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STEREOSPECIFIC POLYMERIZATION OF PROPYLENE ON SYSTEMS TiX_3–$AlEt_3$

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Abstract—It has been shown that replacement of Cl atoms by I and Br atoms leads to decrease in the activity of the catalytis systems $TiCl_3$–$AlEt_3$ owing to decrease in the number of active centres. This decrease is probably due to the fact that a group of titanium atoms bound by halogen bridges, and not a single atom, is involved in the catalytis act. The most effective way of enhancing the isospecificity of the active centre is to induce the iodine-containing compound to act upon the $TiCl_3$ crystal surface. However, no simple correlation between the stereospecificity of the catalytis systems, ion radii of the anions and distances M-M and M-X was found.

INTRODUCTION

The stereospecificities of Ziegler–Natta systems are known to depend on the nature of the cocatalyst. The stereoregularity of polypropylene (PP) increases when a halogen-containing cocatalyst is used, as distinct from $AlEt_3$, according to the series

$$AlEt_2I > AlEt_2Br > AlEt_2Cl$$

Langer [1] assumed that the isotacticity of PP correlates with the stability of the complex between the alkyl metal and the active centre on the $TiCl_3$ surface. The decrease in the acidity of the cocatalyst in the series.

$$AlEt_2I > AlEt_2Br > AlEt_2Cl > AlEt_3$$

leads to destabilization of the complex in which the organometallic component of the catalytic system is the necessary constituent of the isospecific active centre.

According to Keii [2, 3] the interaction of I- or Br-aluminum-alkyl with $TiCl_3$ on the catalyst surface results in the replacement of the Cl atoms by I or Br to an extent corresponding to the number of active centres. In this case, an increase in the stereoregulating ability of the catalyst can be accounted for by the non-equivalence of the ligand surrounding of the Ti atom of the active centre; the greater the non-equivalence, the greater is the ion radius of the halogen atom.

It should be noted that an increase in the stereospecificity of the system is accompanied by a decrease in the polymerization rate. According to Danusso [4], the decrease in the relative polymerization rate of propylene for the catalytic systems $TiCl_3/AlEt_2X$ follows the scheme

$$AlEt_3(100) > AlEt_2Cl(33) \sim AlEt_2Br(33) > AlEt_2F(30) > AlEt_2I \quad (9)$$

Earlier, we showed [5, 6] that the stereoregulating ability of the catalytic systems decreases in the series:

$$\alpha\text{-}TiCl_3 \simeq \delta\text{-}TiCl_3 > CrCl_3 > VCl_3 > FeCl_3$$

(catalyst—$AlEt_3$; polymerization temperature, 70°). This effect may be due to decrease in the distances M-Cl and M-M in the MCl_3 lattice. However the range of the indicated distances is rather small to confirm the validity of this correlation. Generally, there is no correlation between the isospecificity of the active centres and the ion radius of the cation of the trihalogenides involved.

Study of the isospecificity of the catalytic systems on a TiX_3 base, where X = F, Cl, Br or I should help considerably to elucidate this problem.

The purpose of the present paper is to investigate the activity and stereospecificity of catalysts α-$TiCl_3$ and α-$TiBr_3$, β-$TiCl_3$ and β-TiI_3 as well as mixed titanium trihalogenides. Additionally, the catalyst α-$TiCl_3$ treated with titanium trichloride was also used.

Catalysts α-$TiCl_3$, α-$TiBr_3$ and β-TiI_3 were prepared by interacting the corresponding titanium tetrahalogenides with metallic Ti in quartz ampoules [7]. The substances precipitated as large crystals in the colder zones of the ampoules. Chemical analyses have shown that the compositions of titanium trichloride and titanium tribromide are close to stoichiometric (ratio Hal: Ti = 3.0 ± 0.5). For titanium triiodide the ratio I:Ti was 2.8 ± 0.1.

The synthesis of mixed titanium trihalogenides was also carried out in quartz ampoules by interacting the calculated quantities of $TiCl_4$, Ti and Br_2 (or I_2) at temperatures ranging from 500 to 600°. X-ray diffraction analysis has shown that the mixed trihalogenides are solid solutions based on the $TiCl_3$ structure. According to the chemical analysis of the mixed trihalogenide samples, the compositions of the compounds obtained can be expressed thus

$$Cl:Br:Ti = 2.85:0.15:1 \text{ and } Cl:I:Ti = 2.97:0.03:1$$

Analysis of the samples for halogen content was carried out by potentiometric titration using a pH-300 potentiometer equipped with a AgCl electrode.

Treatment of α-$TiCl_3$ with titanium trichloride was carried out at 70° for 40 min. Then the catalyst was washed with heptane and evacuated to remove unreacted $TiCl_3I$. The trichloriodide (liquid at room

Table 1. Stereoregularity of PP fractions

Exp. no.	Catalyst	Iso-fraction Weight (%)	Iso-fraction Macrotacticity M (%)	Iso-fraction D_{841}/D_{973}	Stereo-block fraction Weight (%)	Stereo-block fraction Macrotacticity M (%)	Stereo-block fraction D_{841}/D_{973}	Atactic fraction Weight (%)	Atactic fraction Degree of isotacticity (%)
1	α-$TiCl_3$	74.0	87	0.81	11.5	60	0.50	14.5	70
2	α-$TiBr_3$	75.9	87	0.82	4.3	—	—	19.7	75
3	α-$TiCl_{2.85}Br_{0.15}$	72.3	89	0.78	8.7	51	0.43	18.8	67
4	α-$TiCl_{2.97}I_{0.03}$	91.8	89	0.80	6.1	44	0.33	2.1	—
5	α-$TiCl_3$ treated $TiCl_3J$	73.0	93	0.90	2.5	—	—	24.5	72
6	β-$TiCl_3$	49.4	93	0.88	15.9	49	0.36	34.7	67
7	β-TiI_3	56.4	86	0.75	16.0	43	0.28	27.6	66

temperature) was obtained by mixing the stoichiometric amounts of $TiCl_4$ and TiI_4 [8].

To prepare β-$TiCl_3$, $TiCl_4$ was reduced with diethylaluminum chloride at room temperature, then washed with heptane and evacuated [9].

All the catalyst samples were ground in a ball mill for 10 min. The X-ray patterns of the samples before and after grinding were identical.

X-ray diffraction analyses of the catalyst samples were carried out with a DRON-2 X-ray diffractometer (Co-Kα-radiation, scanning speed—1°(2θ)/min).

The samples were ground in a dry chamber with paraffin oil, smeared on the ground cell and coated with a polystyrene film to prevent hydrolysis during exposure of the samples.

Fractionation of PP into isotactic, atactic and stereo-block fractions was carried out by ordinary extraction with cold and boiling heptane.

The stereoregularity parameters of the PP fractions were determined from the i.r.-spectra recorded with an UR-10 spectrophotometer [5, 10]. The intrinsic viscosities of the PP samples were measrued in tetrahydronaphthalene at 135°; the average viscosity molecular mass ($\bar{M}_v$) was calculated from the Moraglio formula [11]. The gel-chromatograms of the PP samples were obtained with a "Waters" gel-chromatograph in *o*-dichlorbenzene at 135–140°; the average molecular mass (MM) was calculated according to the universal calibration curve, using polystyrene standards [12].

Propylene was polymerized in a steel autoclave in heptane or the bulk liquid at 70°. $AlEt_3$ was used as the cocatalyst.

RESULTS AND DISCUSSION

Table 1 presents the results characterizing the stereospecificity of the catalytic systems under study. Complete replacement of Cl by Br atoms in the α-$TiCl_3$ crystal lattice, as well as partial substitution of Cl by Br or I atoms does not change the stereoregulating ability of the isospecific centres since the parameters of the stereoregularity of the isotactic PP (macrotacticity and the bands ratio D_{841}/D_{973}) remain unaffected. However, alloying of α-$TiCl_3$ with TiI_3 (~1% mol I) leads to an increase in the relative content of the isotactic product in the polymer from 74 to 91% wt. The atactic fraction in this case amounts to only 2% wt. Such a fractional PP composition is unusual in the polymerization of propylene on systems with the participation of $AlEt_3$.

Treatment of α-$TiCl_3$ with titanium trichloriodide slightly improves the quality of the isotactic PP fraction; its weight fraction however is the same. A change in the polymer fraction composition in this case manifests itself in a substantial decrease in the stereoblock fraction.

In all cases, replacement of Cl by I or Br atoms in the α-$TiCl_3$ crystal lattice leads to a decrease in the activity of the TiX_3–$AlEt_3$ catalytic systems, i.e. to a reduction in the polymer yield. Treatment of α-$TiCl_3$ with titanium trichloriodide (Table 2) also produces the same effect.

This effect may be due either to a decrease in the propagation rate constant or to a decrease in the number of active centres in the system. Comparison of the MM values of the PP iso-fractions (Table 2) as well as of the gel-chromatograms (Figs 1 and 2) shows similarity but not identity of the character of the molecular mass distribution (MMD) of the polymers. One thing, however, is clear: the difference in the MMD curves cannot be explained by a decrease in the propagation rate constant.

On the other hand, calculation of the number of iso-chains ($Q/\bar{M}_n$) has shown that the absolute amount of isotactic macromolecules decreases (experiments 1 and 5, Table 2). A larger number of

Table 2. Molecular-mass

Exp. no.	$TiX_3 \times 10^3$ (mol)	$[C_3H_6]$ (mol/l)	Time (min)	Yield $Q \times 10^{-3}$ (gpolym/molTiX_3)	Iso-fraction Weight (%)	Iso-fraction $\bar{M}_v \times 10^{-3}$	Iso-fraction $\bar{M}_w \times 10^{-3}$	Iso-fraction $\bar{M}_n \times 10^{-3}$	Iso-fraction *N* (mol polym/ mol TiX_3)
1	0.90	1.3	150	5.0	74.0	380	730	58	0.064
2	0.92	9.8	285	11.4	75.9	457	876	85	0.100
3	0.67	9.8	240	11.6	72.3	363	—	—	—
4	0.77	9.8	260	6.4	91.8	467	—	—	—
5	1.68	1.2	150	2.8	73.0	478	952	95	0.021
6	0.56	9.8	255	8.9	49.4	467	—	—	—
7	1.49	9.8	270	11.2	56.4	812	1000	115	0.055

*The numbers of the experiments coincide with the numbers in Table 1. Polymerization was carried out at molar ratio Al:Ti = 2:2.6.

Table 3. Characteristics of catalysts

No.	TiX_3	r(M-X) (Å)	r(M-M) (Å)	$r(X^+)$ (Å)
1	α-$TiCl_3$	2.50	3.56	1.81
2	α-$TiBr_3$	—	3.73	1.96
3	α-$TiCl_{2.89}Br_{0.15}$	-	3.55_0	–
4	α-$TiCl_{2.97}I_{0.03}$	—	3.55_5	-
5	β-$TiCl_3$	—	2.91	
6	β-TiI_3	2.76	3.25	2.20

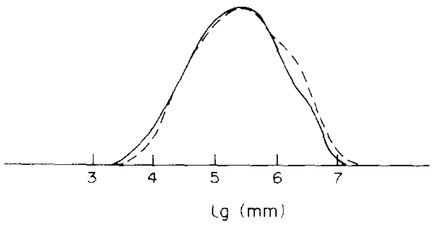

Fig. 1. Gel-chromatograms of isotactic PP fractions: (——) experiment 1, Table 2; (-----) experiment 2.

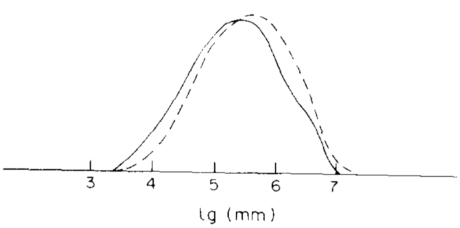

Fig. 2. Gel-chromatograms of isotactic PP fractions: (——) experiment 1, Table 2; (-----) experiment 5.

iso-chains in experiment 2 is undoubtedly associated with a significant fraction of the chain transfer reactions (to the monomer and to the cocatalyst) since the polymerization of propylene in this case took considerably longer and was realized at a much higher monomer concentration. Under comparable conditions (duration and concentration of the monomer) for α-$TiBr_3$-catalyzed polymerization which is stationary in respect of the number of active centres, the amount of polymer chains is of about one order lower.

Thus, a lower activity of Br- or I-containing catalysts is due to decrease in the number of polymerization centres even for small amounts of I or Br atoms in the α-$TiBr_3$ crystals. This is probably due to the fact that not a single Ti atom of the active centre, but a group of atoms bound together by halogen bridges takes part in the catalytic act. According to calculations made by Corradini [13], such a group consists of three Ti atoms. Apparently, these are centres with one vacancy. The appearance of halogen atoms of a large ionic radius in the $TiCl_3$ structure (Table 3) results in a partial blocking of such centres preventing the coordination of the monomer.

The structure α-$TiBr_3$ is similar to that of α-$TiCl_3$ and is characterized by the same degree of asymmetry. Therefore, the stereospecificity of the both catalytic systems is the same.

From comparison of the propylene polymerization on systems with the participation of the β-modification of titanium trihalogenides, we may see that, for practically equal catalyst activity, the quality of the iso-product is better for a system on a β-$TiCl_3$ base, whereas the quantity of the isotactic fraction and its molecular mass is higher when β-TiI_3 is employed (Table 2).

The crystal lattice parameters of the catalysts involved are given in Table 3.

From what has been reported above, we may conclude that there is no simple correlation between the stereospecificity of the catalytic systems, ion radii of the anions and M-M and M-X distances. However, the introduction of I atoms into the $TiCl_3$ crystal structure, or surface treatment of the catalyst with iodine-containing compounds, leads either to an increase in the stereoregulating ability of the isospecific centres or to an increase in the relative iso-fraction content in the polymer. The influence of the iodine-containing compound on the $TiCl_3$ crystal surface is a more effective method of enhancing the isospecificity of the active centres. Obviously, in this case as well as in the case of utilizing $AlEt_2Br$ or $AlEt_2I$ as the cocatalysts, there is an increase in the degree of asymmetry of the original bivacant polymerization centres, the possibility of existence of which has been accepted by a number of investigations [1, 14–16].

Thus, in order to explain the change in the activity and stereospecificity of the catalytic systems involved, due to the introduction of heavy halogen atoms into the catalyst structure, we find it necessary to make use

characteristics of PP fractions*

Stereoblock-fraction					Atactic fraction				
Weight (%)	$\bar{M}_v \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	N (mol polym/ mol TiX_3)	Weight (%)	$\bar{M}_v \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	N (mol polym/ mol TiX_3)
11.5	38	119	10	0.057	14.5	57		–	
4.3	70	149	11	0.045	19.8	42	65	8	0.280
8.7	51			–	19.0	42		–	
6.1	30		–		2.1				
2.5	–	–		–	24.5	35	–		
15.9	–	–	–	–	34.7	42	–	–	
16.0	200	284	17	0.105	27.6	80	147	8	0.386

of the concept concerning the existence of uni- and bivacant active centres which, in turn, suggests that there is simultaneous action of the uni- and bi-metal mechanism of isospecific propylene polymerization on Ziegler–Natta systems.

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