Regioselective Copolymerization of 5-Vinyl-2-norbornene with Ethylene Using Zirconocene–Methylaluminoxane Catalysts: A Facile Route to Functional Polyolefins[1]

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ABSTRACT: Copolymerization of ethylene with 5-vinyl-2-norbornene (VNB) using the dicyclopentadienylzirconium dichloride/methylaluminoxane (zirconocene/MAO) catalyst system has been shown to occur with regioselective insertion of the endocyclic double bond of VNB into the copolymer chain, leaving the exocyclic vinyl double bond as a pendant unsaturation. The pendant vinyl group in the copolymer can be readily converted to the hydroxy/epoxy group with complete conversion under mild reaction conditions, giving rise to the corresponding functionalized copolymers. The copolymers (parent and functionalized) have been characterized using IR, NMR, TGA, DSC, and intrinsic viscosity measurements.

Introduction

The introduction of functional groups in polyolefins has been a much sought after objective in research in recent years.[2,3] This is primarily because polar functionality in polyolefins substantially alters the physical and chemical properties of the polymers such as permeability, dyeability, and adhesion. Furthermore, the functional group offers sites for initiating graft copolymerization, which leads to useful applications such as compatibilization in blends containing polyolefins.

A preferred approach to the synthesis of functional polymers involves the use of precursor monomers possessing functionalities which do not interfere with copolymerization yet can be readily converted to functional polymers by postpolymerization chemical reactions.

Recently, Chung and co-workers have explored borane-containing functional monomers in olefin copolymerization and subsequent conversion of the borane group to polar functionalities.[4] A new approach to end-functionalized polypropylenes has been reported by Mulhaupt et al.[5] and Soga et al.[6] These authors utilized the β-hydride elimination reaction in the polymerization with stereospecific soluble metallocene/methylaluminoxane catalysts to prepare low molecular weight polypropylenes with chain-end unsaturation, which was subsequently converted to a variety of functional groups using standard chemical transformations.

A number of methods are extant in the literature which enable the introduction of pendant unsaturation in a polyolefin. In these methods the olefin is copolymerized with dienes such as α,ω-dienes,[7,8] 4-vinyl-1-cyclohexene,[9] etc. Copolymerization of ethylene with 1,5-hexadiene[8] using a soluble catalyst system, namely, tris(acetylacetonato)vanadium and $AlEt_2Cl$, led to amorphous copolymers in which the diene was copolymerized mainly (70–80%) with 1,2-enchainment. Copolymerization of ethylene with 4-vinyl-1-cyclohexene has been reported by Mulhaupt and co-workers using a Mg–Ti catalyst.[9] However, the level of diene incorporation was very low, ca. 1 mol %. More recently, Lohse et al. have studied the terpolymerization of ethylene and propylene with 5-vinyl-2-norbornene using the $VOCl_3$/ethylaluminum sesquichloride catalyst.[10] It was confirmed by IR that enchainment of the diene in the terpolymer occurred through the endocyclic vinylene bond. The level of incorporation of the termonomer was, however, limited to <1 mol %.

The major drawbacks of the existing approaches are (a) low levels of monomer incorporation and (b) lack of demonstrated evidence of regioselectivity of insertion, especially at higher levels of incorporation. Furthermore, with titanium-based catalysts, enchainment is believed to occur through the exocyclic vinyl bond, leaving the endocyclic vinylene double bond free.[11] Also, it is reported that, with certain heterogeneous Ziegler–Natta catalysts, ring opening metathesis type reactions compete with polymerization.[12]

However, when bicyclic olefins are homo- or copolymerized with soluble metallocene–methylaluminoxane-based catalyst systems, enchainment occurs exclusively through the more strained endocyclic double bond. This is evidenced by the efficient copolymerization of ethylene with bicyclic olefins such as norbornene.[13] Consequently, we reasoned that the copolymerization of 5-vinyl-2-norbornene with ethylene using a soluble catalyst should lead to a copolymer in which enchainment of the bicyclic monomer will occur selectively through the endocyclic double bond, leaving a reactive pendant unsaturation free for further functionalization. In this paper we report our results on the synthesis, characterization, and functionalization of poly(ethylene-*co*-5-vinyl-2-norbornene) using a zirconocene/methylaluminoxane catalyst.[14]

Experimental Section

All manipulations involving air-sensitive compounds were carried out using standard benchtop inert-atmosphere techniques under a stream of ultrahigh-purity nitrogen.

Materials. Toluene (Loba-Chemie AR grade) was purified by refluxing over sodium wire and subsequent distillation under nitrogen. Polymerization-grade ethylene was obtained from the C_2–C_3 gas cracker unit of Indian Petrochemical Corp. Ltd., Nagothane, Maharashtra (O_2 = 3 ppm, H_2O = 4 ppm). Methylaluminoxane (MAO) ([Me]/[Al] = 1.54, free TMA = 35%, 15.5% Al solution in toluene, Schering AG, Germany) was used as a 4.5% solution after dilution. 5-Vinyl-2-norbornene (VNB) (Aldrich, 70:30 endo:exo) was stirred over CaH_2 for 24 h and distilled under N_2 prior to use. Cp_2ZrCl_2, *m*-chloroperbenzoic acid, 9-BBN (0.5 M solution in THF) (all from Aldrich), and Irganox 1010 (Ciba-Geigy) were used as received.

Copolymerization of Ethylene with 5-Vinyl-2-norbornene (1). Ethylene was copolymerized with VNB at 1 atm and 35 °C in a jacketed reactor connected to a 1-L gas buret. Toluene (25 mL) was introduced into the reactor and was saturated with ethylene. VNB (1.17 g, 9.8 mmol) was added to the reactor

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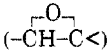
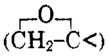
Table 1. Copolymerization of Ethylene with 5-Vinyl-2-norbornene[a]

no.	[ethylene] (M)	[VNB] (M)	10^2[Al] (M)	10^5[Zr] (M)	[Al]/[Zr]	time (min)	yield (g)	conv (%)	activity (kg of copolym/g of Zr)	VNB in feed (mol %)	VNB in copolym[b] (mol %)	$[\eta]$[c] (dL/g)
1	0.11	—	7.5	5.0	1500	20	0.53	100	14.0			2.38
2	0.11	0.28	3.7	2.5	1500	120	0.56	48	4.9	71.7	8	0.41
3	0.11	0.28	3.7	5.0	750	65	0.42	37	3.4	71.7	6.5	0.37
4	0.11	0.28	7.5	5.0	1500	45	0.61	49	7.1	71.7	6	0.50
5	0.11	0.22	7.5	5.0	1500	45	0.79	70	9.3	66.0	nd	0.75
6	0.11	0.33	7.5	5.0	1500	45	0.35	29	4.1	75.0	11	0.37
7	0.11	0.39	7.5	5.0	1500	45	0.39	28	4.6	78.0	10	0.32
8	0.11	0.44	7.5	5.0	1500	45	0.30	20	3.5	80.0	14	0.29

[a] Polymerization conditions: temperature = 35 °C; toluene = 25 mL; ethylene pressure = 1 atm. [b] Calculated from ^{1}H NMR. [c] In 1,2,4-trichlorobenzene at 135 °C.

followed by a toluene solution of MAO (1.875 mmol). The copolymerization was initiated by the addition of a toluene solution of Cp_2ZrCl_2 (0.00125 mmol). Consumption of ethylene was measured by a rise in the level of the gas buret as a function of time. The polymerization was terminated after 45 min by the addition of a 2% solution of HCl in methanol. The copolymer (2) (yield 0.39 g) was washed with methanol containing 0.1% Irganox 1010, filtered, and dried under vacuum at 40 °C for 8 h. IR (film, cm^{-1}): 2950–2850 (C–H stretch), 1638 (C=C stretch), 1470 (C–H def), 990, 910 (CH_2=CH def), 725 (CH_2 rock). ^{1}H NMR (C_6D_6, at 40 °C, ppm): 5.4–6 (=CH), 4.8–5.1 (=CH_2), 2.6–0.95 (backbone and aliphatic H). ^{13}C NMR ($CDCl_3$, at 50 °C, ppm): 144.37 (=CH, exo), 141.70 (=CH, endo), 113.78 (=CH_2, endo), 111.30 (=CH_2, exo), 47.32–34.28 (CH and CH_2 of the bicyclic unit), 30.00 (backbone CH_2).

A larger scale synthesis of the copolymer was carried out in a 1-L SOTELEM reactor at 35 °C and at a constant ethylene pressure of 1.5 atm. Toluene (300 mL), ethylene, VNB (12.62 g, 0.105 mol), and MAO (22.5 mmol) were charged to the reactor. Copolymerization was initiated by the addition of zirconocene solution (0.015 mmol). The reaction was terminated after 25 min. Yield = 7.6 g of copolymer (2).

Functionalization of Poly(ethylene-*co*-5-vinyl-2-norbornene) (EVNB (2)). (a) Epoxidation. A 100-mL, two-necked, round-bottom flask equipped with a Teflon-coated magnetic stirring bar, nitrogen inlet, and septum was cooled under a flow of nitrogen. About 100 mg of EVNB (2) (0.374 mmol of unsaturation) was added to the flask followed by 40 mL of dry toluene, and the mixture was heated at 55 °C till complete dissolution of the copolymer. About 100 mg of *m*-chloroperbenzoic acid (0.575 mmol) dissolved in 10 mL of toluene was added, and the reaction mixture was stirred at 55 °C for 3 h. Then the reaction mixture was poured into methanol, filtered, and dried under vacuum. Yield of 3 = 100 mg. IR (film, cm^{-1}): 2950–2850 (C–H stretch), 1470 (C–H def), 1250 (C–O stretch), 876 (epoxy ring vib), 725 (CH_2 rock). ^{1}H NMR ($CDCl_3$, ppm) 3–2.85  $(-\overbrace{CH-C}^{O}<)$, 2.7–2.85  $(\overbrace{CH_2-C}^{O}<)$, 2.5–0.95 (backbone and aliphatic H).

(b) Hydroboration–Oxidation. A 250-mL, three-necked, round-bottom flask equipped with a reflux condenser, nitrogen inlet, Teflon-coated magnetic stirring bar, and septum was cooled under a flow of nitrogen. About 200 mg of EVNB copolymer (2) (0.748 mmol of unsaturation) was added followed by 100 mL of dry benzene, and the mixture was stirred at 55 °C till complete dissolution of the copolymer. A 2.2-mL aliquot of a 0.5 M THF solution of 9-BBN (1.1 mmol) was added, and the reaction mixture was stirred at 55 °C for 3 h. Oxidation was carried out by addition of 0.2 mL of a 6 N NaOH solution (1.12 mmol) followed by dropwise addition of 0.4 mL of 30% H_2O_2 (3.2 mmol). The mixture was stirred at room temperature for 2 h to ensure complete reaction. The product was poured into methanol, washed to remove boric acid, filtered, and dried. Yield of 4 = 160 mg. IR (film, cm^{-1}): 3350 (O–H stretch), 2950–2850 (C–H stretch), 1470 (C–H def), 1058 (C–O stretch), 725 (CH_2 rock). ^{1}H NMR ($CDCl_3$, ppm): 3.65 (CH_2–O), 2.0–0.95 (backbone and aliphatic H).

Analysis. ^{1}H NMR spectra of the samples as 2 wt % solutions were recorded using a Bruker AC-200 spectrometer at room temperature or 40 °C in $CDCl_3$ or C_6D_6. The ^{13}C NMR spectrum of a 10 wt % solution was recorded using a Bruker MSL 300 spectrometer at 50 °C in $CDCl_3$. IR spectra of films cast from toluene solution were recorded using a Perkin-Elmer PE16 FTIR spectrometer. Thermogravimetric analysis was carried out using a Netzch thermal analysis apparatus (Model STA 409), and differential scanning calorimetric analysis was carried out on a Perkin-Elmer DSC-7. Intrinsic viscosity measurements were done using an Ubbelohde viscometer in 1,2,4-trichlorobenzene at 135 °C.

Results and Discussion

Synthesis and Characterization of Poly(ethylene-*co*-5-vinyl-2-norbornene) (EVNB (2)). Ethylene undergoes facile copolymerization with 5-vinyl-2-norbornene (VNB, 1) in the presence of the zirconocene/MAO catalyst system. By adjusting the feed ratios, copolymers containing as high as 15 mol % VNB could be synthesized (Table 1). Copolymers with high VNB content were completely soluble in toluene at 50 °C, indicating that they were gel-free. As expected, copolymers containing <5 mol % VNB were soluble only at 135 °C in 1,2,4-trichlorobenzene. Catalyst activity in the copolymerization as well as copolymer intrinsic viscosity decreased with increasing comonomer content in the feed. A brief study of the reaction parameters established that the best results were obtained at an [Al]/[Zr] ratio of 1500. Reactivity ratios were determined using a Kelen–Tüdös plot and were found to be $r_{1(\text{ethylene})} = 18.6$, $r_{2(\text{VNB})} = 0.3$, and $r_1r_2 = 5.5$. The selectivity of enchainment of the VNB comonomer was established by ^{1}H NMR and IR spectra. The ^{1}H NMR spectrum of the copolymer (Figure 1a) showed a typical vinyl pattern between 4.8 and 6.0 ppm (exocyclic olefin) and the absence of an intense triplet around 6.1 ppm (endocyclic olefin). Using a suitable physical mixture of ethylene copolymers containing a bicyclic olefin having either an exocyclic or an endocyclic double bond, it was estimated by ^{1}H NMR that the selectivity of copolymerization through enchainment of the endocyclic olefin is >95%. The ^{13}C NMR spectrum of the copolymer showed peaks at 144.37 (=CH, exo), 141.70 (=CH, endo), 113.78 (=CH_2, endo), and 111.30 ppm (=CH_2, exo) indicating the presence of a vinyl double bond and the absence of a peak at 136.9 ppm due to the endocyclic double bond in addition to peaks in the region 47.32–34.28 ppm due to backbone and comonomer carbons. The copolymer IR spectrum shows absorptions at 1638, 990, and 910 cm^{-1}, which are characteristic of vinyl unsaturation (Figure 2a). Absorption at 710 cm^{-1} due to the endocyclic vinylene double bond is absent.

The EVNB copolymers were generally amorphous or showed a T_m in the range 80–110 °C depending on the composition. These properties are similar to those reported for poly(ethylene-*co*-norbornene) of similar composition.[13]

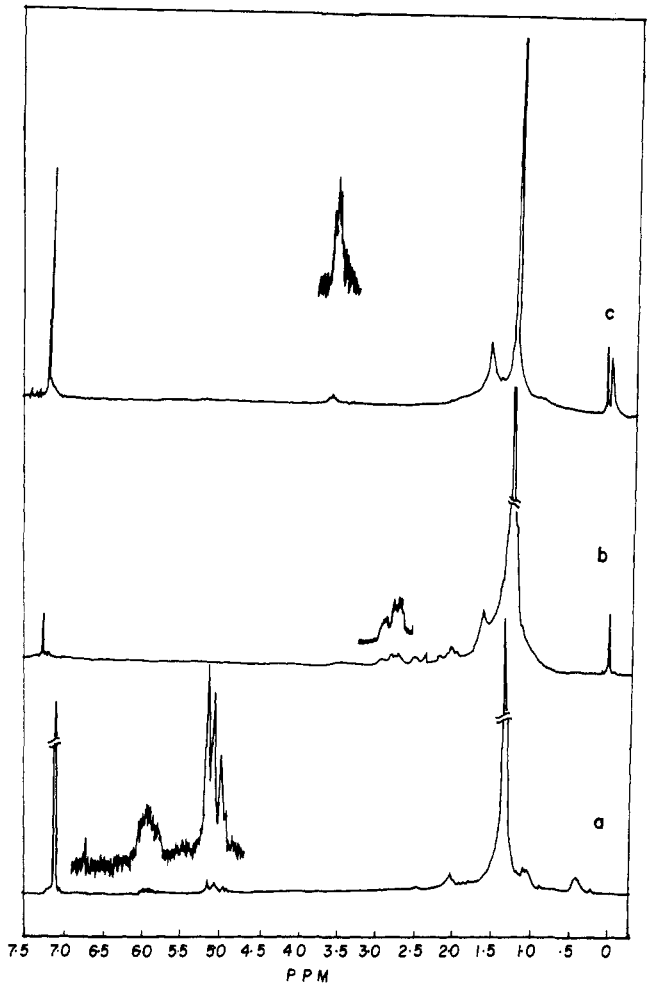


Figure 1. ^1H NMR spectra of (a) poly(ethylene-*co*-5-vinyl-2-norbornene) (2), (b) epoxy-containing copolymer (3), and (c) hydroxy-containing copolymer (4).

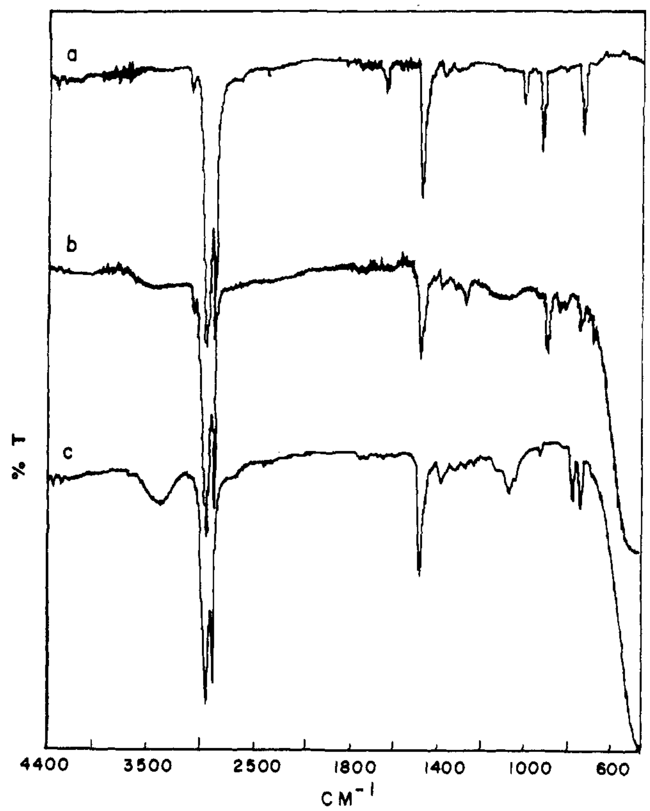
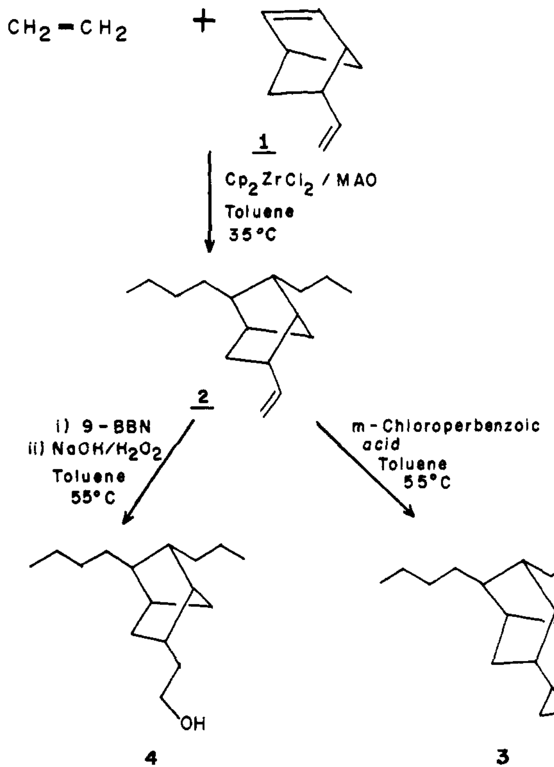


Figure 2. IR spectra of (a) poly(ethylene-*co*-5-vinyl-2-norbornene) (2), (b) epoxy-containing copolymer (3), and (c) hydroxy-containing copolymer (4).

Scheme 1



Functionalization of Poly(ethylene-*co*-5-vinyl-2-norbornene) (EVNB (2)). The copolymer containing 10.5 mol % of VNB (η = 1.0 dL/g) was chosen for functionalization. Epoxidation and hydroboration–oxidation were conducted in homogeneous solution at 55 °C using *m*-chloroperbenzoic acid and 9-borabicyclo[3.3.1]nonane (9-BBN), respectively (Scheme 1). The ^1H NMR and IR spectra of the epoxidized copolymer (3) are shown in Figures 1b and 2b. Complete epoxidation is evident from the disappearance of peaks due to unsaturation and the appearance of peaks due to the epoxy group at 2.5–3.0 ppm. The IR spectrum shows new absorptions at 876 and 1250 cm^{-1} due to the epoxy group.

The epoxy group content in copolymer 3 was estimated from the ^1H NMR spectrum and found to be 9.5 mol %, indicating a nearly quantitative epoxidation of the pendant vinyl double bond. The copolymer was soluble in toluene, 1,2,4-trichlorobenzene, xylene, and $CHCl_3$ above 50 °C. Its intrinsic viscosity was 0.96 dL/g, indicating no main-chain degradation. The copolymer showed a T_m similar to and an IDT lower than that of the precursor copolymer (Table 2).

Hydroboration of 2 using 9-BBN followed by oxidation gave rise to a copolymer (4) containing CH_2OH functionality (Scheme 1). The ^1H NMR spectrum of copolymer 4 (Figure 1c) shows a triplet at 3.55 ppm due to the CH_2O protons. The IR spectrum shows bands at 3350 and 1050 cm^{-1} which are characteristic of CH_2OH groups. The hydroxyl content of the copolymer as estimated from the ^1H NMR spectrum was ca. 10 mol %, indicating nearly quantitative functionalization. The intrinsic viscosity, IDT, and T_m (Table 2) of 4 were similar to those of the precursor copolymer. Copolymer 4 was soluble in toluene, 1,2,4-trichlorobenzene, xylene, and $CHCl_3$ above 50 °C.

Thus copolymerization of ethylene with 5-vinyl-2-norbornene using zirconocene–MAO affords a simple route to polyolefins with pendant vinyl groups. Very high levels of comonomer incorporation with excellent regioselectivity for the endocyclic olefin appear to be the hallmark of the

Table 2. Properties of EVNB (2) and Functionalized Copolymers (3, 4)

no.	copolymer	mol % functionality[a]	$[\eta]$[b] (dL/g)	IDT (°C)	T_m (°C)	ΔH_f (J/g)
1	**2**	10.5	1.00	399	88	36
2	**3**	9.5	0.96	351	88	29
3	**4**	9.9	1.00	391	89	35

[a] Calculated from ^{1}H NMR. [b] In 1,2,4-trichlorobenzene at 135 °C.

metallocene-based catalyst systems. The pendant vinyl group can be quantitatively functionalized using standard organic chemical transformations.

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