4	212.06	18.157	1.464	10	14
polymer	469.86	21.618	$0.034365M^a$	10	13
LKP	T_c (K)	P_c (bar)	ω		ref
CO_2	304.1	73.8	0.225		16
C_2H_4	282.4	50.4	0.089		16
binary interaction parameters	k_{ij}				ref
SAFT	C_2H_4 polymer		$-0.0011847T + 0.27616$		13
$C_2H_4-CO_2$	$0.000491T - 0.0669$				13
polymer$-CO_2$	$-0.001043T + 0.49125$				13
LKP	$C_2H_4-CO_2$		0.957		17

[a] The polymer mass is set to 51 000, as the influence of the molecular mass on the calculations is negligible.

romethane remains homogeneous throughout the reaction.[13] In $scCO_2$, ethylene has been polymerized at two different temperatures and two overall pressures. In Figure 3a, the pressure decay in time is given for all polymerization runs in $scCO_2$. From this figure it can be observed that the pressure decreases even after long reaction times (28−96 h), indicating that at least some of the catalyst remains active. As the pressure is dependent on the composition of the mixture in a complex way, the relation between pressure and conversion is not straightforward. For this purpose, we have modeled the pressure decrease in the polymerizations using the SAFT equation of state for the polymer-rich phase in combination with the LKP equation of state for the supercritical fluid phase. Using the measured final conversions, the model can be validated by predicting the final pressures. As can be seen from Figure 3a, the agreement of the predicted final pressures with the measured final pressures is very good. This now allows for the construction of conversion−time plots for the different experiments (Figure 3b). At initial pressures above 200 bar, the pressure decrease is in the range 25−50 bar, while at lower initial pressures the pressure decrease is only about 8 bar. From Figure 3a,b it can be concluded that this difference is mainly caused by the phase behavior of the system and not by differences in conversion of ethylene.

GPC Analysis. Table 3 shows that the polyethylenes produced in $scCO_2$ have high number-average molecular weights and low polydispersities, although the polymerizations in $scCO_2$ are precipitation polymerizations. This indicates that mass transfer limitations are small during these polymerizations. The polymer synthesized in dichloromethane has a similar molecular weight and molecular weight distribution when compared to the polymers produced in $scCO_2$. The molecular weights determined by light scattering are substantially higher than the molecular weights obtained using polystyrene standards. Agreement of light scattering molecular weights with molecular weights relative to polystyrene is only expected for polymers of very similar structure. At equivalent hydrodynamic volume, polystyrene would be expected to have a larger molecular weight than a linear polyethylene, so that the larger molecular weight determined by light scattering indicates branching. Moreover, the molecular weights obtained from light scattering are considered to be absolute molecular weights. From these results it can be concluded that a high pressure and high temperature lead to the lowest molecular weight (polymer 3), whereas a low pressure and a low temperature lead to the highest molecular weight (polymer 2), i.e., 210 and 332 kg/mol, respectively.

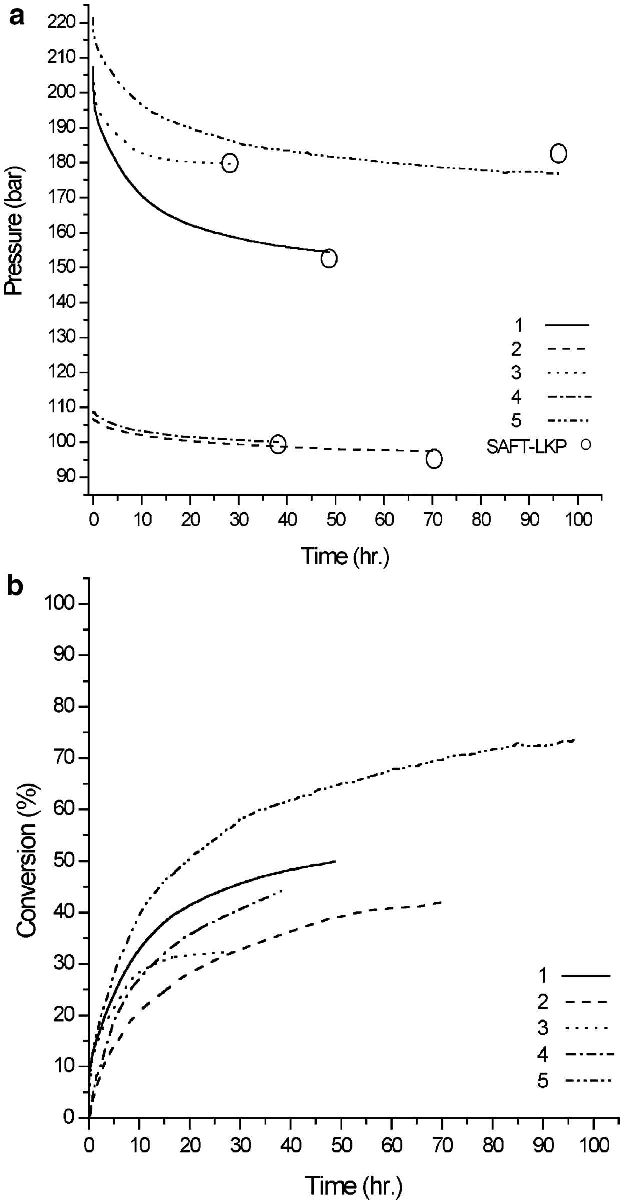

Figure 3. (a) Measured pressure−time plots for the different polymerizations in $scCO_2$. The data points are calculated from measured final conversions using the SAFT-LKP equation of state. (b) Conversion−time plots constructed from the pressure−time plots using the SAFT-LKP equation of state.

DSC Analysis. Figure 4 shows the glass transition temperatures of the polyethylenes formed. The transitions are equally broad; however, the polyethylenes synthesized in $scCO_2$ all have a slightly lower T_g than the polyethylene produced in dichloromethane. Although the polyethylenes are highly amorphous, a small enthalpy of melting can still be observed in the range −50 to −10 °C (see Figure 5). As no melting peaks are observed at higher temperatures, we explain this enthalpic effect as being a melting transition. This shows that the polyethylenes produced in $scCO_2$ are even less

Table 3. Characterization of the Polyethylenes with GPC, ^{1}H NMR, and ^{13}C NMR

polymer sample	1	2	3	4	5	6
M_n (kg/mol)[a]	182	191	123	129	129	159
M_w (kg/mol)[b]	294	332	210	250	300	n.d.
M_w/M_n[b]	2.3	1.9	2.0	1.8	2.2	2.4[a]
T_g (°C)	−68.7	−69.1	−69.3	−68.2	−69.0	−67.4
ΔH_m (J/g)	2.5	2.2	2.4	3.4	2.3	6.6
% crystallinity	0.9	0.8	0.8	1.2	0.8	2.3
branches total ^{1}H NMR[c]	106.5	107.8	107.4	105.1	106.5	99.2
branches total ^{13}C NMR[c]	107.1	106.8	109.3	105.9	107.0	99.1
methyl[c]	36.9	36.7	37.2	36.6	35.1	32.1
-3-methyl-ended branch[c]	6.8	8.2	7.7	7.4	8.1	6.0
ethyl[c]	24.3	24.2	24.7	23.9	24.8	21.7
propyl[c]	2.3	3.2	2.8	2.8	2.5	2.2
butyl[c]	11.4	10.6	11.9	11.4	13.0	10.5
-5-methyl-ended branch[c]	4.5	3.1	3.0	3.0	3.4	2.2
pentyl[c]	4.0	8.6	3.9	3.8	2.8	3.0
hexyl+[c]	28.1	23.5	28.8	27.5	28.8	29.6

[a] Against polystyrene standards. [b] "Absolute" molecular weight based on light scattering. [c] Branches per 1000 °C.

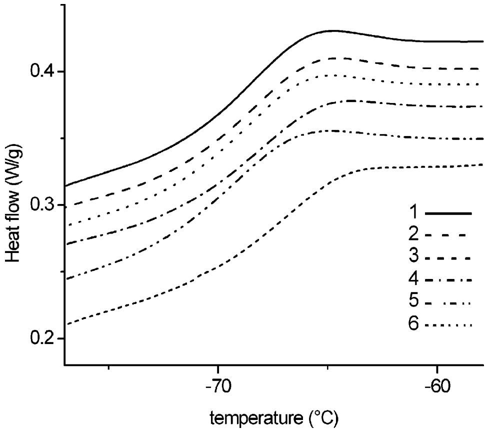

Figure 4. Glass transitions of the polymers: 1 through 5 are synthesized in scCO$_2$; 6 is synthesized in dichloromethane.

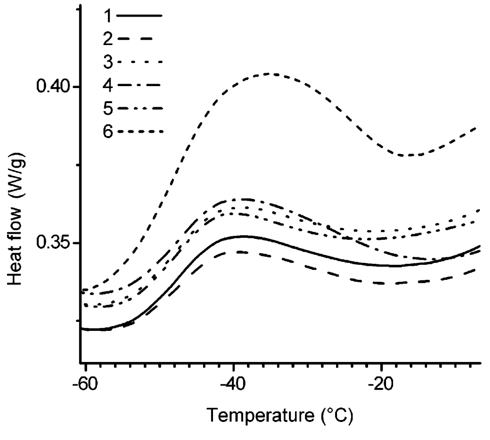

Figure 5. Melting range of the formed polymers: 1 through 5 are synthesized in scCO$_2$; 6 is synthesized in dichloromethane.

crystalline than the polyethylene produced in dichloromethane. Compared to 100% crystalline polyethylene, which has a melting enthalpy of 294 J/g, the polyethylenes produced in scCO$_2$ and dichloromethane have a crystallinity of about 1 and 2%, respectively. Although crystallinities of branched polyethylenes are higher than calculated from the value for 100% crystalline polyethylene due to poor quality of the polymer crystals in branched polyethylene, the relative difference between the polyethylenes produced in scCO$_2$ and dichloromethane remains the same. Furthermore, the melting enthalpy of 100% crystalline polyethylene can be used to determine the crystallinity sufficiently accurate, which is supported by X-ray diffraction and DSC measurements on a series of branched polyethylenes by Mirabella and Bafna.[18]

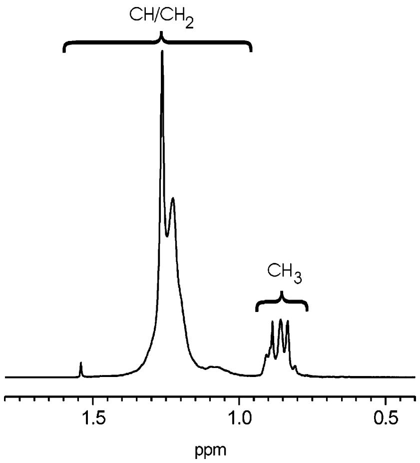

Figure 6. Typical ^{1}H NMR spectrum of the polyethylenes produced by the palladium-based catalyst. Spectrum is a 300 MHz ^{1}H NMR spectrum of polymer 3 (produced at 50 °C in scCO$_2$, 206 bar initial pressure) measured in CDCl$_3$ at 25 °C.

^{1}H and ^{13}C NMR Characterization. Figure 6 shows a typical ^{1}H NMR spectrum of the polymers produced in scCO$_2$ and in dichloromethane. The peaks in the range from 0.76 to 0.94 ppm reflect the large amount of CH$_3$ groups, which indicates that the polymer is highly branched. Although the polyethylenes appear to dissolve completely in CDCl$_3$, phase segregation occurs after a few hours, rendering CDCl$_3$ unsuitable for reliable quantitative ^{13}C NMR measurements. Figure 7 shows the ^{13}C NMR spectrum of the polymer sample 4 produced in scCO$_2$ at 50 °C, 108 bar total pressure, and 74.8 g/L ethylene. The spectrum shows that the polymers produced by the palladium-based catalyst are indeed highly branched. The peaks resulting from resonances of carbons belonging to methyl, ethyl, butyl, pentyl, branches longer than pentyl (hexyl^{+}), and branches belonging to 3-methylbutyl^{+}-ended branches have been assigned according to the literature.[11,19−21] Table 3 shows the number of branches per 1000 carbon atoms of the polyethylenes produced in scCO$_2$ and in dichloromethane. The numbers of branches determined by ^{1}H NMR in CDCl$_3$ and ^{13}C NMR in TCB are very similar, which indicates that CDCl$_3$ can be used to determine the number of branches accurately. The total pressure or the temperature does not influence the type and amount of branches present in the polyethylenes produced in scCO$_2$. The solvent, however, appears to have a small influence on the total branch content of the polyethylenes. The total amount of branches in the polyethylene produced in scCO$_2$ is slightly higher. This increase in total branch content cannot be attributed to a certain type or length of branch but is rather a general increase in the amount of all branches.

Discussion

The DSC experiments show that the polyethylenes produced in scCO$_2$ are more amorphous than the

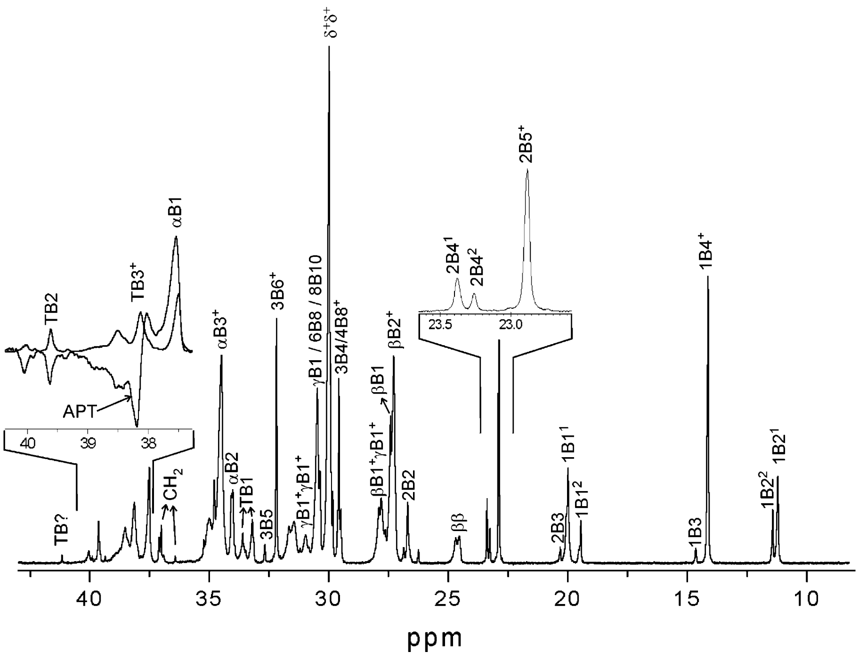

Figure 7. Typical ^{13}C NMR spectrum of polyethylenes produced by the palladium-based catalyst. The spectrum is a 500 MHz ^{13}C NMR spectrum of sample 4 (produced at 50 °C in $scCO_2$, 108 bar initial pressure) measured at 120 °C in 1,2,4-trichlorobenzene. Label xBy in case x is a number: x gives the position of the carbon in a branch of length y, in case x is a Greek symbol: carbon in the main chain with 1, 2, 3, or 4 carbons from a branch respectively denoted as α, β, γ, and δ. Positive peaks in the APT insert (attached proton test) mean CH_2 groups, and negative peaks mean CH or CH_3 groups. Some peak labels contain the superscripts 1 and 2 to distinguish between an ordinary branch and a branch-on-branch structure, respectively.

polyethylenes synthesized in dichloromethane, which is likely to originate from the slightly higher branch content as measured with ^1H and ^{13}C NMR spectroscopy. A study by Mecking et al.[22] using a similar palladium diimine catalyst has shown that branching is strongly dependent on the polymerization medium. A branch content of 65, 66, and 105 branches per 1000 C atoms has been measured in water, gas phase, and dichloromethane, respectively. It was concluded that the mobility of the growing polymer chain is reduced in the precipitation polymerization in the water and the gas phase, which leads to a decrease in the chain-walking process. Apparently, when the polymerizations are performed in $scCO_2$, the carbon dioxide is able to plasticize the precipitated polymer to such an extent that chain walking is still possible. Using the SAFT-LKP model, the solubility of CO_2 in the polymer can be calculated, which ranges from approximately 4.8% up to 6.8%, depending on temperature, pressure, and monomer concentration. Furthermore, swelling experiments with CO_2 at 50 °C result in a swelling between 15 and 25 vol % at pressures between 50 and 90 bar, respectively.

The higher branch content measured for the polymers synthesized in CO_2 compared to the polymers synthesized in dichloromethane is not yet clear. The difference is not likely to originate from the high hydrostatic pressure of CO_2 because the polymers produced at different CO_2 pressures are identical in branch content. Also, within the investigated range, the concentration of ethylene does not change the branch content. Cotts et al.[11] have performed polymerizations in chlorobenzene at ethylene pressures ranging from 0.1 up to 35 bar. It was shown that the SCB was only slightly decreased at higher ethylene pressures, from 99 down to 93 branches per 1000 carbon atoms. A higher branch content would have been expected at higher ethylene pressures if the hydrostatic pressure or the ethylene concentration is the cause of the higher branch content in $scCO_2$. Also, the temperature only affects the molecular weight and not the branching of the polymers. Therefore, the observation that the polyethylenes produced in $scCO_2$ have a higher branch content likely originates from the strong nonpolar environment compared to the relatively polar dichloromethane. In view of the fact that chain walking is much faster than insertion of monomer, a plausible explanation is that in $scCO_2$ insertion of ethylene in secondary carbons attached to the metal center is favored over insertion in primary carbons, resulting in more branching. Since a secondary carbon attached to the metal center is more electron donating than a primary carbon, the former is thermodynamically favored in the nonpolar $scCO_2$.

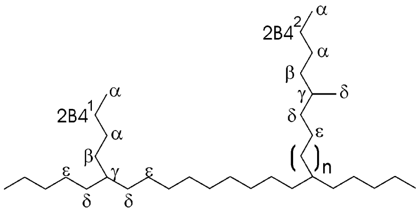

Figure 8. Ordinary butyl branch and 5-methyl-ended branch structure. The symbols α through ε give the distance in carbon atoms from the 2B4 carbon and are used for the chemical shift calculations with the modified Grant and Paul parameters.[13]

There is a strong indication that a new branch on branch structure is identified (see Figure 8). According to the literature, the 2B4 peak occurs at 23.37 ppm. Near that shift an additional resonance can be observed at 23.26 ppm. The sum of the peak areas of both resonances is in all ^{13}C NMR spectra equal in size to the $1B4^+$ minus the $2B5^+$ peak (total amount of "butyl" branches). The shift difference cannot be explained by configurational differences since these are not present in 2B4 peaks in liquid-state NMR. Therefore, the peak has to originate from a different structure. The most likely structure is a 5-methyl-ended branch because the 5-ethyl-ended branch is very likely to give a similar shift as an ordinary butyl branch, as it has the same type of carbons up to four carbons from the carbon in question. When the shifts are calculated using the modified Grant and Paul parameters,[13] a similar trend is observed, although these parameters have been fitted to poly(ethylene-*co*-α-olefin)s, which do not contain structures like the 5-methyl-ended branch. For a normal butyl branch and a 5-methyl-ended branch, a shift is calculated of 23.11 and 23.05 ppm, respectively. Another possible explanation for the presumed 5-methyl-ended branch is the presence of a branch adjacent to the butyl branch. However, this is highly unlikely as the relative amount of the presumed 5-methyl-ended branch is very high, and similar quantities of peaks resulting from branches adjacent to other branches, e.g., methyl, ethyl, or propyl, are absent or very small.

Conclusions

In this paper polymerizations of ethylene in $scCO_2$ have been described using a palladium diimine catalyst. The effect of temperature, pressure, and ethylene concentration has been evaluated experimentally. Additionally, a model based on the SAFT and LKP equations of state has been used to describe the pressure decay upon reaction. From a characterization of the materials it appears that highly branched amorphous polymers of high molecular weight and narrow molecular weight distributions have been formed. As compared to polymerizations in dichloromethane, the polymers produced in $scCO_2$ show a higher degree of short-chain branching. Additionally, analysis of the ^{13}C NMR spectra of the polymers gives a strong indication of a new branch-on-branch structure, which has not been assigned before.

Acknowledgment. We thank Marcel van Genderen for assistance with the ^{13}C NMR measurements, Wieb Kingma for performing the GPC measurements, and Henny Bruinewoud for the help with the DSC measurements.

References and Notes

(1) Kendall, J. L.; Canelas, D. A.; Young, J. F.; DeSimone, J. M. *Chem. Rev.* **1999**, *99*, 543.

(2) Kemmere, M. F.; Van Schilt, M. A.; Cleven, M. H. W.; Van Herk, A. M.; Keurentjes, J. T. F. *Ind. Eng. Chem. Res.* **2002**, *41*, 2617.

(3) Van den Broeke, L. J. P.; Goetheer, E. L. V.; Verkerk, A. W.; De Wolf, E.; Deelman, B.-J.; Van Koten, G.; J. T. F. Keurentjes, J. T. F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4473.

(4) Shaffer, K. A.; Jones, T. A.; Canelas, D. A.; DeSimone, J. M. *Macromolecules* **1996**, *29*, 2704.

(5) Pernecker, T.; Kennedy, J. P. *Polym. Bull. (Berlin)* **1994**, *32*, 537.

(6) Super, M. S.; Berluche, E.; Costello, C. A.; Beckman, E. *Macromolecules* **1997**, *30*, 368.

(7) Hori, H.; Six, C.; Leitner, W. *Macromolecules* **1999**, *32*, 3178.

(8) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

(9) Arthur, S. D.; et al. α-olefins and olefin polymers and processes therefor. Patent Application WO9623010.

(10) De Vries, T. J.; Duchateau, R.; Vorstman, M. A. G.; Keurentjes, J. T. F. *Chem. Commun.* **2000**, 263.

(11) Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules* **2000**, *33*, 6945.

(12) De Vries, T. J. Late-transition-state metal catalyzed polymerizations of olefins in supercritical carbon dioxide. Ph.D. Thesis, Eindhoven University of Technology, 2003.

(13) De Vries, T. J.; Somers, P. J. A.; De Loos, Th. W.; Vorstman, M. A. G.; Keurentjes, J. T. F. *Ind. Eng. Chem. Res.* **2000**, *39*, 4510.

(14) Huang, S. H.; Radosz, M. *Ind. Eng. Chem. Res.* **1991**, *30*, 1994.

(15) Plöcker, U.; Knapp, H.; Prausnitz, J. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 324.

(16) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: London, 1987.

(17) Gmehling, J.; Onken, U.; Arlt, W. *Vapor-Liquid Equilibrium Data Collection;* Dechema: Frankfurt/Main, 1980.

(18) Mirabella, F. M.; Bafna, A. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 1637.

(19) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 901.

(20) Liu, W.; Ray III, D. G.; Rinaldi, P. L. *Macromolecules* **1999**, *32*, 3817.

(21) Randall, J. C. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29*, 201.

(22) Held, A.; Mecking, S. *Chem.—Eur. J.* **2000**, *6*, 4623.

MA035347B