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Copolymerization of Vinyl Chloride and Ethylene with $Cp^*Ti(OCH_3)_3/MAO$ Catalyst

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Summary

Copolymerization of vinyl chloride (VC) and ethylene with $Cp^*Ti(OCH_3)_3/MAO$ catalyst was investigated. The $Cp^*Ti(OCH_3)_3/MAO$ catalyst initiated the copolymerization of VC with ethylene, although the copolymer yields were low. In the ^{13}C NMR spectra of the copolymers, the peaks based on junction part between VC and ethylene was observed, but the signals were small. From DSC measurement of the copolymers, only one glass transition temperature was observed. Thus, it is clear that the copolymerization with $Cp^*Ti(OCH_3)_3/MAO$ catalysts gave the copolymer, and the copolymer consisting of block sequence rather than random copolymer.

Introduction

A large amount of poly(vinyl chloride) (PVC) has been produced by radical polymerization. So far as radical polymerization is used for producing PVC, it is difficult to avoid the formation of anomalous units in the polymer chain, which causes thermal instability of PVC [1]. A precision polymerization of VC for producing polymer consisting of only regular head-to-tail structure seems to be an important factor from the view point of thermal stability of PVC. A low molecular weight plasticizer such as dioctyl phthalate for decreasing a glass transition temperature of PVC was used for production of soft PVC [2]. Copolymerization of VC with other monomers makes it possible to synthesize the internal plasticized PVC. In addition, the copolymerization is an effective way to improve physical properties of PVC, and gives useful information on polymerization mechanism for catalysts examined.

Copolymerization of VC and ethylene with radical initiators such as AIBN [3], BPO [4], R_3B/peroxide [5], and $AlEt_3/CuCl/CCl_4$ [6] has been reported to give a random copolymer. The copolymerization of VC with ethylene by Ziegler-Natta catalysts seems to be difficult by deactivation reaction between VC monomer and polymerization catalysts. Nevertheless, some challenging investigations on copolymerization of VC and ethylene with Ziegler-Natta catalysts have been investigated [7]. Misono and coworkers examined copolymerization of VC and ethylene with $Ti(n\text{-}BuO)_4$ in combination with $EtAlCl_2$ or Et_2AlCl [8], and stated that the copolymer composition and copolymer yield were depended strongly on the Al/Ti mole ratios, while random copolymer was obtained at lower Al/Ti molar ratios. The copolymer composition curve was also different from that obtained with radical initiators. By addition of donor compounds such as THF and Et_3N to the catalyst, the activity for the copolymerization of VC and ethylene increased, and an anionic mechanism was suggested. Similarly, $VO(OEt)_3/Et_xAlCl_{x-3}$ catalysts gave copolymers consisting of VC and ethylene units [9].

Metallocene catalysts are known to be able to initiate polymerization of polar vinyl monomers such as methyl methacrylate [10]. Although polymerization of VC with Zr-based metallocene catalysts was reported to give atactic polypropylene owing to polymerization of propylene produced by β-chloride elimination during the polymerization of VC [11], $Cp^*Ti(OCH_3)_3/MAO$ (Cp^* indicates pentamethyl cyclopentadienyl group) catalyst gave a high molecular weight PVC in a good yield by selecting ligands of the titanium that is less electron-withdrawing than halogens and MAO instead of alkylaluminums [12]. Since the $Cp^*Ti(OCH_3)_3/MAO$ catalyst initiate polymerization of ethylene [13], copolymerization of VC and ethylene with $Cp^*Ti(OCH_3)_3/MAO$ catalyst will be expected to induce to give copolymers. In addition, it will be also possible to elucidate polymerization mechanism for polymerization of VC with $Cp^*Ti(OCH_3)_3/MAO$ catalyst. From these points, we investigated the copolymerization of VC and ethylene with $Cp^*Ti(OCH_3)_3/MAO$ catalyst. In this article, we report on the copolymerization of VC and ethylene with $Cp^*Ti(OCH_3)_3/MAO$ catalyst.

Experimental

Materials

VC purchased from Sumitomo Fine Chem. Co. was used after distillation over CaH_2. Commercially available ethylene was used after passed through a aluminum column. $Cp^*Ti(OCH_3)_3$ purchased from Strem Chem. Inc. was used without further purification, and was used after dilution with CH_2Cl_2. Pure MAO kindly supplied from Tosoh Co. was used without further purification as toluene solution. Other reagents were used after purification by conventional methods.

Copolymerization Procedure

Copolymerization was carried out in a 300 cm^3 glass reactor equipped with a stirrer and connected to a vacuum line. The required amounts of CH_2Cl_2 (40 mL), $Cp^*Ti(OCH_3)_3$ diluted with CH_2Cl_2 (3.4×10^{-3} mol/L) and MAO (3.4×10^{-2} mol/L) were charged in this order into the glass reactor by syringe through a rubber septum under nitrogen atmosphere. VC (400-80 mmol) was, then, introduced into the glass reactor at –78°C by vacuum distillation over CaH_2. After charging VC, ethylene (20 mmol) was admitted into the glass reactor. After the copolymerization, the contents of the glass reactor were poured into a large amount of methanol containing a few percent of hydrochloric acid to precipitate the copolymer formed. The precipitate was collected by filtration and washed well with an excess of methanol. The resulting copolymer was dried under vacuum at room temperature. Copolymer yields were determined by gravimetry.

Characterization of copolymer

The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the copolymer were estimated by GPC using a Waters 150 CV in *o*-dichlorobenzene at 120°C calibrated as polystyrene standards. The copolymer composition was determined by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H- and ^{13}C-NMR spectra were taken using a JEOL A-400 spectrometer in C_6D_6/*o*-dichlorobenzene (3/7 volume ratio) at 120°C with hexamethyl disiloxane as an internal standard. DSC measurement was conducted using a SEIKO EXSTAR 6000 instrument with a heating rate of 10°C/min, and a nitrogen purge was maintained over the samples during the measurement.

Results and discussion

Copolymerization of VC and Ethylene

Copolymerization of VC and ethylene with $Cp^*Ti(OCH_3)_3$/MAO catalyst was conducted, and the results are listed in Table 1. The copolymerization of VC and ethylene with the $Cp^*Ti(OCH_3)_3$/MAO catalyst gave a white powder polymer with high molecular weight, although the copolymer yields were low regardless of VC content in the feed. We conducted the copolymerization under the optimum conditions for the polymerization of VC as reported previously [12], but not for ethylene polymerization that required a large amount of MAO is needed to reach high activity for the polymerization [13]. As a result of the copolymerization under such conditions, the obtained copolymer was rich in VC content, but the copolymer composition did not change significantly by changing the VC content in the feed. On the other hand, the copolymer yields increased with an increase of VC concentration in the feed

Table 1 Copolymerization of VC with Ethylene with $Cp^*Ti(OCH_3)_3$/MAO in CH_2Cl_2 at 20°C for 24h [a)]

Run No.	[VC] in Comonomer (mol %)	Copolymer			
		Yield (g)	[VC] in Copolymer (mol %)	$M_n \times 10^{-4}$	M_w/M_n
1	100[b)]	1.10	100	2.5	2.0
2	95	0.23	78	6.1	1.5
3	90	0.21	74	2.9	1.4
4	80	0.10	72	1.5	1.6
5	0	trace	---	--	---

[a] Ethylene = 20 mmol, [Ti] = 3.4×10^{-3} mol/L, MAO/Ti = 10 mol ratio

[b][VC] =3.5 mol/L.

The copolymer composition curve obtained from the copolymerization of VC and ethylene with $Cp^*Ti(OCH_3)_3$/MAO is depicted in Figure 1, in which the previously reported results for that obtained with benzoyl peroxide (BPO) [4] is also indicated to comparison. The copolymer composition curve for the copolymerization of VC and ethylene with the $Cp^*Ti(OCH_3)_3$/MAO catalyst was different from that obtained with radical initiators [3,4], which is consistent with the previously reported results for the copolymerization with $Ti(n\text{-}BuO)_4/Et_xAlCl_{x-3}$ catalysts [8]. This suggests that the copolymerization of VC and ethylene with the $Cp^*Ti(OCH_3)_3$/MAO catalyst seems to be excluded through a radical mechanism, and an ionic mechanism seems to be suggested.

The copolymer obtained with the Cp*Ti(OCH_3)$_3$/MAO catalyst did not dissolve in THF, suggesting that the resulting copolymer does not contain homopolymer of VC. Then, the GPC measurement was carried out in *o*-dichlorobenzene at 120°C. Figure 2 shows the typical elution curve of GPC for the copolymer obtained from copolymerization of VC and ethylene with the Cp*Ti(OCH_3)$_3$/MAO catalyst (run no. 4). The elution curve was unimodal and the value of M_w/M_n of the copolymer was 1.6. Similar elution curves were also observed for other copolymers and the M_w/M_n of the copolymers is below 2.0 regardless of the VC contents in the feed as listed in Table 1. This suggests that the copolymerization of VC and ethylene with the Cp*Ti(OCH_3)$_3$/MAO catalyst proceeds at a single site.

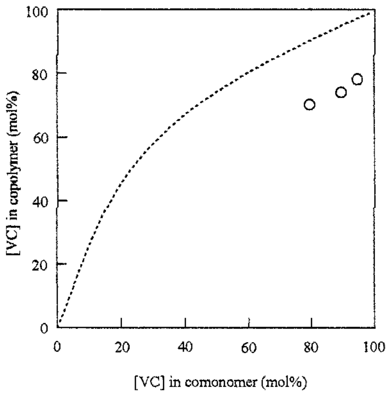

Figure 1. Copolymer composition curve for the copolymerization of VC with ethylene with (1) Cp*Ti(OCH_3)$_3$/MAO (O), (2) BPO (----).

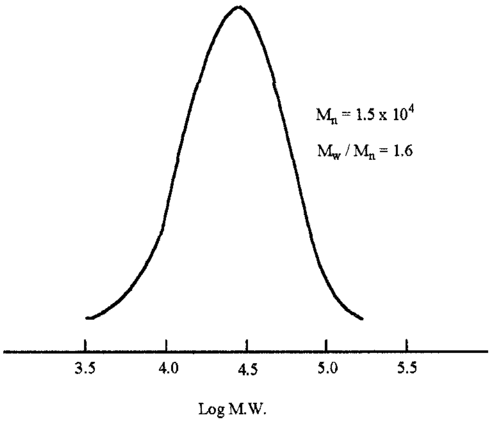

Figure 2. GPC elution curve of the copolymer of VC and ethylene (run no. 4): Measured at 120℃ in *o*-dichlorobenzene.

Structure of Copolymer

Copolymerization of vinyl monomer and olefin with transition metal catalysts sometimes gave a homopolymer mixture. To elucidate this point, the structure of the copolymer obtained from the copolymerization of VC and ethylene with the Cp*Ti(OCH_3)$_3$/MAO catalyst was analyzed by ^{13}C-NMR spectroscopy. The internal double bond introduced surely in the chain in the case of radical polymerization of VC [14] was not observed in alkenes region. This was confirmed by ^{1}H NMR spectra of the copolymers. If the copolymer contains internal double bond, they will appear at 4.0~4.1 ppm and 5.7~5.8 ppm due to olefin protons to the structures of ~CH=CH-C$\underline{H}_2$Cl~ and ~CH_2-CH=C$\underline{H}$-CHCl-, respectively [15]. However, such signals were not observed on the ^{1}H NMR spectra of the copolymers.

Figure 3 shows the expanded ^{13}C NMR spectrum of copolymer obtained from copolymerization of VC and ethylene with Cp*Ti(OCH_3)$_3$/MAO catalyst. The signals appeared at 45~48 ppm, 55~58 ppm as main peaks, based on methine and methylene carbon of PVC units and 29~30 ppm based on methylene carbon of ethylene units. In addition, the signals assigned to the junction part of VC and ethylene unit were observed as shown in Figure 3. These signals were in an agreement with the calculated value [16]. However, the peak intensity of the junction part is small as compared with that of VC or ethylene units. Namely, copolymer with block sequence is suggested.

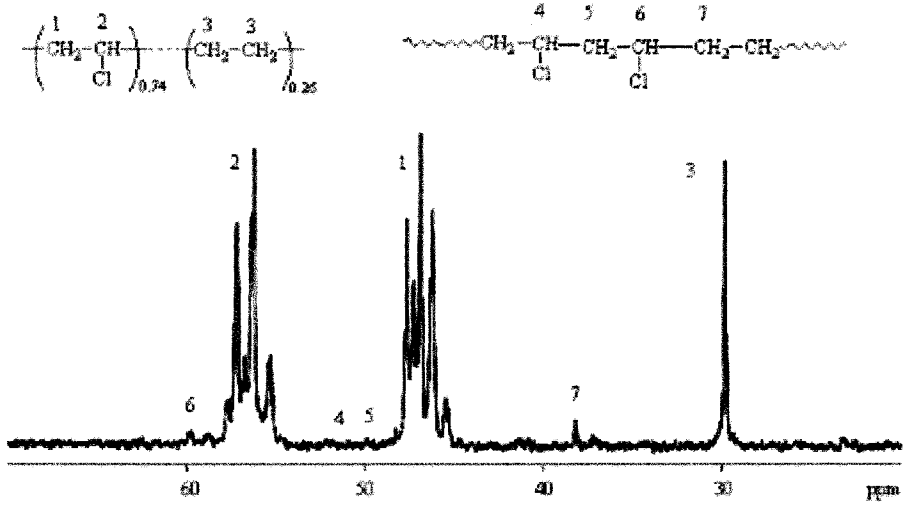

Figure 3. ^{13}C-NMR spectrum of copolymer of VC and ethylene (run no.4) measured at 120°C in C_6D_6/o-dichlorobenzene

If the product obtain from copolymerization of two monomers is not a homopolymer mixture, only one glass transition temperature (T_g) will be observed. To clarify this point, the T_g was determined from DSC measurement. Figure 4 shows the DSC curve of the copolymer obtained from copolymerization of VC and ethylene with the $Cp^*Ti(OCH_3)_3$/MAO catalyst (run no.4). Only one T_g for the copolymer was observed at 78.3°C. This value was lower than that of the copolymer with similar molecular weight and copolymer composition obtained with radical initiator (T_g = 83.4°C). Thus, we presumed that the copolymer obtained from the copolymerization of VC and ethylene with the $Cp^*Ti(OCH_3)_3$/MAO consists of the block sequence of both monomers rather than random sequence.

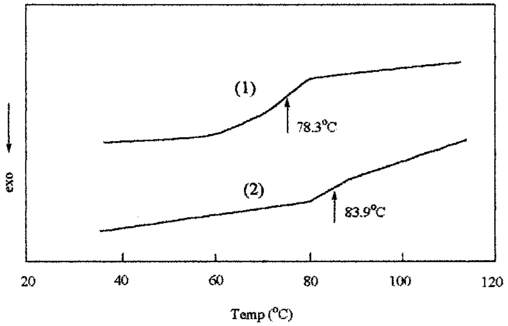

Figure 4. DSC chart of copolymer of VC and ethylene with (1) radical copolymerization ([VC] = 65mol %), and (2) with $Cp^*Ti(OCH_3)_3$/MAO catalysts (run no. 4)

In conclusion, the $Cp^*Ti(OCH_3)_3$/MAO catalysts were found to initiate the copolymerization of VC with ethylene, although the polymerization rate was slow. The copolymer obtained from the copolymerization with the $Cp^*Ti(OCH_3)_3$/MAO catalysts have block sequences.

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