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Propylene copolymerization with non-conjugated dienes and α-olefins using supported metallocene catalyst

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Abstract

Propylene was copolymerized with 7-methyl-1,6-octadiene, 1,9-decadiene and α-olefins using dimethylsilanyl*bis*(2-methyl-4-phenyl-1-indenyl)zirconium dichloride supported on methylaluminoxane modified silica. Additional methylaluminoxane was needed to activate the catalyst. Comonomer incorporations were 1.5 mol% or less. In propylene/7-methyl-1,6-octadiene copolymers there was no indication of long-chain branching and molar masses were low. Adding a small amount of 1,9-decadiene caused very high molar masses and broad molar mass distributions. A possible long-chain branching in propylene/1,9-decadiene copolymers was evaluated by stress-controlled dynamic rheometer. Changed rheological behavior and especially raised Arrhenius-type flow activation energy along with change in polymer properties indicated long-chain branching in propylene/1,9-decadiene copolymers.
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1. Introduction

Polypropylene has a good impact strength, rigidity, chemical resistance and a low cost. An improved melt strength could enable new possibilities in blow molding, foaming, thermoforming, fiber spinning and extrusion coating. A key feature of metallocene catalyzed polymer is the narrow molar mass distribution, which then is associated with a narrow processing window due to poor shear thinning [1]. Processability of polypropylene could be enhanced by introducing long-chain branches into the polymer.

The easiest method is to make a blend of polypropylene with desired properties and low-density polyethylene with good processability, but typically all the good properties of polypropylene are lost in the mixing, especially the film transparency, film strength and heat resistance [2,3].

Dienes have been used with propylene to introduce long-chain branching or terminal unsaturations into the copolymer [3,4]. These unsaturations can react with functional comonomers, which typically contaminate metallocene catalysts in direct copolymerizations [5]. The unsaturations also enable sterilization with gamma radiation without molar mass loss or significant decomposition [6]. This is particularly attractive in medical devices made of or containing propylene/diene copolymer.

The melt strength of polypropylene can be enhanced with crosslinkage or long-chain branching. A route to obtain modified polypropylene is either by chemical means using peroxides [7] or by copolymerizations with silanes [8] or dienes [6].

One possibility to modify polypropylene is after-treatment solely [9] or with combination with other mentioned methods [10,11]. Using ionizing radiation [9] in the presence of oxygen causes chain-cission and polymer degradation but could lead to improved processability. A few higher molar mass chains formed by irradiation could induce increased entanglement of polypropylene chains, which thereby leads to higher melt strength [11]. During this degradation process uniformity is lost and also the good properties of polypropylene are affected. Another disadvantage in after-treatment is that oxidation occurs uncontrolled. Postal treatment is performed in several phases and is therefore time-consuming and costly. Use of strong chemicals such as mercaptans and dienes could leave

residues in the polymer if used in excess and cause undesirable odour effects.

The aim in our present study was to improve the rheology of polypropylene by introducing long chain-branches via direct copolymerization with non-conjugated dienes. Selected dienes were 7-methyl-1,6-octadiene and 1,9-decadiene to avoid ring formation typical to shorter dienes. The amount of comonomer used was kept really very low in order to avoid bad odour, which is very common in propylene/diene copolymers causing troubles in commercialization. The effect of low comonomer incorporations on polymer properties and rheology was examined.

2. Materials

The heterogeneous catalyst used in the polymerizations was dimethylsilanyl*bis*(2-methyl-4-phenyl-1-indenyl)zirconium dichloride supported on methylaluminoxane modified silica surface. After heterogenezation the zirconium content was 0.21 wt% and aluminum content 12.6 wt%. The comonomers 1,9-decadiene (Shell), 7-methyl-1,6-octadiene (Aldrich), 1-hexene (Aldrich) and 1-tetradecene (Merck) were dried with molecular sieves. 7-methyl-1,6-octadiene was further purified by distilling over sodium in vacuum before use. *n*-heptane (p.a.) was obtained from Merck and purified before use by circulating the liquid through 3 Å molecular sieve, BASF R3-11 copper catalyst and activated Al_2O_3 columns. Methylaluminoxane (MAO, a 10 wt% solution in toluene) and triisobutylaluminum (TIBA) were obtained from Witco GmbH (Bergkamen, Germany) and used as received. Propylene (grade 2.8 from AGA) was purified by conducting it through columns containing 3 Å molecular sieves, BASF R3-11 copper catalyst and activated Al_2O_3.

3. Polymerizations

The polymerization experiments were carried out in a $0.5\ dm^3$ stainless steel autoclave reactor equipped with a propeller-like stirrer. The reactor was evacuated and flushed with nitrogen several times before adding *n*-heptane and cocatalyst. The suspension of the catalyst in *n*-heptane was prepared in a glove box and introduced to the reactor with nitrogen pressure. The total volume of polymerization medium was $300\ cm^3$. The mixture was stirred and the polymerization reaction was initiated by introducing the monomer. Comonomer was added batchwise with a dosing pump in the beginning of the polymerization. The stirring speed was $1000\ min^{-1}$, polymerization temperature 80 °C, and propylene overpressure 5.0 bar. With high temperature crosslinking and cyclication can be reduced. Polymerization temperature was kept constant during reaction by circulating water in the reactor jacket. Partial pressure of the monomer was maintained constant with an electronic

pressure controller. Propylene consumption was monitored during polymerization. The polymerization was stopped by cutting off the propylene feed. The reactor was degassed, and the polymer was precipitated with a mixture of ethanol and a small amount of concentrated hydrochloric acid. The product was isolated by filtering, washed with ethanol and *n*-pentane, and dried in vacuum at 40 °C.

4. Polymer characterization

The molar masses and molar mass distributions of the polymers were determined with a Waters 150-C ALC/GPC gel permeation chromatograph operating at 140 °C and equipped with three Waters Styragel HMW columns (HT6, HT4 and HT3) and a refractive index detector. The solvent 1,2,4-trichlorobenzene was applied at a flow rate of $1.0\ cm^3$/min. The columns were calibrated with narrow molar mass distribution polystyrene standards using a universal calibration method. Polypropylene standard with known molar mass value was used as reference in the selection of Mark–Houwink parameters K and α for the samples.

Melting temperatures (T_m) and enthalpies (ΔH_m) were determined with a Mettler Toledo DSC 821^e differential scanning calorimeter. Indium was used for the calibration of the temperature scale. The melting endotherms were measured upon reheating of the polymer sample to 190 °C at a heating rate of 10 °C/min.

The FTIR spectra were measured with Nicolet Magna FTIR spectrometer 750 from melt-pressed polymer sample films.

The ^{13}C NMR spectra of polypropylenes were recorded on a Varian Gemini 2000 300 MHz spectrometer at 125 °C from samples dissolved in 1,2,4-trichlorobenzene/benzene-d6 (90/10 w/w). The [mmmm] methyl signal of polypropylene was used as an internal standard and was given the chemical shift δ 21.8 ppm.

Rheological analyses were performed on a Rheometric Scientific SR-500 stress controlled dynamic rheometer. Frequency sweeps were carried out at three different temperatures 200, 220 and 240 °C under nitrogen atmosphere. A 25 mm plate–plate geometry and a 1 mm sample gap were used for stiff materials, a 25 mm cone-plate geometry and a 0.045 mm sample gap otherwise. The angular frequency was from 0.01 to 100 rad/s. Frequency sweep measurements were carried out within the linear viscoelasticity region, which was ensured by a stress sweep. The thermal stability of selected samples was examined with a 90-minute time sweep. Thermal stability throughout the rheological testing was checked by repeating one low-frequency measurement point ($\omega = 0.02$ rad/s) after the primary frequency sweep. In every sample the change in storage modulus G' during the frequency sweep was less than 5%. To prevent degradation during measurement 2000 ppm Irganox B215 antioxidant (Ciba-Geigy, Basel,

Switzerland) and 500 ppm calcium stearate were added. Rheometrics RSI Orchestrator software version V6.5.3 was used to extrapolate zero shear viscosities using Ellis model fit method and to shift the moduli curves along the frequency axis to construct the master curves and to determine the shift factor a_T. The shift factors were then plotted against $1/T$ to obtain the Arrhenius-type flow activation energy E_a. Only the E_a from the time-temperature superposition measurements with correlation coefficient of 0.99 and higher were accepted for further evaluation.

5. Results

5.1. Copolymerization of propylene and 7-methyl-1,6-octadiene

The reaction conditions and all polymerization results are presented in Table 1. The polymer structures formed can be seen in Fig. 1. Adding 7-methyl-1,6-octadiene (PP/MOD) into the reaction affected activity and molar masses. Compared to the activity in homopolymerization of propylene (PP) 12 000–88 000 kg/(mol$_{Zr}$ h), comonomer addition decreased activity to 1200–18 000 kg/(mol$_{Zr}$ h). These calculated polymerization activities are greatly

affected by an alteration in polymerization time or the amount of catalyst. The decline in activity could also be detected with 1-hexene, but 1-tetradecene or 1,9-decadiene had a slighter effect on the activity. Walter et al. [12] eliminated the activity drop by adding a very small amount of ethylene during the initial phase of the polymerization.

7-methyl-1,6-octadiene behaved like an excellent chain transfer agent. Compared to the molar mass of homopolymer 122–180 kg/mol, adding 7-methyl-1,6-octadiene lowered molar mass of the polymer to as low as 68–83 kg/mol even with so low comonomer quantities, which were undetectable by ^{13}C NMR from the copolymer. Molar mass distributions were narrow 2.0–2.3.

An increase in comonomer incorporation lowered melting temperatures. With further increase in comonomer incorporation also the melting enthalpies dropped. The same phenomenon was detected when 1-hexene and 1-tetradecene were used as comonomer.

Propylene/7-methyl-1,6-octadiene copolymers were highly isotactic as were also the homopolymers. Comonomer incorporations were determined from the ^{13}C NMR spectra [13]. The spectrum of propylene/7-methyl-1,6-octadiene copolymer is presented in Fig. 2. Intensity of peaks at δ 43.8 ppm (α), δ 35.7 ppm (C6), δ 33.8 ppm (br), δ 27.3 ppm (C4), δ 25.6 ppm (C1, in *trans* position to the
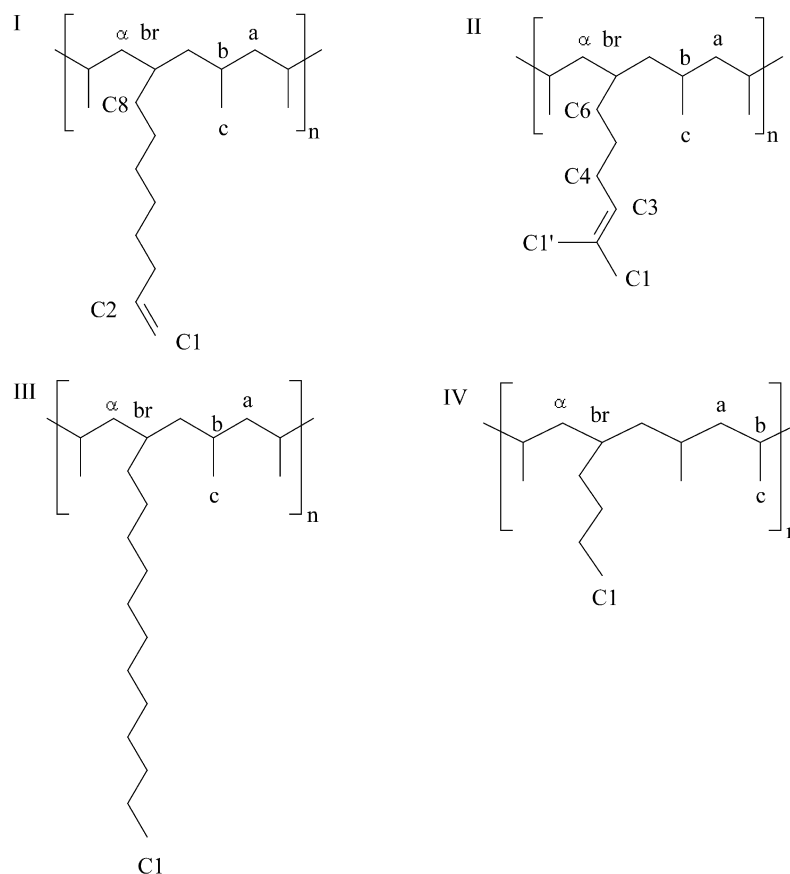

Fig. 1. Copolymer structures. I polypropylene/1,9-decadiene (PP/DD), II polypropylene/7-methyl-1,6-octadiene (PP/MOD), III polypropylene/1-tetradecene (PP/14C) and IV polypropylene/1-hexene (PP/Hx).

Table 1
Polymerization results

Experiment	n (Zr) (μmol)	Comonomer concentration (mol/dm^3)	Polymerization time (min)	Activity (kg/(mol h))	T_m (°C)	ΔH_m (kJ/mol)	M_w (kg/mol)	M_w/M_n	[mmmm] [%]	Comonomer incorporation (mol%)
PP1	4.0[a]	0	30	12 000	155.1	107	128	2.1	95.5	0
PP2	1.7	0	30	15 000	156.4	112	122	2.4	94.6	0
PP3	1.0	0	15	53 000	155.4	105	180	2.4	n.d.	0
PP4	1.1	0	15	88 000	154.5	110	120	2.5	n.d.	0
PP5[b]	2.5[a]	0	30	0[b]	n.d.[b]	n.d.[b]	n.d.[b]	n.d.[b]	n.d.[b]	n.d.[b]
PP/MOD6	6.0	0.014	45	1200	141.8	94	76	2.0	96.6	0.20
PP/MOD7	6.4	0.011	20	5800	151.3	91	68	2.1	96.6	0.10
PP/MOD9	4.0	0.014	20	18 000	154.5	102	83	2.3	93.2	0[c]
PP/DD1	4.6	0.014	10	14 000	139.0	76	544	9.1	93.3	0.64
PP/DD2	1.2	0.028	15	57 000	151.2	100	368	4.8	94.7	0.40
PP/DD3	0.8	0.028	20	54 000	150.7	90	977	12.0	94.5	0.15[d]
PP/DD4	0.5	0.032	30	22 000	137.1	76	991	6.8	n.d.	n.d.
PP/DD5	3.6	0.014	27	10 000	142.7	85	n.d.[e]	n.d.	n.d.	n.d.
PP/Hx1	1.0	0.027	30	31 400	150.7	100	152	2.3	95.4	0.15
PP/Hx2	0.8	0.015	30	19 500	147.0	95	176	2.3	93.5	0.38
PP/Hx3	0.8	0.033	60	8800	137.8	83	192	2.4	95.6	1.07
PP/14C1	4.0[a]	0.006	30	3900	154.3	100	171	2.4	95.0	0.04
PP/14C3	0.6	0.034	30	2200	132.0	68	207	2.7	n.d.[f]	n.d.
PP/14C2	1.0	0.029	30	46 100	144.9	86	149	2.3	95.1	0.56

Reactor volume 0.5 dm^3, 300 cm^3 n-heptane, propylene overpressure 5.0 bar, polymerization temperature 80 °C, Al/Zr ratio 2000 mol/mol.

[a] Al/Zr ratio was only 1000 mol/mol.
[b] TIBA was used as cocatalyst, but unfortunately could not activate the catalyst.
[c] No comonomer detected by ^{13}C NMR.
[d] Only carbons attached directly to the main chain detected by ^{13}C NMR.
[e] Partially insoluble in TCB.
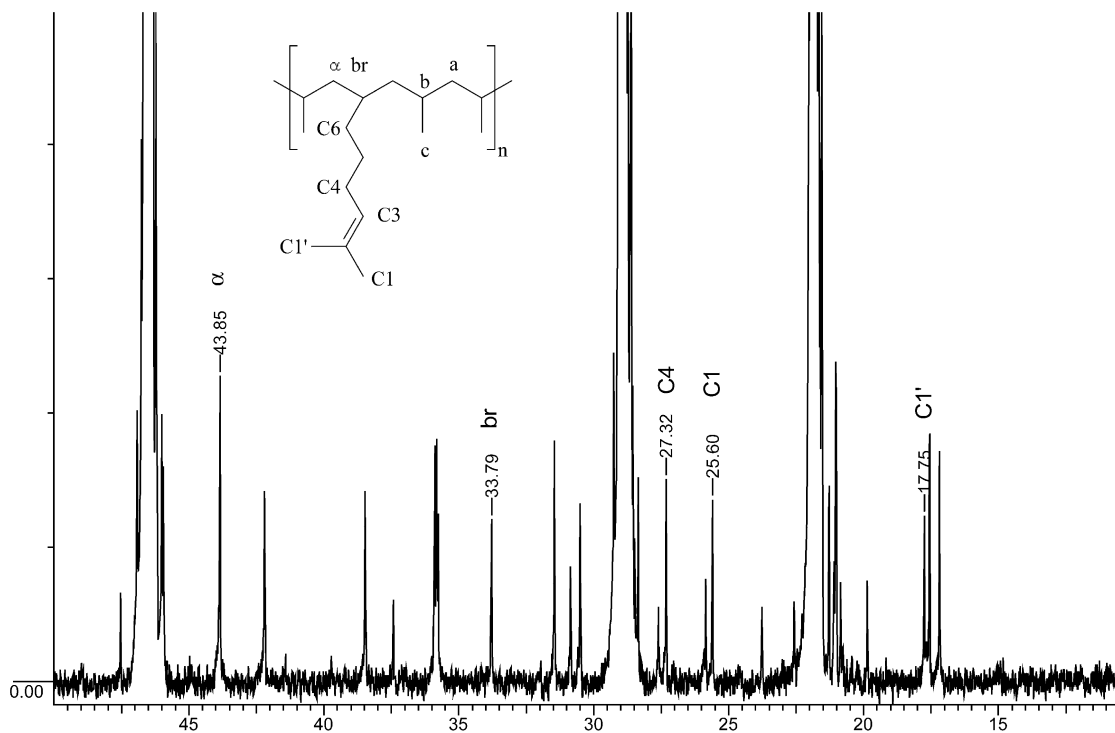[f] Not enough material for ^{13}C NMR measurements due to very low yield.

Fig. 2. ^{13}C NMR spectrum of 7-methyl-1,6-octadiene/propylene copolymer.

comonomer chain) and δ 17.8 ppm (C1$'$, in *cis* position to the comonomer chain) were used for the quantitative determination of comonomer incorporations. Also the double bond at δ 125.5 ppm (C3) was visible. Comonomer incorporations were calculated to be less than 0.2 mol%. No indication of intramolecular cyclization was detected. Due to extremely low amounts of comonomer in polymer, comonomer incorporation was difficult to detect with NMR and the calculations were not as precise as desired. Comonomer incorporations below 0.05 mol% were overlaid by the noise of the base line with our measuring system. Conventionally low comonomer incorporations are determined with FTIR [13,14] but no double bonds were detected from FTIR spectra because of very low comonomer incorporations or disturbance of silica residue from the catalyst support in the same spectral frequency region. High comonomer incorporation should be avoided because the mechanical properties of polypropylene are maintained only if the amount of comonomer is kept very low [14].

2,1 misinsertions were quantitated from intensity of peaks at δ 17.2 ppm, δ 17.5 ppm, δ 30.5 ppm, δ 31.5 ppm, δ 35.8–35.9 ppm, δ 38.5 ppm and δ 42.2 ppm. The amount of 2,1 misinsertions was in the range 0.36–0.39 mol% in all the examined polymers. 3,1 misinsertions were quantitated from intensity of peaks at δ 19.9 ppm, δ 27.6 ppm, δ 30.9 ppm and δ 37.4 ppm. The amount of 3,1 misinsertions was in the range 0.10–0.16 mol% in all the examined polymers. The total amount of regioerrors varied between 0.46 and 0.55 mol% and was independent of comonomer incorporation or comonomer used.

5.2. Copolymerization of propylene and 1,9-decadiene

The structure of the copolymer is presented in Fig. 1. Reaction conditions and results from the polymerizations are displayed in Table 1. Activity in copolymerizations 10 000–57 000 kg/(mol$_{Zr}$ h) was in the same range as in homopolymerizations 12 000–88 000 kg/(mol$_{Zr}$ h). These calculated polymerization activities are greatly affected by alterations in polymerization time and amount of catalyst.

1,9-decadiene (PP/DD) had a great influence on molar masses. Even small amounts of comonomer raised molar masses to 368–991 kg/mol. Molar masses of homopolymers were 122–180 kg/mol. Copolymer PP/DD2 had a clear shoulder in the GPC curve and all the other propylene/1,9-decadiene copolymers had bimodal molar mass or even more peaks. The effect of comonomer incorporation on the molar mass can be seen in Fig. 3. Molar mass distributions were broad 4.8–12.0. PP/DD3 and PP/DD4 had very high molar masses and also even larger fractions, which could not flow through GPC columns and were cut off from the curve so the actual molar masses could be even higher. Copolymer PP/DD5 was insoluble in 1,2,4-trichlorobenzene so neither molar mass nor comonomer incorporation could be determined for this sample. Broad molar mass distributions, an increase in molar mass and gel formation imply slight crosslinkage in the copolymer. Molar masses and molar mass distributions grew very high with polymerization times of 20 min or longer. This might indicate increase in the level of crosslinkage as the double bonds react further during longer reaction times.
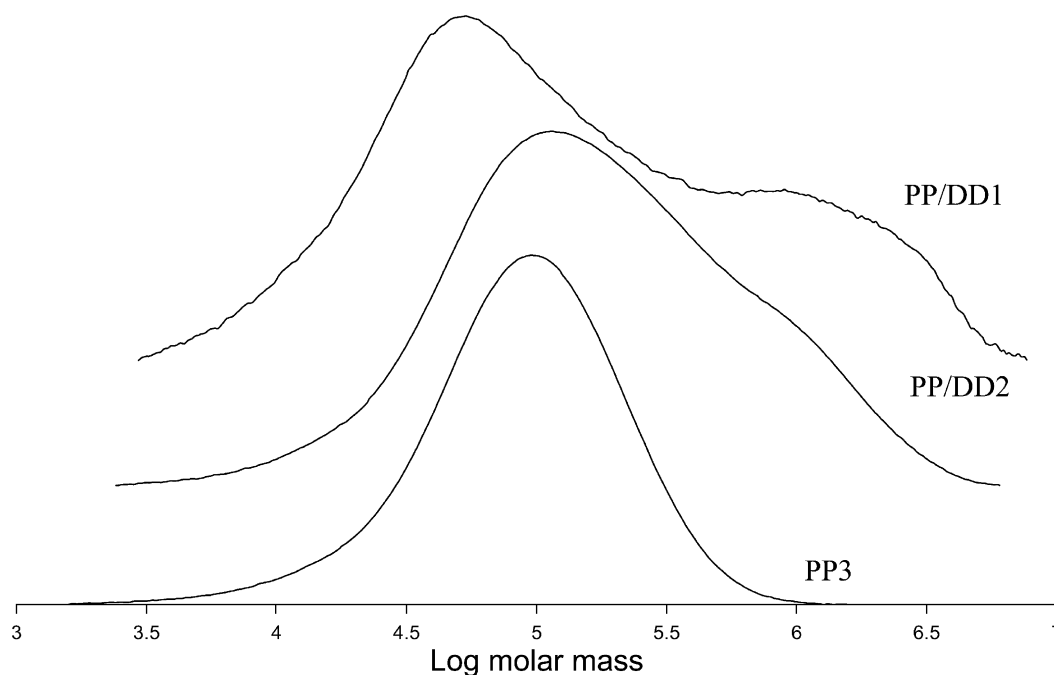
Fig. 3. Effect of increasing crosslinkage on GPC curve. Comonomer incorporation, molar mass and molar mass distribution increases from bottom to top in samples PP3, PP/DD2 and PP/DD1.

Melting temperatures 137–151 °C and enthalpies 76–100 kJ/mol of propylene/1,9-decadiene copolymers are lower than for the homopolymers. This implies a formation of side chains as in Fig. 1 or the rigid structure of slightly crosslinked polymer.

Propylene/1,9-decadiene copolymers were highly iso-tactic as were also the homopolymers. Comonomer incorporations were determined from the ^{13}C NMR spectra [13,15]. The spectrum of propylene/1,9-decadiene copoly-mer is presented in Fig. 4. Intensity of peaks at δ 43.9 ppm (α), δ 36.1 ppm (C8) and δ 33.8 ppm (br) were used for the quantitative determination of comonomer incorporations. Also the double bonds at δ 139.0 ppm (C2) and δ 114.3 ppm (C1) were visible. Comonomer incorporations were 0.15–0.64 mol%. Incorporations were very low, actual incorpor-ations were difficult to determine from the ^{13}C NMR spectra and incorporations in some copolymers were estimated from only two peaks (α and C8). Such low quantities of diene in copolymer caused no undesired odour in the end product. Strong odours could limit the range of possible applications. Amount of comonomer added was very low in all the cases and did not affect the comonomer incorpor-ations as much as for example the activity of the polymerization reaction. Quantitative ^{13}C NMR analysis is in good accordance with the assumption of domination of linear 1,2-addition over intramolecular cyclization. On the account of cyclization, the broadening of the transition in the vicinity of δ 43.9 ppm suggested presence of magneti-cally non-equivalent S_{aa} carbons adjacent to C8 branch. However, quantification of the relative amounts of linear versus cyclic structures turned out to be impossible due to

overlapping transitions thus it can be only concluded that linear addition of DD is dominant. The amount of 2,1 and 3,1 misinsertions was in the same range as in all the other examined polymers.

Reasonably good copolymers for further analyses were acquired in short polymerizations of 10–15 min. An increase in polymerization time caused ultra-high molar masses, broad molar mass distributions, partial insolubility, gel formation and a disappearance of side-chain carbons from the ^{13}C NMR spectrum. This implied reaction of both double bonds of 1,9-decadiene and a crosslinkage of the polymer during longer reaction times.

5.3. Homopolymerization of propylene and copolymerization with α-olefins

Homopolymerization of propylene (PP) and copolymer-ization with 1-hexene (PP/Hx) or 1-tetradecene (PP/14C) were performed for comparison. In addition, also homo-polymerizations (PP5) without additional MAO using TIBA as cocatalyst were tested but TIBA alone could not activate the catalyst although the support was treated with MAO. Activity in copolymerizations was in the same range as in homopolymerization. Comonomer incorporation did not affect tacticity or molar masses but it decreased melting temperatures and enthalpies.

Comonomer incorporations were determined from the ^{13}C NMR spectra [16]. The spectrum of propylene/1-hexene copolymer is presented in Fig. 5. Intensity of the peaks at δ 43.9 ppm (α), δ 33.8 ppm (br) and δ 14.1 ppm (C1) were used for determination. Comonomer incorporations of
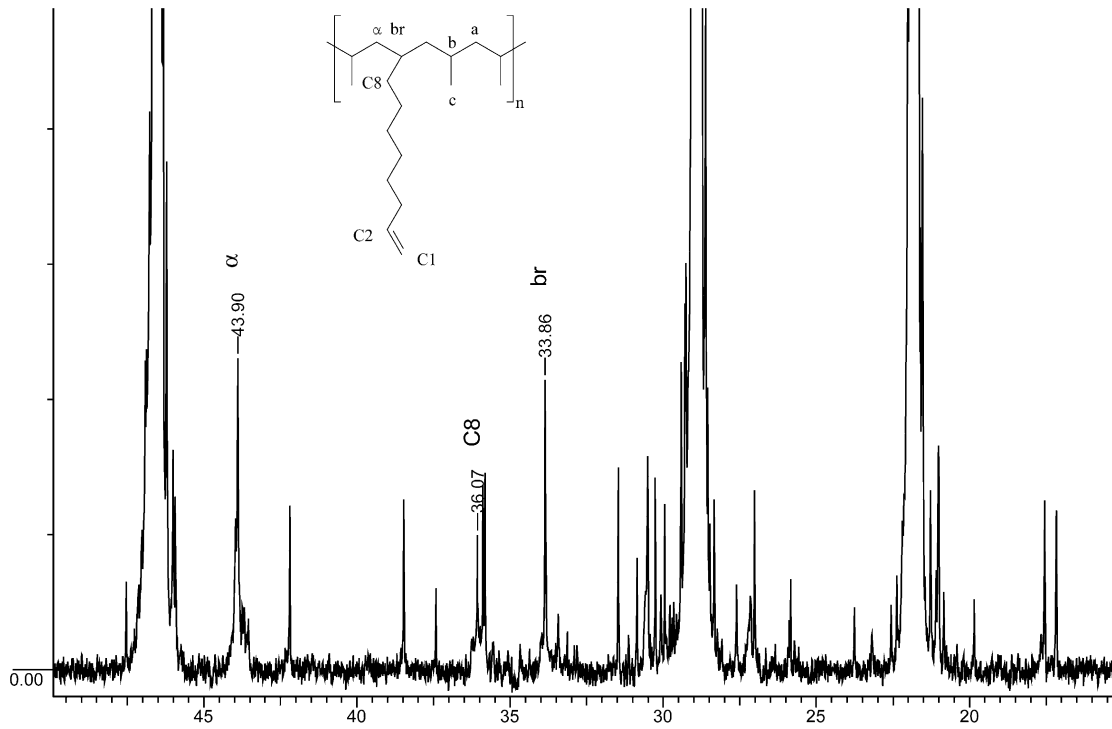
Fig. 4. ^{13}C NMR spectrum of 1,9-decadiene/propylene copolymer.

1-hexene were 0.15–1.07 mol% and of 1-tetradecene 0.04 mol% and 0.56 mol%. The amount of 2,1 and 3,1 misinsertions was in the same range as in all the other examined polymers.

5.4. Dynamic rheological measurements

The most intriguing polymer samples were selected for the rheological tests. Two polypropylene/1,9-decadiene
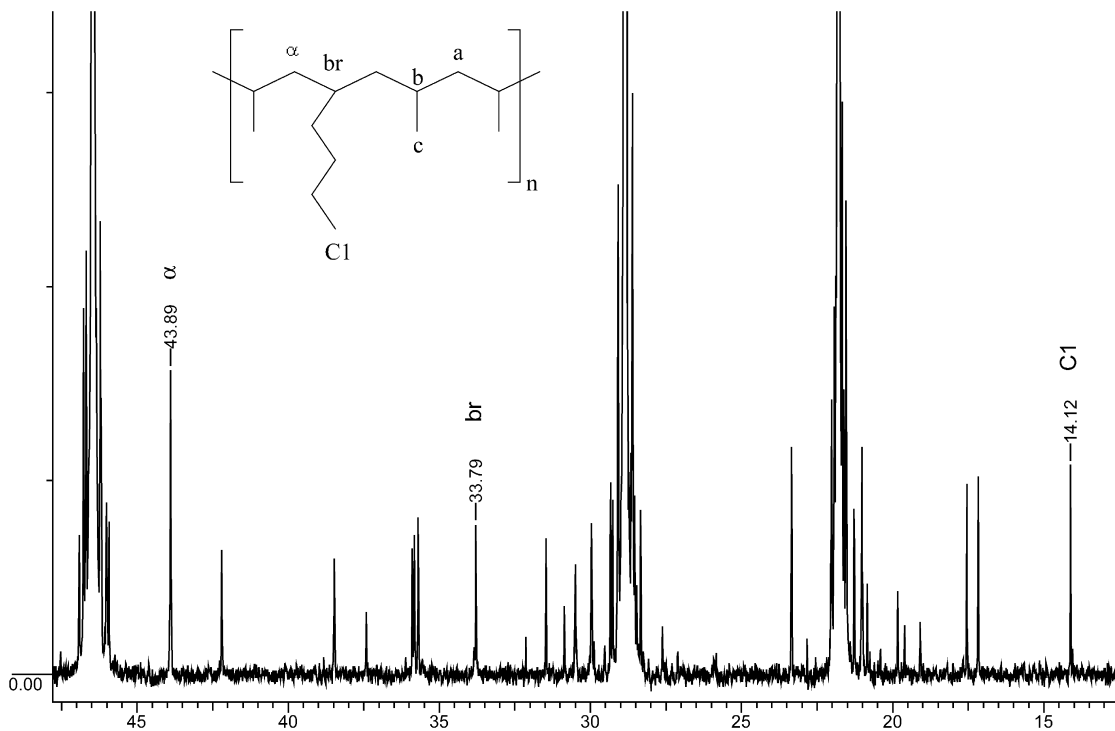
Fig. 5. ^{13}C NMR spectrum of 1-hexene/propylene copolymer.

samples were PP/DD1 and PP/DD2. For comparison one polypropylene/1-hexene (PP/Hx2), one polypropylene/1-tetradecene (PP/14C1) and one polypropylene (PP3) were also examined. In addition, one polypropylene PP6 with a higher molar mass of 387 kg/mol closer to molar masses of the PP/DD copolymers was used as reference.

Reliable measurements could be made with the molar mass range of 150–800 kg/mol. With lower molar masses the polymer melts were too fluid and with higher molar masses relaxation times grew too long. This restriction greatly diminished the variety of samples available for the evaluation of rheological properties. For example, only two polypropylene/1,9-decadiene copolymers had a molar mass low enough for the rheological tests.

Unfortunately all the propylene/7-methyl-1,6-octadiene had too low molar masses for a reliable measurement, but according to the earlier analyses the PP/MOD copolymers and the homopolymer resembled each other to a great extent and the polypropylene modification seemed to be minimal. Also the homopolymers, polypropylene/1-hexene and polypropylene/1-tetradecene copolymers had quite low molar masses but one sample of each had a moderate molar mass for rheological studies. In addition to these polymers polymerized at the same conditions, one reference sample produced in a pilot reactor was tested in order to eliminate effects of the molar mass differences between polypropylene/1,9-decadiene copolymers and other polymers. The results from the dynamic rheological measurements are presented in Table 2.

Zero shear viscosities of the measured samples were extrapolated from the complex viscosity curves. Zero shear viscosity is dependent mainly on the molar mass as can be seen from the reference samples. The PP/DD copolymers gave much higher zero shear viscosity than would have been expected based on the molar masses. One obvious reason could be the much broader molar mass distributions [17] as seen from GPC measurements (Fig. 2). Zero shear viscosity is also greatly affected by a high molar mass tail as well as long-chain branching or crosslinkage. Crosslinkage can be ruled out because PP/DD1 and PP/DD2 were completely soluble in TCB used as solvent in GPC and NMR analysis. This distinguished change in rheological behaviour is best observed in the difference between samples PP/DD2 and the polypropylene reference PP6 with almost the same molar mass. (Table 2 and Fig. 6)

Though broad molar mass distribution increases shear thinning, a shear thinning behaviour this strong and sharp as seen in the Fig. 6 indicates also other reasons such as long-chain branching or crosslinkage behind this phenomenon [12,18].

When comparing the dynamic moduli of polypropylene/1,9-decadiene copolymers in Figs. 7 and 8 with dynamic moduli of homopolymer in Fig. 9 clear differences were detected. In PP/DD1 the contribution of the storage modulus G' was greater. In both PP/DD copolymers the $G'–G''$ moduli crossover occurred at a lower frequency.

Table 2
Dynamic rheological test results

Experiment	T_m (°C)	ΔH_m (kJ/mol)	M_w (kg/mol)	M_w/M_n	Comonomer incorporation (mol%)	η_0 extrapolated at 200 °C	E_a (kJ/mol)	G' at G'' (2000) at 200 °C	G' at G'' (5000) at 200 °C	G' at G'' (10 000) at 200 °C
PP3	155.4	105	180	2.4	0	892	49	350	1460	4160
PP6	154.6		387	2.4	0	13 631	44	388	1410	3860
PP/DD1	139.0	76	544	9.1	0.64	80 709	68	2980	7630	15 000
PP/DD2	151.2	100	368	4.8	0.40	39 798	100	1640	4820	10 700
PP/Hx2	147.0	95	176	2.3	0.38	634	39	241	1100	3390
PP/14C1	154.3	100	171	2.4	0.04	847	42	381	1510	4220

Eta* at 200 °C
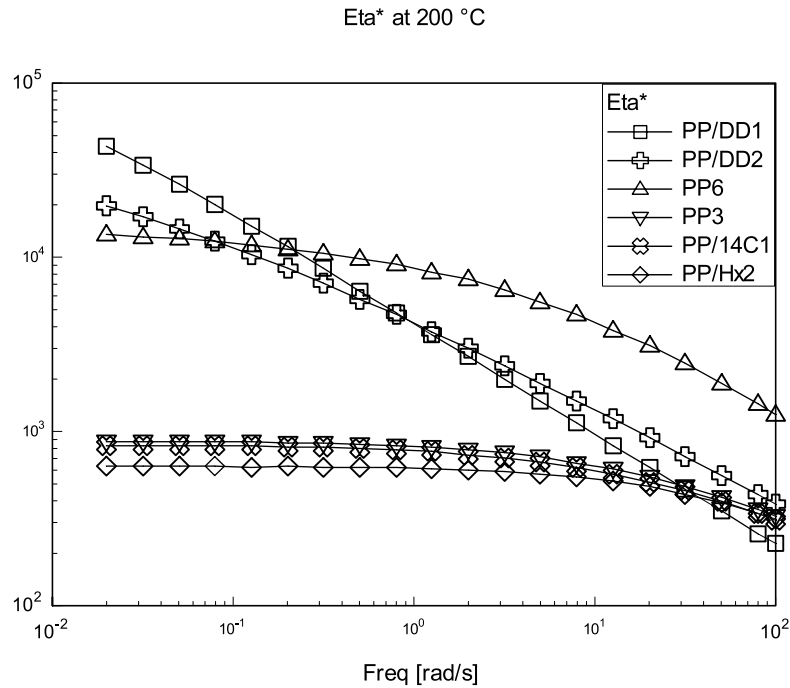

Fig. 6. Eta* of the selected samples at 200 °C used for Eta$_0$ extrapolation.

This indicates the startup of a secondary network structure and could mean very early stages of crosslinking [19]. Dynamic moduli were very linear which implied long-chain branching but the same effect can be seen in homopolymers with broad molar mass distribution as was the case in both copolymers PP/DD1 and PP/DD2. A typical problem with the rheological analysis is that the effect of molar mass distribution can obscure the rheological response associated with long-chain branching.

According to the literature, in linear isotactic polypropylenes the Arrhenius-type flow activation energies E_a vary from 27 to 40 kJ/mol [20,21]. For syndiotactic linear polypropylene the E_a of 51 kJ/mol is slightly higher [21]. E_a is independent of molar mass distribution. For isotactic polypropylene with molar mass distributions changing from 5 to 10 E_a has been reported to be 42–43 kJ/mol [22]. With branched polypropylene where branches have been induced by an electron beam treatment the E_a was 55 kJ/mol, which

Frequency PP/DD1 at 200 °C

Fig. 7. Frequency sweep of propylene/1,9-decadiene copolymer PP/DD1 at 200 °C.
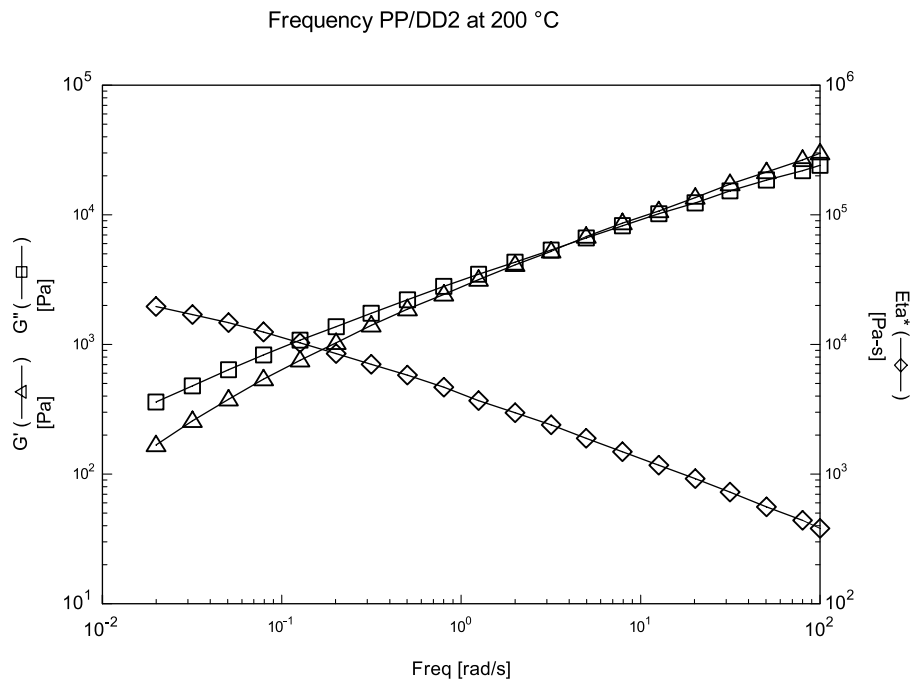
Frequency PP/DD2 at 200 °C

Fig. 8. Frequency sweep of propylene/1,9-decadiene copolymer PP/DD2 at 200 °C.

was significantly higher than with linear polypropylene [23].

When comparing the Arrhenius-type flow activation energies of the reference samples acquired in this work to what has been published earlier, the E_a 39–49 kJ/mol measured for our reference samples was in the same range as reported in the literature for linear isotactic polypropylene.

Differences in polymerization activity and the level of propylene consumption could cause the variation of E_a.

For the two tested polypropylene/1,9-decadiene copolymers, the E_a were 68 kJ/mol for PP/DD1 and 100 kJ/mol for PP/DD2. Compared to the literature, these acquired E_a values were on a much higher level than would be expected for a linear polypropylene. Also the
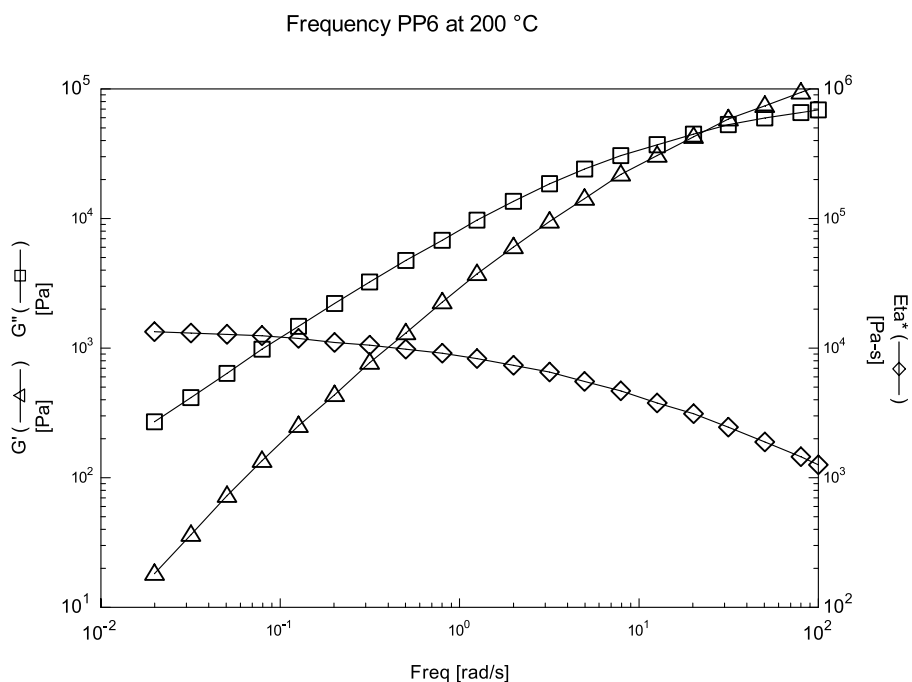
Frequency PP6 at 200 °C

Fig. 9. Frequency sweep of polypropylene reference PP6 at 200 °C.

difference to the E_a measured for the reference samples is evident.

Although there is a slight variation in the Arrhenius-type flow activation energies, the E_a measured for propylene/1,9-decadiene copolymers are clearly on a higher level than the E_a measured for the reference samples. The exact E_a might depend slightly on the equipment used but the E_a measured here are comparable to each other.

One explanation for this kind of rheological behaviour might be a chain extension or crosslinkage of the polymer chains because of thermal degradation during measurement or sample preparation. Even a small amount of high molar mass fraction has a big influence on rheological behaviour. But as was found out in the time sweeps, the stability of 1,9-decadiene/propylene copolymers during a 90-minute measuring time was sufficient throughout the whole temperature range used for sample preparation and rheological measurements from 200 to 240 °C. During sample preparation, the polymers were exposed to a temperature of 200 °C only for a period of ten minutes. As for the stability of the sample during a single frequency sweep, the change in storage modulus G' was less than 5% for all the selected samples and for the most interesting propylene/1,9-decadiene copolymers the change was 1.5% or less. Furthermore in DSC measurements performed prior to and after the rheological measurements thermal behaviour remained unaltered.

6. Discussion

In 7-methyl-1,6-octadiene the methyl group next to the other double bond creates steric hindrance and decreases the reactivity thus protected from crosslinkage and cyclization [13,14,24] which is typical for shorter linear dienes [15]. Also the selected polymerization temperature diminishes crosslinkage of dienes as a lower polymerization temperature favours crosslinkage as reported in literature [25]. Unfortunately the steric hindrance prevented the formation of long-chain branching.

In 1,9-decadiene linear addition was dominant over cyclization as would be expected. According to literature, DD cyclizates very rarely due to a longer carbon chain between the two vinyl groups of DD [26,27]. Cyclization is favored by lower temperatures [27] and is also catalyst sensitive [27,28].

In contradiction to an earlier study with ethylene and long dienes [25], crosslinking was not avoided in long polymerizations though high reaction temperature was used. A crosslinking reaction cannot compete with more reactive ethylene the same way it does with propylene.

The formation of a long-chain branch via reaction with DD is pictured in Scheme 1. A growing polypropylene chain reacts with DD and continues to grow. Free double bond of DD branch reacts with another growing polypropylene chain. As both chains continue to grow, DD acts as a bridge

between two polypropylene chains and an H-like molecule with two long branches is created. DD has to link two quite long polypropylene chains together in order to produce long-chain branching. With shorter polypropylene chains or if only one of the double bonds of DD has reacted, no long-chain branching in the rheological sense is formed. This might explain why higher flow activation energy was measured for PP/DD2 (100 kJ/mol, 0.40 mol%) than for PP/DD1 (68 kJ/mol, 0.68 mol%) with higher diene incorporation and why long-chain branching does not correlate with comonomer incorporation. In addition, the comonomer incorporations detected by ^{13}C NMR were very close to each other. Therefore it might be insignificant to the long-chain branching whether the polymer has 0.40 or 0.64 mol% diene.

Aside from copolymerization with dienes, another reason for long-chain branching in polypropylene might be macromonomer incorporation formed in situ [19] or by using previously prepared macromonomers, where long-chain branch length and distribution can be controlled [29]. Although the monomer partial pressure in the gas phase was kept constant during polymerization, the variation in the monomer consumption might have caused differences in the monomer concentration in the liquid phase, as the propylene is not immediately passed into *n*-heptane, and thereby the lower monomer concentration favours the incorporation of macromonomer over propylene. Especially in very short and highly active polymerizations, macromonomer incorporation might have occurred more easily. As this was the case for both samples in which long-chain branching was detected, macromonomer incorporation cannot be completely excluded.

In contrary to Walter et al. [16] we have used ^{13}C NMR instead of ^{1}H NMR to determine comonomer incorporations. If polymerization occured as described in Scheme 1, the amount of double bonds would not have given useful information about comonomer incorporation as both double bonds had reacted. The determination of the amount of branches had its own disadvantages because each 1,9-decadiene had two reactive double bonds and formed two branches. On the other hand, the detection of branches was an important part of proving the existence of long-chain branching.

Differences in the methods to determine comonomer incorporations or the longer chain of diene might be the reason why we did not see an equally dramatic drop of melting temperature as Walter et al. When looking at the effect of comonomer on the molar masses, in the research of Walter et al. 1,7-octadiene caused a serious drop in molar masses and the effect with DD in our study was the exact opposite.

Apart from viscosity measurements done similarly to Walter et al., we have concluded a more thorough rheological analysis and used Arrhenius-type flow activation energy to assure the existence of long-chain branches. We
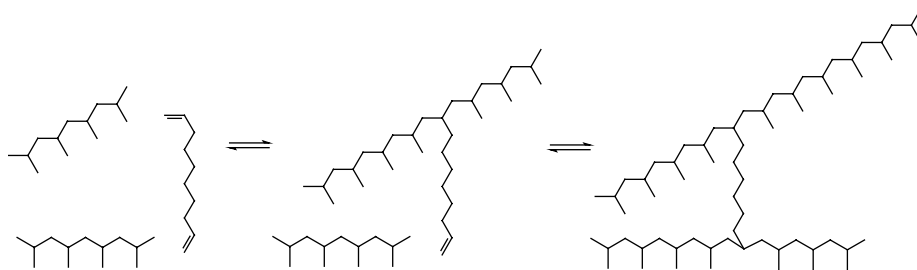
Scheme 1. The formation of long-chain branching in propylene 1,9-decadiene copolymerization.

achieved higher values of E_a than Kurzbeck et al. [23] with electron-beam irradiated polypropylene with LCB.

7. Conclusions

Polypropylene/7-methyl-1,6-octadiene and propylene/1,9-decadiene copolymers with comonomer content under 1 mol% were successfully polymerized. In polypropylene/7-methyl-1,6-octadiene copolymers there was no indication of long-chain branching or crosslinkage and the molar masses were rather low.

Comonomer branches were detected from the ^{13}C NMR spectrum. Use of 1,9-decadiene as comonomer caused very high molar masses and broad molar mass distributions even in low concentrations. Molar mass distributions of the PP/DD copolymers were 5–12. The typical molar mass distribution for homopropylene produced by metallocene is 2.0–2.5. Polymerization times of 20 min or longer seemed to further increase the effect on the molar mass. This implies reaction of both double bonds of 1,9-decadiene and a crosslinkage of the polymer during longer reaction times.

The propylene/1,9-decadiene copolymer affected strongly on the elasticity index of the material. Elevated zero shear viscosity, increased shear thinning along with changed rheological behaviour and especially raised Arrhenius-type flow activation energies of 68 and 100 kJ/mol indicated long-chain branching in polypropylene/1,9-decadiene copolymers.

Long-chain branching improves process abilities of the isotactic polypropylene produced by metallocene catalyst and enables new applications.

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