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COMMENT ON THE LETTER OF A. P. FIRSOV, B. N. KASHPROV, YU. V. KISSIN, AND N. M. CHIRCOV

In a Letter to the Editor, J. Polymer Science, Firsov, et al. on the basis of some experiments state that the deduction of Natta and co-workers about the dependence of the stereoregularity of polypropylene on the type of $Me(C_2H_5)_n$ used is "in error" (1).

Furthermore, they argue that Natta and co-workers "erroneously assumed" on the basis of the solubility of polypropylene in n-heptane that "the fractionation of the polymer is determined only by its content of stereoregular and atactic structures."

Concerning the first point, an approximate evaluation of the stereospecificity of a catalytic system in the propylene polymerization could be obtained at least on two different bases:

(I) The total amount of crystallizable sections present in the polymer sample, disregarding the steric structure of each macromolecule as a whole (e.g., isotactic or stereoblock macromolecules).

(II) The amount of isotactic macromolecules (2).

In the first case, a rough indication of the stereospecificity of the catalytic system may be given by the total crystallinity of the polymer as determined, for example, by x-ray (3).

In the second case for a polypropylene in tetralin at 135°C. having $[\eta]$ higher than 0.25, the stereospecificity of the catalyst is conventionally evaluated on the basis of the percentage of a boiling heptane non-extractable fraction. This method was introduced in practice because it was much more significant than others in the evaluation of the properties of the catalyst.

In fact, the solvent extraction is up to now the only simple method to separate in a substantially quantitative way isotactic high molecular weight macromolecules and stereoblock macromolecules.

In the case of very low molecular weight polymers, the heptane extraction cannot be applied as the very low molecular weight isotactic polymers have higher solubility and lower melting temperatures (5,6).

Whichever criterion is assumed, we would like to point out that the views of Natta and co-workers about the different stereospecificity of catalysts prepared starting from $Be(C_2H_5)_2$ and $Al(C_2H_5)_2$ actually do not appear to be contradicted by the Chirkov et al. experimental data (see Table I).

Furthermore, it seems to us that the comparison made by Chirkov and co-workers between the stereospecificity of $Zn(C_2H_5)_2$-$TiCl_3$ catalyst and one of the other two catalytic systems is not completely satisfactory. In fact, the polymerization experiments with the $TiCl_3$-$Zn(C_2H_5)_2$

TABLE I

Analysis of Firsov and Co-workers' Data on the Fractionation of Polypropylenes Obtained by α-$TiCl_3$-$Be(C_2H_5)$ or α-$TiCl_3$-$Al(C_2H_5)_3$ Catalysts

$Me(C_2H_5)_n$	Fraction	Crystallinity I.R. spectrum, %	Crystallinity x-ray spectrum, %	Average % of crystallinity calculated for the total polymer
	%			
$Be(C_2H_5)_2$	Boiling heptane insoluble	91–98	60.5–69.5	61.6
$Al(C_2H_5)_3$	Boiling heptane insoluble	77–80	57 –62	54–57	46.7
	Boiling heptane soluble and cold heptane insoluble	8–12	55	55	5.5
	Cold heptane soluble	8–13	18 –32		2.6

54.8

TABLE II

Conditions Adopted by Firsov and Co-workers for the Polymerization of Propylene by α-$TiCl_3$ Catalysts, in Heptane

Organometallic compound	R [a]	Pressure	Temperature, °C.
$Al(C_2H_5)_3$	~3	200–600 mm. Hg	30–70
$Be(C_2H_5)_2$	~3	200–600 mm. Hg	30–70
$Zn(C_2H_5)_2$	$5.4 \cdot 10^{-2}$	4– 9 atm.	50–70

[a] R is the ratio between the moles of the organometallic compound and the moles of the transition metal compound.

system have been carried out by Firsov and co-workers in conditions very different from those adopted by them in the case of $TiCl_3$-$Al(C_2H_5)_3$ and of $TiCl_3$-$Be(C_2H_5)_2$ systems (see Table II).

On the basis of the data previously reported by us (7), if the stereospecificity of the polymerization is determined according to method (2), the $Zn(C_2H_5)_2$-$TiCl_3$ catalytic system should be much less stereospecific than the $Al(C_2H_5)_3$-$TiCl_3$ and $Be(C_2H_5)_2$-$TiCl_3$ systems. However, we agree that the application of method (2) for polymers obtained with $Zn(C_2H_5)_2$-$TiCl_3$ catalysts does not yield very satisfactory results, due to the very low molecular weight of the polymers.

We believe that further work is necessary in order to evaluate more precisely the stereospecificity of the $TiCl_3$-$Zn(C_2H_5)_2$ catalytic system, particularly because of the quite low molecular weight of the polymers obtained, which has been attributed (8) to a very high rate of chain transfer reaction with the alkyl groups bound to the Zn atoms, in comparison with that observed in the $TiCl_3$-AlR_3 catalytic system.

Concerning the second remark of Firsov and co-workers, Natta and co-workers have already pointed out that the fractionation of a polypropylene is determined not only by its content of stereoregular and atactic structures. In fact, they stated that the steric configuration of the macromolecules influences the solubility much more than the molecular weight, at least for molecular weights between 10^4 and 10^6 (2).

Furthermore, the influence of molecular weight on the solubility of isotactic polymers has been already emphasized in other papers in which ether soluble crystalline polypropylene has been described (9).

In conclusion, we think that the dependence of the catalyst stereospecificity on the nature of both the transition metal compound and the met-