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입체규칙성이 다른 Ziegler-Natta 촉매에 의한 올레핀의 삼원 공중합

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Olefins Terpolymerization with Ziegler-Natta Catalysts of Different Stereoregularity

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요 약: 고입체규칙성 촉매와 비입체규칙성 촉매를 이용하여 프로필렌/1-헥센/1-헥사데센 삼원공중합을 행하였다. 고입체규칙성인 Solvay $TiCl_3$-Cp_2TiMe_2를 사용한 삼원공중합에서 1-헥센과 1-헥사데센의 단량체 공급비가 증가할 때 중합속도가 가속화되고 삼원공중합체 내의 1-헥센 및 1-헥사데센의 함량이 증가하였다. 반면에 비입체규칙성 $MgCl_2$/$TiCl_3$-TEA 촉매계를 사용한 경우에는 공단량체가 첨가됨에 따라 촉매활성과 공단량체의 함량이 감소하였다. 이러한 결과를 단량체 확산의 개념으로 설명하였다.

ABSTRACT: Terpolymerizations of propylene/1-hexene/1-hexadecene had been carried out with high-isospecific and nonisospecific catalysts. For high-isospecific Solvay $TiCl_3$-Cp_2TiMe_2 catalyst system, polymerization rate accelerated and incorporation of 1-hexene and 1-hexadecene in terpolymer increased when feed ratio of 1-hexene and/or 1-hexadecene increased. In contrast, catalyst activity and comonomers content decreased with addition of comonomers for nonisospecific $MgCl_2$/$TiCl_3$-TEA catalyst system. These phenomena might be explained with the concept of monomer diffusion limitation.

Keywords: *terpolymerization, Solvay $TiCl_3$-Cp_2TiMe_2, $MgCl_2$/$TiCl_3$-TEA.*

INTRODUCTION

Copolymerization and terpolymerization of olefins are important methods in the manufacturing of polyolefin products. For copolymerization of olefins, it was well-known that rate enhancement can be observed due to the presence of a small amount of comonomer,[1-4] which is called as "comonomer effect" by Chien et al.[5] The reason of rate enhancement is one of the unsolved problems in the fields of Ziegler-Natta polymerization of olefins, but one possible explanation is based on the monomer diffusion limitation through high crystalline polymer layer to active site.[6-8]

If monomer diffusion limitation is one reason of rate enhancement, the effect of comonomer could be dependent on the crystallinity(i.e., tacticity) of polymers produced by catalysts of different isotacticity. In other words, not only catalyst activity but polymer composition may be depen-

dent on stereoregularity of catalysts.

From the previous studies, it had been found that Solvay $TiCl_3$-Cp_2TiMe_2 catalyst system[9] gave very high isotactic ([mmmm]=98.7) polypropylene (PP) while $MgCl_2$/$TiCl_3$-triethylaluminum (TEA) catalyst system[10] produced totally atactic PP.

In this study, terpolymerizations of propylene/1-hexene/1-hexadecene were carried out with high-isospecific Solvay $TiCl_3$-Cp_2TiMe_2 and nonisospecific $MgCl_2$/$TiCl_3$-TEA catalyst systems. The catalyst activity and polymer composition were examined, and results were correlated with the isospecificity of catalyst systems.

EXPERIMENTAL

Materials. Propylene was purified by passing through NaOH and P_2O_5 columns. Commercial 1-hexene and 1-hexadecene were purified by the usual procedures. Solvay $TiCl_3$ (from Showa Denko Co.) was used without further treatment. Cp_2TiMe_2 was prepared according to the reported procedures,[11] diluted into 0.25 mol/dm^3 of heptane and stored as stock solution. Nonisospecific $MgCl_2$/$TiCl_3$ catalyst was obtained with the method described previously.[10]

Terpolymerization. Terpolymerization was carried out in a 200 cm^3 glass reactor equipped with a magnetic stirrer. 1.0 mol of $TiCl_3$ was suspended in 92 cm^3 of heptane and comonomer (1-hexene and/or 1-hexadecene) under nitrogen atmosphere. After the temperature was raised to 40 ℃, propylene was saturated with continuous flow under a total pressure of 1 atm and 2.0 mmol of Cp_2TiMe_2 (8 cm^3 of heptane solution) was added to start the polymerization. The concentration of propylene in heptane was calculated according to Henry's equation quoted by Kissin.[12] Polymerization was conducted at 40 ℃ for 15 min and terminated by adding a dilute hydrochloric acid solution in methanol. The precipitated polymer was adequately washed and dried in vacuum.

Characterization of Polymers. The composition of polymers were determined by ^{13}C-NMR, according to the method reported by Randall et al.[13] ^{13}C-NMR spectra were recorded on a JEOL FX-100 spectrometer operating at 25.14 MHz or JEOL GX-270 spectrometer operating at 67.20 MHz under proton decoupling in the Fourier Transform (FT) mode. Instrument conditions were $\pi/4$ pulse of 9.0 s, 8.0 s repetition time. Sample solution of polymer was prepared at a concentration of 10 g/dL in 1,2,4-trichlorobenzene/benzene-d_6 (vol. ratio 3:1) mixture with internal hexamethyldisiloxane.

RESULTS AND DISCUSSION

To study the comonomer effect for catalysts having different isospecificity, terpolymerization of propylene (C_3)/1-hexene (C_6)/1-hexadecene (C_{16}) had been carried out with high-isospecific Solvay $TiCl_3$-Cp_2TiMe_2 and nonisospecific $MgCl_2$/$TiCl_3$-TEA catalyst systems. The catalyst activity and polymer composition had be examined and correlated with isospecificity of catalysts.

With high-isospecific Solvay $TiCl_3$-Cp_2TiMe_2 catalyst system, catalyst activity and polymer composition for terpolymerization of C_3/C_6/C_{16} were compared with those of C_3/C_6 copolymer as shown in Table 1.

As shown in Table 1, the catalyst activity of C_3/C_{16} copolymer was smaller than that of C_3 homopolymer due to the presence of C_{16} and content of C_{16} in copolymer was found to be small. For 1.00/0.22 feed mole ratio of C_3/C_{16}, the catalyst activity decreased in a great extent and comonomer effect could not be observed due to the some amount of C_{16}. The rate enhancement could be observed in the presence of only a small amount of C_6 (0.04 mole/L).[7]

Table 1. Catalyst Activity and Polymer Composition for High-isospecific Solvay $TiCl_3$-Cp_2TiMe_2 Catalyst System

Monomers	Concentration (mol/L)	Feed ratio (mole ratio)	Activity (g-polymer/ g-Ti-hr)	Polymer composition (mol%)
C_3	0.45	–	111.9	–
C_3/C_{16}	0.45/0.10	1.00/0.22	13.4	99.5/0.5
$C_3/C_6/C_{16}$	0.45/0.04/0.10	1.00/0.09/0.22	22.1	97.3/1.2/1.5
	0.45/0.10/0.10	1.00/0.22/0.22	134.0	93.3/3.1/3.6
	0.45/0.04/0.20	1.00/0.09/0.44	160.3	94.9/1.2/3.9

With more addition of a small amount of C_6 to the C_3/C_{16} copolymerization system, catalyst activity increased more than half to show the comonomer effect. Surprisingly C_{16} content became 3 times larger than that in C_3/C_{16} copolymer.

By increasing C_6 feed ratio more than 2.5 times, catalyst activity increased up to 6 times and C_6 content increased upto 2.5 times as expected. In addition, C_{16} content increased more than double in spite of unchanged feed ratio of C_{16}.

On the other hand, double increment of C_{16} with fixed amount of C_6 resulted in remarkable increase of catalyst activity as well as unexpected high C_{16} content while C_6 content is almost unchanged.

The above unexpected results could be explained with consideration that the higher α-olefin comonomer has the less diffusivity through crystalline polymer layer to active site due to its bulkiness.

For noncrystalline polymer layer produced by nonisospecific catalyst, it could be expected that monomer diffusion limitation may be less serious and the comonomer effect is not observed.

To check the above expectation, terpolymerization was also carried out with nonisospecific catalyst system and the results were shown in Table 2.

Compared with copolymerization behaviors of

Table 2. Catalyst Activity and Polymer Composition for Nonisospecific $MgCl_2/TiCl_3$-TEA Catalyst System

Monomers	Concentration (mol/L)	Feed ratio (mole ratio)	Activity (g-polymer/ g-Ti-hr)	Polymer composition (mol%)
C_3	0.45	–	6000	–
C_3/C_{16}	0.45/0.10	1.00/0.22	1169	99.5/9.5
$C_3/C_6/C_{16}$	0.45/0.04/0.10	1.00/0.09/0.22	459	96.2/2.4/1.4

high-isospecific catalyst system, the catalyst activity decreased in a great extent by adding C_{16} comonomer while comonomer content was larger due to its less difussion limitation. By further addition of C_6, the catalyst activity decreased remarkably and C_{16} content became less due to its lower reactivity. In addition, C_6 content was larger than C_{16} content due to its smaller size even if the feed ratio of C_6 was smaller.

To confirm the rate enhancement of comonomer, C_3 feed flow rates corresponding to polymerization rates had been measured for different C_6 and/or C_{16} contents with high-isospecific catalyst system and given in Fig. 1.

The polymerization rate increased slightly with addition of small amount of C_6 and/or C_{16} and

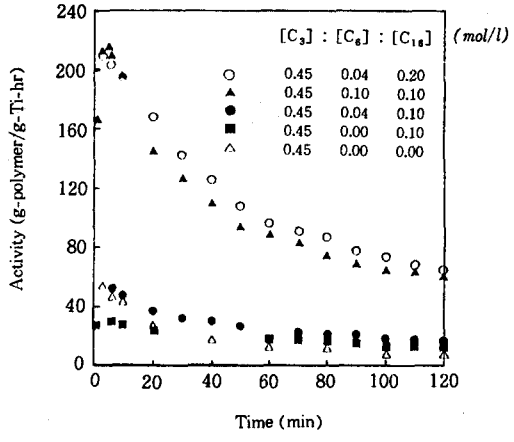

Figure 1. Effect of feed olefin compositions on rate profile of polymerization using high-isospecific Solvay $TiCl_3$-Cp_2TiMe_2 catalyst system.

rate enhancement was profound for larger addition of comonomers. The polymerization rate profile was found to be decay-type and the decay was accelerated by the more addition of C_6 and/or C_{16}. The reason of accelerated decay with addition of C_6 and/or C_{16} is not clear yet, but this phenmomenon might be a supporting evidence for the idea of monomer diffusion limitation.

CONCLUSION

For terpolymerizations of propylene/1-hexene/1-hexadecene with high-isospecific Solvay $TiCl_3$-Cp_2TiMe_2 catalyst system and nonisospecific Mg Cl_2/$TiCl_3$-TEA catalyst system, the followings had been found; (1) For high-isospecific catalyst system, catalyst activity and incorporation of 1-hexene and 1-hexadecene in terpolymer increased with feed ratio of 1-hexene and/or 1-hexadecene. (2) For nonisospecific catalyst system, catalyst activity and comonomers content decreased with addition of comonomers. (3) For high-isospecific catalyst system, polymerization rate increased and rate decay accelerated with addition of 1-hexene and/or 1-hexadecene.

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