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**Synthesis of Optically Active *Cis*-1,4 Poly(1,3-Pentadiene) by  
Asymmetric Induction**

by

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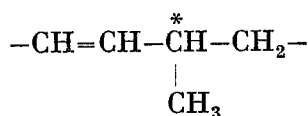
## Synthesis of Optically Active *Cis*-1,4 Poly(1,3-Pentadiene) by Asymmetric Induction

By GIULIO NATTA, LIDO PORRI, and SALVATORE VALENTI

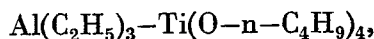
(Eingegangen am 10. Mai 1963)

It has been recently reported<sup>1)</sup> that by polymerizing the *trans* isomer of 1,3-pentadiene with stereospecific catalysts prepared from aluminum trialkyls and titanium tetraalkoxides, crystalline polymers having a prevailingly *cis*-1,4 enchainment (up to about 85 %) have been obtained. Investigation of the crystalline structure by X-ray spectroscopy has shown that the polymers contain sequences of *cis*-1,4 units in which the asymmetric carbon atoms exhibit an isotactic configuration.

In this type of polymer every isotactic sequence is to be considered optically active, as the groups directly bonded to the asymmetric carbon atoms are chemically different even if considered in the immediate proximity of the asymmetric carbon atoms\*):

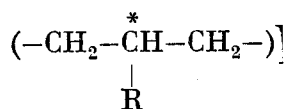


The polymers obtained with the usual catalysts, such as



are inactive because they contain isotactic sequences of opposite configurations which compensate themselves.

\*) This is not the case for the isotactic polymers of vinyl monomers, in which the asymmetry of the tertiary carbon atoms



depends on the different length and configuration of the chain sections, and also on the nature of the end-groups. In a high polymer such asymmetry is generally not sufficient to give rise to an appreciable optical activity<sup>3)</sup>.

By analogy with the results obtained in this Institute in the case of other isotactic polymers of substituted butadienes<sup>2a,b</sup>), it seemed possible that the use of a suitable optically active catalyst would yield an optically active *cis*-1,4 polypentadiene, that is a polymer containing a preponderance of isotactic sequences having the same configuration.

An optically active catalyst could be obtained using either an optically active aluminum trialkyl in combination with an inactive titanium tetraalkoxide or an inactive aluminum trialkyl in combination with an optically active titanium tetraalkoxide.

In view of the information which could possibly be derived regarding the mechanism of the stereospecific polymerization, it appeared of interest to compare the two types of optically active catalysts with regard to their ability to induce asymmetry in the *cis*-1,4 isotactic polypentadiene.

In this communication we briefly report some results of the polymerization of 1,3-pentadiene with each of the two following systems:

- 1) (+)tri(2-methylbutyl)aluminum and titanium tetrabutoxide, and
- 2) triethyl aluminum and (-) titanium tetramenthoxide.

The high molecular weight polymers obtained by catalyst system 1) do not present an optical activity (Table 1). Only in the very low molecular weight polymers, it was possible to detect a low optical activity.

On the contrary, the polymers obtained with system 2) exhibit a remarkable optical activity. This was observed both in low and in high molecular weight polymers. By ozonolysis of the polymers, optically active methyl succinic acid was obtained; this shows that the optical activity of the polymers arises, at least in part\*), from the asymmetric carbon atoms of the 1,4-units, which are prevailing of one configuration.

By fractionating the products obtained from system 2), polymers having different *cis*-1,4 contents (from about 50 to about 85%) were isolated. The rotatory power was highest in the fractions having the greatest *cis*-1,4 content, as is shown in Table 1. This seems to indicate that the optical activity is prevailing due to *cis*-1,4 isotactic sequences, which are largely of one configuration\*\*).

The fact that the optical activity appears only when the asymmetric groups are bonded to titanium seems to confirm that the active site in the

\*) We do not know, at present, whether or not a contribution to the optical activity due to conformational factors also exists.

\*\*\*) The *trans*-1,4, the 1,2, and the 3,4 units also present asymmetric carbon atoms and therefore could also contribute to the optical activity if their configuration is influenced by the asymmetric induction.

co-ordination catalysts, contains the transition metal. The asymmetric induction can be accounted for by assuming that the polymer grows on titanium or, at least, that the monomer coordinates to titanium before its incorporation into the growing chain. The presence of asymmetric groups bonded to titanium would influence the configuration of the incorporating unit.

Table 1. Optical Activity of *Cis*-1,4 Isotactic Polypentadiene Obtained by Optically Active Catalyst Systems

Catalyst system (1)	<i>Cis</i> -1,4 content of the polymer		$\alpha_D^{18}$ (3)	$[\alpha]_D^{18}$	$[\eta]$ dl./g. (4)
	(%)	(2)			
(+) $\text{Al}(i\text{-C}_5\text{H}_{11})_3\text{-Ti}(\text{OC}_4\text{H}_9)_4$ (5)	73.6	a	0	—	5.97
	82	c	0	—	6.4
	69.2	a	0	—	1.67
	83	c	0	—	7
	69	a	0	—	3
	57	b	-0.03	-1.76	0.62
$\text{Al}(\text{C}_2\text{H}_5)_3\text{-(-)Ti}(\text{OC}_{10}\text{H}_{19})_4$ (6)	55	b	-0.86	-7.8	0.96
	78	c	-0.88	-22.8	6.8
	75	c	-0.21	-19	4.1
	72	c	-0.17	-16.3	—
	79	c	-0.25	-21.6	6.5
	65	a	-0.11	-13	7
	55	b	-0.07	-4.16	1.09
	65	c	-0.08	-13.3	3.5

- (1) Polymerization conditions: Solvent (benzene or toluene), ml. 25; titanium tetraalkoxide 0.625 mmole; Al/Ti (molar ratio) 7; 1,3-pentadiene (98% *trans* isomer, 2% *cis* isomer) ml. 7; polymerization temp. 0°C.; polymerization time 80–100 hrs. Crude polymer obtained 1,5–2 g.
- (2) The crude polymerization product was fractionated by dissolving in benzene and reprecipitating with methylethylketone (MEK). Analyses refer to a) crude polymerization products, b) MEK soluble, and c) MEK insoluble fractions.
- (3) Determined in *n*-hexane solution ( $l = 4$  dm).
- (4) Determined in toluene at 30°C.
- (5) (+)  $\text{Al}(i\text{-C}_5\text{H}_{11})_3$ :  $[\alpha]_D^{25} + 25,6^\circ$  ( $c = 15,42$  g./100 ml., toluene); optical purity about 81%<sup>4</sup>).
- (6) (-)  $\text{Ti}(\text{OC}_{10}\text{H}_{19})_4$ :  $[\alpha]_D^{25} - 98,3$  ( $c = 5,54$  g./100 ml., benzene); optical purity 98–99%<sup>5</sup>).

With regard to the polymers obtained from system 1) we do not know, at present, whether the weak activity observed in the low molecular

weight polymers results only from the 2-methylbutyl end-groups or also from the asymmetric carbon atoms in the chains. In this second case, the low activity could be accounted for by assuming that only the first sequence of a chain (which starts on a metal-2-methylbutyl bond) grows under the influence of the asymmetric group. The following sequences would exhibit a statistical distribution of the configurations, not being influenced by the optically active group present at the extremity of the growing chain\*).

Further work is in progress and more complete results will be published in a future paper.

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\*) This is presumably the case for the *trans*-1,4 isotactic polymers of 1,3-pentadiene obtained with the heterogeneous system  $(+)Al(i-C_5H_{11})_3 \cdot (C_2H_5)_2O-VCl_3$  <sup>2c</sup>). Actually these polymers show an optical activity which is rather low and decreases with the molecular weight, as one would expect when only the beginning of a chain grows under asymmetric influence.

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