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POLYMERIZATION OF ETHYLENE AND PROPYLENE WITH VCL_4-BUTYLLITHIUM CATALYSTS

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ABSTRACT

Polymerization of ethylene and propylene with VCl_4-BuLi (Bu = *n*-Bu, *sec*-Bu, *tert*-Bu) catalysts was investigated. The VCl_4-BuLi catalysts were found to initiate the polymerization of ethylene and propylene. The VCl_4-BuLi catalysts gave an ultra high molecular polyethylene. The effect of the Li /V mole ratio on the polymerization of ethylene with the VCl_4-BuLi catalysts was observed, and the catalyst gave an optimum rate at the Li/V ratio of about 3.0. The polyethylene obtained with the VCl_4-BuLi catalyst was found to be a linear structure. In the polymerization of propylene with the VCl_4-BuLi catalyst, the polymers contain mm contents of 56-66% were produced.

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INTRODUCTION

Since the discovery of Kaminsky *et al.* [1-3], and the polymerizations with soluble metallocene catalysts are one of the most investigated area for both industrial and academic aspects in polymer synthesis. On the other hand, V-based catalysts are also known to be effective soluble catalysts for polymerization of olefins [4-11]. Syndiotactic polypropylene has been synthesized by V-based catalysts such as $VCl_4/Al(C_2H_5)_2Cl$ and $VOCl_3/Al(C_2H_5)_2Cl$[4-5], and a living polymerization of propylene was also achieved with V-based catalysts such as $V(acac)_3/Al(C_2H_5)_2Cl$ and V(2-methyl-1,3-butanedionato)/$Al(C_2H_5)_2Cl$ [6-8]. Thus, V-based catalysts have still attractive feature as the soluble polymerization catalysts of olefins.

Zambelli *et al.* [11] reported that polymerization of olefins with V-based catalyst depended on the cocatalyst, and the activity for the polymerization and the reduction power to vanadium compounds decreased in the following.

For polymerization: $AlEt_3$>$BeEt_2$>$GaEt_3$>$AlEt_2I$>$AlEt_2Cl$>$CdEt_2$> LiBu> $ZnEt_2$

For reduction: LiBu>$CdEt_2$>ZnEt2>$BeEt_2$>$AlEt_3$>$AlEt_2Cl$>$AlEt_2I$ (Et: ethyl, Bu:butyl)

Although VCl_4-BuLi catalyst was reported to initiate the polymerization of styrene [12], the polymerizations of olefins with the VCl_4-BuLi catalyst were not found in the literature. The VCl_4-BuLi catalyst as well as $TiCl_4$-BuLi cata lysts [13-16] has a potential to make novel block copolymers through a transformation reaction from anionic to coordination route, since the living polymers initiated with BuLi can be regarded as a polymeric lithium compound. So, it is interesting to know the activity for the polymerization of ethylene and propylene with the VCl_4-BuLi catalysts.

In this paper, we will describe on the polymerization of ethylene and propylene with the VCl_4-BuLi catalysts.

EXPERIMENTAL

Materials

Ethylene was used after passed through a 5Å molecular sieve column. Propylene was used after removed water over a calcium hydride. VCl_4 kindly supplied from Shinkoh Chemical Co. was used as received. *n*-BuLi, *sec*-BuLi and *tert*-BuLi diluted with solvents, purchased from Kanto Chemical, was used without further purification. $AlEt_3$ kindly supplied from Tosoh Akuzo Co. were used after a dilution with solvent. Solvents and other reagents were used after purification by conventional methods.

Polymerization Procedure

The polymerizations were carried out using a 300 cm^3 glass reactor equipped with a stirrer and connected to a vacuum line. The required amounts of reagents into the reactor were performed by a syringe under nitrogen atmosphere through a rubber septum. Ethylene and propylene were introduced into a reactor through a stainless tube column packed with a 5Å molecular sieve from the bomb.

Polymerization was carried out in the reactor at a constant temperature for a given time. After the polymerization, isopropyl alcohol was added to terminate the polymerization reaction. Then, the contents of the reactor were poured into a large amount of methanol containing a small amount of hydrochloric acid to precipitate the polymer formed. The resulting polymer was filtered through a glass filter and washed with a large amount of methanol, and dried under high vacuum at 25°C. Polymer yields were determined by gravimetry.

Characterization of the Polymers

The viscosity of the polymers was measured in *o*-dichlorobenzene at 130°C using Ubbelohde viscometer. The viscosity-average molecular weight (M_v) of the polyethylene was calculated from the following equation: $[\eta] = (1.542 \times 10^{-4}) \times M_v^{0.8}$. The polymer structure was determined by NMR spectroscopy. The ^{13}C-NMR spectra of the polymers are recorded on JEOL A-400 NMR spectrometer in d_6-benzene and *o*-dichlorobenzene at 120°C.

RESULTS AND DISCUSSION

Polymerization of Ethylene with the VCl_4-BuLi Catalysts

Polymerization of ethylene with VCl_4-BuLi (Bu: *n*-butyl, *sec*-butyl, *tert*-butyl) catalysts was conducted in toluene at -78°C. The results are shown in Table 1, in which the results for the polymerization of ethylene with VCl_4-$AlEt_3$ catalyst are also indicated to comparison. The VCl_4-BuLi catalysts was found to initiate the polymerization of ethylene even at -78°C to give high polymers.

TABLE 1. Polymerization of Ethylene with VCL_4/Alkylmetal Catalysts in Toluene at -78°C for 30 minutes[a)]

Alkylmetal	Activity (g-PE / g-VCl_4)	M_v x 10^{-6}
n-BuLi	17.4	0.88
sec-BuLi	22.9	0.96
tert-BuLi	39.0	1.17
$AlEt_3$	42.3	0.57

a) Ethylene pressure = 2.0 kg·cm^{-2}, [VCl_4] = 3.0 x 10^{-2} mol / L,*n*-BuLi / VCl_4 = 3.0 (mole ratio), $AlEt_3$ / VCl_4 = 3.0 (mole ratio).

The catalytic activity for the polymerization depended on the BuLi used, and decreased in the following order; *tert*-BuLi >*sec*-BuLi > *n*-BuLi. The VCl_4-*tert*-BuLi catalyst gave highest activity for the polymerization of ethylene, and its activity was not so different from that of the VCl_4-$AlEt_3$ catalyst.

From viscosity measurement of the resulting polymers, the M_v of the polymers obtained with the VCl_4-BuLi catalysts were always higher than that obtained with VCl_4-$AlEt_3$ catalyst, and the VCl_4-*tert*-BuLi catalyst gave a polymer having M_v of more than 10^6, i.e., an ultra high molecular weight polyethylene (UHMWPE) with a great impact toughness, good corrosion resistance and excellent environmental stress crack resistance [17] was synthesized with the VCl_4-*tert*-BuLi catalyst.

Since no polymerization of ethylene was induced with only each catalyst component, both components are required to form active species for the polymerization. In the binary catalyst systems, the polymerizations are known to be influenced by the ratio of both components. To check this point, the effect of the Li/V mole ratios on the polymerization of ethylene with the VCl_4/*n*-BuLi catalyst at -78°C was examined. As shown in Figure 1, an optimum polymerization rate was observed at the Li/V mole ratio of about 3, which is coincided with the previous reported results for the polymerization of ethylene with $TiCl_4$-BuLi catalysts [18]. Namely, the active species for the polymerization of ethylene with the VCl_4/*n*-BuLi catalyst are likely to be reduced alkyl-vanadium complexes, since BuLi can serve as both reducing and alkylating agents for the vanadium compounds [19, 20].

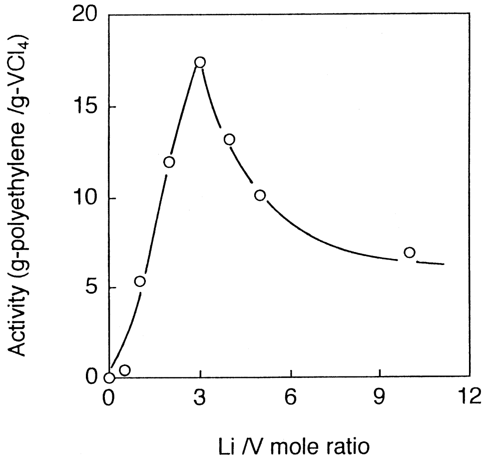

Figure 1. Effect of Li/V mole ratio on polymerization of ethylene with the VCl_4/*n*-BuLi catalyst in toluene at -78°C for 0.5 hours: Ethylene pressure = 2.0 kg/cm_2, $[VCl_4] = 3.0\times10^{-2}$ mol / L, Total volume = 100 cm^3.

The effect of the reaction temperatures from -78°C to 60°C on the polymerization of ethylene with the VCl_4-*n*-BuLi catalyst was investigated, and the results are shown in Figure 2. The polymer yields increased as a function of polymerization time at each reaction temperature, and an optimum polymeriza-

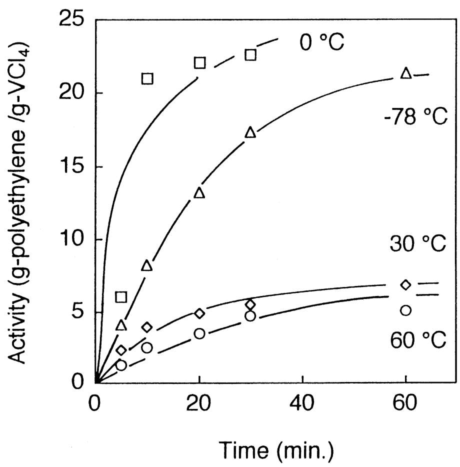

Figure 2. Time-conversion curves for polymerization of ethylene with the VCl_4/*n*-BuLi catalyst in toluene: Ethylene pressure = 2.0 kg/cm^2, [VCl4] = 3.0×10^{-2} mol/L, *n*-BuLi /Vcl_4 = 3.0 (mole ratio), Total volume = 100 cm^3.

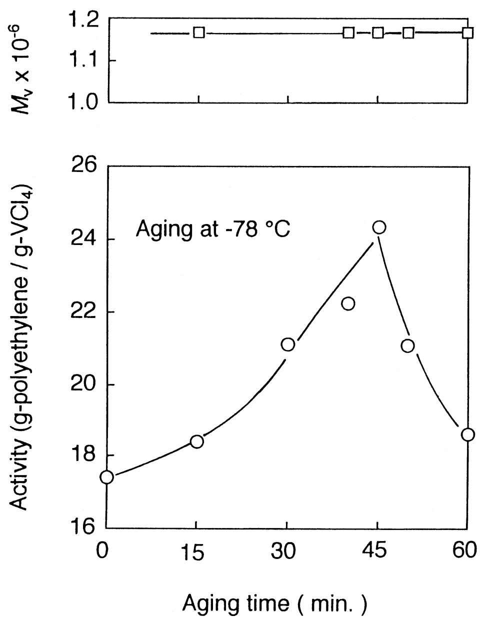

Figure 3. Effect of catalyst aging on polymerization of ethylene with the VCl_4/*n*-BuLi catalyst in toluene at -78°C for 0.5 hours: Ethylene pressure = 2.0 kg/cm^2, [VCl_4] = 3.0×10^{-2} mol/L, *n*-BuLi /Vcl_4 = 3.0 (mole ratio), Total volume = 100 cm^3.

tion rate was observed at 0°C, suggesting that the active species derived from the VCl_4-*n*-BuLi catalyst are not so thermal stable.

The effect of aging time of the VCl_4-*n*-BuLi catalyst on the polymerization of ethylene was examined, and the results are shown in Figure 3. The activity for the polymerization was found to depend on the aging time of the catalyst, and an optimum condition on the activity for the polymerization was 3/4 hour. The activity for the polymerization with aged catalyst was higher than that the catalyst without aging. However, the molecular weights of the polymers did not depend significantly on the aging time of the catalyst.

It is generally known that the polyethylene obtained from the polymerization with Ti-based Ziegler-Natta catalysts have short branches [21]. To clarify this point, the structure of the polymer (Mv $\geq$ 1.2 x 10^6) obtained with the VCl_4-*n*-BuLi catalyst at -78°C was checked by ^{13}C-NMR spectroscopy. Figure 4 shows the ^{13}C-NMR spectrrum of the polyethylene obtained with the VCl_4-*n*-BuLi catalyst, in which the spectrum of commercially UHMWPE is also shown to comparison.

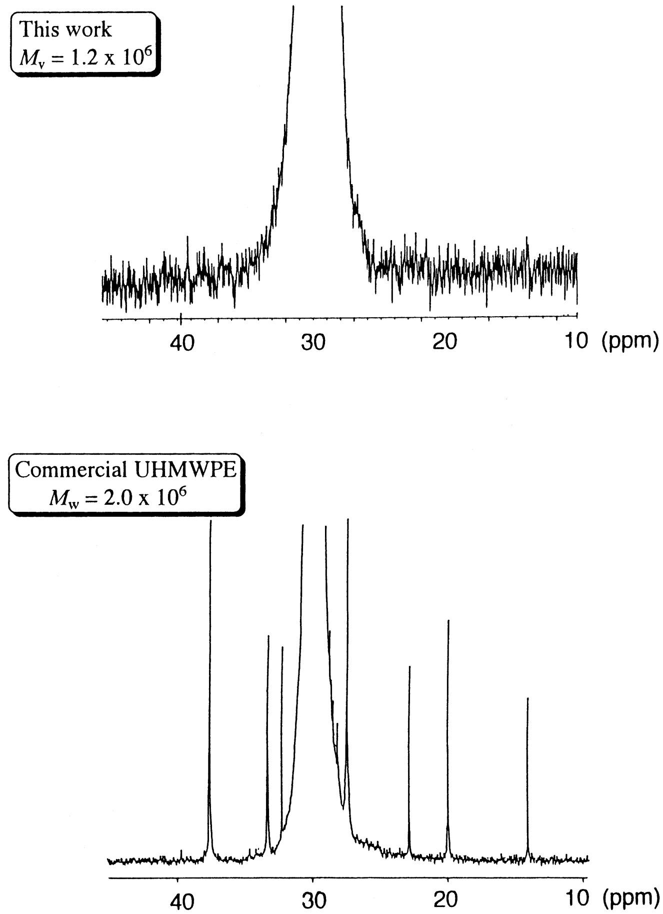

Figure 4. ^{13}C-NMR spectra of polyethylene obtained with the VCl_4-*n*-BuLi catalyst (1) and commercial UHMWPE (2).

The ^{13}C-NMR spectrrum of the polyethylene obtained with the VCl_4-*n*-BuLi catalyst shows only one peak at 29.6 ppm based on the methylene carbon in the main chain, and other peaks did not appear in the spectra of the polymers. On the other hand, the ^{13}C-NMR spectrum of the commercial polyethylene (Mw $\geq$ 2.0 x 10^6) showed many small peaks besides a main peak based on the methylene carbon in the main chain. [21]. These small peaks were assigned as branches of polyethylene. Accordingly, it is clear that the polyethylene obtained with the VCl_4-*n*-BuLi catalyst has a linear structure.

TABLE 2. Polymerization of Propylene with VCL_4-n-BuLi Catalyst in Toluene for 5 hours [a)]

Temp (°C)	Activity (g-polypropylene / g-VCl_4)	Tacticity (%)		
		mm	*mr*	*rr*
-78	0.24	60.5	23.7	15.8
0	1.66	63.7	24.0	12.3
30	0.96	66.5	21.5	12.0
60	0.57	56.4	24.6	19.0

a) [propylene] = 7.1×10^{-1} mol / L, [VCl_4] = 9.8×10^{-3} mol / L, [*n*-BuLi] / [VCl_4] = 3.0.

Polymerization of Propylene with the VCl_4-n-BuLi Catalyst

Polymerization of propylene with the VCl_4-*n*-BuLi catalyst in toluene was conducted, and the results are shown in Table 2. The polymerization of propylene was induced with the VCl_4-*n*-BuLi catalyst, and an optimum temperature for the polymerization was found to be at 0°C, which is in a good agreement with the result for the polymerization of ethylene with the same catalyst as described above, but the activity for the polymerization of propylene was slower than that of ethylene.

The Ziegler-Natta catalysts can give a stereoregular polypropylene depending on the catalysts used [22]. The stereoregularity of the polymers obtained with the VCl_4-*n*-BuLi catalyst was examined by the ^{13}C-NMR spectrum of polypropylene. The ^{13}C-NMR spectrum of the polymer is shown in Figure 5. Since the methyl carbon of the side chain is sensitive to stereoregularity of the polymer, the splitting of the peaks based on the methyl carbon was used to estimate the triad tacticity of the polypropylene. From the area ratio of the splitting peak, the triad tacticity of polypropylene was determined, and the results are listed in Table 2. The mm contents of the polymer did not depend significantly on the polymerization temperature, and the polymers having mm contents of 56.4-66.5% was obtained with the VCl_4-*n*-BuLi catalyst.

It is noted that the mm rich polypropylene was obtained from the polymerization of propylene with the VCl_4-*n*-BuLi catalyst even at -78°C, although the VCl_4-$Al(C_2H_5)_2Cl$ catalyst gave syndiotactic polymers [5].

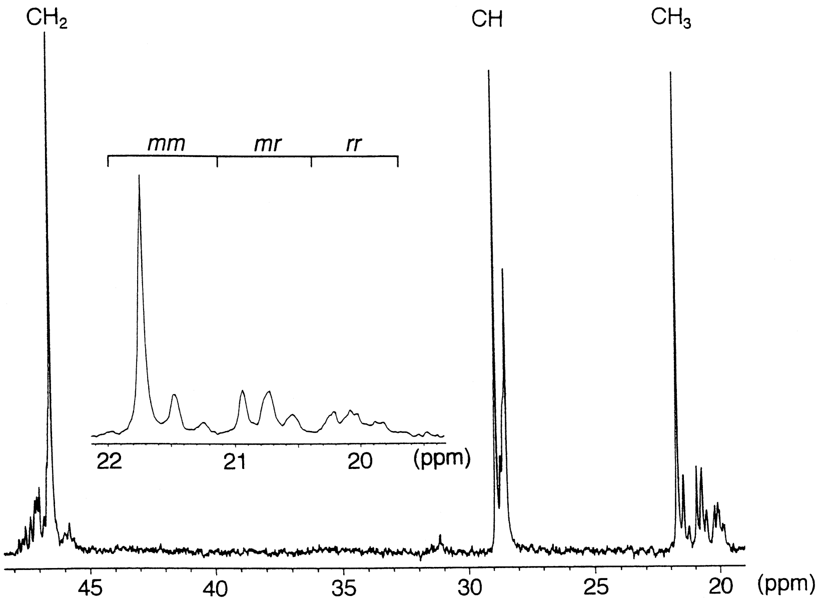

Figure 5. ^{13}C-NMR spectrum of polypropylene obtained with the VCl_4-*n*-BuLi catalyst in toluene at -78°C for 0.5 hours: [Propylene] = 0.7 mol/l, [VCl_4] = 9.8×10^{-3} mol/L, *n*-BuLi/VCl_4 = 3.0 (mole ratio).

CONCLUSION

The VCl_4-BuLi catalyst were found to be effective catalyst for the polymerizations of ethylene and propylene. In the polymerizations of ethylene, effects of Li/V mole ratios were observed, and optimum rate was obtained at the Li/V mole ratio of about 3. The ultra high molecular polyethylene (Mv $\geq 10^6$) was obtained with the VCl_4-*tert*-BuLi catalyst. From the analysis of ^{13}C-NMR spectra of the polymer, the resulting polyethylene has a linear structure. Polypropylene obtained with VCl_4-*n*-BuLi catalyst was found to be rich in isotactic contents.

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