CHEMISTRY LETTERS, pp. 425-428, 1982.

THE ROLE OF ADDITIVES ON THE IMPROVEMENT OF THE ISOTACTICITY OF POLYPROPYLENE —— A POSSIBLE INTERPRETATION

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Polymerization of propylene and isoprene were conducted with the catalytic systems of $TiCl_4/Al(C_2H_5)_3$ and $TiCl_4/MgCl_2/Al(C_2H_5)_3$ using ethyl benzoate and 2,2,6,6-tetramethylpiperidine as Lewis bases. With increasing the concentration of these Lewis bases, the stereospecificities increased toward more isotactic and more trans-1,4-addition. The role of Lewis bases on the stereospecificities was proposed based on the result.

Numerous publications, particularly in patent literatures, have recently claimed a number of additives (Lewis bases) for Ziegler-Natta catalysts to improve the isotacticity of polypropylene. Among the Lewis bases reported so far, ethyl benzoate (EB)[1) and 2,2,6,6-tetramethylpiperidine (TMPip)[2) seem to be most effective. These compounds easily react with titanium chloride ($TiCl_3$ or $TiCl_4$), $MgCl_2$ and $Al(C_2H_5)_3$ to form the corresponding complexes. Giannini et al. have recently prepared a single crystal of $TiMgCl_6(CH_3COOC_2H_5)_4$ from the reaction between $TiCl_4$, $MgCl_2$ and ethylacetate and determined the structure of the complex.[3) However, the complex doesn't show the activity for propylene polymerization, and it rapidly decomposes on adding $Al(C_2H_5)_3$. Kinetic studies of propylene polymerization using Lewis bases have shown that an increase in stereospecificity is often accompanied by a decrease in catalytic activity, especially in the case of supported catalysts.[4) On increasing the Lewis bases / $Al(C_2H_5)_3$ ratio, a dramatic decrease of the atactic fraction takes place, while the amount of isotactic polymer decreases only a very little, which seems to indicate that catalytic centers having different stereospecificities exist in the catalytic systems. From such a viewpoint, some authors have proposed the mechanism in which the isotacticity is controlled by the number of vacant sites in the catalytic centers. However, it seems very difficult to confirm the validity of the mechanism.

On the other hand, it is also well known in the polymerization of dienes by transition metal compounds that the change in stereoregularity depends very much on the type of bases used. The factors govering the stereoregularity of polydienes are still unknown. A tenable possibility is that geometric isomerism is controlled by the π-allylic polymer-metal bond with the syn-form favouring trans-polymerization and the anti-form cis-addition.5) Syn/anti-orientations would be dependent on the coordinating ability of the double bond nearest the π-allylic polymer end, i.e. the penultimate double bond. However, the possibility was denied by Furukawa based on the nmr study of π-crotyl nickel halides.6) Another suggestion most frequently made is that the stereoregularity of polymers is dependent on the conformation of the monomer complexed at the active site prior to insertion. Dawans and Teyssie7) have suggested that cis-1,4-polymer is obtained from s-cis-coordinated monomer while the trans-1,4-structure results from monomer coordination involving only one double bond with the molecule in its s-trans-form.

More recently, Tornqvist et al. have studied the polymerization of 1,3-butadiene in detail using the $TiCl_3 \cdot nAlI_3/Al(C_2H_5)_3$ system combined with THF and found that trans-1,4-addition becomes predominant with increasing the concentration of THF.8) The result has been explained as follows: cis-1,4-forming species have two vacant sites to which the diene monomer can coordinate in cisoid form. When a Lewis base is added, one of the vacant sites may first be blocked, which forces the monomer to coordinate via one double bond and add in a transoid conformation, and gives trans-1,4-polydiene in consequence.

From these standpoints, we have examined both propylene and isoprene polymerization with the catalytic systems of $TiCl_4/Al(C_2H_5)_3$ and $TiCl_4/MgCl_2/Al(C_2H_5)_3$ using EB and TMPip as Lewis bases.

The $MgCl_2$-supported $TiCl_4$ catalyst was prepared by grinding the mixture of $MgCl_2$ and $TiCl_4$ (1.80×10^{-3} mol $TiCl_4$/g-catalyst). Research grade propylene, isoprene, EB and TMPip were purified according to the usual procedures. Extra pure grade $TiCl_4$ and $Al(C_2H_5)_3$ were commercially obtained and used without further purification. Polymerizations of propylene and isoprene were conducted in a 100 ml stainless steel reactor equipped with a magnetic stirrer. The polymerizations were terminated by adding an excess of a dilute hydrochloric acid solution in methanol. The precipitates (polymers) were dried i. vac. at room temperature. The isotacticity of polypropylene and the microstructure of polyisoprene were determined by IR and ^{1}H NMR, respectively.

In Table 1 are shown the results obtained.

Table 1. Change in activity and stereospecificity as a function of the concentration of EB or TMPip.

Run No.	Additives (mmol)		Activity (g/g-Ti• h)		Iso-tacticity (%)	Microstructure (%)		
	EB	TMPip	C_3H_6 Total (Iso)	C_5H_8 Total (3,4- & trans-1,4-)		cis-1,4-	3,4-	trans-1,4-
1	0		530	220	60	91.8	2.9	5.3
2	0.025		190	280	75	87.7	1.8	10.5
3	0.25		27	340	77	82.4	4.0	13.6
4	0.40		7.0	30	86	63.4	0.4	36.2
5	0.50		4.9	13	89	29.2	3.0	67.8
6		0.10	89	110	77	80.2	2.7	17.1
7		0.25	79	50	85	68.7	4.5	26.8
8		0.50	40	67	87	20.5	5.0	74.5
9	0		3300 (1848)	260 (75)	56	71.1	2.6	26.3
10	0.01		4200 (2646)	250 (75)	63	70.0	3.4	26.6
11	0.04		3300 (2310)	130 (60)	70	53.7	3.5	42.8
12		0.04	4100	140	88	37.7	4.7	57.6
13	0.11		3100 (2449)	58 (38)	79	35.2	2.4	62.4
14	0.15		2900 (2465)	25 (17)	85	31.0	2.4	66.6

Polymerization was conducted at 65 °C by using (Runs No. 1-8) 0.5 mmol of $TiCl_4$ and 0.5 mmol of $Al(C_2H_5)_3$, (Runs No. 9-14) 0.10 g of the $TiCl_4/MgCl_2$ catalyst and 0.2 mmol of $Al(C_2H_5)_3$.

In Figures 1 and 2 are plotted the relation between the isotacticity and the cis-1,4-content. A marked increase in the isotacticity was accompanied by a remarkable decrease in the cis-1,4-content with both catalytic systems.

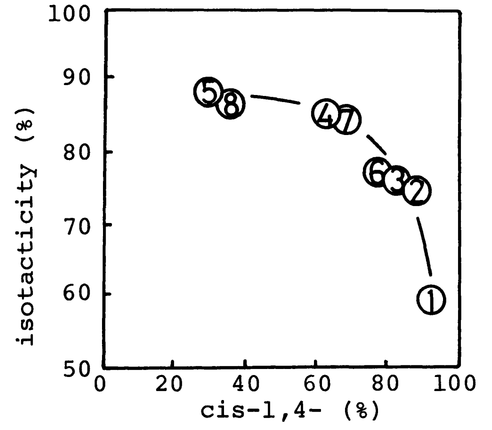

Fig. 1 Relation between the isotacticity and cis-1,4-content with $TiCl_4/Al(C_2H_5)_3$.

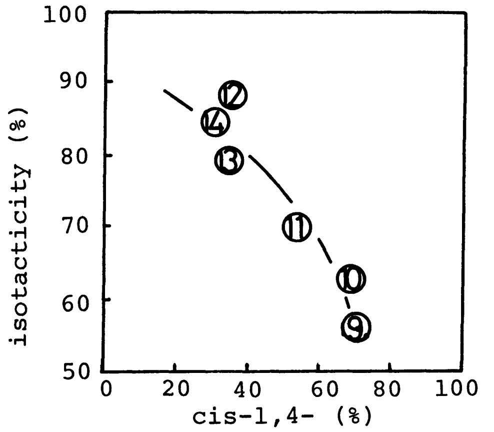

Fig. 2 Relation between the isotacticity and cis-1,4-content with $TiCl_4/MgCl_2/Al(C_2H_5)_3$.

From these results we propose the following mechanism for the stereospecific polymerizations of propylene and isoprene. There exist two types of active species. The species having two vacant sites give the atactic polypropylene and cis-1,4-polyisoprene, while the species having only one vacant site give the isotactic polypropylene and trans-1,4- or 3,4-polyisoprene. When a Lewis base such as EB or TMPip is added, one of the vacant sites of the former species may be blocked and consequently the species may become inactive or turn into the latter species. If the vacant site of the latter species is blocked, the species become inactive.

Such Lewis bases as EB and TMPip are known to form complexes with $Al(C_2H_5)_3$. Therefore it is not sure at present whether the vacant site is blocked by such a Lewis base or by the complex with $Al(C_2H_5)_3$. The activity of the latter species producing the isotactic polypropylene seems to be much less affected by a Lewis bases,$^{9)}$ which might be attributed to the difference in acidity between the two species.

Then, the change in activity by adding EB or TMPip is briefly discussed. In the case of the $TiCl_4/Al(C_2H_5)_3$ system, the activity producing polyisoprene significantly increased by the addition of a small amount of EB, while that producing polypropylene greatly decreased (c.f. Runs no 1, 2 and 3 in Table 1). On the other hand, in the case of the $TiCl_4/MgCl_2/Al(C_2H_5)_3$ system, the activity producing trans-1,4- or 3,4-polyisoprene decreased monotonously with an increase in the amount of EB, while that producing isotactic polypropylene clearly increased at first, followed by a slight decrease (for more details see Table 1). These inconsistent results in the activity cannot be explained at the present stage.

A more detailed study is now being carried out and the results will be reported in another paper.

References

1) Montedison S.P.A., Japan Pat. (Open), 48-16986 (1973); Mitsui Petrochemical Industries, Japan Pat. (Open), 50-126590 (1975).
2) A. W. Langer, T. J. Burkhard and J. J. Steger, "MMI International Symposium on Transition Metal Catalyzed Polymerization (Midland)", preprint, p 13 (1981).
3) E. Albizzati, J. C. J. Bart, U. Giannini and S. Parodi, "IUPAC International Symposium on Macromolecules (Florence)", preprint, vol. 2, p 40 (1980).
4) P. Pino and R. Mulhapt, Angew. Chem. Int. Ed. Engl., <u>19</u>, 857 (1980).
5) S. Ohtsuka, Kogyo Kagaku Zasshi, <u>68</u>, 776 (1968).
6) D. A. Dolgoplosk, "Polymerization of dienes by metal π-allyl complex", Nauka, Moscow, 1968, p 97.
7) F. Dawans and Ph. Teyssie, Organic Coatings and Plastics, Chemistry Division, ACS/CIC Meeting, Vol. 30, p 208, Toronto, 1970.
8) E. Torniqvist, C. Cozewith and W. F. Libby, "IUPAC International Symposium on Macromolecules (Florence)", preprint, vol. 2, p 79 (1980)
9) N. Kashiwa, "MMI International Symposium on Transition Metal Catalyzed Polymerization (Midland)", preprint, p 13 (1981)
T. Keii, ibid., p 6 (1981).

(Received November 9, 1981)