to the conclusion that an asymmetric synthesis of the poly-
mer has in fact been achieved.

These results demonstrate a new method for the synthesis of optically active polymers.

Experimental:
Polyvinylacetophenone was prepared according to Kenyon[6], and (+)-a-methylbenzyl alcohol according to Červinka[3] with [α]D = +19.5° (homogeneous), in 45–48% optical yield. (+)-Poly-[4-(2-hydroxyethyl)styrene] (2):
LAI4H4 (2.112 g, 0.0553 mole) was added in tetrahydro-
furan (250 ml), quinine ([α]D = −172°; 16.2 g, 0.05 mole) was added, and the mixture was boiled for 10 min. A solution of (1) (4 g, 0.0274 unit mole) in tetrahydrofuran (50 ml) was added dropwise during 10 min and the whole boiled under reflux for 6 h. The polymer was precipitated by pouring the mixture into 3% sulfuric acid and was reprecipitated from tetrahydrofuran by 3% sulfuric acid and then from tetra-
hydrofuran by saturated sodium hydrogen carbonate solution and water. Yield 2.5 g.

Received: December 11, 1967 [Z 690 IE]
German version: Angew. Chem. 80, 236 (1968)

[*] Prof. Dr. Rolf C. Schulz and Dipl.-Chem. H. Mayerhöfer
Organisch-chemisches Institut der Universität
65 Mainz, Johann-Joachim-Becher-Weg 18–20 (Germany)

[**] Part of the dissertation by H. Mayerhöfer, Mainz D 77.

[***] We are grateful to the Deutsche Forschungsgemeinschaft
and the Fonds der Chemischen Industrie for financial support.


Formation of Poly(methylene)alumina


Complex formation between biscyclopentadienyltitanium(iv) compounds (Cp2TiCl2 and Cp2Ti(CH3)2) and trimethyl-
aluminum has a half-reaction time of < 10−2 seconds even at 45°C. In both cases the complex formation is accom-
panied by a very slow reaction. This is indicated by develop-
ment of an absorption band at 460 nm which is at first syn-
chronous with an evolution of methane. It thus seemed
likely that the reaction should be considered as formation of the compounds with CH2 bridges between Ti and Al that
C. Feay[1] had isolated.

However, we observed that further methane was evolved after the band at 460 nm had developed; the reaction was
therefore studied without use of a solvent and with a large ex-
cess of Al(CH3)3. The rate of initial evolution of methane followed the rate law:
\[ \text{d(CH}_4)/\text{dt} = k \text{[Ti][Al(CH}_3)_3] \]

If the initial molar ratio Cp2TiCl2/Al(CH3)3 was 1:100, the evolution of methane increased after ca. 100 hours at room

temperature. The viscosity of the mixture increased from 0.9

cp to > 100 cp; after 350 hours the reaction mass solidified,

We therefore propose formula (1), where n is probably
about 100. (If this were not so, more DCH3 would be formed
by reaction with the end groups.)

\[ \frac{\text{-Al-C-CH}_2}{\text{Cl}}_n \]

In this connection the compound (2) that was obtained by H. Lehmkohl and R. Schaefler[1] by a quite different route
should be noted.

Before the extraction, the reaction mass evolves only traces of Al(CH3)3 in a high vacuum. It dissolves in tetrahydrofur-
an. Viscosity determination (on the basis of the Staudinger relation that is valid for polystyrene) gave a mean degree of
polymerization \( P_n = 3(1 - p) = 20 \), corresponding to a degree of reaction \( p = 0.95 \), whereas we expected \( p = 0.85 \) to 0.90 on the basis of the amount of methane evolved.

The extraction residue, swollen and suspended in benzene, reacts with titanium tetrachloride with formation of a
voluminous, almost black, mass. A suspension of this com-

pound in hydrocarbons is an efficient catalyst for the poly-
reaction of ethylene and \( \alpha \)-olefins.

Received: December 13, 1967 [Z 689 IE]

German version: Angew. Chem. 80, 190 (1968)

[6*] Prof. H. Sinn, Dipl.-Chem. H. Hinck, and Dr. F. Bandermann
Lehrstuhl für Angewandte Chemie,
Institut für Organische Chemie, Chemisches Staatsinstitut
2 Hamburg, Papendamm 6 (Germany)

[6**] Doz. Dr. H. F. Grützmacher
Institut für Organische Chemie, Chemisches Staatsinstitut
2 Hamburg, Papendamm 6 (Germany)


N-(Fluoriformyl)iminosulfur Dichloride and
N-(Chloroformyl)iminosulfur Dichloride

By H. W. Roesky and R. Meiss[6*]

As part of our study of sulfur-nitrogen compounds we have prepared iminosulfur dichlorides -N-SCl2 from the corresponding fluor derivatives. N-(Fluoriformyl)iminosulfur dichloride (1) [2] reacts with phosphorus pentachloride at room temperature, giving N-(fluoriformyl)iminosulfur dichloride (2) and phosphorus pentachloride.

\[ \frac{\text{O}}{\text{F}} \cdot \text{C} \cdot \text{N} = \text{S} \cdot \text{Cl} \rightarrow 5 \text{P} \cdot \text{C} \cdot \text{N} = \text{S} \cdot \text{Cl} + 2 \text{PCl}_5 \]

33 g of (1) is added dropwise with ice cooling to 23.1 g of PCl5. The mixture is then stirred for 2 h at 0°C and for 24 h at room temperature. The volatile products are removed in a