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Study on the copolymerization of propylene with norbornene using metallocene catalysts

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Abstract The copolymerization of propylene with norbornene, using the metallocene catalysts $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ and $Ph_2C(Flu)(Cp)ZrCl_2$ was evaluated. The presence of norbornene decreases the polymerization activity in both systems. In the $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ system, the decrease is ca. 80 % using 0.5 mL of norbornene while the addition of 2 mL reduces the activity by 97 %. The molecular weight of the materials decreases between 27,000 and 37,000 g/mol in the presence of norbornene. The $Ph_2C(Flu)(Cp)ZrCl_2$/MAO system has the same tendency, but the norbornene has a lesser effect on the activity, with 2 mL of comonomer reducing the activity ca. 80 %. The molecular weight decreased significantly with this system as well. The elongation at break of some of the materials was 80 times higher than the homopolymer and the Young's modulus slightly superior to the homopolymer. This indicates that it is possible to generate materials that keep the properties of a syndiotactic polypropylene but with good elastomeric properties.

Keywords Polypropylene copolymerization · Norbornene ·
Metallocene catalyst · Physical properties

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Introduction

The ability of metallocenes to copolymerize ethylene with cyclic hindered monomers has been demonstrated using a variety of catalytic systems [1–6]. These materials show very different properties than either homopolymer, and vary greatly depending on the composition and molecular weight of the final material. The copolymerization of ethylene with cyclic monomers is well known, and has been extensively studied by this and other groups. In particular, works describing the effect of monomer concentration, catalyst selection, and polymerization conditions have been widely reported [3, 5, 7–9]. However, due to a number of factors (e.g., difficulty in working with propylene, analysis of the microstructure of the polymer), the copolymerization of propylene with such monomers has been reported less, and typically by few research groups. One of the first reports of such a copolymerization was reported in 1997 by Henschke [10–17]. Nonetheless, the copolymer materials are of great interest as the incorporation of small concentrations (<1 mol%) result in significant changes to the thermal and mechanical properties which enable the materials to be used over a wider range [6, 18, 19].

The combination of polypropylene with sterically bulky and hindered monomers was a natural continuation of existing research efforts for this group [7, 17, 20]. As the study of polymerization catalysts and polymeric materials has continued, one of the foci has been on the incorporation of controlled amounts of copolymers in order to better understand and control the polymerization process as well as the polymer properties of the resulting materials. Recently, the use of styrene as a chain termination agent in the polymerization of propylene was reported, the efficacy of styrene in terminating the polymer chain being related to the catalyst structure as well as the polymerization conditions [21]. This led to an interest in the effect that other sterically blocky monomers might have on the polymerization process as well as the polymer properties.

In previous work, it has been noted the activity of copolymerizations using both norbornene and dicyclopentadiene with both ethylene and propylene are low compared to the homopolymerization reactions; this is due in large part to the steric demands of the monomer. In work in our lab with dicyclopentadiene–ethylene copolymerizations, it was noticed that the materials showed interesting properties which were very sensitive to the concentration of the comonomer incorporated as well as the reaction conditions [7]. In previous work involving propylene copolymers [17], polymerization conditions were selected to produce high molecular weight polymers with low incorporations. This involved the use of low pressures and temperatures, which may not be possible in industrial conditions. Boggioni et al. [10, 12] reported on the characterization of propylene–norbornene copolymers, however, the focus was primarily on the NMR analysis of the polymers. The effect of the fluorenyl ring substituents in titanium-based catalysts was studied by Cai et al. [22], where it was found that the introduction of substituents to the fluorenyl ring produced significant effects on the polymerization activity.

It was therefore decided to investigate the copolymerization of propylene with norbornene, shown in Scheme 1, and dicyclopentadiene using two metallocene catalysts, one which produces isotactic materials and the other which produces syndiotactic materials, in order to evaluate how sterically bulky and hindered monomers affect the thermal and mechanical properties of the final copolymer and also how the syndiospecificity of the catalysts affects the incorporation of the monomers.

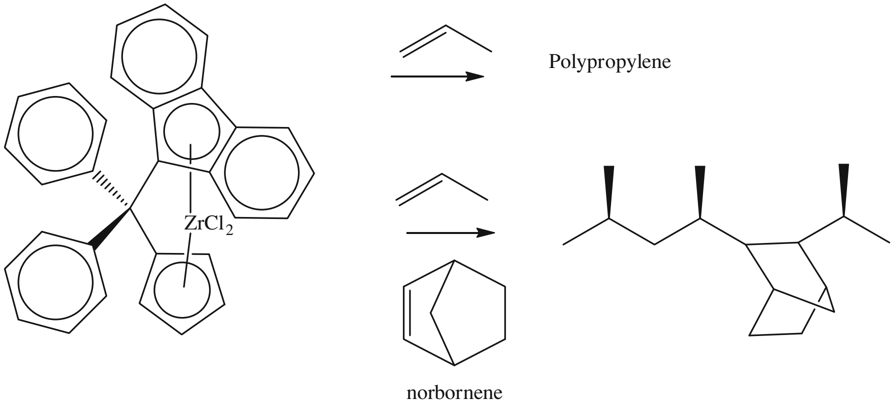
Materials and procedures

Materials

The metallocene catalysts, dimethylsilyl(2-methylindenyl)zirconium chloride ($Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$) and diphenylmethylidene(cyclopentadienyl)(fluorenyl)zirconium dichloride ($Ph_2C(Flu)(Cp)ZrCl_2$), were obtained from Boulder Scientific Company and used without further purification. Methylaluminoxane (MAO) was purchased from Huntsman (10.7 wt% in toluene) and used as received. Toluene was purified by distillation from sodium metal and benzophenone and dispensed under nitrogen. Dicylcopentadiene and norbornene (Aldrich) were stirred over CaH_2, vacuum distilled, and stored under nitrogen prior to use. Polymerization grade propylene (99.9 %) was obtained from Petroquim and purified by passage through columns of BASF R3-11G and BASF R3-12 catalysts and 4 Å molecular sieves.

Homo- and copolymerization reactions

Polymerizations were carried out in a 1 L Buchi glass polymerization reactor, thermostated at the temperature indicated using a recirculating bath. The reactor was dried in an oven at 150 °C for a minimum of 3 h prior to use and assembled hot, evacuated and purged with nitrogen three times. Freshly distilled toluene (600 mL) was then transferred under nitrogen into the reactor. A solution of MAO was injected into the reactor, followed by the introduction of propylene at the reaction



Scheme 1 Reaction of propylene and norbornene with a metallocene catalyst

pressure (2 bar). The [Al]/[Zr] molar ratio was 2,000 in each of the reactions. The toluene–MAO solution was allowed to stir under propylene pressure for 30 min at the reaction temperature. A solution of the catalyst, prepared in a nitrogen glovebox, was then injected into the reactor. The polymerization was carried out for 30 min and was terminated by the injection of 10 mL of a 10 wt% solution of HCl in methanol. The polymers were allowed to precipitate over night, and then were filtered, washed with acetone and ethanol, and then allowed to dry overnight. The reactions were repeated at least once and the average values of activity are reported.

Characterization of the copolymers

Polymer samples were analyzed using differential scanning calorimetry (DSC) measurements on a TA Instruments Modulated DSC 2920. The samples were exposed to two thermal cycles, from 20 to 220 °C, at a heating rate of 10 °C/min, the values reported are from the second cycle in order to eliminate any thermal history.

The molecular weight of the polymers was determined by viscometry as previously described [21]. The tacticity and comonomer content in the homo- and copolymers was determined by ^{1}H and ^{13}C NMR on a Varian Innova 300 spectrometer operating at Lamor frequencies of 300 and 75 MHz, respectively [23]. 1,1,2,2-tetrachloroethane-D2 was used as the solvent and the samples were run at 120 °C.

The mechanical properties were measured using a HP D500 dynamometer. The samples were melt pressed at 165 °C and 50 bars pressure using a hydraulic press to a thickness of ca. 0.2 mm and cooled under pressure. Samples for analysis were then cut using a stainless steel die to the dimensions and shape specified in ASTM D638M-I. The dynamometer was run at a rate of 50 mm/min at 25 °C and 35 % RH. A minimum of three samples were tested for each material and the average values are reported.

Results and discussion

Copolymerizations with $Me_2Si(2\text{-}Me\text{-}Ind)ZrCl_2$

As this system had been used in previous work with ethylene-*co*-dicyclopentadiene copolymers, it was decided to use this system as a starting point for the copolymerization of propylene with the cyclic monomers as well. Polymerizations using dicyclopentadiene/propylene as the comonomers resulted in polymerization activities which were reduced by 80 % at low loadings of dicyclopentadiene. This was not unexpected as the presence of the cyclic monomers has been shown in previous work to diminish the polymerization activity. The very low activity, combined with a low molecular weight of the materials, however, made the production of high molecular weight materials untenable using laboratory scale equipment. Therefore, it was decided to focus on norbornene copolymerizations, as these materials could be generated in sufficient quantities to study the mechanical properties.

The effect of the norbornene concentration on yield is readily apparent with even a small concentration resulting in a significant decrease in the activity, Table 1. The addition of just 0.0075 mol/L (0.5 mL) norbornene decreases the activity of the polymerization from ca. 11,000 (kg/mol·h·bar) for the homopolymerization to ca. 2,100 (kg/mol·h·bar) for the copolymerization. This decrease in activity continues with increasing monomer concentration, with the reactions carried out using just 0.030 mol/L (2 mL) of comonomer in the reaction mix resulting in yields which are ca. 3 % than that of the homopolymer. This decrease in activity is likely due to the high steric demands of the monomer which hinders access for subsequent monomer coordination and insertion. As might be expected, the molecular weight of the materials decreased greatly in the presence of the comonomer with the molecular weight decreasing from 165,000 to about 30,000 g/mol regardless of the amount of comonomer used. This could be the result of a decreased solubility of the copolymer produced. The incorporation of the norbornene into the polymer was dependent on the initial comonomer concentration. The tacticity of the materials decrease slightly with the incorporation of norbornene, to ca. 94 % compared to 95 % for the homopolymer. The melting temperature of the materials decreased with the incorporation of the norbornene with the melting points decreasing from 8 to 23 °C. The cause of this decrease is likely a combination of the decrease in molecular weight as well as the incorporation of the sterically bulky norbornene which would make the packing of the molecule less crystalline.

In the study of the Young's modulus of the materials, a significant decrease was found at relatively low norbornene content with just 2.4 mol% norbornene incorporation, reducing the Young's modulus by ca. 30 % and by ca. 60 % at 3.4 mol% loading. At higher incorporations, the materials became too brittle to press. Incorporation of a small amount of norbornene nearly doubled the elongation at break compared to the homopolymer. This is particularly interesting for use in polymer composites in which the elongation at break often suffers following melt blending or processing. Increasing the incorporation even slightly results in a large decrease in the elongation at break.

Table 1 Polymerization reactions with the polymerization catalyst $Me_2Si(2\text{-}Me\text{-}Ind)ZrCl_2$

Sample	Norbornene (mol/L)	Yield (g)	Activity (kg/mol·h·bar)	I^a (mol%)	T^b (%)	$T_m{}^c$ (°C)	Mw^d (10^{-3} kg/mol)	YM^e (MPa)	e^f (%)
1	0.0	55.6	11,000	–	95.2	143	165	1,025	6
2	0.0075	10.3	2,100	2.4	94.5	136	37	730	12
3	0.015	6.3	1,200	3.4	94.0	126	32	393	3
4	0.030	1.5	300	7.3	93.5	120	27	ND	ND

Polymerization conditions: $Me_2Si(Ind)_2ZrCl_2$, $[Zr] = 3 \times 10^{-6}$, $[Al]:[Zr] = 2{,}000:1$, propylene pressure: 2 bar, reaction time 30 min, reaction temp 55 °C

ND not detected

[a] Incorporation determined by ^{13}C NMR, [b] Tacticity (rrrr), [c] Melting temperature, [d] Molecular weight, [e] Young's modulus, [f] Elongation at break

Copolymerizations with the syndiotactic polymerization catalyst $Ph_2C(Flu)(Cp)ZrCl_2$

The results obtained using $Ph_2C(Flu)(Cp)ZrCl_2$ (Table 2) were consistent with previously reported results when reaction conditions are considered, and showed similar trends as the ($Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$) in the presence of the comonomer with the activity and molecular weight decreasing substantially in the presence of comonomer. This system showed increased activity compared to previously reported studies, however, in this study, a higher [Al]:[Zr] ratio was used, making direct comparisons difficult; however, the effect on activity and molecular weight show similar trends, likely indicating that the differences are due to the different reaction conditions. When norbornene was used as a comonomer in this system, the reduction of activity was much less than that observed in system 1. The addition of 0.5 mL reduced the activity ca. 32 %, which is much less than the ca. 80 % observed at the same loading for system 1. The activity continues to decrease with increasing initial monomer concentration and reaches 1,400 kg/mol·h·bar, when 0.120 mol/L (8 mL) norbornene is used. This is due to the steric demands of the comonomer which slows the insertion of the next monomer. In the case of the syndiotactic materials, it was observed that the catalyst was able to tolerate the presence of the monomers better which is most likely due to its more open structure. While this produces higher activities the comonomer incorporation is lower for system 2 for a given comonomer incorporation. For instance, when 0.0075 mol/L (0.5 mL) norbornene are used an incorporation of just 0.1 mol% is observed, this is significantly <2.4 mol% observed at the same initial comonomer concentration in system 1. Even though system 2 incorporates the comonomer less effectively, it was possible to produce materials with an incorporation of up to 8 mol% when 8 mL of norbornene was used. In this system, it is possible to observe the effect of the norbornene on the tacticity of the system. The presence of norbornene in the polymerization decreases the tacticity due to an increase in back-skips following the

Table 2 Polymerization results using $Ph_2C(Flu)(Cp)ZrCl_2$

Sample	Norbornene (mol/L)	Yield (g)	Activity (kg/mol·h·bar)	I^a (mol%)	T^b (%)	Mw^c (10^{-3} kg/mol)
5	0.0	53.9	18,000	0.0	95.6	322
6	0.0075	37.0	12,000	0.1	94.4	298
7	0.015	28.9	9,500	0.4	94.8	253
8	0.030	11.3	3,700	1.3	94.2	170
9	0.045	6.6	2,200	4.0	93.6	93
10	0.060	5.6	1,900	6.9	92.2	44
11	0.090	6.0	2,000	7.9	92.7	35
12	0.120	4.2	1,400	8.0	86.3	21

Polymerization conditions: $Ph_2C(Flu)(Cp)ZrCl_2$, $[Zr] = 3 \times 10^{-6}$, $[Al]:[Zr] = 2{,}000:1$, propylene pressure 2 bar, reaction time 30 min, reaction temp 55 °C

[a] Incorporation determined by ^{13}C NMR, [b] Tacticity (rrrr), [c] Molecular weight

insertion of norbornene. As the tacticity decreases with increasing monomer concentration, it would seem that the insertion of the norbornene causes the generation of stereoirregularities in the polymer chain. This has been described previously, [17] in that work a lower tacticity was generally observed, although that may have been the result of differing experimental conditions. The molecular weight of the polymers produced decrease with increasing initial norbornene content, however, high molecular weight materials (170,000 g/mol) are still produced when 2 mL norbornene are used, increasing the initial comonomer loading to 0.120 mol/L results in the production of materials with low molecular weights (21,000 g/mol).

The physical properties of the materials generated by system 2 (Table 3) are extremely sensitive to the incorporation of norbornene. At very low concentrations (0.1 mol%), the Young's modulus increases slightly, but the elongation at increases from 5.6 % for the homopolymer to 408 %, which is a tremendous change. Increasing the incorporation slightly to 0.4 % produces a decrease in the Young's modulus of 42 % to 485 MPa while at the same time decreasing the elongation at break to 286 %. Further increases to the incorporation results in deteriorating properties, and at ca. 4 mol% incorporation the samples become fragile when pressed into films making the measurement of the physical properties difficult if not impossible. As such the physical properties of the materials at higher loadings were not measured.

The graphs of the DSC analysis are shown in Fig. 1. The materials produced with the $Ph_2C(Flu)(Cp)ZrCl_2$ catalyst at low comonomer incorporation show the characteristic double melting point of syndiotactic materials which has been previously discussed [17, 20]. This double peak is actually better defined in the polymers produced in samples 6 and 7 than in the homopolymer. This is interesting as it indicates that the growth of one of the crystal phases of the material is being significantly hindered at even low incorporations of comonomer. The melting point is further depressed with increased comonomer incorporation; however, the effect of the comonomer content on the melting point decreases with increasing incorporation. When the comonomer incorporation is more than 4 mol%, the materials are

Table 3 Physical properties of the materials results using $Ph_2C(Flu)(Cp)ZrCl_2$

Sample	Norbornene (mol/L)	T_m[a] (°C)	T_g[b] (°C)	YM[c] (MPa)	e[d] (%)
5	0.0	127/132	−2.02	844	5.6
6	0.0075	127/132	−1.55	900	408
7	0.015	128/132	−1.13	485	286
8	0.030	124	−0.017	250	2.6
9	0.045	108	0.76	ND	ND
10	0.060	102	1.39	ND	ND
11	0.090	98	1.98	ND	ND
12	0.120	96	2.3	ND	ND

ND not detected

[a] Melting temperature, [b] Glass transition temperature, [c] Young modulus, [d] Elongation at break

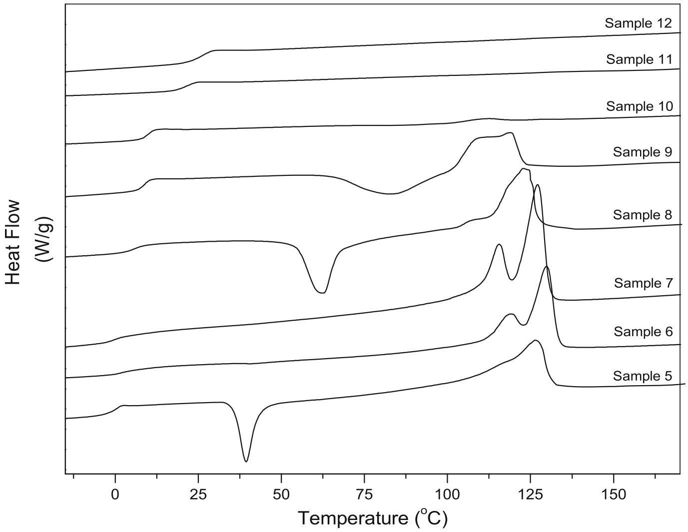


Fig. 1 DSC of copolymers produced using $Ph_2C(Flu)(Cp)ZrCl_2$

nearly amorphous and only show a glass transition in the DSC. The T_g shifts to slightly higher temperatures with increasing commoner content. At higher comonomer contents (8 mol%), the T_g is shifted to significantly higher temperatures (Table 3).

Endgroup analysis of the copolymers was conducted using ^{1}H NMR (Sample 12 is shown as an example in Fig. 2). It was possible to evaluate the termination behavior as a function of initial norbornene concentration using the methodology described by Boggioni et al. [10]. It is possible to separate the three types of terminal groups and identify the insertion which preceded the chain termination. This is possible because vinyl groups arise via from termination followed by a methyl transfer from a 1,2 metal coordinated polymer chain and vinylidene groups from a similar 1,2 coordinated polymer chain. Only vinylene terminal groups arise following a 2,1 monomer insertion. As shown in Table 4, 10–28 % of the terminal units in the materials produced by the syndiotactic catalyst are those following an inverted (2,1) propylene insertion. This percentage decreases as the initial concentration of norbornene increased. Similarly, the materials produced by the isotactic catalyst have 11–29 % of vinylene groups. Chain transfers after an inserted norbornene unit are difficult, so chain termination only occurs following the insertion of a propylene or inverted propylene unit [10] .

Examples of the ^{13}C NMR spectra of the isotactic (a) and syndiotactic (b) polypropylene–norbornene copolymers are shown in Fig. 3. The resonance at 27.1 ppm which is due to block norbornene sequences (where two or more norbornene insertions occur in a row, e.g., PNN, NNP, and NPN where N = norbornene and P = propylene) are absent in the samples except for sample 12, which has a low (<1 %) concentration. The absence of a peak in the range of 29.77–30.06 ppm and a resonance at 37.35 ppm suggests that 1,3 propylene insertion units are not present. The presence of some small resonances at

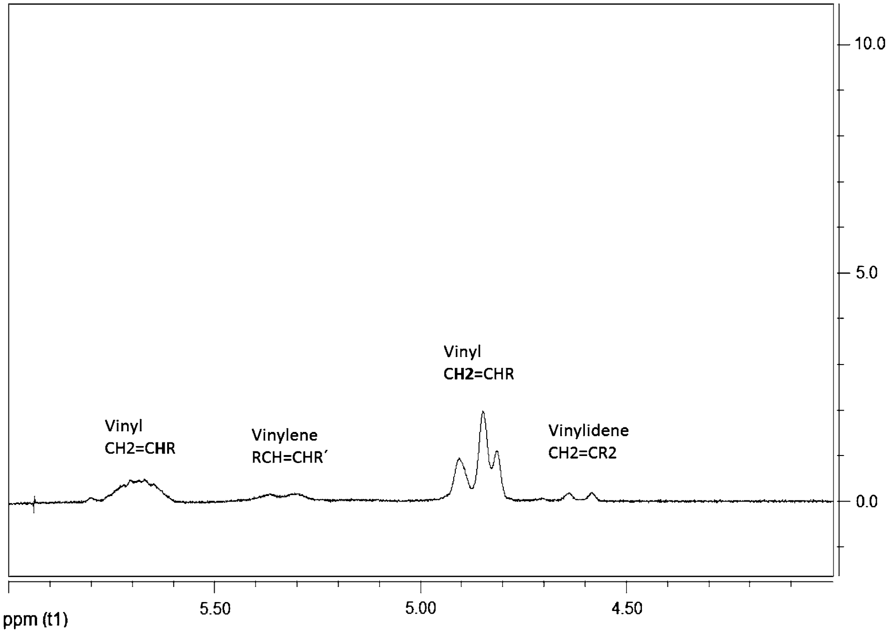


Fig. 2 Expanded ^{1}H NMR of the unsaturated terminal groups of sample 12

Table 4 Percentage of olefin terminal groups in the propylene–norbornene copolymers calculated by ^{1}H NMR

Sample	Terminal groups			Norbornene (mol%)
	Vinyl	Vinylidene	Vinylene	
2	0.69	0.20	0.11	2.4
3	0.52	0.19	0.29	3.4
4	0.47	0.25	0.27	7.3
6	0.42	0.30	0.28	0.06
7	0.64	0.16	0.20	0.4
8	0.60	0.15	0.25	1.3
9	0.67	0.11	0.22	4.0
10	0.79	0.09	0.12	6.9
11	0.79	0.07	0.14	7.9
12	0.84	0.06	0.10	8.0

17.10–18.45 ppm suggests the presence of low concentrations of inverted propylene (2,1 insertions) sequences [12].

Conclusion

The ability of the two catalysts used in this study to incorporate norbornene varied greatly when compared using the same initial comonomer concentration. However,

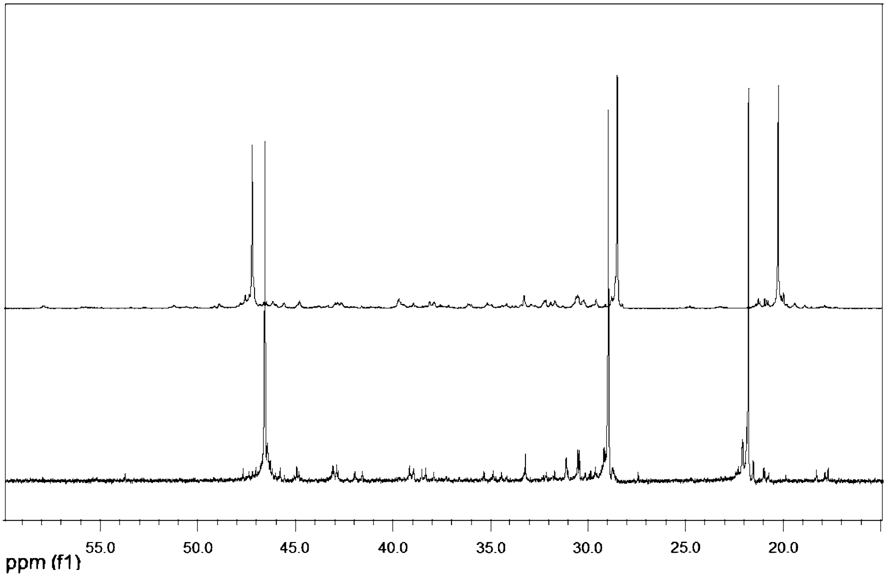


Fig. 3 **a** Sample 4 ($I = 7.3$ mol%) catalyst: $Me_2Si(Ind)_2ZrCl_2$; **b** Sample 12 ($I = 8.0$ mol%) catalyst: $Ph_2C(Flu)(Cp)ZrCl_2$

in the end both catalysts were able to incorporate ca. 8 mol% norbornene. The impact of the norbornene concentration on the physical properties was significant, as the incorporation of a low concentration of norbornene into the polymer produced increases in the elongation at break in both systems. In the case of the $Ph_2C(Flu)(Cp)ZrCl_2$ system, the incorporation of just 0.1 mol% norbornene increased the elongation at break to 408 %, which is a substantial increase, a small further increase in the incorporation resulted in a decrease to 286 and 2.6 % at 0.35 and 1.34 mol%, respectively. This suggests that it may be possible to produce polypropylene-based materials with significantly increased elongation properties if the incorporation can be well controlled and limited to ca. 0.1 mol% norbornene.

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