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Copolymerizations of ethylene with α-olefin-ω-ols by highly active vanadium(III) catalysts bearing [N,O] bidentate chelated ligands

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ABSTRACT

The copolymerizations of ethylene with polar hydroxyl monomers such as 10-undecen-1-ol, 5-hexen-1-ol and 3-buten-1-ol were investigated by the vanadium(III) catalysts bearing bidentate [N,O] ligands (**1**, [PhN=C(CH_3)CHC(Ph)O]$VCl_2(THF)_2$; **2**, [PhN=CHC_6H_4O]$VCl_2(THF)_2$; **3**, [PhN=CHC(Ph)CHO]$VCl_2(THF)_2$). The polar monomers were pretreated by alkylaluminum before the polymerization. High catalytic activities and efficient comonomer incorporations can be easily obtained by changing monomer masking reagents and polymerization conditions in the presence of diethylaluminium chloride as a cocatalyst. The longer the spacer group, the higher the incorporation of the monomer. Under the mild conditions, the incorporation level of 10-undecen-1-ol reached 13.9 mol% in the resultant copolymers was obtained. The reactivity ratios of copolymerization ($r_1 = 41.4$, $r_2 = 0.02$, $r_1r_2 = 0.83$) were evaluated by Fineman–Ross method. According to ^{13}C NMR spectra, polar units were located both on the main chain and at the chain end. The end-hydroxylated polymers were probably obtained due to the formation of dormant species after the insertion of the comonomer followed by the chain transfer to alkylaluminum. In addition, the signals derived from polar monomer inverse insertion were detected for the first time.

1. Introduction

The incorporation of polar groups in polyolefin chains not only can provide the polymers with improved properties, but also offers the sites for initiating graft copolymerization [1–10]. Direct copolymerizing olefin with polar monomer in which functional group closes to vinyl bond by traditional Ziegler–Natta or metallocene catalysts is restricted since the nonbonded electron pairs of heteroatoms tend to form complexes with the metal center. Thus, a preferred current approach to the synthesis of functional polyolefins is the use of monomers possessing long methylene spacers between polar and vinyl groups like in the case of 5-hexen-1-ol, 10-undecen-1-ol and 10-undecenoic acid etc. [11–32]. A number of metallocene catalysts were efficiently tested to produce ethylene/polar monomers copolymers. For example, Seppala, Lofgren and their coworkers explored ethylene/10-undecen-1-ol copolymerizations using a series of metallocene catalysts in the presence of excess methylaluminoxane (MAO) as the cocatalyst and monomer masking reagent [11–13]. Fink and his coworkers utilized $Me_2Si(Ind)_2ZrCl_2$/MAO system to promote the copolymerizations of ethylene with 10-undecene-1-oxytrimethylsilane or 10-undecene-1-oxytriisopropylsilane, in which high catalytic activities and comonomer incorporations were obtained with the triisopropylsilyl protected monomers [14]. Imuta established the end-site-selective introduction of an alcohol group into polyolefins by the combination of metallocene "IF catalyst" with alkylaluminums as a monomer masking reagent, which provided the strategic basis for controlling the regioselectivity in the one-pot synthesis of hydroxyl-capped polyolefins [17]. Shiono and his colleagues reported the copolymerization of ethylene or propylene with 5-hexen-1-ol by $Me_2Si(Flu)_2ZrCl_2$, and alternating poly(ethylene-*co*-5- hexen-1-ol)s were easily obtained under the mild conditions [20].

Compared with group IV metals, vanadium compounds or metal exhibits the reduced oxophilicity. Therefore, the enhanced functional group tolerance makes them much attractive for the incorporation of polar monomers into polyolefin backbone. In recent years, a number of well-defined vanadium catalysts have been used in ethylene polymerization or copolymerization with α-olefins [34–48]. However, successful examples concerning the controlled copolymerization of ethylene with polar monomers by vanadium catalysts are limited so far. Our interest is to explore ethylene/polar monomers copolymerizations with vanadium catalysts, further to prepare polyolefins bearing functional groups in the side chain. The 10-Undecen-1-ol, 5-hexen-1-ol and 3-buten-1-ol with different

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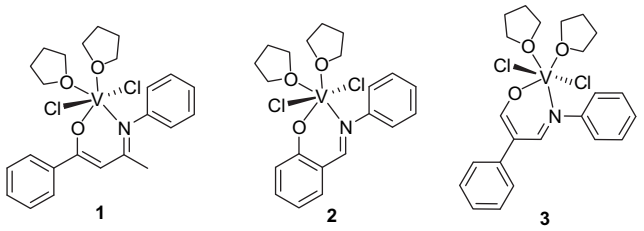

Scheme 1. Vanadium(III) complexes **1**–**3**.

spacer lengths between the functional group and the polymerizable double bond are selected as the polar comonomers to incorporate functional groups into polyolefin chains. In this contributor, we thus explored the copolymerization of ethylene with these functional α-olefins using the vanadium(III) catalysts bearing [N,O] ligands (Scheme 1). These catalysts exhibited remarkable activities and copolymerization abilities in the presence of alkylaluminums as the monomer masking reagents, yielding the copolymers with high functional comonomer incorporation.

2. Experimental

2.1. General

All manipulation of air- and/or moisture-sensitive compounds was carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from an MBraun SPS system. Commercial ethylene was directly used for polymerization without further purification. The polar comonomers such as 10-Undecen-1-ol, 5-hexen-1-ol and 3-butylene-1-ol, and ethyl trichloroacetate (ETA) were purchased from Aldrich, dried over calcium hydride at room temperature and then distilled. Diethylaluminium chloride (DEAC), triisobutylaluminum (TiBA), triethylaluminum (TEA) and trimethylaluminum (TMA) were purchased from Albemarle Corporation. The vanadium complexes **1**–**3** were synthesized according to the procedures reported previously [33,34].

2.2. Characterization of the polymers

The ^{1}H and ^{13}C NMR data of copolymers were obtained on a Varian Unity-400 MHz spectrometer at 110 °C with *o*-$C_6D_4Cl_2$ as a solvent. The DSC measurements were performed on a Perkin–Elmer Pyris 1 Differential Scanning Calorimeter at a rate of 10 °C/min. The weight-average molecular weight (MW) and the molecular weight distribution (MWD) of polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three Plgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd).

2.3. Ethylene/polar monomer copolymerization

The copolymerization was carried out under atmospheric pressure in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. The reactor was charged with 30 mL of toluene and the prescribed amount of polar monomer (10-undecen-1-ol, 5-hexen-1-ol, or 3-butylene-1-ol) and an equivalent amounts of protection reagent (DEAC, TMA, TEA or TiBA), then the ethylene gas feed was started followed by equilibration at desired polymerization temperature. After 10 min, a solution of DEAC in toluene and a solution of ETA in toluene were added. Subsequently, a toluene solution of catalyst was added into the reactor with vigorous stirring (900 rpm) to initiate polymerization. The total volume of the liquid phase was 50 mL. After a prescribed time, ethanol (10 mL) was added to terminate the polymerization reaction. The resulted mixture was added to acidic ethanol. The solid polymer was isolated by filtration, washed with ethanol and acetone, and dried at 60 °C for 24 h in a vacuum oven.

2.4. Ethylene/hexene copolymerization

The copolymerization was also carried out under atmospheric pressure in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. The reactor was charged with 30 mL of toluene and the prescribed amount of 1-hexene, and then the ethylene gas feed was started followed by equilibration at desired polymerization temperature. After 10 min, a solution of DEAC in toluene and a solution of ETA in toluene were added. Subsequently, a toluene solution of catalyst was added into the reactor with vigorous stirring (900 rpm) to initiate polymerization. After a prescribed time, ethanol (10 mL) was added to terminate the polymerization reaction. The resulted mixture was added to acidic ethanol. The solid polymer was isolated by filtration, washed with ethanol and acetone, and dried at 60 °C for 24 h in a vacuum oven.

Table 1
Copolymerization of ethylene/polar comonomers protected with different alkyaluminums.[a]

Entry	Cat. (μmol)	Comonomer	AlR_3[b]	Yield (g)	Activity[c]	Incorp.[d] (mol%)	T_m[e] (°C)	M_W[f] ($\times 10^{-3}$)	M_W/M_n[f]
1	**1**(1.0)	10-undecen-1-ol	TIBA	0.33	1.98	2.2	115	14.9	1.8
2	**1**(1.0)	10-undecen-1-ol	TEA	0.54	3.24	2.3	116	8.90	1.9
3	**1**(1.0)	10-undecen-1-ol	TMA	1.39	8.34	2.5	117	9.00	2.0
4	**1**(1.0)	10-undecen-1-ol	DEAC	1.62	9.72	3.7	112	13.3	2.0
5	**1**(1.0)	5-hexen-1-ol	DEAC	1.42	8.50	2.7	122	14.4	2.1
6	**1**(1.0)	3-buten-1-ol	DEAC	0.65	3.90	0.4	128	16.9	1.9
7	**2**(1.0)	10-undecen-1-ol	DEAC	1.45	8.70	4.0	111	8.90	2.0
8	**3**(1.0)	10-undecen-1-ol	DEAC	1.86	11.2	3.4	113	11.7	2.0
9[g]	**4**(1.0)	10-undecen-1-ol	DEAC	Trace	–	–	–	–	–
10[g]	**4**(5.0)	10-undecen-1-ol	DEAC	0.20	0.24	2.5	115	10.5	2.0

[a] Reaction conditions: 1 μmol catalyst, DEAC/V (molar ratio) = 4000, ETA/V (molar ratio) = 500, 0.1 mol/L comonomer, V_{total} = 50 mL, 1 atm ethylene pressure, at 50 °C in toluene for 10 min.
[b] 1.0 equivalent of alkylaluminums to comonomer added as protecting reagents.
[c] Activity in kg/mmol$_v$ h.
[d] Comonomer incorporation determined by ^{1}H NMR.
[e] Determined by DSC.
[f] GPC data in 1,2,4-trichlorobenzene versus polystyrene standard.
[g] MMAO as cocatalyst.