TABLE II

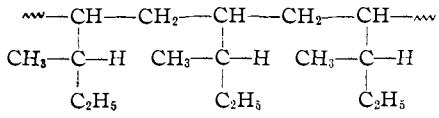
RESOLUTION OF RACEMIC POLY-4-METHYL-1-HEXENE SAMPLES HAVING DIFFERENT STEREOREGULARITY[a]

Sample: Solubility	$[\eta]$ 100 cm.³/g.[b]	Melting temp., °C.[c]	$[\alpha]_D$ in benzene[d]: First fraction	$[\alpha]_D$ in benzene[d]: Last fraction	$\Sigma_i\{[\alpha]_D\}_i\, w_i/W$[e]: Negative fractions	$\Sigma_i\{[\alpha]_D\}_i\, w_i/W$[e]: Positive fractions	R[g]
Acetone soluble	n.d.	...	−29.7°[f]	+10.8°[f]	−4.22°[f]	+2.94°[f]	26.5
Acetone in soluble, diethyl ether soluble	0.67	85–95	− 7.6°	+73.0°	−5.21°	+5.10°	25.6
Diisopropyl ether insoluble, isoöctane soluble	1.52	146–148	−21.0°	+97.5°	−8.46°	+8.02°	22.0

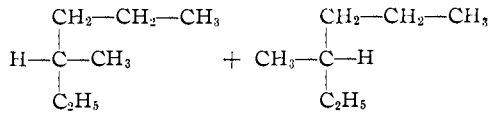
[a] Obtained by solvent extraction at the solvent boiling point. [b] At 120° in tetralin. [c] Determined using a Kofler melting point apparatus. [d] At 40°, if not otherwise indicated. [e] w_i = weight of the fraction having $\{[\alpha]_D\}_i$; W = total weight of the eluted polymer. [f] The optical activity measurements were carried out at 25°. [g] R = weight of supporting polymer/weight of supported polymer.

atoms of the lateral chains in optically active isotactic poly-3-methyl-1-pentene and poly-4-methyl-1-hexene,[8,9] we can now assume that the supporting polymer adsorbs more strongly the macromolecules in which most of the lateral chains possess asymmetric carbon atoms with the same absolute configuration of the corresponding asymmetric carbon atoms which are present in the lateral chains of the supporting polymer.

The remarkable difference between the affinity of the poly-(R)-4-methyl-1-hexene and poly-(S)-4-methyl-1-hexene for the poly-(S)-3-methyl-1-pentene used as chromatographic support, could depend mainly on the interactions between the lateral chains of the supported and the supporting polymers. Since our attempts to resolve low molecular weight hydrocarbons such as the 3-methylhexane (IV) at room temperature, by the same supporting medium, have failed, it appears, at least in the case of low molecular weight hydrocarbons having m.p. well below the fractionation temperature, that the different interactions of the *sec*-butyl groups having opposite absolute configurations of the racemic hydrocarbons, with the *sec*-butyl groups present as lateral chains in the optically active supporting polymer are not strong enough to allow resolution of a racemic hydrocarbon.



III



IV

The conformation of the principal chains of the polymer to be resolved should therefore play an important role in the resolution of the racemic poly-hydrocarbons. In other words macromolecules having the same conformation of the supporting polymer (*e.g.*, helical conformation of the same screw sense) are much more strongly adsorbed than macromolecules having different conformations.

From the point of view of the stereospecific polymerization mechanism these results nicely confirm that the highly stereospecific catalysts (*e.g.*, $TiCl_3$ + $Al(i\text{-}C_4H_9)_3$), are able to choose predominantly one or the other enantiomer from the racemic monomer in order to build up a single macromolecule.

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RECEIVED JANUARY 24, 1962

(8) P. Pino, G. P. Lorenzi, L. Lardicci and F. Ciardelli, *Vysokomol. Soedineniya*, **3**, 1597 (1961).

(9) P. Pino, Lecture given at the Summer School of Macromolecular Chemistry, Varenna, Italy, 18–30 September, 1961.

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

(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).

TABLE I

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

Catalytic system						Polymer obtained, g.	Relative index of crystallinity for the syndiotactic polymer[a]	Intrinsic viscosity [η] 100 cm.³/g.[b]
Vanadium compound	Moles	Organometallic compound	Moles	Al/V ratio	Solvent, 100 cm.³			
VA_3	1.4×10^{-3}	$Al(C_2H_5)_2F$	7×10^{-3}	5	Toluene	3	0.80	Not detd.
VA_3	1.4×10^{-3}	$Al(C_2H_5)_2Cl$	7×10^{-3}	2	Toluene	0	..	.....
VA_3	1.4×10^{-3}	$Al(C_2H_5)_2Cl$	7×10^{-3}	5	Toluene	1.2	0.65	0.39
VA_3	1.4×10^{-3}	$Al(C_2H_5)_2Cl$	14×10^{-3}	10	Toluene	10.0	0	Not detd.
VCl_4·An	$Z \times 10^{-3}$	$Al(C_2H_5)_2Cl$	5×10^{-3}	5	Toluene	7.5	1	Not detd.
VCl_4·An	1×10^{-3}	$Al(C_2H_5)_2Cl$	10×10^{-3}	10	Toluene	10.0	0.90	1.04
VCl_4·An	1×10^{-3}	$Al(C_2H_5)_2Cl$	2×10^{-3}	2	Toluene	0.1	>0	Not detd.
VCl_4·An	1×10^{-3}	$Al(i\text{-}C_4H_9)_2Cl$	5×10^{-3}	5	Toluene	10.0	1.30	0.99
VCl_4·An	1×10^{-3}	$Al(neo\text{-}C_5H_{11})_2Cl$	5×10^{-3}	5	Toluene	2.3	1.85	0.78
VCl_4·An	1×10^{-3}	$Al(i\text{-}C_4H_9)Cl$	5×10^{-3}	5	*n*-Heptane	2.5	2.05	0.606
VCl_4·An	1×10^{-3}	$Al(neo\text{-}C_5H_{11})_2Cl$	5×10^{-3}	5	*n*-Heptane	2.4	2.05	0.7

[a] The crystallinity index for the syndiotactic polymer is referred to the polymer obtained by the system VCl_4·An; Al(C_2H_5)Cl; (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°.

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 $\simeq 5$, and if one operates at temperatures below 0° (*e.g.*, −78°). With regard to systems prepared from VCl_4, 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 systems prepared by us (*e.g.*, starting from VCl_4–anisole–AlR_2Cl), is that their stereospecificity is considerably influenced by the nature of the alkyl groups contained in the aluminum dialkyl monohalide. For instance, the stereospecificity increases when passing from $Al(C_2H_5)_2Cl$ to $Al[CH_2C(CH_3)_2]_2Cl$ or $Al[CH_2C(CH_3)_3]_2Cl$.

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 polymer (4). 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.

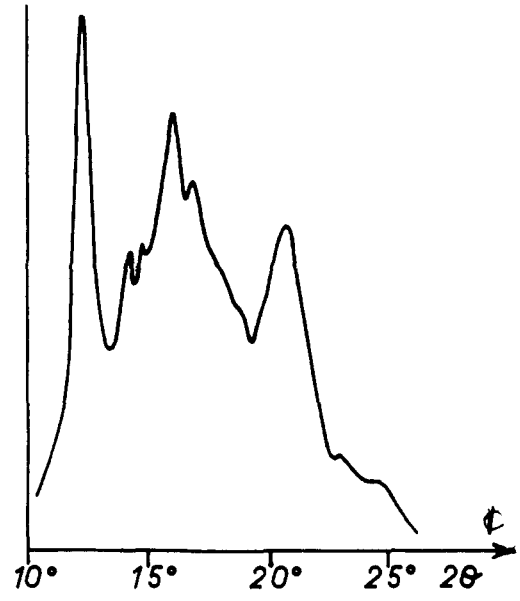

Fig. 1.—X-Ray Geiger spectra (CuKα) of syndiotactic polypropylene (partially crystalline product).

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 the aid of the last catalytic system reported in Table I. The product examined is only partially

(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).

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.

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RECEIVED JANUARY 6, 1962

THE LABELLING OF PHOSPHOMONOESTER END GROUPS IN AMINO ACID ACCEPTOR RIBONUCLEIC ACIDS AND ITS USE IN THE DETERMINATION OF NUCLEOTIDE SEQUENCES

Sir:

To date the sequence shown in partial representation I[1] is known to be common for the presumed twenty different amino acid-acceptor ribonucleic acids.[2] While some progress has been made[3] in the determination of sequences in the vicinity of the CpCpA terminus, nothing is known about the sequences at the opposite terminus except that by alkaline hydrolysis guanosine-2′(3′),5′-diphosphate (pGp) has been identified.[4] In this communication we report on the specific conversion of the terminal phosphomonester groups in the amino acid acceptor ribonucleic acids to the C^{14}-labelled phosphoroanilidates (I→II) and on the information which we have already obtained concerning nucleotide sequences nearest to that end.

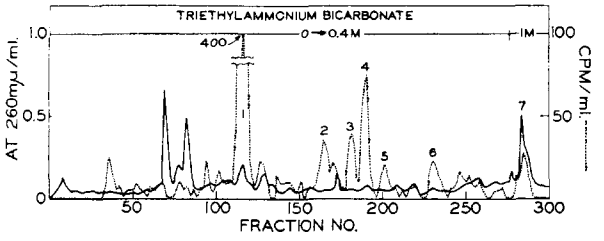
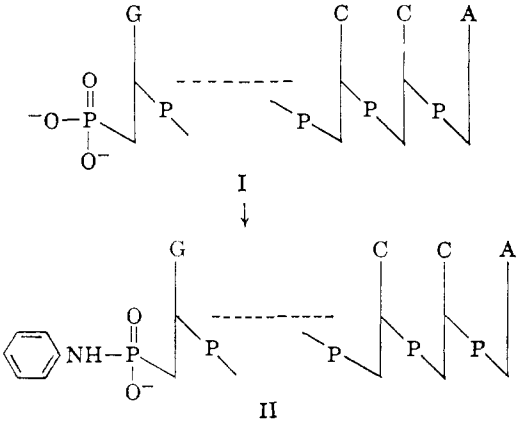


Fig. 1.—Chromatography of labelled oligonucleotides (approximately 270 optical density units at 260 mμ) on a DEAE-cellulose (carbonate) column (1 cm. × 50 cm.): elution was with a linear gradient 0 → 0.4 *M* triethylammonium bicarbonate (*p*H 7.5) with 2 l. in each vessel; rate of flow was 0.5 ml./min., ten ml. fractions being collected; one ml. of each tube was plated and radioactivity measured in a thin end window gas flow counter.



Labelling experiments were carried out with either yeast amino acid acceptor ribonucleic acid itself or with the oligonucleotide mixture[5] obtained by pancreatic ribonuclease digestion of the ribonucleic acid followed by removal of mono- and dinucleotides[5] by column chromatography. Since the results were similar, only the experiments on oligonucleotide mixture are herein summarized. Approximately 500 optical density (260 mμ) units of the mixture as triethylamine salt were treated in a mixture of water (0.3 ml.), dimethylformamide (0.6 ml.) and *tert*-butyl alcohol (0.6 ml.) with diisopropylcarbodiimide (0.12 ml.) and aniline (0.075 ml., containing 0.1 mC. of C^{14}-label) at room temperature. The pH was maintained at 8 by means of a pH stat which continually added hydrochloric acid to neutralize the guanidine (III) formed. After one day, about 80% of the total end groups were converted to the phosphoroanilidates, the 3′-phosphate end groups being converted simultaneously to 2′,3′-cyclic phosphate groups. After work-up, the total product was digested with spleen phosphodiesterase to enrich the oligonucleotides containing the 5′-phosphoroanilidate groups.[6] The resistant oligonucleotide mixture was freed from the resulting mononucleotides by column chromatography. The recovery at this stage was about 20% of the total material subjected to the action of spleen phosphodiesterase. This oligonucleotide mixture was again digested with pancreatic ribonuclease to open the 2′,3′-cyclic phosphates and the resulting mixture gave after chromatography the elution pattern shown in Fig. 1.[7]

Alkaline hydrolysis of radioactive peaks 1–7 showed that most of the radioactivity was released in compounds of the type IV (R = purine). The technique is, therefore, specific in providing a handle at the 5′-phosphomonoester ends of the polynucleotide chains and the interference from any random incorporation of label is not serious. The bulk of the radioactivity in the peak 1 is associated with the compound V which has been isolated pure and characterized. Peaks 2–6 and the peak immediately following peak 2 apparently contain mixtures of trinucleotides of the general structure VI and

(1) For the system of diagrammatic representations and abbreviations for polynucleotides see H. G. Khorana, "Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest," John Wiley and Sons, New York, N. Y., 1961, Chapter 5.

(2) *Cf.* P. C. Zamecnik, "Harvey Lectures," LIV, 256 (1958–1959).

(3) U. Lagerkvist, P. Berg, M. Dieckmann and F. W. Platt, *Fed. Proc.*, **20**, 363 (1961).

(4) M. F. Singer and G. L. Cantoni, *Biochim. Biophys. Acta*, **39**, 182 (1960); W. Zillig, D. Schachtschabel and W. Krone, *Z. Physiol. Chem.*, **318**, 100 (1960).

(5) By analysis, this contained all the oligonucleotides containing pG and pA end groups that were present in the original ribonucleic acid. However, there was identified free pUp in the dinucleotide fraction discarded.

(6) Oligonucleotides released by ribonuclease from the interior of the ribonucleic acid chains would contain free 5′-hydroxyl end groups and should be degraded by the spleen phosphodiesterase. The oligonucleotides bearing 5′-phosphate or 5′-phosphoroanilidate groups would be resistant (for references, see) H. G. Khorana, in "Phosphodiesterases," "The Enzymes," Vol. V., P. D. Boyer, H. A. Lardy and K. Myrback, eds., Academic Press, New York, N. Y., 1961, p. 79).

(7) The presence of the two large peaks of nucleotide material essentially free from radioactivity shows that the digestion with spleen phosphodiesterase was not complete.