

STEREOSPECIFIC CATALYSTS FOR THE HEAD-TO-TAIL POLYMERIZATION OF PROPYLENE TO A CRYSTALLINE SYNDIOTACTIC POLYMER

Sir:

Propylene can be polymerized stereospecifically to yield two types of crystalline polymers having monomeric units with a head-to-tail attachment: these polypropylenes are isotactic and syndiotactic. A polymer which may be considered as a third type of crystalline polypropylene having a head-to-head and tail-to-tail attachment and a di-syndiotactic structure can be obtained by the alternate copolymerization of ethylene with *cis*-butene-2.¹

The catalytic systems described up to now and used for obtaining crystalline head-to-tail syndiotactic polymers of propylene consist predominantly of complexes which are specific for the polymerization of isotactic polypropylene. In fact, at the very best, the syndiotactic fraction has a low order of crystallinity, and is present only in small amounts in the crude polymer together with large amounts of isotactic polymer.² The syndiotactic fraction was separated from the isotactic one by adsorption chromatograph.²

We now have found some catalytic systems that permit the polymerization of propylene to polymers which crystallize without purification or fractionation, and whose crystallinity derives only from the presence of head-to-tail syndiotactic polypropylene.

Some of these catalytic systems, obtained from a vanadium compound and aluminum dialkylmonohalide are listed in Table I. Systems prepared from these compounds have been used previously for the copolymerization of α -olefins with ethylene, for obtaining amorphous polymers with elastomeric properties.³ However we have observed that the systems studied by us are stereospecific in the polymerization of propylene to a syndiotactic polymer only if the Al/V ratios are within a certain range (see Table I) depending on the vanadium compound and if one operates at low temperature. If these specific conditions are neglected, the system is either inactive or will yield a completely amorphous polymer.

For example, the catalytic systems obtained from vanadium triacetylacetonate and aluminum dialkylmonochloride (or aluminum dialkylmonofluoride) are stereospecific in the polymerization of propylene to a syndiotactic polymer, only if the Al/V ratio is ≈ 5 , and if one operates at temperatures below 0° (e.g., -78°). With regard to systems prepared from VCl₄, the Al/V ratio is less important than in the preceding case; however, it is better if it ranges between 3 and 10. In this case, both stereospecificity and catalytic activity are considerably improved by the addition of weak Lewis bases (e.g., anisole) to the system with a molar ratio 1/1 in respect to the vanadium compound.

Another interesting aspect of the catalytic

(1) G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvassori and A. Zambelli, *J. Am. Chem. Soc.*, **83**, 3343 (1961).

(2) G. Natta, I. Pasquon, P. Corradini, M. Peraldo, M. Pegoraro and A. Zambelli, *Rend. Acc. Naz. Lincei*, [8] **28**, 539 (1961).

(3) G. Natta, G. Mazzanti, A. Valvassori, G. Sartori and D. Fiumani, *J. Polymer Sci.*, **51**, 411 (1961).

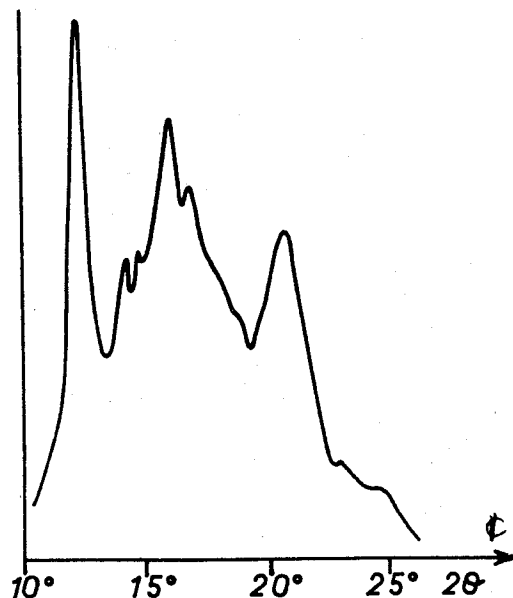


Fig. 1.—X-Ray Geiger spectra (CuK α) of syndiotactic polypropylene (partially crystalline product).

systems prepared by us (e.g., starting from VCl₄-anisole-AlR₂Cl), is that their stereospecificity is influenced by the nature of the alkyl groups contained in the aluminum dialkyl monohalide. For instance, the stereospecificity increases when passing from Al(C₂H₅)₂Cl to Al[CH₂C₂(CH₃)₂]₂Cl or Al[CH₂C(CH₃)₂]₂Cl.

Another interesting property of the catalytic systems studied by us derives from the fact that their stereospecificity, in the polymerization of propylene to a syndiotactic polymer, is not conditioned by the presence of a heterogeneous phase in the system, in which the polymerization is carried out. On the contrary, this condition is essential in the case of the polymerization of propylene to give an isotactic polymer⁴. In fact, the catalytic systems reported in Table I act in a homogeneous solution. This is also confirmed by the fact that from the crude polymer obtained, it is practically impossible to separate (e.g., by extraction with solvents) fractions of polymer with a steric regularity very different from that of the crude polymer, contrary to what is generally observed for the crude polymers obtained by heterogeneous catalytic systems.

It must be borne in mind that even in the case of the polymerization of butadiene to syndiotactic 1,2 polymer, the stereospecific catalysts are soluble in the polymerization medium.^{4,5}

The structure of head-to-tail syndiotactic polypropylene already has been described in previous papers.² The identity period of the chain along the *c* axis is of 7.4 Å. and it corresponds to 4 monomeric units per pitch. The elementary unit cell has the constants: $a = 14.5 \pm 0.15$ Å, $b = 5.8 \pm 0.1$ Å, $c = 7.4 \pm 0.1$ Å. Figure 1 shows the X-ray spectra of crude polypropylene obtained with

(4) See for instance G. Natta, *Chimica e Industria*, **42**, 1207 (1960).

(5) G. Natta, L. Porri, G. Zanini and A. Palvarini, *Chimica e Industria*, **41**, 1163 (1959); G. Natta, L. Porri, G. Zanini and L. Fiore, *ibid.*, **41**, 526 (1959).

TABLE I

POLYMERIZATION OF PROPYLENE TO A SYNDIOTACTIC POLYMER (AT -78°) (A = ACETYLACETONIC RESIDUE, An = ANISOLE)

Vanadium compound	Moles	Catalytic system		Al/V ratio	Solvent, 100 cm. ³	Polymer obtained, g.	Relative index of crystallinity for the syndiotactic polymer ^a	Intrinsic viscosity $[\eta]$ 100 cm. ³ /g. ^b
		Organometallic compound	Moles					
VA ₃	1.4×10^{-3}	Al(C ₂ H ₅) ₂ F	7×10^{-3}	5	Toluene	3	0.80	Not detd.
VA ₃	1.4×10^{-3}	Al(C ₂ H ₅) ₂ Cl	7×10^{-3}	2	Toluene	0
VA ₃	1.4×10^{-3}	Al(C ₂ H ₅) ₂ Cl	7×10^{-3}	5	Toluene	1.2	0.65	0.39
VA ₃	1.4×10^{-3}	Al(C ₂ H ₅) ₂ Cl	14×10^{-3}	10	Toluene	10.0	0	Not detd.
VCl ₄ ·An	1×10^{-3}	Al(C ₂ H ₅) ₂ Cl	5×10^{-3}	5	Toluene	7.5	1	Not detd.
VCl ₄ ·An	1×10^{-3}	Al(C ₂ H ₅) ₂ Cl	10×10^{-3}	10	Toluene	10.0	0.90	1.04
VCl ₄ ·An	1×10^{-3}	Al(C ₂ H ₅) ₂ Cl	2×10^{-3}	2	Toluene	0.1	>0	Not detd.
VCl ₄ ·An	1×10^{-3}	Al(<i>i</i> -C ₄ H ₉) ₂ Cl	5×10^{-3}	5	Toluene	10.0	1.30	0.99
VCl ₄ ·An	1×10^{-3}	Al(neo-C ₅ H ₁₁) ₂ Cl	5×10^{-3}	5	Toluene	2.3	1.85	0.78
VCl ₄ ·An	1×10^{-3}	Al(<i>i</i> -C ₄ H ₉) ₂ Cl	5×10^{-3}	5	<i>n</i> -Heptane	2.5	2.05	0.606
VCl ₄ ·An	1×10^{-3}	Al(neo-C ₅ H ₁₁) ₂ Cl	5×10^{-3}	5	<i>n</i> -Heptane	2.4	2.05	0.70

^a The crystallinity index for the syndiotactic polymer is referred to the polymer obtained by the system VCl₄·An; Al-(C₂H₅)₂Cl; (Al/V = 5). ^b Measured in tetralin at 135°. Starting monomer, 90 g.; length of time of the runs, 20 hr.; temperature of preparation of the catalyst and of polymerization, -78° .

the aid of the last catalytic system reported in Table I. The product examined is only partially crystalline; but it is free from crystalline isotactic polypropylene.

The nature of the catalytic complexes, which are stereospecific in the polymerization of propylene

to syndiotactic polymer, will be discussed in another paper.

ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO
PIAZZA LEONARDO DA VINCI
32 MILANO, ITALY

G. NATTA
I. PASQUON
A. ZAMBELLI

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