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Short Communication

POLYMERIZATION OF PROPYLENE OVER SOLVAY/Cp_2TiMe_2 CATALYST

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Abstract—Propylene polymerization behavior of a highly isospecific catalyst, Solvay/Cp_2TiMe_2, was investigated. Polypropylene from the Solvay/Cp_2TiMe_2 system showed higher I.I% with less dependence on reaction temperature than that produced from the Solvay/DEAC system.

Key words: *Propylene Polymerization, Solvay Catalyst, Cp_2TiMe_2, Isotacticity, Morphology*

INTRODUCTION

Recent researches on propylene polymerizing catalysts have focussed on the development of catalysts producing polypropylene of high impact strength or of high stiffness. Higher stiffness of polypropylene by enhancing the stereoregularity can improve the mechanical properties of the polymer to the value of the general purpose engineering plastics and wide applications of the polypropylene can be achieved. Stiffness of polypropylene is closely related with crystallinity and a high isospecific catalyst suitable for this purpose should be developed.

Solvay/Cp_2TiMe_2 catalyst, known as one of the most isospecific catalysts was developed initially by Soga et al. They tested this catalyst system for propylene polymerization [Sun and Soga, 1989], ethylene/styrene copolymerization [Soga et al., 1988], propylene/styrene copolymerization [Soga and Yanagihara, 1989] and polymerization of other α-olefins [Soga and Yanagihara, 1988; Soga et al., 1990].

In this study, the Solvay/Cp_2TiMe_2 catalyst was prepared with Cp_2TiMe_2 and Solvay lynx-900. Solvay lynx-900 contained extremely small quantity of polypropylene through prepolymerization. Propylene polymerization behavior of the catalyst together with properties of the produced polypropylene was explored in detail.

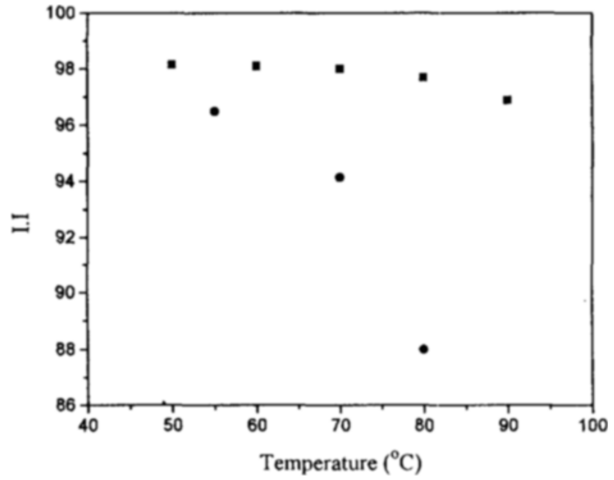


Fig. 1. Effect of polymerization temperature on I.I.% of polypropylene produced over Solvay/Cp_2TiMe_2 (■) and Solvay/DEAC (●) system.
$[Cp_2TiMe_2]/[Solvay]=1.0$, $[DEAC]/[Solvay]=10.0$
Polymerization time : 2 hours
Polymerization pressure : 6 atm

EXPERIMENTAL PART

Solvay type catalyst was the commercially available Solvay lynx-900. Cp_2TiCl_2 and MeLi (Aldrich Chemical Co, U.S.A), n-pentane (Janssen Chimica, Belgium) and DEAC were used as supplied. n-Heptane (Katayama Chemical Co, Japan), toluene and diethylether (Ducksan Chemical Co, Korea) were purified twice in a recycling distillation system under nitrogen atmosphere with sodium metal and benzophenone.

Cp_2TiMe_2 was synthesized from Cp_2TiCl_2 and MeLi according to the procedure reported by Clauss and Bestian [1962]. Polymerization was carried out in an 1 L autoclave. 600 ml of heptane was added to the autoclave followed by serial injection of heptane solutions containing Solvay catalyst and Cp_2TiMe_2 respectively.

Polymerization was started by introduction of propylene gas to an appropriate pressure. The polymer obtained was precipitated in a methanol-hydrochloric acid solution, washed with methanol several times and dried in vacuum at 50℃. Isotactic index of polypropylene was determined as the weight fraction of polymer insoluble in boiling heptane (I.I%).

Melting point of polypropylene was measured with a Perkin-Elmer DSC-7 at a heating rate of 10℃/min. The polymer was kept at 200℃ for 5 min and then cooled down to room temperature at 5℃/min to obtain the crystallization point.

RESULTS AND DISCUSSION

Isotactic index of polypropylene produced over Solvay/Cp_2TiMe_2 is compared with that obtained from Solvay/DEAC as shown in Fig. 1.

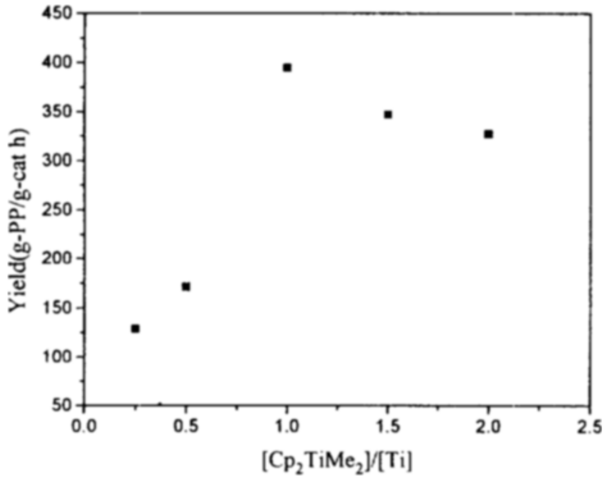


Fig. 2. Melting point from 1st scan DSC thermogram of polypropylene as a function of polymerization temperature.
Catalyst : Solvay/Cp_2TiMe_2 (■), Solvay/DEAC (●)
$[Cp_2TiMe_2]/[Solvay]=1.0$, $[DEAC]/[Solvay]=10.0$
Polymerization time : 2 hours
Polymerization pressure : 6 atm

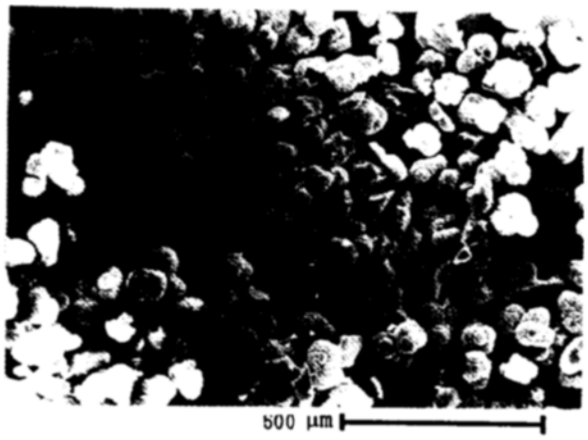
The former catalyst system produces polypropylene of higher I.I% than the latter one does. Effect of polymerization temperature on the I.I% appears less significant in the former case than in the latter one. Sun and Soga [1989] suggested a plausible model to explain the high isospecific character of the Solvay/Cp_2TiMe_2 catalyst: Cp_2TiMe_2 blocks the two vacant aspecific sites of the solvay catalyst leaving only one vacant isospecific site. It is generally known that the decrease in I.I% is due not only to the loss of stereoregularity but also to the production of lower molar mass polypropylene molecules at elevated polymerization temperatures.

The relationship between melting point of polypropylene synthesized over Solvay/Cp_2TiMe_2 and polymerization temperature is shown in Fig. 2. The melting point of polypropylene decreases somewhat as the polymerization temperature goes up from 50℃ to 90℃.

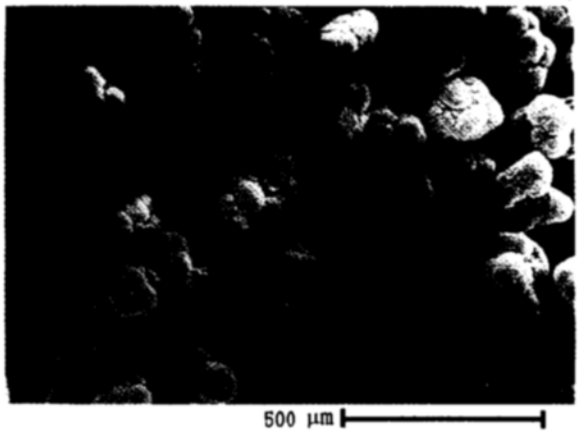
The solubility of the polypropylene in trichlorobenzene was too low to measure the molecular weight by a gel permeation chromatography. Therefore the molecular weight of the polymer obtained at higher polymerization temperatures seems to be high enough not to cause the decrease of the melting point as shown in Fig. 2. Instead, the slight reduction of stereoregularity at higher temperatures must be responsible for the decrease of the melting point.

In SEM micrographs (Fig. 3), it is worth mentioning that some interwound morphology of polypropylene produced at 90℃ is found. It is certain that this is not ascribed to melting of the polymer particles during the polymerization because the catalyst activity at that temperature as depicted in Fig. 4 is not high enough to cause the polymer to melt. The morphology in Fig. 4 does not have a coweb structure which is known to form as a result of the polymerization rate at the surface different from that in the interior of catalyst particle. It is thought to reflect trace of dissolution of molecules soluble in the hot n-heptane.

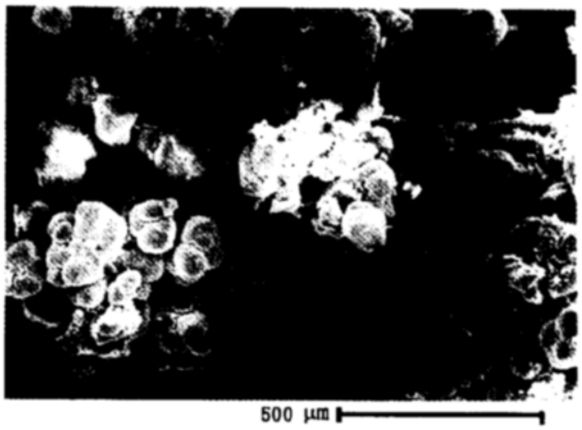
From the above results, it can be concluded that even the highly isospecific catalyst, Solvay/Cp_2TiMe_2, produces a slight quantity of stereoirregluar polypropylene molecules at higher polymerization temperatures and that the isotacticity of polypropylene depends not only on the structure of the active sites but also on the insertion rate of propylene molecules into the active sites in comparison with the migration rate of the polymer-transition metal bond.



(a) 50℃



(b) 70℃



(c) 90℃

Fig. 3. SEM micrographs (×80) of polypropylene produced over Solvay/Cp_2TiMe_2 at different temperatures.

The catalyst activity increases up to 80℃ and then drops abruptly with further increase of the polymerization temperature. The decrease of the polymerization rate results from deterioration of

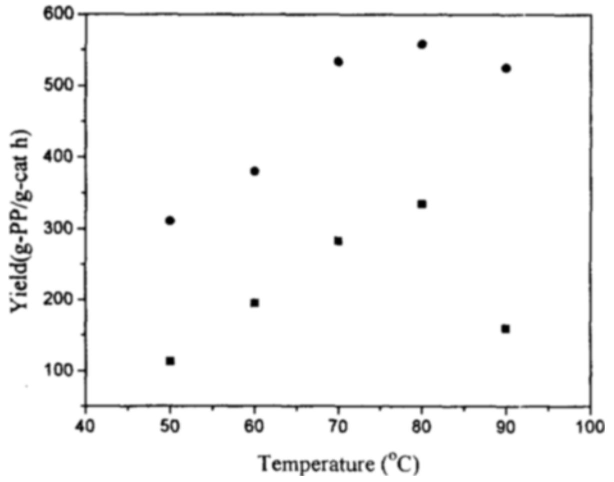


Fig. 4. Effect of polymerization temperature on the Solvay/Cp$_2$TiMe$_2$ catalyst activity.
Catalyst : Solvay/Cp$_2$TiMe$_2$ (■), [Cp$_2$TiMe$_2$]/[Solvay]=1.0, Solvay/DEAC (●), [DEAC]/[Solvay]=10.0
Polymerization pressure : 6 atm

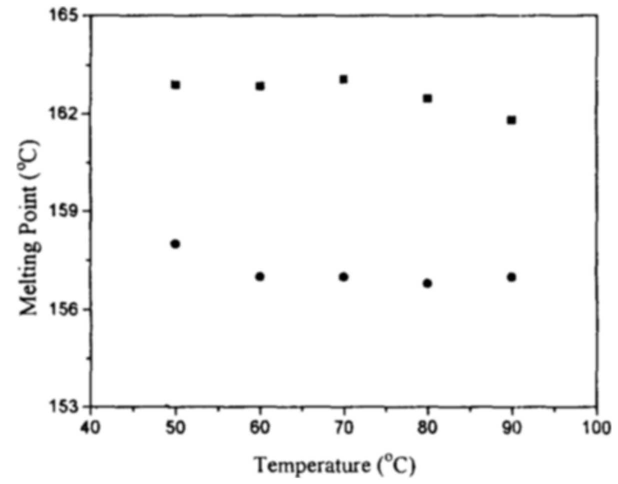


Fig. 5. Effect of [Cp$_2$TiMe$_2$]/[Solvay] on the catalyst activity.
Polymerization temperature : 70℃
Polymerization time : 2 hours
Polymerization pressure : 6 atm

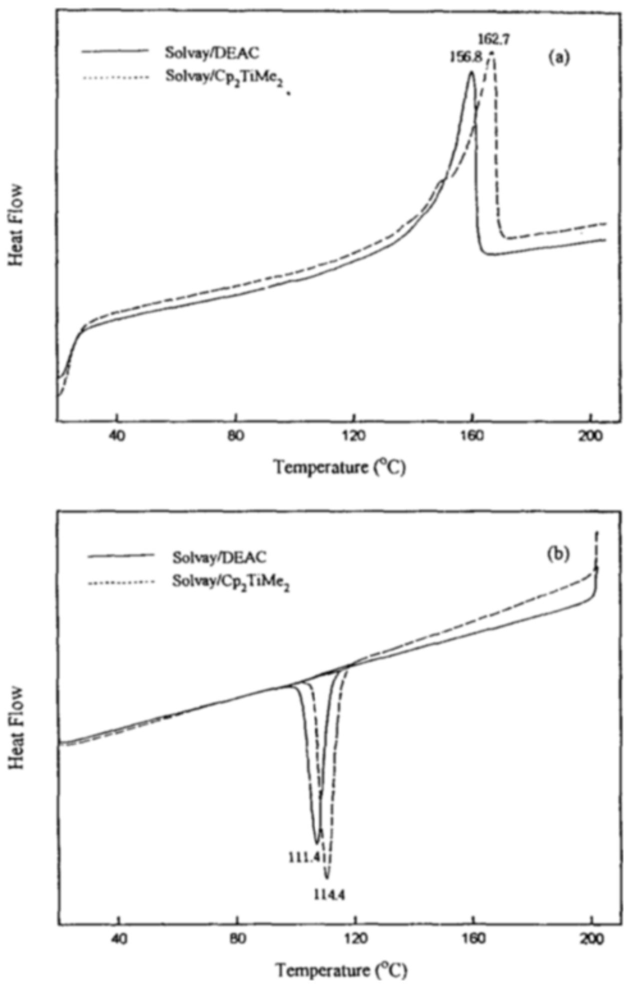


Fig. 6. DSC thermograms [(a) melting and (b) crystallization] of polypropylene prepared with Solvay/Cp$_2$TiMe$_2$ and Solvay/DEAC system.
[Cp$_2$TiMe$_2$]/[Solvay]=1.0, [DEAC]/[Solvay]=10.0
Polymerization temperature : 80℃
Polymerization pressure : 6 atm

the active sites and from reduction of monomer concentration at the catalyst surface due to increase of partial pressure of n-heptane molecules in the vapor phase as well as decrease of monomer solubility in the solution as the temperature rises because the polymerizations proceeded at a fixed total pressure.

Effect of Cp$_2$TiMe$_2$ concentration on the catalyst activity is shown in Fig. 5. The catalyst activity reaches a maximum at [Cp$_2$TiMe$_2$]/[Solvay]=1.0.

Fig. 6 demonstrates melting and crystallization temperatures of polypropylene made by Solvay/Cp$_2$TiMe$_2$ and Solvay/DEAC catalyst system, respectively. Polypropylene from Solvay/Cp$_2$TiMe$_2$ catalyst shows higher melting point (Fig. 2) and heat of fusion. It has also higher crystallization temperature and enthalpy of crystallization than that from Solvay/DEAC catalyst indicating the former polypropylene is more crystalline and more easily crystallizable than the latter one.

ACKNOWLEDGEMENT

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