SHORT COMMUNICATIONS

Polymerization of Vinyl Chloride with Cp*Ti(OCH₃)₃-Methylaluminoxane Catalyst

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Metallocene catalysts are the subject of continuing interest area of polymer synthesis.[1-9] Some of metallocene catalysts such as Cp*LnR (Cp* $=\eta^5$-C₅(CH₃)₅, Ln=Sm, Lu, Yb, R=H, CH₃)[9-11] and (C₂H₄Ind₂)ZrMe₂/[Ph₃C][B (C₆F₅)₄]/Zn(C₂H₅)₂[12, 13] were effective catalysts for polymerization of methyl methacrylate. We believe that metallocene catalysts are applicable to the polymerization of vinyl chloride (VC), and give polymers without anomalous units introduced into the polymer chain in radical polymerization.[14-18] However, we could not find the polymerization of VC with metallocene catalysts in the literature, although the polymerization of VC has been attempted with Ziegler type catalysts.[19-21]

In the polymerization of VC with modified Ziegler catalysts, titanium-*tetra-n*-butoxide in combination with Et₂AlCl polymerized VC,[20, 21] in which the ligand of the titanium compound is less electron-withdrawing than halogens, and cocatalysts are less reactive than alkylaluminium toward chlorinated compounds. Thus, we selected Cp*Ti(OCH₃)₃ as a transition metal compound, and polymerization of VC was investigated with Cp*Ti(OCH₃)₃ in combination with methylaluminoxane (MAO). The polymerization of VC with Cp*TiCl₃-MAO catalyst was examined for comparison. This paper briefly reports the polymerization of VC with Cp*TiX₃ (X=Cl or OCH₃)-MAO catalysts.

EXPERIMENTAL

Materials

Cp*TiCl₃ and Cp*Ti(OCH₃)₃ (Strem Chem. Inc.) were used without further purification. PMAO kindly supplied from Tosoh-Akzo Co. was used as received. Other reagents were used after purification by conventional methods.

Polymerization

Polymerization was carried out in a sealed glass tube with a rubber stopper or a 300 cm³ glass reactor equipped with a stirrer and connected to a vacuum line. Required amounts of reagents were charged in the glass tube by syringe through a rubber septum. VC was introduced into the tube at −78°C by a vacuum distillation over CaH₂. After polymerization, the contents of the tube were poured into excess methanol containing a small amount of hydrochloric acid to precipitate the polymer. Polymer yields were determined by gravimetry.

Characterization of Polymers

The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymer were determined by GPC using tetrahydrofuran (THF) as an eluent at 38°C calibrated as standard polystyrenes. The structure of the polymer was determined by ¹H and ¹³C NMR spectroscopy and elemental analysis. The tacticity of the polymers was determined from ¹³C NMR spectra of the polymers. ¹H and ¹³C NMR spectra were taken using a JEOL A-400 spectrometer in C₆D₆/o-dichlorobenzene (3/7 v/v%) at 120°C with hexamethyldisiloxane (HMDS) as the internal standard.

RESULTS AND DISCUSSION

Polymerization of VC with Cp*TiX₃-MAO (X=Cl, OCH₃) catalysts was conducted, and the results are listed in Table I. The polymerization of VC proceeded with Cp*TiX₃-MAO catalysts, but the polymerization rate was very slow. In the polymerization of styrene and substituted styrenes with Cp*TiX₃-MAO catalysts, the active species were strong electrophiles and organotitanium complex cations.[22] When the polymerization of styrene was carried out with the Cp*TiX₃-MAO catalysts at low MAO/Ti mole ratio of 10, polymer yield was low (4%) as compared with that of VC, suggesting that the active site for the polymerization of VC differs from that of styrene. However, the active site for the polymerization of VC with the Cp*TiX₃-MAO catalysts seems to have strong electrophiles. Thus, the slow polymerization of VC with the Cp*TiX₃-MAO catalysts is due to the fact that the active site formed from the Cp*TiX₃-MAO catalysts in the polymerization of VC is blocked by a free electron pair from the chloro atom of the VC. This suggests that changing of a Lewis acidity of the central metal of the active site by the ligand influences activity for the polymerization of VC. As shown in Table I, the activity for the polymerization of VC with the Cp*Ti(OCH₃)₃-MAO catalyst was higher than that with the Cp*TiCl₃-MAO catalyst. In the polymerization of styrene with the Cp*TiX₃-MAO catalysts, the active site does not contain Ti–X bonds. If Ti–X bond is not present

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Table I. Polymerization of VC with Cp*TiX$_3$-MAO catalyst at 20°C[a]

No.	Cp*TiX$_3$	Solvent	$\dfrac{\text{Time}}{\text{h}}$	$\dfrac{\text{Yield}}{\%}$	$M_n \times 10^{-4}$	M_w/M_n
1	Cp*TiCl$_3$	CH$_2$Cl$_2$	6	8.0	1.1	1.7
2	Cp*TiCl$_3$	CH$_2$Cl$_2$	10	8.1	1.1	1.7
3	Cp*TiCl$_3$	Toluene	24	0.3	—	—
4	Cp*Ti(OCH$_3$)$_3$	CH$_2$Cl$_2$	4	22.6	1.7	1.8
6	Cp*Ti(OCH$_3$)$_3$	CH$_2$Cl$_2$	42	50.0	2.5	2.0
7	Cp*Ti(OCH$_3$)$_3$	Toluene	48	2.7	0.3	3.0

[a] [Ti] = 5×10^{-3}mol L^{-1}, [VC] = 3.52 mol L^{-1}, MAO/Ti = 10 mole ratio.

Figure 1. ^{1}H NMR spectra of PVC obtained with (a) Cp*TiCl$_3$-MAO catalyst and (b) Cp*Ti(OCH$_3$)$_3$-MAO catalyst.

at the active site for the polymerization of VC, such effect of the ligand is not observed, although more detailed study is necessary to confirm this assumption.

In the polymerization in CH$_2$Cl$_2$ solvent, polymer yields and the molecular weight of the polymers were higher than in toluene, which is consistent with the previous reported results for the polymerization of styrene and propylene with metallocene catalysts, for which a transition from a contact pair metallocene/MAO in toluene to free separated species in CH$_2$Cl$_2$ is suggested. [23, 24]

The structure of the polymers was first checked by elemental analysis. Carbon and hydrogen content of the polymer obtained with the Cp*Ti(OCH$_3$)$_3$-MAO catalyst (C ; 38.40% and H ; 4.82%, respectively) was in a good agreement with calculated values for assuming that the polymer consists of –CH$_2$–CHCl– units (C ; 38.42%, H ; 4.80%). Whereas, carbon and hydrogen content of the polymers obtained with the Cp*TiCl$_3$-MAO catalyst (C ; 40.12%, H ; 5.03%) was higher than the calculated values, suggesting that side reactions such as elimination of HCl and methylation took place during the polymerization.

The elimination reaction of HCl leads to the formation of double bonds in the polymer chain. Methylation between the resulting polymer and catalyst possibly yields methyl branches in the polymer. To elucidate these points, the structures of the resulting polymers were examined by ^{1}H NMR spectroscopy. Figure 1 shows the ^{1}H NMR spectra of the polymers obtained with the Cp*TiCl$_3$-MAO catalyst and Cp*Ti(OCH$_3$)$_3$-MAO catalyst. The polymer obtained with the Cp*TiCl$_3$-MAO catalyst revealed signals at 4.0—4.1 ppm and 5.7—5.8 ppm based on olefinic proton for the structures of ~CH=CH–CHCl ~ and ~CH$_2$–CH=CH–CH$_2$Cl. A signal based on methyl proton was observed at 0.9 ppm.[17] This indicates that the elimination of HCl from the polymer and methylation of the polymer took place during the polymerization with the Cp*TiCl$_3$-MAO catalyst. Such signals were not detected in the ^{1}H NMR spectrum of the polymer obtained with the Cp*Ti(OCH$_3$)$_3$-MAO catalyst. The signal based on head–head structure[16] was not observed in the ^{1}H NMR spectrum. This indicates that the polymers obtained with the Cp*Ti(OCH$_3$)$_3$-MAO catalyst have no anomalous structures. The polymers, thus, consist of repeating regular –CH$_2$–CHCl– units.

Since the Cp*Ti(OCH$_3$)$_3$-MAO catalyst was found to give a high polymer consisting of only regular structure, the polymerization of VC with the Cp*Ti(OCH$_3$)$_3$-MAO
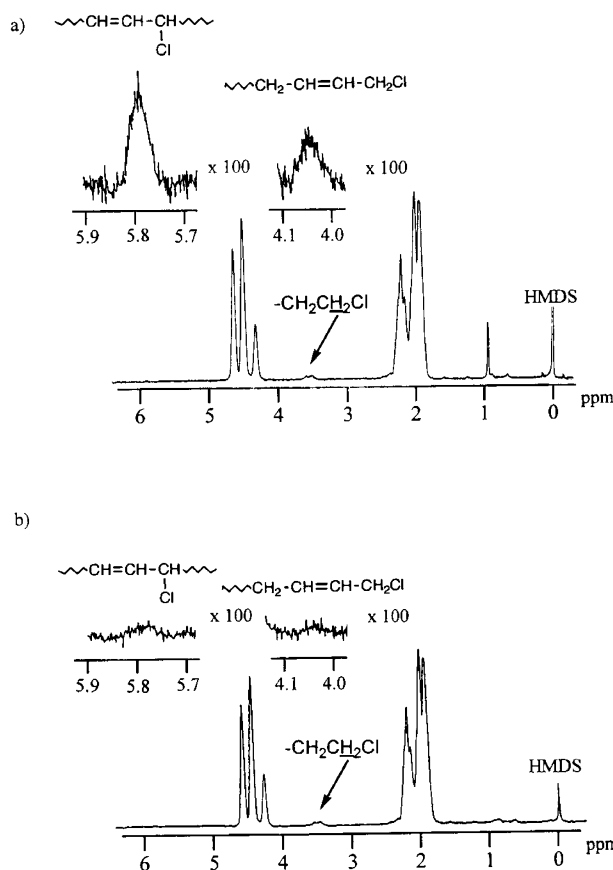
catalyst was further investigated. Figure 2 shows kinetic curve for the polymerization of VC with the Cp*Ti (OCH$_3$)$_3$-MAO catalyst. Polymer yields and M_n increased as a function of reaction time. The GPC elution curves of the polymers were unimodal and polydispersities were 1.8—2.0, suggesting the polymerization to proceed at a single active site.

Figure 3 shows the effects of MAO/Ti mole ratios on the polymerization of VC with the Cp*Ti(OCH$_3$)$_3$-MAO catalyst. Polymer yields were strongly dependent on the MAO/Ti molar ratio. An optimum condition for polymer yields was observed at the MAO/Ti molar ratio of about 10, which is in contrast to the polymerization of olefins with metallocene catalysts for which excess MAO is required to reach high activity.[6]

The tacticity of poly(vinyl chloride) (PVC) obtained with the Cp*Ti(OCH$_3$)$_3$-MAO catalyst in CH$_2$Cl$_2$ was determined from ^{13}C NMR spectroscopy. Pentad tacticity of PVC was determined from the intensity of methine carbon resonance in the main chain at 55.1—57.4 ppm according to the literature.[18] The results are listed in Table II. Tacticity obtained with α,α'-azobis(isobutyronitrile) (AIBN) is indicated for comparison. Pentad tacticity of the PVC obtained with the Cp*Ti(OCH$_3$)$_3$-MAO catalyst was somewhat different from that obtained with AIBN, but the high stereoregular PVC was not synthesized with the Cp*Ti(OCH$_3$)$_3$-MAO catalyst.

The polymerization of VC with the Cp*Ti(OCH$_3$)$_3$-MAO catalyst was carried out in the presence of radical inhibitors such as 2,2,6,6-tetramethylpiperidine-1-oxyl
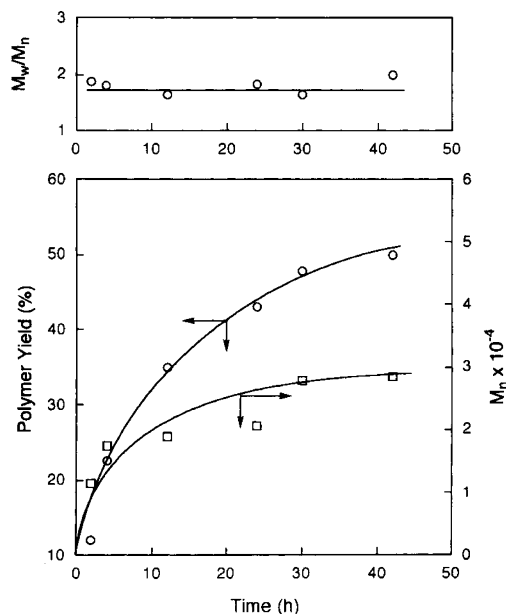
Figure 2. Kinetic curve for the polymerization of VC with the $Cp^*Ti(OCH_3)_3$-MAO catalyst in CH_2Cl_2 at $20\,^\circ\!C$: [VC] = 3.52 mol L^{-1}, $[Cp^*Ti(OCH_3)_3] = 5 \times 10^{-3}$ mol L^{-1}, MAO/Ti = 10 mole ratio.

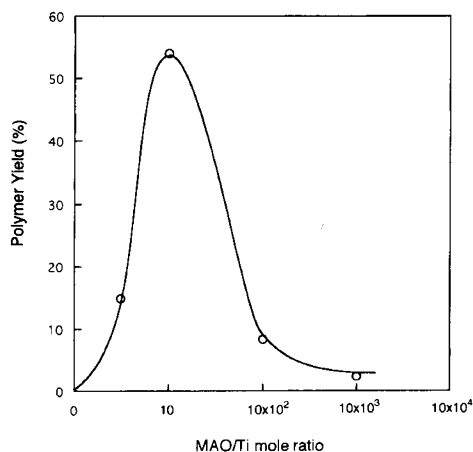**Figure 3.** Effects of MAO/Ti mole ratios on the polymerization of VC with the $Cp^*Ti\,(OCH_3)_3$-MAO catalyst in CH_2Cl_2 at $20\,^\circ\!C$: [VC] = 3.52 mol L^{-1}, $[Cp^*Ti\,(OCH_3)_3] = 5 \times 10^{-3}$ mol L^{-1}.

(TEMPO) and 2,6-ditert-butyl-cathechol. The results are shown in Table III. Even in the presence of the radical inhibitors, the polymerization was not inhibited, although polymer yields somewhat decreased. The polymerization of VC with the $Cp^*Ti(OCH_3)_3$-MAO catalyst did not proceed through radical mechanism. Thus, the polymerization of VC with the $Cp^*Ti(OCH_3)_3$-MAO catalyst may proceed through a coordination polymerization mechanism, A detail study is now underway to clarify the polymerization mechanism.

In conclusion, the Cp^*TiClX_3-MAO (X : Cl and OCH_3) catalysts initiated the polymerization of VC, although the polymerization rate was slow. The $Cp^*Ti(OCH_3)_3$-MAO catalyst in CH_2Cl_2 gave high molecular weight polymers in good yields. From elemental analysis and ^1H NMR spectra of the polymers, the $Cp^*Ti(OCH_3)_3$-MAO catalyst was found to give polymers consisting of repeating regular $-CH_2-CHCl-$ units.

Table II. Pentad tacticity of PVC

Catalyst	rr			mr			mm		
	mrrm	rrrm	rrrr	mmrm rmrr + rmm	rmrr + mmrr	mmmm	rmmm	rmmr
AIBN[b]	4.8	16.1	11.1	20.8	30.1	3.2	8.1	5.8
Cp*Ti(OCH₃)₃-MAO	13.6	15.0	6.3	34.3	15.2	6.1	6.3	3.3

[a] Sample No. 6 of Table I was used.   [b] Polymerized at $30\,^\circ\!C$.

Table III. Polymerization of VC with the $Cp^*Ti(OCH_3)_3$-MAO catalysts in the presence of radical inhibitors at $20\,^\circ\!C$ for 48 h[a]

Radical inhibitor	[inhibitor]/mol L^{-1}	Yield/%	$M_n \times 10^{-4}$	M_w/M_n
None	—	53	2.5	1.8
p-t-Butylcatechol	3.4×10^{-3}	40	2.3	1.9
TEMPO	3.4×10^{-3}	38	2.4	2.0

[a] [VC] = 3.52 mol L^{-1}, [Ti] = 3.4×10^{-3} mol L^{-1}, MAO/Ti = 10 mole ratio.

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