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THE POLYMERIZATION OF PROPYLENE USING AN OPTICALLY ACTIVE CATALYST SYSTEM

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Abstract—The incorporation of the first monomer unit in a growing chain of isotactic polypropylene affords an asymmetric carbon atom, and the orientation of subsequent monomer units has been explained on the basis of asymmetric induction. This hypothesis has now been tested by carrying out the polymerization of propylene in the presence of an optically active trialkylaluminium and α-titanium trichloride. The absence of optical activity in the resulting polymer, and in the products of its pyrolysis, would appear to disprove the above hypothesis. Polymerizations carried out in an optically active medium also failed to produce an optically active polypropylene.

THE use of special Ziegler catalyst systems, such as triethylaluminium in combination with α-titanium trichloride, has enabled Natta and his collaborators[1] to attain highly stereospecific polymerization of propylene and other α-olefines. Investigation of the structures of the resulting isotactic polymers by means of X-ray crystallography has shown that, in any one polymer chain

$$\text{—}CH_2{\cdot}\overset{*}{C}HR{\cdot}CH_2{\cdot}\overset{*}{C}HR{\cdot}CH_2{\cdot}\overset{*}{C}HR{\cdot}CH_2{\cdot}\overset{*}{C}HR\text{—}$$

the asymmetric carbon atoms display the same configuration (i.e. all D or all L), at least over long sections of the chain. The isotactic polymers are composed of racemic mixtures of these enantiomorphic chains, which assume helical conformations (right- or left-handed screws).†

The mechanism of olefine polymerization in the presence of catalyst systems of the Ziegler type has been the subject of much varied speculation.[2] It is generally agreed, however, that the polymerization must proceed by insertion of the incoming monomer units between metal atoms or ions in the catalyst complex and the growing chains. In the formation of isotactic polypropylene, asymmetric synthesis takes place at each propagating active centre, and this must be due to the presence of some element of asymmetry. This might be supplied originally by the first incorporated monomer unit, which affords an asymmetric carbon atom, either in the D- or the L-configuration, as in A. The next incoming propylene molecule might therefore be incorporated under the

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† In this communication the term "enantiomorphic" as applied to isotactic polymer chains refers to the asymmetric carbon atoms only, asymmetry due to the helical nature of the chains being neglected in order to avoid confusion.

[1] See e.g. G. Natta, [a] *Angew. Chem.* **68**, 393 (1956); [b] *Chem. & Ind.* 1520 (1957); [c] *J. Inorg. Nuclear Chem.* **8**, 589 (1958); [d] *J. Polymer Sci.* **34**, 21 (1959).

[2] See N. G. Gaylord and H. F. Mark, *Polymer Reviews* Vol. 2. Interscience, New York (1959) and references quoted therein. R. Robinson, *Chem. Age. Lond.* **74**, 997 (1956); *Gazz. chim. ital.* **89**, 265 (1959). Later papers include [a] J. Furukawa and T. Tsuruta, *J. Polymer Sci.* **36**, 275 (1959); [b] R. van Helden, A. F. Bickel and E. C. Kooyman, *Tetrahedron Letters* No. 12, 18 (1959); [c] C. Beerman and H. Bestian, *Angew. Chem.* **71**, 618 (1959); [d] A. Gumboldt and H. Schmidt, *Chem. Z.* **83**, 636 (1959); [e] G. Natta and G. Mazzanti, *Tetrahedron* **8**, 86 (1960); [f] W. L. Carrick, F. J. Karol, G. L. Karapinka and J. J. Smith, *J. Amer. Chem. Soc.* **82**, 1502 (1960); [g] P. Cossee, *Tetrahedron Letters* No. 17, 12, 17 (1960); [h] W. L. Carrick, A. G. Chasar and J. J. Smith, *J. Amer. Chem. Soc.* **82**, 5319 (1960); [i] C. M. Fontana and R. J. Osborne, *J. Polymer Sci.* **47**, 522 (1960).

influence of an asymmetric centre, and might be expected to take up one of the two possible configurations preferentially.[3]† Continuation of this process of asymmetric induction with successive monomer units could thus result in a stereospecific polymerization.

A $\text{metal—CH}_2\cdot\overset{*}{\text{C}}\text{HMeR}$ (where R is the group originally attached to the metal)

This hypothesis is not without defects, but it was thought worthwhile to test it by polymerizing propylene with α-titanium trichloride and an optically active trialkylaluminium containing a resolved asymmetric carbon atom in the β-position with respect to the metal atom, as in A. If the above hypothesis were correct, the use of this catalyst system would be expected to produce a preponderance of one enantiomorphic form of isotactic polypropylene.‡ Such a polymer would probably not exhibit a measurable optical activity[5] unless it also contained a preponderance of one helical form. Although helices of a single screw sense are prevalent in the stereoregular polymers of certain optically active olefines,[6] it is apparent from Natta's description of the structure of isotactic polypropylene that either a right- or left-handed helix can be formed by any one polypropylene chain, irrespective of the configuration of the asymmetric carbon atoms in the chain back-bone. Thus unidirectional helix formation would not be expected to occur in the single enantiomorphic form of isotactic polypropylene envisaged above. However, if the polymer chains were subjected to a suitable fragmentation process, such as pyrolysis, optical activity might be detected in the fragments, provided they contained undisturbed asymmetric centres and were of a relatively low molecular weight.[7]

The synthesis of a suitable optically active trialkylaluminium was accomplished as follows.

(+)-2-Methylpent-4-enoic acid (I), obtained in the known manner,[4] was hydrogenated to afford (+)-2-methylpentanoic acid (II), which by reduction with lithium aluminium hydride yielded (−)-2-methylpentan-1-ol (III). The alcohol was then converted into (−)-1-chloro-2-methylpentane (IV) by means of thionyl chloride in pyridine. Reaction of the Grignard compound prepared from IV with mercuric chloride in tetrahydrofuran furnished (+)-di(2-methylpent-1-yl) mercury (V), which on treatment

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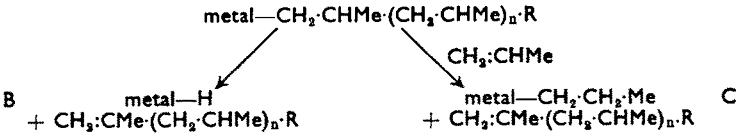
† It is known that *partial* asymmetric synthesis can occur during the formation of a new asymmetric centre in the β-position with respect to a resolved asymmetric carbon atom (cf. e.g. ref. 4).

‡ A *pure* enantiomorphic form could not be expected even under conditions of 100% asymmetric synthesis, since chain-termination processes such as the following[1d]



would result in the formation of the new catalytic species B and C, and thus enable new chain-growth to start in the absence of the desired asymmetric influence.

[3] *Cf.* R. L. Burwell, *Chem. Revs.* **57**, 895 (1957); D. J. Cram and K. R. Kopecky, *J. Amer. Chem. Soc.* **81**, 2748 (1959).

[4] G. I. Fray and N. Polgar, *J. Chem. Soc.* 2036 (1956).

[5] See N. G. Gaylord and H. F. Mark, *Polymer Reviews* Vol. 2, Chap. 4. Interscience, New York (1959).

[6] P. Pino and G. P. Lorenzi, *J. Amer. Chem. Soc.* **82**, 4745 (1960).

[7] *Cf.* J. v Schooten and P. W. O. Wijga in *High Temperature Resistance and Thermal Degradation of Polymers* (*S.C.I. Monograph No.* 13), p. 432. Society of Chemical Industry, London (1961).

with aluminium in 2,2,4-trimethylpentane finally afforded a solution of (+)-tri(2-methylpent-1-yl)aluminium(VI). The corresponding racemic compound, (±)-tri(2-methylpent-1-yl)aluminium, was obtained from (±)-2-methylpentanoic acid in a similar way.

I $CH_2{:}CH\cdot CH_2\cdot CHMe\cdot CO_2H$
II $CH_3\cdot (CH_2)_2\cdot CHMe\cdot CO_2H$
III $CH_3\cdot (CH_2)_2\cdot CHMe\cdot CH_2OH$
IV $CH_3\cdot (CH_2)_2\cdot CHMe\cdot CH_2Cl$
V $(CH_3\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2)_2Hg$
VI $(CH_3\cdot CH_2\cdot CH_3\cdot CHMe\cdot CH_2)_3Al$

During the course of this work, which was carried out in 1958–59, Pino *et al.*[8] reported the synthesis of the etherate of (+)-tri(2-methylbutyl)aluminium (VII) from (−)-2-methylbutanol (VIII) by a route which differed from ours only in that the Grignard compound obtained from the chloro-derivative (IX) was converted directly into the final product VII by reaction with aluminium chloride in ether. The optical purity of VII was proved by treatment with oxygen, followed by hydrolysis, which yielded the alcohol (VIII) with essentially the same rotation as that of the starting material. Moreover, it was shown that negligible racemization occurred on treatment of the active trialkylaluminium (VII) with titanium trichloride at 80–90° for 13 hours.

VII $(CH_3\cdot CH_2\cdot CHMe\cdot CH_2)_3Al$
VIII $CH_3\cdot CH_2\cdot CHMe\cdot CH_2OH$
IX $CH_3\cdot CH_2\cdot CHMe\cdot CH_2Cl$
X $(CH_3\cdot CH_2\cdot CHMe\cdot CH_2)_2Hg$

Recently, however, Murahashi *et al.*[9] have prepared (+)-tri(2-methylbutyl)aluminium (VII) from the (−)-alcohol (VIII) *via* the (+)-dialkylmercury (X), and reported that a sample of VIII obtained by reconversion of VII had an optical purity of only 27 per cent.† This prompted us to check the optical purity of our (+)-trialkylaluminium (VI) by the same means. The result was similar, the derived alcohol (III) having an optical purity of 38 per cent, i.e. the (+)-trialkylaluminium (VI) contained 69 per cent of the (+)- and 31 per cent of the (−)-enantiomorph. The ratio of the (+)-to the (−)-form was therefore greater than 2:1, and this was considered to be sufficient to provide a valid test of the original hypothesis.

The solutions of (+)- and (±)-tri(2-methylpent-1-yl)aluminium were used directly for comparative polymerization experiments with propylene. The resulting samples of isotactic polypropylene had identical melting points, and no optical activity could be detected in the polymer prepared with the optically active catalyst system‡ nor in the products of its pyrolysis. It seems, therefore, that the stereospecific orientation of the

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† The partial racemization occurring in the synthetic procedure evidently took place during the reaction of the (+)-dialkylmercury with aluminium. The synthesis of (+)-tri(2-methylbutyl)aluminium of high optical purity has now been achieved by Pino and his collaborators[10] by treating the appropriate (+)-alkyllithium with aluminium chloride in benzene.

‡ Similar results have been reported for the polymerization of styrene using (+)-tri(2-methylbutyl) aluminium and α-titanium trichloride.[9]

[8] P. Pino, L. Lardicci and G. P. Lorenzi, *Ann. Chim. Italy* **48**, 1426 (1958).

[9] S. Murahashi, S. Nozakura and S. Takeuchi, *Bull. Chem. Soc. Japan* **33**, 658 (1960).

[10] L. Conti, L. Lardicci and P. Pino, *Chimica e Industria* **43**, 414 (1961).

monomer units in isotactic polypropylene is not due to asymmetric induction under the influence of the asymmetric centres in the growing chains.†

We await with interest the experimental testing of other suggestions concerning the stereospecific control of the polymerization.

In additional experiments, the possibility that unidirectional helix formation might be induced in a growing polymer chain under the influence of an asymmetric environment[12] was investigated. Propylene was polymerized in (+)-pinane, employing as catalysts (a) triethylaluminium and α-titanium trichloride, and (b) triethylaluminium and titanium tetrachloride. The resulting specimens of isotactic polymer differed from those prepared in e.g. 2,2,4-trimethylpentane in that they were obtained in a fibrous rather than a granular form, but there was little difference in melting point, and no optical activity was detected.

EXPERIMENTAL

Unless otherwise stated, α refers to homogeneous liquids (*l* 0·5).

(+)-2-*Methylpent-4-enoic acid* (I)

(±)-2-Methylpent-4-enoic acid was prepared, and resolved via the quinine salt, in the known manner[4,13] to afford the (+)-enantiomorph, b.p. 100–102°/21 mm, α_D^{21} 7·82° (*l* 1), $[\alpha]_D^{21}$ +8·20°. Fray and Polgar[4] recorded α_D^{21} +7·86° (*l* 1), $[\alpha]_D^{19}$ +8·24°; Ställberg-Stenhagen recorded α_D^{16} +7·62° (*l* 1) (ref. 13) and α_D^{20} +7·88° (*l* 1) (ref. 14).

Further quantities of the (+)-acid were obtained from the mother-liquors of the crystallizations of the quinine salt by the racemization and re-resolution procedure described by Fray and Polgar.[4]

(+)-2-*Methylpentanoic acid* (II)

The above unsaturated acid (18·5 g) was hydrogenated in ethanol at room temp and atm press in the presence of 2% palladized strontium carbonate to yield (+)-2-methylpentanoic acid (17·7 g, 94%), b.p. 98–100°/19 mm, $[\alpha]_D^{22}$ +18·5°. Ställberg-Stenhagen[13] recorded $[\alpha]_D^{16}$ +18·5°; Holliday and Polgar[15] gave $[\alpha]_D^{14}$ +18·08°.

(±)-2-*Methylpentanoic acid*

Carboxylation of the Grignard reagent obtained from (±)-2-bromopentane (150 g) and magnesium (24 g) in ether (300 cc) afforded the (±)-acid (71 g, 62%), b.p. 102–104°/23 mm.

(−)-2-*Methylpentan*-1-*ol* (III)

Reduction of (+)-2-methylpentanoic acid (15·0 g) with lithium aluminium hydride (8 g) in ether (300 cc) gave the (−)-alcohol (10·9 g, 83%), b.p. 149–150°/773 mm, n_D^{18} 1·4185, α_D^{20} −5·28°, $[\alpha]_D^{20}$ −12·9°. Holliday and Polgar[15] recorded n_D^{14} 1·4182, $\alpha_D^{11\cdot5}$ −8·36°.‡

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† An optically active isotactic *trans*-1,4-polymer of penta-1,3-diene has recently been obtained by Natta *et al.*,[11] using vanadium trichloride and (+)-tri(2-methylbutyl) aluminium etherate as polymerization catalyst, and the authors consider that the rotatory power of the polymer must result from the asymmetric carbon atoms in the chains

$$\text{—}CH_2.CH{:}CH.\overset{*}{C}HMe.CH_2.CH{:}CH.\overset{*}{C}HMe.CH_2.CH{:}CH.\overset{*}{C}HMe\text{—}.$$

There are, however, obvious fundamental differences between this case and that of isotactic polypropylene.

‡ This figure was probably in error (private communication from Dr. N. Polgar).

[11] G. Natta, L. Porri, A. Carbonaro, and G. Lugli, *Chimica e Industria*, **43**, 529 (1961).

[12] *Cf*. N. G. Gaylord and H. F. Mark, *Polymer Reviews* Vol. 2, Chap. 5, pp. 59, 60. Interscience, New York (1959).

[13] S. Ställberg-Stenhagen, *Arkiv Kemi, Mineralog. Geol.* **23A**, No. 15 (1946).

[14] S. Ställberg-Stenhagen, *Arkiv Kemi* **1**, No. 18 (1950).

[15] I. A. Holliday and N. Polgar, *J. Chem. Soc.* 2934 (1957).

(±)-2-*Methylpentan*-1-*ol*

Similar reduction of (±)-2-methylpentanoic acid (40 g) gave the (±)-alcohol (29 g, 82%), b.p. 149–152°/769 mm.

(−)-1-*Chloro*-2-*methylpentane* (IV)

Thionyl chloride (9·9 g, 0·5 mol.) was added dropwise, with stirring, to a cold (ice-salt bath) mixture of (—)-2-methylpentan-1-ol (17·0 g, 1 mol.) and pyridine (13·2 g, 1 mol.); more thionyl chloride (19·8 g, 1 mol.) was then added rapidly. Next day the mixture was kept at 95–100° (bath) for 24 hr, and the upper layer was separated and diluted with ether. Ice was added, and the ethereal solution was washed successively with water, saturated sodium carbonate solution, and water again. The dried ($MgSO_4$) solution was then distilled to yield (−)-1-*chloro*-2-*methylpentane* (15·0 g, 75%), b.p. 127–129°/774 mm, n_D^{21} 1·4195, d_4^{23} 0·875, $[\alpha]_D^{25}$ −4·73° (Found: C, 60·0; H, 10·9; Cl, 29·1. $C_6H_{13}Cl$ requires: C, 59·7; H, 10·9; Cl, 29·4%).

(±)-1-*Chloro*-2-*methylpentane*

Treatment of (±)-2-methylpentan-1-ol (12·0 g) with thionyl chloride in pyridine similarly afforded the (±)-chloro-compound (9·4 g, 66%), b.p. 127–129°/759 mm.

(+)-*Di*(2-*methylpent*-1-*yl*)*mercury* (V)

The Grignard reagent was prepared from (−)-1-chloro-2-methylpentane (7·9 g) and magnesium (1·6 g) in tetrahydrofuran (100 cc), and the clear solution decanted under nitrogen. Mercuric chloride (7·3 g) in tetrahydrofuran (15 cc) was added dropwise, with stirring, to the Grignard solution refluxing under nitrogen, and after the addition (1½ hr) the stirring and refluxing were continued for 2 days. The mixture was filtered, and most of the solvent was removed from the filtrate by evaporation. The residue was treated with water, then with a little dil sulphuric acid, and the product was collected with ether. The dried ($MgSO_4$) ethereal solution was evaporated, and the residue distilled to give (+)-*di*(2-*methylpent*-1-*yl*)*mercury* (8·9 g, 89% on the mercuric chloride), b.p. 93–95°/0·35 mm, n_D^{21} 1·4907, d_4^{25} 1·51, $[\alpha]_D^{27}$ +7·35° (Found: C, 39·7; H, 7·2. $C_{12}H_{26}Hg$ requires: C, 38·9; H, 7·1%).†

(±)-*Di*(2-*methylpent*-1-*yl*)*mercury*

Similar treatment of the Grignard compound from (±)-1-chloro-2-methylpentane (20·0 g) with mercuric chloride (18·0 g) in tetrahydrofuran afforded (±)-*di*(2-*methylpent*-1-*yl*)*mercury* (19·2 g, 78% on the mercuric chloride), b.p. 92–94°/0·3 mm, n_D^{20} 1·4910 (Found: C, 39·9; H, 7·1. $C_{12}H_{26}Hg$ requires: C, 38·9; H, 7·1%).†

(+)-*Tri*(2-*methylpent*-1-*yl*)*aluminium* (VI)

A mixture of (+)-di(2-methylpent-1-yl)mercury (8·6 g), aluminium "flitters" (0·7 g), and 2,2,4-trimethylpentane (100 cc) was stirred and refluxed under nitrogen for 3 days. The resulting mixture was allowed to cool and settle, and the clear solution of (+)-*tri*(2-*methylpent*-1-*yl*)*aluminium* was decanted under nitrogen. The aluminium content of the solution was estimated by precipitation of the aluminium as the "oxinate," followed by acidification and bromometric determination of the liberated oxine; the concentration of the solution was found to be 30 g/l. (corresponding to a yield of ca. 70%). A sample of the solution, $[\alpha]_D^{24}$ ca. +12°, when treated successively with oxygen and dil. sulphuric acid, afforded partially racemized (−)-2-methylpentanol, α_D^{26} −2·03° (optical purity 38%).

(±)-*Tri*(2-*methylpent*-1-*yl*)*aluminium*

Treatment of (±)-di(2-methylpent-1-yl)mercury (15·0 g) with aluminium (1·0 g) in 2,2,4-trimethylpentane (100 cc) similarly afforded a solution of the (±)-trialkylaluminium, containing 56 g/l. (ca. 75% yield).

Polymerization experiments with (+)- *and* (±)-*trialkylaluminium*

Materials. The above solutions of (+)- and (±)-tri(2-methylpent-1-yl) aluminium were used directly. α-Titanium trichloride (Stauffer Chemical Co.) was stored and handled as a suspension in

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† High carbon values were obtained on repeated analyses.

degassed liquid paraffin. 2,2,4-Trimethylpentane was dried over sodium. Propylene was purified by passage through a drying-train containing calcium chloride and magnesium perchlorate and then through a hydrocarbon solution of trialkylaluminium.

(a) *Using (+)-tri(2-methylpent-1-yl)aluminium.* Propylene was passed for 6 hr into a stirred mixture of α-titanium trichloride (3·5 mmoles), (+)-tri(2-methylpent-1-yl)aluminium (5·0 mmoles), and 2,2,4-trimethylpentane (total volume 225 cc) at 80–85°. Ethanol containing a little conc hydrochloric acid was added, and the solid polymer collected by filtration. The polypropylene was treated overnight with ethanolic hydrochloric acid, washed successively with ethanol and ether, and dried. It was then extracted with boiling n-heptane in a Soxhlet apparatus for 24 hr, affording heptane-insoluble (4·3 g) and heptane-soluble (0·5 g) fractions. The melting behaviour of the heptane-insoluble polymer was examined using a hot-stage microscope with crossed Nicols; the temp at which the polymer was completely molten was 166°. No optical activity could be detected in the heptane insoluble fraction (thin film). The heptane-soluble fraction likewise had no measurable rotation (*l* 2, *c* 0·3 in CCl_4).

(b) *Using (±)-tri(2-methylpent-1-yl)aluminium.* A similar experiment using the (±)-trialkylaluminium (5·0 mmoles) yielded polypropylene of which 6·4 g was heptane-insoluble and 0·8 g heptane-soluble. The heptane-insoluble fraction was completely molten at 166°.

Pyrolysis experiments

The following experiments were carried out using the heptane-insoluble fraction of the polymer prepared with the (+)-trialkylaluminium.

(a) The polymer was heated rapidly in an open vertical tube; the waxy material which condensed on the cooler part of the tube had no measurable rotation (*l* 2, *c* 1·0 in CCl_4).

(b) Variation of the rate and duration of heating in a similar experiment produced a distillate which contained a waxy solid and an oil. These were separated by extraction with cold acetone; neither fraction showed optical activity (*l* 1, *c* 1·0 in CCl_4).

(c) The polymer (1·0 g) was heated in a distillation flask (under nitrogen) at such a rate that steady distillation occurred. Fractions of b.p. 100–150° (0·19 g) and b.p. 150–210° (0·57 g) were collected; neither fraction had a measurable rotation (homog, *l* 0·5).

Polymerization experiments carried out in (+)-pinane†

(a) *Using triethylaluminium and α-titanium trichloride.* A polymerization experiment similar to those described above was carried out in (+)-pinane (200 cc) using triethylaluminium (5 mmoles) and α-titanium trichloride (3·5 mmoles). The resulting polypropylene, which had a fibrous appearance, was extracted with n-heptane as above. The heptane-insoluble fraction (0·12 g), m.p. 167°, had no measurable rotation (thin film), and the heptane-insoluble material (0·01 g) also showed no optical activity (*l* 1, *c* 0·5 in $CHCl_3$).

(b) *Using triethylaluminium and titanium tetrachloride.* Triethylaluminium (1·7 mmoles) was added to a stirred solution of titanium tetrachloride (5 mmoles) in (+)-pinane (150 cc), and the resulting mixture was kept at 80–85° for 2 hr. More triethylaluminium (13·3 mmoles) was then added, and propylene was passed in for 1 hr at the same temp. The resulting fibrous polymer furnished a heptane-insoluble fraction (0·35 g), m.p. 161°, showing no rotation (thin film), and a heptane-soluble fraction (0·40 g), also having no measurable rotation (*l* 2, *c* 0·2 in $CHCl_3$).

† The (+)-pinane ($[\alpha]^{24}_{D}$ +21·6°) was kindly supplied by Boake Roberts & Co.