Copolymerization of ethylene and 4-vinylcyclohexene by various metallocenes in the presence of Al(\(i\)Bu)\(_3/\)\([\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]\)

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Abstract: Copolymerizations of ethylene and 4-vinylcyclohexene (VCH) were carried out with isospecific \(\text{rac-1,2-ethylenebis(1-indenyl)Zr(N(CH}_3)_2\text{)}_2}\) \([\text{rac-(EBI)}\text{Zr(NMe}_2\text{)}_2]\) and syndiospecific isopropylidene(cyclopentadienyl)(9-fluorenyl)ZrMe\(_2\) \([\text{iPr(Cp)}(\text{Flu})\text{ZrMe}_2]\) compounds combined with Al(\(i\)Bu)\(_3/\)\([\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]\) as a cocatalyst system. VCH was regioselectively inserted into the copolymer through the vinyl double bond, leaving the endocyclic double bond unreacted. \(\text{rac-(EBI)}\text{Zr(NMe}_2\text{)}_2\) catalyst showed a higher polymerization rate but lower VCH reactivity than the \(\text{iPr(Cp)}(\text{Flu})\text{ZrMe}_2\) catalyst. The calculation of copolymerization parameters according to Kelen-Tüdös resulted in \(r_E = 131.49\) and \(r_{\text{VCH}} = 0.02\) for the \(\text{iPr(Cp)}(\text{Flu})\text{ZrMe}_2\) catalyst. When [VCH] in feed was 90.5 mol-%, [VCH] in polymer was 1.88 and 8.04 mol-% for \(\text{rac-(EBI)}\text{Zr(NMe}_2\text{)}_2\) and \(\text{iPr(Cp)}(\text{Flu})\text{ZrMe}_2\) catalysts, respectively. The resulting copolymers were characterized using NMR, Raman and intrinsic viscosity measurements.

Introduction

Recently, much work has been conducted on the co- and terpolymerizations of diolefins for syntheses of polymers with pendant unsaturated double bonds, as these polymers are useful for the introduction of functional groups into polyolefins. The functionalized polyolefins can serve as interfacial modifiers to improve their adhesion to and compatibility with other polar materials.

Ethylene and/or propylene have been copolymerized with dienes, such as 1,4-hexadiene [1], 4-vinylcyclohexene (VCH) [2], and 5-vinyl-2-norbornene [3]. These dienes are copolymerized with the olefin regioselectively in the presence of a metallocene compound, leaving an unsaturated double bond in the pendant group.

5-Vinyl-2-norbornene is copolymerized through the endocyclic double bond leaving the vinyl group unreacted, because of the higher ring strain of the endocyclic double bond [3,4]. In case of VCH, vinyl double bonds were reported to take part in the polymerization reaction, as the endocyclic double bond shows little ring strain and large steric hindrance [2,5]. However, no detailed reports have been published to investigate the effect of the metallocene structure on the copolymerization of ethylene and VCH.
In this paper we investigate the copolymerization of ethylene and VCH by two metalloocene catalysts, isospecific rac-1,2-ethylenebis(1-indenyl)Zr(NMe₂)₂ (rac-(EBI)Zr(NMe₂)₂, CAT-1) and syndiospecific isopropyldiene(cyclopentadienyl)(9-fluorenyl)ZrMe₂ ([Pr(Cp)(Flu)]ZrMe₂, CAT-2), combined with Al(ιBu)₃/[Ph₃C][B(C₆F₅)₄] as a cocatalyst system.

Experimental part

Materials

All reactions were carried out under a purified nitrogen atmosphere using standard dry box and Schlenk techniques. Ethylene and propylene (SK Co., Korea) of polymerization grade were purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. VCH was stirred with triisobutylaluminium (Al(ιBu)₃) for 72 h and distilled prior to use. Solvents were distilled from Na/benzophenone and stored over molecular sieves (4A). Al(ιBu)₃ from Aldrich was used without further purification. Metalloocene compounds, rac-(EBI)Zr(NMe₂)₂ [6] and Me₂C(Cp)(Flu)ZrMe₂ [7] and the anionic [Ph₃C][B(C₆F₅)₄] compound [8] were synthesized according to literature procedures.

Copolymerizations

Copolymerizations were carried out in a 250 mL glass reactor equipped with a magnetic stirrer and a thermometer. In a dry box, the reactor was filled with 80 mL of toluene, Al(ιBu)₃, VCH, and metalloocene catalyst. The reactor was immersed in a constant-temperature bath previously set to the desired temperature. When the reactor temperature had been equilibrated to the bath temperature, ethylene was introduced into the reactor after removing nitrogen in vacuum. When no more absorption of ethylene or propylene into toluene was observed, a prescribed amount of [Ph₃C][B(C₆F₅)₄] dissolved in toluene was injected into the reactor and then the polymerization was started. The polymerization rate was determined at every 0.01 s from the rate of consumption and was measured by a hot-wire flow-meter (model 5850 D, Brooks Instrument Div.) connected to a personal computer through an analogue-to-digital converter. Polymerization was quenched by the addition of methanol. The polymer obtained was filtered, washed with an excess amount of methanol and dried in vacuum at 50°C for 24 h.

Characterization

¹³C NMR spectra of the polymers were recorded at 120°C on a Varian Unity Plus 300 spectrometer. Samples were prepared by dissolving the polymer in CDCl₃-tetrachloroethane (1/5 v/v). Melting curves were recorded with a DuPont differential scanning calorimeter (DSC, Model 910) at 10°C/min. The intrinsic viscosities of polymers were determined in decalin at 135°C using an Ubbelohde viscometer. Raman spectra were recorded on a Bruker IFS55 FTIR spectrometer with the Raman modulus (FRA 106), CaF₂ beam splitter, and Ge detector. The excitation source was a diode pumped Nd YAG laser operated at 1064 nm. The laser power was 350 mW.
Results and discussion

Figs. 1 and 2 show the copolymerization rate \( (R_p) \) curves of ethylene/VCH measured at 30°C at different ratios of [VCH]/[ethylene] in the feed by using CAT-1 and CAT-2, respectively, in the presence of Al(\( \text{Bu} \))\(_3\) and [Ph\(_3\)C][B(C\(_6\)F\(_6\))\(_4\)] as a cocatalyst formulation. CAT-1 showed much higher activity than CAT-2 and the polymerization behaviours are quite different from each other. The initial rate decreases monotonously as the amount of VCH in feed increases for both catalysts. There was no acceleration of activity by adding comonomer, which has been generally found in the copolymerization of ethylene and \( \alpha \)-olefin by using metallocene catalysts. When 1-hexene was used as a comonomer, the polymerization rate enhanced very much with similar catalytic systems [9,10,11]. With stereo-rigid catalysts like CAT-1 and CAT-2, the rate enhancement effect of the comonomer may arise mainly from relieving diffusion limitation due to the polymer becoming soluble in the reaction medium [9,12]. However, a pronounced change in the viscosity of the polymerization medium was observed in the copolymerizations by using both CAT-1 and CAT-2 catalysts during the early stage. In this stage fibrous polymer was sticking on the magnetic stirrer bar, and then precipitated as particulates or agglomerates. These results demonstrate that the diffusion limitation is not relieved by the addition of VCH, as in the case of ethylene/1-hexene copolymerizations.

The polymerization rate with CAT-1 reaches its maximum within a minute followed by a decay of \( R_p \). In cases of homopolymerization of ethylene (Fig. 1(a)) and copolymerizations at a low amount of VCH (Fig. 1(b) and (c)), there were sudden decays of \( R_p \). In this stage the viscosity of the polymerization medium changes dramatically, resulting in the precipitation of polymer particles out of solvent. As a result the sharp decrease of \( R_p \) may come from the prevention of diffusion of ethylene into the active sites.

In the presence of CAT-2 (Fig. 2), the initial rate is not as high as with CAT-1 and an induction period (1 - 2 min), which increases with the amount of VCH in the feed, can be observed. The lower initial rate results in a slower viscosity change of the polymerization medium so that the decay of \( R_p \) after reaching its maximum is moderate.

![Graph](image)

Fig. 1. \( R_p \) versus time curve obtained with the CAT-1/Al(\( \text{Bu} \))\(_3\)/[Ph\(_3\)C][B(C\(_6\)F\(_6\))\(_4\)] system. Polymerization conditions are described in Tab. 1: (a) run no. 1 in Tab. 1, (b) no. 6, (c) 7, (d) 8, (e) 9, and (f) 10
Fig. 2. $R_p$ versus time curve obtained with the **CAT-2**/Al(Bu)$_3$[Ph$_3$C][B(C$_6$F$_6$)$_4$] system. Polymerization conditions are described in Tab. 1: (a) run no. 16 in Tab. 1, (b) no. 17, (c) 18, (d) 19, and (e) 20

Fig. 3. Copolymerization diagrams of ethylene/VCH: (a) **CAT-1** and (b) **CAT-2**

The VCH content incorporated in copolymer was determined by $^{13}$C NMR spectroscopy according to the literature [2]. The results are summarized in Tab. 1 together with polymerization results. Fig. 3 shows the plot of VCH percentage in feed versus VCH percentage in copolymer obtained with **CAT-1** and **CAT-2**. Even if both catalysts do not show high VCH reactivity, **CAT-2** is featured by much higher VCH reactivity than **CAT-1** at the same polymerization conditions.

The calculation of copolymerization parameters according to Kelen-Tüdös resulted in $r_E = 131.49$, $r_{VCH} = 0.02$ ($r_E \times r_{VCH} = 3.02$; E = ethylene, VCH = 4-vinylcyclohexene) for the **CAT-2**/Al(Bu)$_3$[Ph$_3$C][B(C$_6$F$_6$)$_4$] system, but we failed to get those for the **CAT-1**/Al(Bu)$_3$[Ph$_3$C][B(C$_6$F$_6$)$_4$] system due to too low comonomer reactivity. The higher reactivity towards VCH of **CAT-2** may be rationalized by the higher electron-donating effect of the fluorenyl group compared to the indenyl group and larger space so that bulky VCH can collide with the active central metal. Similar results were reported for the copolymerization of ethylene and higher $\alpha$-olefins [13-15].
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<th>[Zr]/μmol</th>
<th>( T_p ) in °C</th>
<th>[VCH]_{in polymer} in mol-%</th>
<th>( \bar{R}_p \times 10^{-6} )</th>
<th>( T_m ) in °C</th>
<th>( \Delta H_f ) (J/g)</th>
<th>[( \eta )] (dL/g)</th>
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a) Polymerization conditions: \( P_{ethylene} = 5 \) psig, \([Al]/[Zr] = 80, [(Ph_3C)(B(C_6F_5)_4)]/[Zr] = 1\), toluene = 80mL.  

b) Determined by \(^{13}\)C NMR.  
c) Average rate of polymerization in g PE/(mol Zr· h).  
d) \( T_m \) and \( \Delta H_f \) are melting temperature and heat of fusion, measured by DSC.  
e) Intrinsic viscosity measured in decalin at 135°C.
Copolymerization of ethylene and VCH was also carried out at various polymerization temperatures ranging from 30 to 70°C, in order to investigate the effect of temperature on the copolymerization behaviour. As summarized in Tab. 1, the average rate of polymerization increases as the temperature increases; however, the reactivity of VCH decreases as the temperature increases at the same [VCH]/[E] ratio.

Copolymerizations of propylene and VCH were also carried out at 30°C in the presence of CAT-1 and CAT-2 at polymerization conditions similar to those shown in Tab. 1. However, $^{13}$C NMR and Raman spectra of the resulting copolymers showed no peaks indicating the existence of VCH in polymer. As a result it might be assumed that the reactivity of VCH be negligible in the copolymerization of propylene and VCH using CAT-1 and CAT-2.

**Characterization of poly(ethylene-co-VCH)**

Fig. 4 shows the $^{13}$C NMR spectrum of poly(ethylene-co-VCH) containing 8.04 mol-% of VCH (run no. 20 in Tab. 1). The copolymer microstructure and the copolymerization mechanism can be realized from the reactivity ratios and the $^{13}$C NMR spectra. There are no peaks of VCH showing alternating or blocky structure. Recalling that the copolymer represents a blocky character when the product of the two reactivity ratios ($r_E \times r_{VCH}$) is larger than unity, poly(ethylene-co-VCH) copolymers obtained by CAT-2 would appear to be composed of ethylene blocks and VCH distributed randomly.

![NMR spectrum](image)

**Fig. 4.** $^{13}$C NMR spectrum of poly(ethylene-co-VCH) made with the CAT-2/Al(iBu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] catalyst system (run no. 20 in Tab. 1)

The vinyl double bond in VCH takes part in the homopolymerization, as the endocyclic double bond has little ring strain and large steric hindrance [2,5]. Chien and coworkers [5] investigated the homopolymerization of VCH, vinylcyclohexane and cyclohexene in order to elucidate which unsaturated group is involved in the polymerization reaction, vinyl or endocyclic double bonds, and reported that the
polymerization activity of VCH or vinylcyclohexane is 10 times greater than that of cyclohexene. The preference of vinyl double bonds was also observed in the copolymerizations. It can be confirmed from the absence of peaks at 112.2 and 143.5 ppm, which are assigned to be =CH₂ and =CH of the vinyl group, and the presence of peaks at 126.9 and 127.3 ppm, which are assigned to be =CH of the endocyclic double bond (Fig. 4).

FT Raman spectra of poly(ethylene-co-VCH) were recorded, in order to get deeper insight into the microstructure of copolymers. Fig. 5 shows Raman spectra of polyethylene and poly(ethylene-co-VCH) produced with CAT-2. Fig. 5(a) represents a typical Raman spectrum of a high-density polyethylene in the 700 - 1700 cm⁻¹ spectral region [16]. As the amount of VCH incorporated in copolymer increases, the amorphous part of copolymers increases. This result is verified from the decrease of the crystalline peaks of polyethylene at 1170 and 1417 cm⁻¹ and the increase of the amorphous peak of polyethylene at 1080 cm⁻¹, together with the decreasing heat of fusion of the copolymers obtained by DSC as the amount of VCH incorporated in copolymer increases (Tab. 1).

![Raman Spectra](image)

Fig. 5. Raman spectra of copolymers produced with CAT-2: (a) run no. 11 in Tab. 1, (b) no. 16, (c) 17, (d) 18, (e) 19, and (f) 20

The peaks at 1653 and 873 cm⁻¹ are assigned to be C=C (3.4 in Fig. 4) stretching vibration of endocyclic double bonds and C-C (say, 1, 6 and 5, 6 in Fig. 4) vibration of cyclic units, respectively. The intensities of these peaks increase linearly as [VCH] in polymer increases. As a result they may be utilized for quantitative analysis. The quantitative analysis was carried out by comparing the intensity ratio of peaks of Raman spectra with the amount of VCH determined by ¹³C NMR. The peaks at 1437 and 1295 cm⁻¹ are used as reference peaks; they are assigned to be CH₂ deformation and twisting vibrations of polyethylene [16], respectively. Baselines were drawn among 768, 985, 1225, 1398, 1528, 1619 and 1693 cm⁻¹ for the determination of peak intensities. The plots of intensity ratios I₈₇₃/I₁₂⁹₅ and I₈₇₃/I₁₄₃₇ were not suitable for the quantitative analysis, since they gave r² values of 0.860 and 0.662, respectively. The r² value is a measure of the linear correlation between the
experimental points (intensity ratio in Raman spectra) and the actual amount of VCH in copolymer (determined by $^{13}$C NMR). The plots of the intensity ratios $I_{1653}/I_{1295}$ and $I_{1653}/I_{1437}$ versus the amount of VCH in copolymer determined by $^{13}$C NMR gave good linear relationships expressed as:

$$I_{1653}/I_{1295} = 0.0486 \text{ (mol-% of VCH in copolymer)} - 0.0251 \quad (1)$$

$$I_{1653}/I_{1437} = 0.0334 \text{ (mol-% of VCH in copolymer)} - 0.0001 \quad (2)$$

The $R^2$ values are 0.991 and 0.989 for Eqs. (1) and (2), respectively. These results demonstrate that Raman spectroscopy can be used as a quick estimation of the amount of comonomer incorporated in polymer.

**Conclusions**

The isospecific **CAT-1** showed much higher polymerization rate than **CAT-2** in the copolymerization of ethylene and VCH; however, **CAT-2** showed much higher incorporation of VCH than **CAT-1**. The calculation of copolymerization parameters according to Kelen-Túdös resulted in $e = 131.49$ and $r_{\text{VCH}} = 0.02$ for **CAT-2**. The insertion of VCH proceeded through the vinyl double bond regioselectively, leaving the endocyclic double bonds unreacted. The incorporation of VCH in the copolymerization of propylene and VCH was negligible for both catalysts. The relatively low reactivity of VCH may be attributed to the ability of the cyclohexene ring to form ring conformations which enhance its steric repulsion towards the ligands of the active centers. The endocyclic double bond of VCH makes VCH sterically bulky by arranging the cycle more planar.

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