

Is isoprene capable of being a comonomer under metallocene catalysis to reach side chain-unsaturated isotactic polypropylene?

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Abstract

Isoprene (2-methyl-1,3-butadiene) was attempted as a comonomer in metallocene-catalyzed propylene polymerization to prepare side chain-unsaturated isotactic polypropylenes (*i*-PP). Hydrogen was added into the sluggish copolymerization of propylene and isoprene mediated by a highly isospecific metallocene complex *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂/MAO. Catalyst activity was restored due to breaking by hydrogen of the stable π -allyl zirconocene species caused by 1,4-isoprene insertion. Stunningly, it was found that the generated Zr–H species had been able to take the accompanying vinylidene-terminated polymer chain for insertion as a preemptive mode of re-initiation. With a consecutive action of chain release followed by in situ reinsertion, the hydrogen-induced catalyst reactivation was not accompanied by chain termination. With the smooth occurrence of the copolymerization, the 1,2-insertion of isoprene led to the preparation of *i*-PP bearing pendant vinylidene groups. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Isoprene; Comonomer; Side chain-unsaturated polypropylene

1. Introduction

Isotactic polypropylene (*i*-PP) finds widespread applications because of its excellent material properties coupled with low cost and superior processibility [1–4]. However, its major drawback of lacking functional groups in polymer chain has posed serious problems in applications where adhesion, dyeability, printability or compatibility with other polymers is paramount [5]. For the functionalization of *i*-PP, one classical approach is to use side chain-unsaturated *i*-PP polymers as an intermediate to conduct selective and versatile functional transformations at the unsaturated groups [6]. For such a purpose, *i*-PP containing pendant olefinic groups has long been a material target in coordinative stereospecific propylene polymerization over both traditional heterogeneous Ziegler–Natta and single-sited metallocene catalysts, via copolymerization

with diolefins [7,8]. In this art, it has also been acknowledged that a metallocene catalyst is usually preferred than Ziegler–Natta catalyst because the former usually possesses much better copolymerization capability than the latter and will endow an unsaturated *i*-PP intermediate polymer with controlled incorporation and homogeneous distribution of pendant olefinic groups [9,10].

Most of the diolefin monomers reported to prepare side chain-unsaturated *i*-PP by metallocene catalysts fall in the categories of symmetric α,ω - [11–13] and asymmetric diolefins [7,14–16], for example, 1,5-hexadiene, 1,7-octadiene, 1,11-dodecadiene, 1,4-hexadiene, and 4-methyl-1,4-hexadiene, etc. Conjugated 1,3-butadiene, which is commercially available in large volume, is usually thought to be not eligible, for it may seriously impair both the catalyst activity and copolymer molecular weight. This is because the 1,4-insertion of butadiene into metallocene active sites forms a stable π -allyl species that performs dormant in the subsequent polymer chain propagation. Interestingly, Shiono and co-workers recently unraveled this mystery by adding hydrogen into the

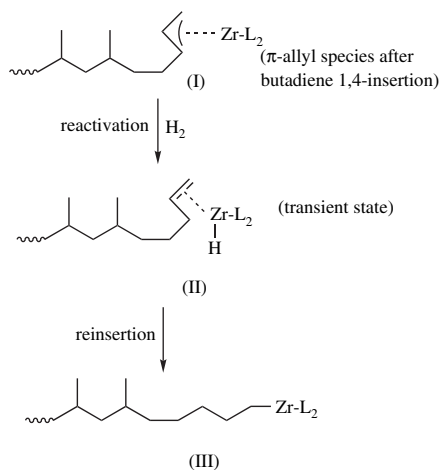
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copolymerization of propylene and 1,3-butadiene mediated by a metallocene catalyst, successfully preparing *i*-PP containing pendant vinyl groups [17]. In fact, the catalyst reactivation effect of hydrogen in Ziegler–Natta and metallocene propylene polymerizations has been well cited from both homopolymerization [18] and copolymerization with styrene (or its derivatives) [19–21]. Reactivation generally takes place by releasing the formed polymer chain from the metal center, generating a new metal–hydride (M–H) species to take monomer (usually the higher reactivity one) for insertion to start a new polymer chain propagation. The aftermath is usually the restoration of catalyst activity at the expense of polymer molecular weight. However, in the case of propylene/butadiene copolymerization, Shiono's success has largely relied on an unusual, unique hydrogen reactivation process that simultaneously restored both the catalyst activity and polymer molecular weight, as illustrated in Scheme 1. The polymer chain end vinyl group formed by 1,4-butadiene insertion followed by hydrogen addition prompted, due to a preferred coordination to the synchronously generated Zr–H species to propylene and butadiene monomers, a preemptive reinsertion of the polymer chain into Zr–H, which not only restored catalyst activity, but also resumed polymer chain propagation.

Intrigued by Shiono's work, we have been wondering if isoprene (2-methyl-1,3-butadiene) [22–25], another large volume conjugated diolefin, is also capable of being a comonomer under metallocene catalysis to reach side chain-unsaturated *i*-PP. Despite the fact that isoprene differs from butadiene by only an extra 2-methyl substituent, the predictable formation of a vinylidene moiety instead of vinyl at polymer chain end in the transient state (II) is of worrisome in that vinylidene, unlike vinyl, has yet to be reported to be able to insert into either a M–C or a M–H species in Ziegler–Natta and metallocene olefin polymerization. Under the circumstances, the reinsertion of the temporarily released end-unsaturated polymer chain in the transient state (II) into Zr–H, a crucial step for resuming polymer chain propagation



Scheme 1. Shiono's chemistry for propylene/butadiene copolymerization assisted by hydrogen.

after hydrogen reactivation, is not assured. This poses a major threat to polymer molecular weight of the copolymerization. On the other hand, an attempt to use isoprene other than butadiene to prepare side chain-unsaturated *i*-PP is also of practical significance, which is not limited to provide a second source of large volume diolefins. As a conjugated diolefin composed of a vinyl moiety and a vinylidene moiety, isoprene is expected to enchain in its copolymerization with propylene through both 1,4- and 1,2-insertion fashions. The 1,2-insertion of isoprene will result in pendant vinylidene group that differs in many aspects from vinyl group. The thus-formed *i*-PP containing pendant vinylidene groups will also become a new polymer material that by any means deserves a pursuit.

2. Experimental part

2.1. Materials and instruments

All O₂- and moisture-sensitive manipulations were carried out inside an argon-filled vacuum atmosphere dry box equipped with a dry train. CP grade toluene was deoxygenated by argon purge before refluxing for 48 h and distilling over sodium. Methylaluminoxane (MAO) (10 wt% in toluene) was purchased from Albermarle and used as received. The catalyst, *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂, was synthesized according to a published procedure [26]. Isoprene and polymerization-grade propylene were supplied by Yanshan Petrochemical Co. of China. Isoprene was dried over CaH₂ and distilled before use. High-purity hydrogen gas (>99.999%) was used without further purification.

All high-temperature ¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 instrument in *o*-dichlorobenzene-*d*₄ at 110 °C. The melting temperature of the polymers was measured by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC-7 instrument controller with a heating rate of 10 °C/min. The molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) using a Waters Alliance GPC 2000 instrument equipped with a refractive index (RI) detector and a set of u-Styragel HT columns of 10⁶, 10⁵, 10⁴, and 10³ pore size in series. The measurement was performed at 150 °C with 1,2,4-trichlorobenzene as the eluent with a flow rate of 1.0 mL/min. Narrow molecular weight PS samples were used as standards for calibration.

2.2. Copolymerization of propylene and isoprene

A 250 ml three-necked flask equipped with a magnetic stirrer was charged with 50 mL of toluene and 5.7 mL of MAO (10 wt% in toluene), when it was saturated with 0.1 MPa of propylene at 0 °C. A certain amount (demonstrated in Table 1) of isoprene was injected into the reactor and 4 μmol of *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ catalyst in toluene solution was then added to the rapidly stirring solution to initiate the polymerization reaction. In the case of using hydrogen in the copolymerization, 2.23 mmol of hydrogen was charged to the flask through a measuring tube before polymerization.

Table 1

Conditions^a and results of propylene/isoprene copolymerization catalyzed by *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂/MAO in the absence of hydrogen

Run no.	Isoprene (mmol)	H ₂ (mmol)	Yield (g)	Activity (kg/mol Zr h)	Isoprene units in copolymer ^b		<i>M_n</i> (×10 ³)	<i>M_w</i> (×10 ³)	<i>M_w</i> / <i>M_n</i>	<i>T_m</i> (°C)	Δ <i>H</i> (J/g)
					<i>f</i> _{1,4} (mol%)	<i>f</i> _{1,2} (mol%)					
Control 1	0	0	0.78	194.0	—	—	117.1	770.9	6.58	159.3	73.5
1	0.6	0	0.22	55.0	0.005	0.002	88.0	410.0	4.66	157.4	73.0
2	2.0	0	0.10	25.2	0.031	0.031	52.1	182.2	3.50	154.8	49.9
3	6.0	0	~0	~0	—	—	—	—	—	—	—
4	10.0	0	0	0	—	—	—	—	—	—	—

^a Other conditions: 0.1 MPa propylene, 50 mL toluene, Zr = 4.0 × 10⁻⁶ mol, [MAO]/[Zr] = 2000, polymerization temperature = 0 °C, polymerization time = 60 min.

^b *f*_{1,4}, 1,4-inserted isoprene unit, *f*_{1,2}, 1,2-inserted isoprene unit.

After 60 min reaction at 0 °C, acidic ethanol was added to terminate the polymerization. The precipitated polymer was isolated and washed with ethanol repeatedly before being dried under vacuum.

3. Results and discussion

3.1. Copolymerization of propylene and isoprene in the absence of hydrogen

The copolymerization of propylene and isoprene was first studied in the absence of hydrogen. The highly active, highly isospecific metallocene complex *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂/MAO was employed as a catalyst. Polymerization reactions were carried out in toluene solution under an atmospheric pressure of propylene. Polymerization temperature was set at 0 °C in order to prevent isoprene evaporation during the polymerization. Table 1 summarizes the results.

In general, in the absence of hydrogen, the copolymerization of propylene and isoprene can be conceived ineffective. Catalyst activity decreased significantly upon addition of a very small amount of isoprene in the copolymerization reaction (0.6 mmol of isoprene addition caused a decrease of catalyst activity from 194 kg PP/(mol Zr h) for propylene homopolymerization to 55 kg PP/(mol Zr h), an almost 2-fold reduction). Moreover, the catalyst activity continued decreasing with the increase of isoprene feeding. Under the adopted reaction conditions, the catalyst completely lost its function when the added amount of isoprene reached 6.0 mmol. Due to very limited comonomer feedings, the incorporations of isoprene in the obtained copolymers were generally poor.

Fig. 1 compares ¹H NMR spectra of two propylene/isoprene copolymers (runs 1 and 2 in Table 1) with that of a neat PP (control 1 in Table 1). Despite the limited isoprene incorporations, the copolymers are easily recognized with both 1,4- and 1,2-inserted isoprene units. As shown in Fig. 1(b) and (c), in addition to the major chemical shifts at 0.95–1.65 ppm corresponding to CH₃, CH₂ and CH groups in propylene repeating unit, two minor chemical shifts are observed around 4.65 and 5.25 ppm, which are unambiguously assignable to protons on the two types of unsaturated groups (side chain vinylidene and main chain vinylene groups, shown in Chart 1) formed by 1,2- and 1,4-isoprene insertions. By comparing the peak integrations at 4.65 and 5.25 ppm with that at

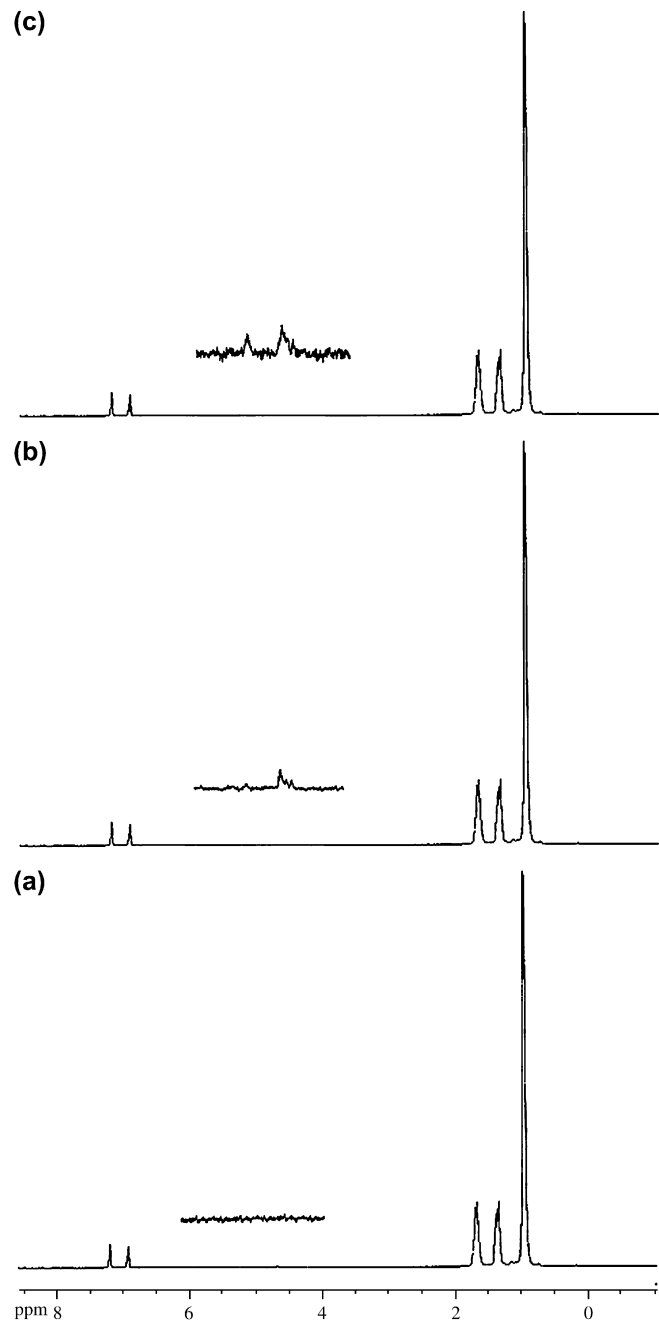


Fig. 1. ¹H NMR spectra of (a) a neat polypropylene (control 1 in Table 1) and two propylene/isoprene copolymers prepared with (b) 0.6 (run 1 in Table 1) and (c) 2.0 mmol (run 2 in Table 1) of isoprene feedings in the absence of hydrogen (solvent: *o*-dichlorobenzene-*d*₄; temperature: 110 °C).

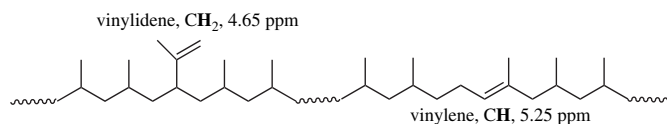


Chart 1. Hydrogen-absent propylene/isoprene copolymer structure and proton chemical shifts of unsaturated groups caused by 1,2- and 1,4-isoprene insertions.

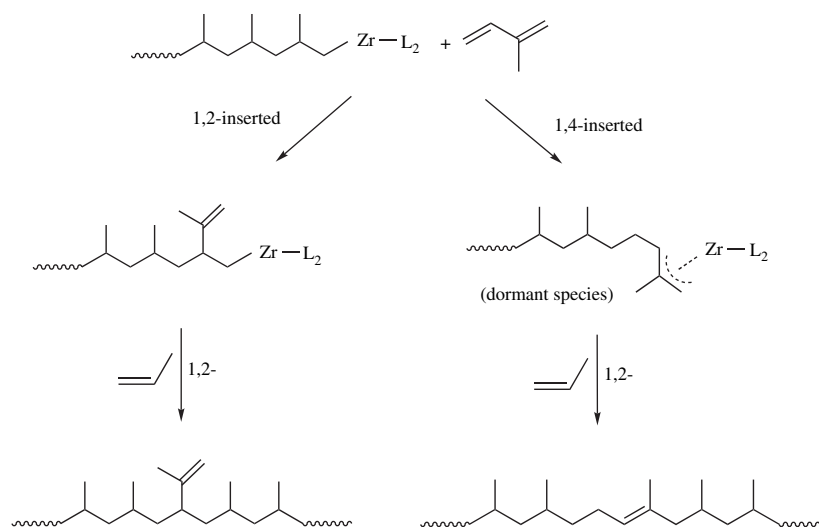
0.95–1.65 ppm, together with a consideration of number of protons each peak represents, the relative amounts of isoprene enchainments through 1,4- and 1,2- fashion were calculated. The results are included in Table 1.

Scheme 2 illustrates the reaction pathways for the copolymerization. The 1,2-insertion seems a natural choice for isoprene incorporation, which exerts no significantly negative effect on the continuous polymer chain propagation. However, the 1,4-insertion of isoprene generates a stable π -allyl species at the propagating Zr–C site. This species performs dormant in further monomer insertion. In consequence, polymer chain propagation slows down (if not completely halt), so does the overall polymerization rate. In fact, as shown in Table 1, besides catalyst activity decreasing, both the number- and weight-average molecular weights of the obtained copolymers

(runs 1 and 2 in Table 1) are proportionally reduced with their isoprene feedings as compared with those of the neat PP homopolymer (control 1 in Table 1).

3.2. Copolymerization of propylene and isoprene in the presence of hydrogen

Hydrogen was introduced into the copolymerization, to break the stable π -allyl species formed by 1,4-isoprene insertion and regenerate active species to continue the polymerization cycle. However, unlike propylene/butadiene copolymerization reported by Shiono et al. where addition of hydrogen to the stable π -allyl species after 1,4-butadiene insertion left a vinyl-terminated polymer chain [20], the active site regeneration by hydrogen in propylene/isoprene copolymerization would rather generate, along with the Zr–H species, a vinylidene-terminated polymer chain. Since, to our best knowledge, there has been no example describing the insertion of a vinylidene group into either a Zr–C or Zr–H species because of the bulky 2,2-substitutions of vinylidene, the reinsertion of the vinylidene-terminated polymer chain into Zr–H, a key step for polymer chain propagation resumption to ensure high polymer molecular weight, would be in



Scheme 2. Copolymerization of propylene and isoprene in the absence of hydrogen.

Table 2

Conditions^a and results of propylene/isoprene copolymerization catalyzed by *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂/MAO in the presence of hydrogen

Run no.	Isoprene (mmol)	H ₂ (mmol)	Yield (g)	Activity (kg/mol Zr h)	Isoprene units in copolymer ^b		M _n (×10 ³)	M _w (×10 ³)	M _w /M _n	T _m (°C)	ΔH (J/g)
					f _{1,4} (mol%)	f _{1,2} (mol%)					
1	0.6	2.23	0.86	215.0	0	~0	102.3	293.7	2.87	159.1	81.8
2	2.0	2.23	0.76	190.0	n.d. ^c	0.018	103.0	224.0	2.17	156.2	82.0
3	6.0	2.23	0.66	166.0	n.d.	0.087	99.4	282.9	2.85	152.2	79.7
4	10.0	2.23	0.38	94.7	n.d.	0.15	70.1	190.3	2.72	145.9	74.8
5	40.0	2.23	0.19	46.7	4.23	0.57	52.7	204.8	3.89	127.6	46.5

^a Other conditions: 0.1 MPa propylene, 50 mL toluene, Zr = 4.0 × 10⁻⁶ mol, [MAO]/[Zr] = 2000, polymerization temperature = 0 °C, polymerization time = 60 min.

^b f_{1,4}, 1,4-inserted isoprene unit, f_{1,2}, 1,2-inserted isoprene unit.

^c Not determined.

doubt. It would be very likely that hydrogen addition at the stable π -allyl species after 1,4-isoprene insertion leads to real chain release and termination.

The hydrogen-present propylene/isoprene copolymerization was carried out under similar reaction conditions as those adopted in the case of hydrogen-absence. Details of the copolymerization are summarized in Table 2. In general, in terms of reaction efficiency, hydrogen effectively restored catalyst activity and rendered successful polymerization reaction. As displayed in Table 2, with the presence of 2.23 mmol of hydrogen in the copolymerization, catalyst activities at isoprene feedings being 0.6 and 2.0 mmol were found to be 215.0 and 190.0 kg PP/(mol Zr h), respectively, which were close to that of propylene homopolymerization (194.0 kg PP/(mol Zr h)) and far more increased as compared with those conducted in the absence of hydrogen (55.0 and 25.2 kg PP/(mol Zr h), respectively). This had made a further increase of isoprene feeding in the copolymerization possible in order to obtain higher isoprene incorporations. As also shown in Table 2, isoprene feeding in the copolymerization was further increased through 6.0 and 10.0 mmol to as high as 40.0 mmol, when the catalyst activity maintained a fairly high value.

In Fig. 2 are shown ^1H NMR spectra of three propylene/isoprene copolymers obtained in the presence of hydrogen (runs 2, 4 and 5 in Table 2). It is very interesting to find that only the side chain vinylidene protons show their chemical shift at 4.65 ppm, the intensity of which increases with isoprene feeding in the copolymerization; nevertheless, the chemical shift at 5.25 ppm, which represents main chain vinylene proton in the propylene/isoprene copolymers obtained in the absence of hydrogen, completely disappears. At a first glance, these results may give a false impression that 1,4-insertion of isoprene was suppressed due to a hydrogen presence. However, after ^{13}C NMR spectra (Fig. 3) of one of the copolymer samples (run 5 in Table 2) were examined, it became evident that 1,4-isoprene insertion did take place, only that it was followed by an immediate hydrogen addition, causing a consecutive action of chain release followed by in situ reinsertion to completely saturate the 1,4-inserted isoprene units.

Fig. 3 shows these ^{13}C NMR spectra. The resonances at 111.0 and 149.0 ppm are assigned to the two side chain vinylidene carbon atoms due to 1,2-isoprene insertion. In the aliphatic region, in addition to the three major chemical shifts ($\delta = 21.6, 28.5,$ and 46.2 ppm) corresponding to CH_3 (mmmm), CH , and CH_2 groups in PP backbone, some minor ones are observed at 24.4, 30.6, 37.5, and 38.7 ppm, which are ascribable to the incorporated hydrogenated 1,4-isoprene units. Chart 2 illustrates the polymer structure along with the carbon chemical shifts of the incorporated isoprene units through both 1,2- and 1,4-insertions. It is very interesting to note that, although located in seemingly similar chemical environments, the two methylene carbons at 38.7 and 37.5 ppm show slightly different chemical shifts. The steric difference between the adjacent structures of the two methylenes (one is in a stereospecific *i*-PP configuration and the other in a randomly incorporated isoprene unit) must have contributed to this faint yet discernible differentia.

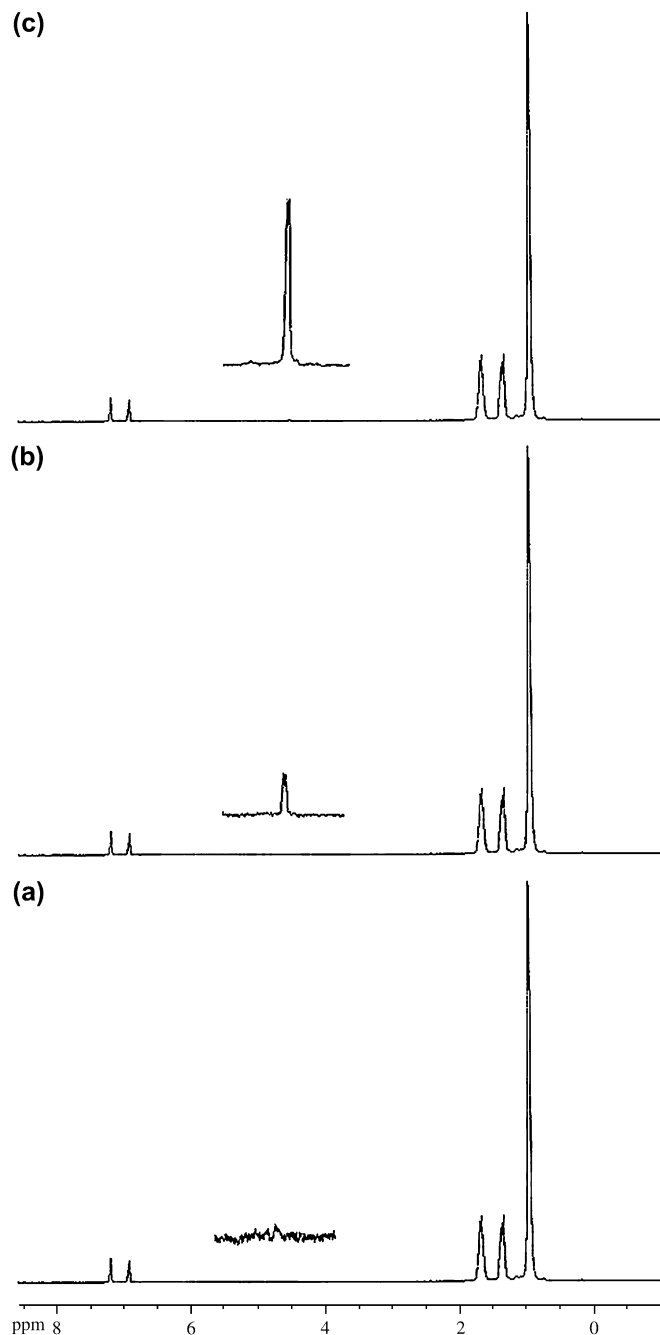


Fig. 2. ^1H NMR spectra of three propylene/isoprene copolymers containing (a) 0.018, (b) 0.15, and (c) 0.57 mol% of pendant vinylidene groups (1,2-inserted isoprene units) obtained in the presence of hydrogen (runs 2, 4, and 5 in Table 2) (solvent: *o*-dichlorobenzene- d_4 ; temperature: 110°C).

Scheme 3 illustrates the reaction pathway concerning 1,4-isoprene insertion in the presence of hydrogen. The formation of stable π -allyl species (II) due to isoprene 1,4-insertion into the propagating polymeric active site (I) endangers the copolymerization, causing a significant reduction of catalyst activity as well as polymer molecular weight. These have been observed in reality in the hydrogen-free experiments of propylene/isoprene copolymerization (shown in Table 1). However, in the presence of hydrogen, hydrogen is able to break the stable π -allyl species (II) by separating the polymer chain

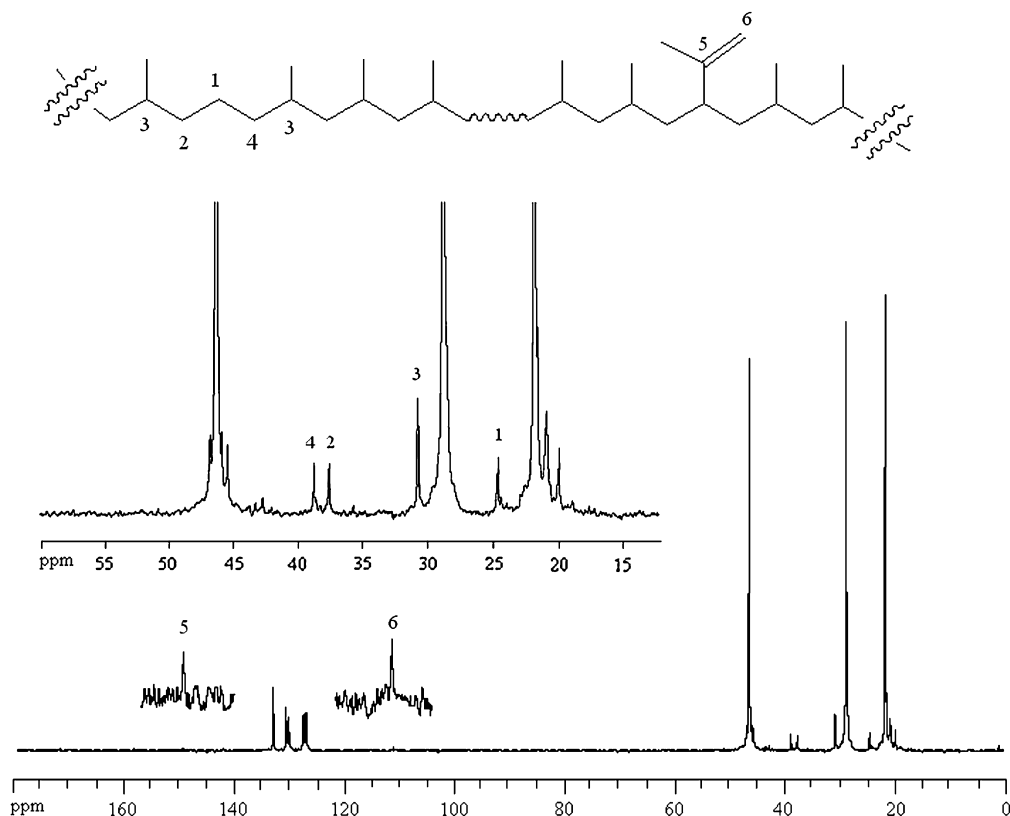


Fig. 3. ^{13}C NMR spectra of a propylene/isoprene copolymer containing 0.57 mol% of pendant vinylidene groups (1,2-inserted isoprene units) prepared in the presence of hydrogen (run 5 in Table 2) (solvent: *o*-dichlorobenzene- d_4 ; temperature: 110 °C).

from the metal center to form a Zr–H species and a vinylidene-terminated polymer chain. As the terminal vinylidene group remains in the coordination sphere of the metal, a spontaneous reinsertion into Zr–H occurs, irrespective of the substantial steric hindrance caused by the 2,2-substitutions of the unsaturation group as well as the presence in the polymerization reaction of propylene and isoprene monomers that pose competition in complexation and insertion. These series of actions caused by hydrogen effectively counteract the nearly fatal effect of 1,4-isoprene insertion on the copolymerization. Polymer chain then resumes its propagation and the overall polymerization is recovered. Apparently, the key step in this process is the unusual insertion of the terminal vinylidene group into Zr–H, an active species that has been demonstrated to possess an extraordinary capability in sucking sterically hindered bulky monomers as compared with Zr–C [27].

Polymer molecular weight and molecular weight distribution (M_w/M_n) were measured by high-temperature GPC. The results are included in Tables 1 and 2. Polymers obtained in the absence of hydrogen were found to possess broad molecular weight

distributions (between 3 and 7), one sample (run 1 in Table 1) even showing an apparent shoulder for low molecular weight portion. This should be attributed to the inhomogeneity of the copolymerization caused by 1,4-isoprene insertion that inflicts serious retardation on partial polymer chain propagation. Fig. 4 compares two sets of GPC curves between polymers synthesized in the presence and absence of hydrogen. It is very interesting to note that, under similar reaction conditions, polymers obtained in the presence of hydrogen (runs 1 and 2 in Table 2) show even higher values of number average molecular weight than their hydrogen-free counterparts (runs 1 and 2 in Table 1). Considering the unavoidable chain transfer to hydrogen during PP polymer chain propagation, these results further support the validity of the above proposed mechanism for the effective resumption of polymer chain propagation by hydrogen after 1,4-isoprene insertion.

3.3. Synthesis and properties of polypropylene containing pendant vinylidene groups

With the successful copolymerization of propylene and isoprene assisted by hydrogen, the 1,2-isoprene insertion naturally led to the allocation of pendant vinylidene groups at polymer side chains. As shown in Table 2, with the increase of isoprene concentration in the copolymerization feed, the 1,2-inserted isoprene incorporations increased gradually. With a 40.0 mmol of isoprene feeding (run 5 in Table 2),

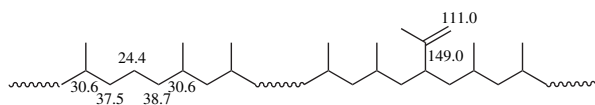
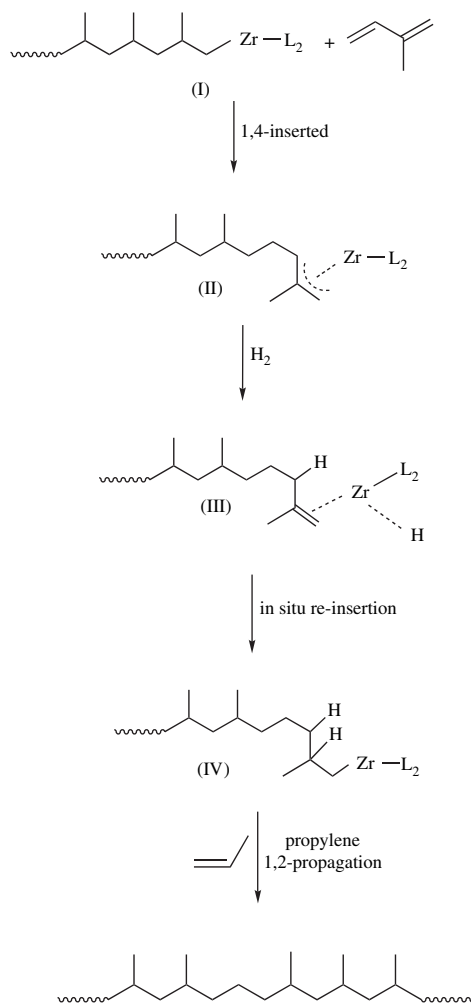


Chart 2. Hydrogen-present propylene/isoprene copolymer structure and carbon chemical shifts (ppm) of incorporated isoprene units through 1,2- and 1,4-insertions.



Scheme 3. Copolymerization of propylene and isoprene in the presence of hydrogen.

a 0.57 mol% of pendant vinylidene content was obtained in the copolymer. Considering the number average molecular weight of the copolymer to be 52,700, the average number of pendant vinylidene groups was roughly estimated to be seven per polymer chain, which would be sufficient for further functional modifications to access polarity-enhanced functional polypropylenes. It is obvious that the pendant vinylidene groups cannot represent the whole incorporations of isoprene units in the copolymer. A substantial amount of isoprene units was incorporated via 1,4-insertion and were saturated and consumed in the polymer main chain.

The PP copolymers containing pendant vinylidene groups exhibit sufficiently high molecular weights, which are largely independent of their vinylidene contents. This again confirms the effectiveness of hydrogen in the resumption of polymer chain propagation endangered by 1,4-isoprene insertion. The molecular weight distributions fall in a narrow range of 2.0–4.0, which reflect a single-sited polymerization and herald also narrow composition distributions of the copolymers.

Fig. 5 compares DSC curves of four vinylidene-bearing PP copolymers (runs 2–5 in Table 2) with that of a neat PP (control 1 in Table 1). The collected data of melting points and thermal

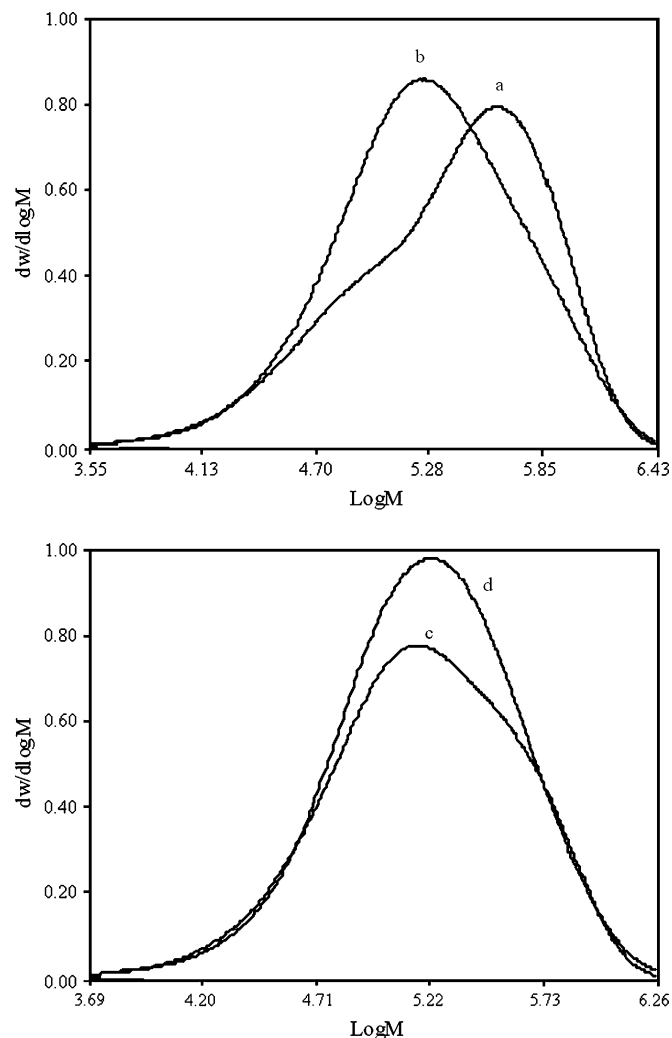


Fig. 4. GPC profile comparisons between propylene/isoprene copolymers prepared in the absence and presence of hydrogen at two isoprene feedings. (a) [Isoprene] = 0.6 mmol, in the absence of hydrogen (run 1 in Table 1), (b) [isoprene] = 0.6 mmol, in the presence of hydrogen (run 1 in Table 2), (c) [isoprene] = 2.0 mmol, in the absence of hydrogen (run 2 in Table 1), and (d) [isoprene] = 2.0 mmol, in the presence of hydrogen (run 2 in Table 2).

enthalpies during melting are included in Tables 2 and 1. Both the copolymers' melting points and thermal enthalpies show reciprocal relations with their vinylidene contents (as well as their 1,4-inserted isoprene units). With a 0.57 mol% of vinylidene implantation (which is accompanied by 4.23 mol% of 1,4-inserted isoprene units) (run 5 in Table 2), this copolymer shows a remarkable decrease in melting point (down to 127.6 °C) as well as thermal enthalpy (down to 46.5 J/g).

4. Conclusions

In summary, we have successfully shown that isoprene was applicable as a diolefin comonomer in metallocene-catalyzed propylene polymerization to reach side chain-unsaturated *i*-PP. Catalyst deactivation due to 1,4-isoprene insertion was effectively reimbursed by introducing hydrogen into the copolymerization. The formed Zr–H and vinylidene-terminated

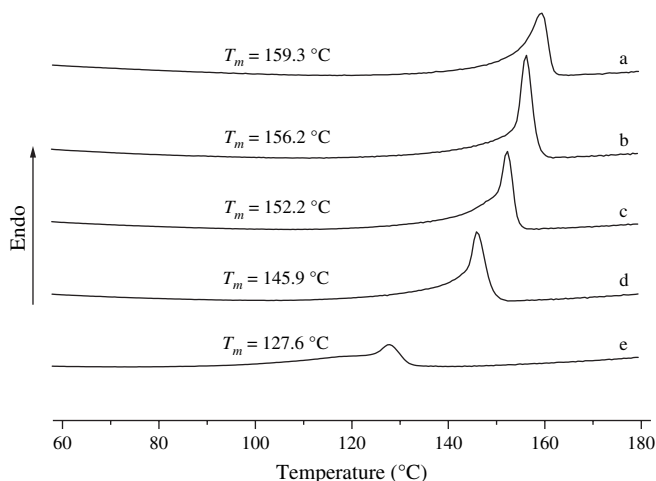


Fig. 5. DSC curves of (a) a neat polypropylene (control 1 in Table 1) and four propylene/isoprene copolymers containing 0.018, 0.087, 0.15, and 0.57 mol% of pendant vinylidene groups (1,2-inserted isoprene units) (runs 2–5 in Table 2).

polymer chain were found to be able to together perform a spontaneous in situ reinsertion as a preemptive mode for Zr–H re-initiation. With a consecutive action of chain release followed by in situ reinsertion, the hydrogen-induced catalyst reactivation was not accompanied by chain termination. With the smooth occurrence of the copolymerization, the enchainment of isoprene via 1,2-insertion fashion led to the formation of *i*-PP bearing pendant vinylidene groups.

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