

to the conclusion that an asymmetric synthesis of the polymer 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 (+)- α -methylbenzyl alcohol according to *Červinka*^[3] with $[\alpha]_{589} = +19.5^\circ$ (homogeneous), in 45–48% optical yield.

(+)-Poly-[4-(2-hydroxyethyl)styrene] (2):

LiAlH_4 (2.112 g, 0.0553 mole) was suspended in tetrahydrofuran (250 ml), quinine ($[\alpha]_{\text{D}} = -172^\circ$; 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 tetrahydrofuran by saturated sodium hydrogen carbonate solution and water. Yield 2.5 g.

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Formation of Polymethyl(methylene)aluminum

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Complex formation between biscyclopentadienyltitanium(IV) compounds (Cp_2TiCl_2 and $\text{Cp}_2\text{TiClCH}_3$) and trimethylaluminum has a half-reaction time of $< 10^{-2}$ seconds even at -45°C . In both cases the complex formation is accompanied by a very slow reaction. This is indicated by development of an absorption band at 460 nm which is at first synchronous with an evolution of methane. It thus seemed likely that the reaction should be considered as formation of the compounds with CH_2 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 excess of $\text{Al}(\text{CH}_3)_3$. The rate of initial evolution of methane followed the rate law:

$$d[\text{CH}_4]/dt = k[\text{Ti}][\text{Al}(\text{CH}_3)_3]^{0.5}$$

If the initial molar ratio $\text{Cp}_2\text{TiCl}_2/\text{Al}(\text{CH}_3)_3$ 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,

yet slowly evolved more methane. In sum, almost 1 mole of methane was liberated per mole of $\text{Al}(\text{CH}_3)_3$.

The solidified mass does not dissolve in petroleum ether, and swells in benzene; components of low molecular weight and products formed from the titanium compound are removed by extraction in a glass Soxhlet apparatus with benzene. The residue is a pale greyish powder with the composition $\text{C}_2\text{H}_5\text{Al}$. It reacts quantitatively with deuterium chloride:



We therefore propose formula (1), where n is probably about 100. (If this were not so, more DCH_3 , would be formed by reaction with the end groups.)



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

Before the extraction, the reaction mass evolves only traces of $\text{Al}(\text{CH}_3)_3$ in a high vacuum. It dissolves in tetrahydrofuran. Viscosity determination (on the basis of the Staudinger relation that is valid for polystyrene) gave a mean degree of polymerization $P_n = 1/(1-p) = 20$, 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 compound in hydrocarbons is an efficient catalyst for the polymerization of ethylene and α -olefins.

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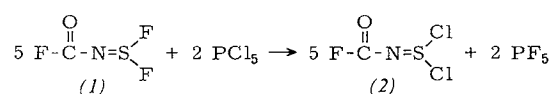
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N-(Fluoroformyl)iminosulfur Dichloride and N-(Chloroformyl)iminosulfur Dichloride

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As part of our study of sulfur-nitrogen compounds^[1] we have prepared iminosulfur dichlorides $-\text{N}=\text{SCl}_2$ from the corresponding fluoro derivatives. N-(Fluoroformyl)iminosulfur difluoride (1)^[2] reacts with phosphorus pentachloride at room temperature, giving N-(fluoroformyl)iminosulfur dichloride (2) and phosphorus pentafluoride.



33 g of (1) is added dropwise with ice cooling to 23.1 g of PCl_5 . 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