CHEMISTRY LETTERS, pp. 833-836, 1973. Published by the Chemical Society of Japan

POLYMERIZATION OF α-OLEFINS WITH THE SUPPORTED ZIEGLER TYPE CATALYSTS; INFLUENCE OF THE CRYSTALLINE STRUCTURE OF THE CATALYSTS ON THE ISOTACTICITY OF POLYPROPYLENE

Kazuo SOGA*, Masahiro AKIYOSHI, and Tsutomu KAGIYA
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University * Present Adress; Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguro-ku, Tokyo 152

Various transition metal compounds were supported on magnesium hydroxide and propylene polymerization was carried out by using them as catalyst. The isotacticity of polypropylene was remarkably increased in comparison with that obtained with the use of carrier free catalyst, from which it has been concluded that the stereoregulation of polymer is mainly based on the crystalline structure of the catalyst not on the transition metal compound.

In the previous paper1), the present authors have examined the influence of the various supports mainly on the isotacticity of polypropylene by using $TiCl_4$ as a transition metal compound and found that some magnesium compounds such as $Mg(OH)_2$ and Mg(OH)Cl show the most excellent property as a support for the stereospecific polymerization catalyst.

In this paper, we have examined the influence of the transition metal compounds on the isotacticity of polypropylene with the use of $Mg(OH)_2$ as a support. The support, $Mg(OH)_2$, was prepared by heating a commercial GR-grade $Mg(OH)_2$ at 150°C for 4 hrs under vacuum. $TiCl_3(OBu^n)$ was synthesized from $TiCl_4$ and $Ti(OBu^n)_4$ according to the usual method. The supported catalysts were prepared as shown below. 3g portion of $Mg(OH)_2$ was placed in a three-necked 200 ml glass flask with a magnetic stirrer. After the flask was completely substituted with nitrogen, 25 ml portion of purified n-heptane and 20 g portion of each transition metal compound were added.

In the case of $TiCl_4$, the supported catalyst was also prepared by using only 1g portion of $TiCl_4$. The mixture was vigorously stirred at 98°C for 1.5 hrs under a nitrogen atmosphere. After most of the soluble part was syringed out, the precipitate was washed several times with n-heptane and then dried in a vacuum at room temperature overnight. As for the reactions of these transition metal compounds with $Mg(OH)_2$, some discussions were previously made1). Polymerizations of propylene were carried out at 50°C for 2 hrs with the same apparatus and procedures as reported in the previous paper1), by using 100 ml portion of n-heptane as solvent, ca 1g portion of each transition metal compound (with or without $Mg(OH)_2$), and 10 ml portion of $Al(C_2H_5)_3$ or $Al(C_2H_5)_2Cl$ (10 wt-% of n-heptane solution), by adding in this order.

The isotacticity of polypropylene was determined by high-resolution NMR. The NMR spectra were measured in 1.2.4-trichlorobenzene solutions (0.05 g/ml) at 100°C with a 220 MHz spectrometer. A typical NMR spectrum is shown in Figure 1. Figure 2 shows the calibration curve obtained by using commercial isotactic and syndiotactic polypropylene.

The values of the isotacticity calculated on the basis of Figure 2 are shown in Table 1. The isotacticity differs to some extent by changing the transition metal compound, however, it increases remarkably by using a $Mg(OH)_2$ support.

Taking into account that the crystalline structure of $Mg(OH)_2$ or Mg(OH)Cl is very close to that of α-$TiCl_3$, it can be said that the stereoregulation of the polymer is mainly based on the crystalline structure of the catalyst not on the transition metal compound used. The precise study is now in progress.

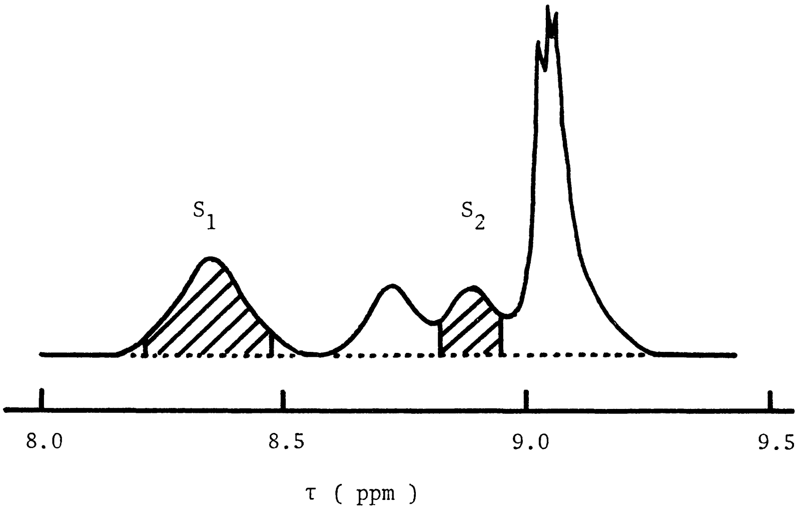

Figure 1 Typical NMR spectrum of polypropylene

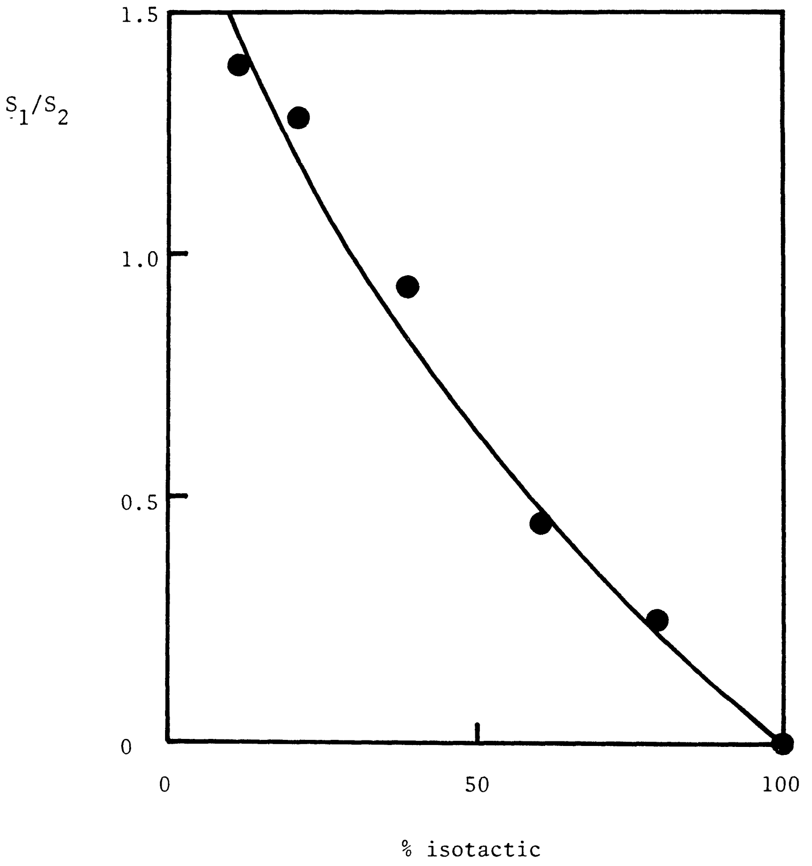

Figure 2 Calibration curve

Table 1 Isotacticity of polypropylene with various catalytic systems

Transition metal compound	Support	$Al(C_2H_5)_3$	$Al(C_2H_5)_2Cl$
$TiCl_4$	with (w)	60 (62*)	51
	without (w/o)	53	~0
$TiCl_3(OBu^n)$	(w)	40	36
	(w/o)	34	~0
$Ti(OBu^n)_4$	(w)	36	48
	(w/o)	~0	~0
VCl_4	(w)	53	45
	(w/o)	50	~0
$VOCl_3$	(w)	45	55
	(w/o)	~0	~0

* Catalyst was prepared by using only 1 g $TiCl_4$

Reference

1) Kazuo Soga, Satoshi Katano, Yoshiyuki Akimoto and Tsutomu Kagiya
Polymer Journal in press

(Received April 16, 1973)