

Catalytic polymerization of acetylene by titanium(III) complexes

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Polyacetylene was obtained by contacting the gaseous acetylene at room temperature and atmospheric pressure with catalytic system containing various titanium(III) complexes and magnesium bis(cyclopentadienide) in aprotic coordinating solvents. The probable reaction mechanism of the catalytic polymerization of acetylene is discussed.

Был получен полиацетилен при контакте газообразного ацетилена при лабораторной температуре и атмосферном давлении с каталитической системой, содержащей различные комплексы титана(III) и бис(циклопентадиенид) магния в апротонных координирующих растворителях. Обсуждается вероятный механизм реакции каталитической полимеризации ацетилена.

The polymerization reactions of acetylene, though known for several decades [1—4], have become objects of renewed interest recently. This is chiefly due to the recent observation that polyacetylene (polyvinylene), $(\text{CH})_x$, which is the simplest of all possible conjugated organic polymers and which is the nearest analogue to conventional inorganic semiconductors, can be chemically doped by various donors and acceptors to give n-type or p-type semiconductors [5—8]. When the pure polyacetylene, which is known to be a semiconductor [9, 10], is doped by iodine or arsenic(V) fluoride, its electrical conductivity increases sevenfold and the material thus formed has the highest room-temperature electrical conductivity from among all covalent organic polymers.

Natta *et al.* [11, 12] prepared polyacetylene using the catalyst $\text{Ti}(\text{OC}_3\text{H}_7)_4 - (\text{C}_2\text{H}_5)_3\text{Al}$. It gave, however, the yield of only 2 g of dark insoluble polymer per 1 g of catalyst. One of the first systematic studies of standard Ziegler—Natta catalysts for polymerization of acetylene was made by Watson *et al.* [13], but the yields of polyacetylene per gram of catalyst were also low. In a series of papers by Shirakawa *et al.* [14—17], the synthesis and properties of crystalline films of polyacetylene prepared using Ziegler—Natta catalysts were investigated and a method for determination of *cis*- and *trans*-isomer was reported [16—18]. Hsu *et al.* [8] found that acetylene polymerizes at atmospheric pressure by contacting the gas with

solution of $\mu-(\eta^1:\eta^5\text{-cyclopentadienyl})\text{tris}(\eta\text{-cyclopentadienyl})\text{dтитанium}(\text{Ti-Ti})$ in hexane without presence of an alkylaluminium cocatalyst. At room temperature chiefly *trans*-polyacetylene was formed; by a polymerization reaction at -80°C predominantly copper-coloured gelatinous *cis*-polyacetylene was obtained. Removing the solvent very slowly under vacuum, it was possible to prepare from this gel a glossy polyacetylene film of grey metallic appearance.

The aim of our present work was the study of catalytic polymerization of acetylene to linear polyacetylene using cyclopentadienyl titanium(III) complexes. The latter were prepared by a direct reaction of titanium(III) chloro complexes whose composition was $\text{TiCl}_3 \cdot 3\text{L}$ and $\text{TiCl}_3 \cdot 2\text{L}$ (L = tetrahydrofuran, acetonitrile, pyridine, methanol, ethanol, 1-propanol, 1-butanol) with magnesium bis(cyclopentadienide), $\text{Mg}(\text{C}_5\text{H}_5)_2$, in aprotic coordinating and noncoordinating solvents (tetrahydrofuran, benzene) [19].

Experimental

With regard to the extremely easy oxidability of titanium(III) complexes all experiments were made in closed glass apparatuses and under inert atmosphere [20]. Synthesis of the starting complexes and purification of solvents are described in papers [20—24]. Magnesium bis(cyclopentadienide) was prepared by direct synthesis of magnesium with thermally cracked dicyclopentadiene [25] and was used in the form of benzene or tetrahydrofuran solution, which was also protected against the action of oxygen and moisture.

A schematic drawing of the apparatus for automatic control and registration of acetylene consumed in the reaction used for the investigation of catalytic activity of titanium(III) complexes in solution is shown in Fig. 1. An electrolyzer (1), a mercury storage flask (2), a gauging tube (3) with a platinum resistance wire (11), a small mercury manometer (4), a control bubble trap (5), a reaction vessel (6), system of bubblers for controlling the inlet (31, 32) and outlet (33) of gas, electric blocks-sources of electrical current, and a registration device constitute the main parts of the apparatus.

In the course of the reaction of the gaseous acetylene with the solution of the catalytic system the gas pressure in the apparatus decreases. As a consequence of this a contact in the manometer (4) is switched on and the electric device sets the electrolyzer (1) in action. By electrolysis of approximately 20% of solution of sodium hydroxide a gas evolves (mixture of oxygen and hydrogen) which extrudes the mercury out of the tube till the reacting gas (acetylene) equilibrates a required pressure which can be adjusted with the aid of a sliding contact of the manometer (4). Then the manometer contacts are switched on and the electric block stops the work of the electrolyzer. The amount of gas consumed in the course of the reaction is registered automatically. The main part of the recording device is the resistor (11) (i.e. a thin platinum wire stretched on a glass rod along the tube wall), which changes with the height of the mercury column. Change of the resistance of the platinum wire brings about change in voltage at constant current and this is recorded by a compensation recorder.

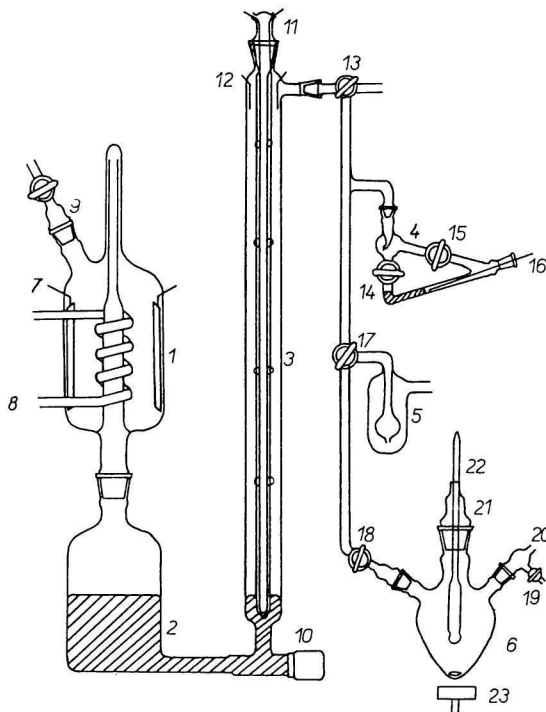


Fig. 1. Apparatus for investigation of catalytic activity of complexes in solution.

A typical experiment proceeded in the following way: Into 100 cm³ of brownish green solution consisting of 80 cm³ benzene, 20 cm³ tetrahydrofuran, 10⁻⁵ mole TiCl₃ · 3C₄H₈O, and 10⁻⁴ mole (C₃H₅)₂Mg, gaseous acetylene was introduced in an absorption apparatus (Fig. 1). After about 2 min the solution started turning red, which proceeded from a bright red to reddish purple. After about 5 min a purplish black flaky precipitate began separate out from this solution which itself turned brownish red to brownish olive green. After about 2 h such an amount of polyacetylene separated out that the suspension could be mixed with difficulties only and the sorption of acetylene slowed down. The solid polyacetylene was separated by filtration and then was washed with benzene and tetrahydrofuran, upon which it agglomerated and formed hard clods of considerable strength. The yield was about 0.3 g, *i.e.* about 10³ moles C₂H₂ per 1 mole of catalyst Ti(III). The filtrate was brownish green and it was able to catalyze again the polymerization of further portion of acetylene.

Results and discussion

The basic experiments were made with the solutions of TiCl₃ · 2C₄H₈O in benzene and with solutions of TiCl₃ · 3C₄H₈O in tetrahydrofuran [22]. By interac-

tion of magnesium bis(cyclopentadienide) with suspension of titanium(III) chloride in tetrahydrofuran, titanium(III) bis(cyclopentadienyl) chloride was formed [26, 27], which is dimeric in benzene solution, $\text{Cp}_2\text{TiCl}_2\text{TiCp}_2$ ($\text{Cp} = \text{C}_5\text{H}_5$) [28, 29]. Various colourings of this substance are reported: green [27], greenish brown [28—30], and violet brown [27]. By the action of monodentate ligands on the dimer $(\text{Cp}_2\text{TiCl})_2$ the monomers $\text{Cp}_2\text{TiCl}\cdot\text{L}$ ($\text{L} = \text{C}_5\text{H}_5\text{N}$, NH_3 , NH_2CH_3 , etc.) are formed [26]. By reaction of sodium cyclopentadienide with titanium(III) bis(cyclopentadienyl) chloride the green tris(cyclopentadienyl)titanium(III) was prepared in which according to [31] one of the cyclopentadienyl ligands is σ -bonded. According to X-ray diffraction analysis [32] the third cyclopentadienyl ligand is bonded through two carbon atoms forming a three-centre four-electron bond.

In our experiments we investigated the successive formation of cyclopentadienyl titanium(III) complexes in a system which contained 0.01 M benzene solution of trichloro-bis(tetrahydrofuran)titanium(III) with a successively increasing content of magnesium bis(cyclopentadienide). The colour of the solution changes consecutively from the original green to reddish brown, olive green, grass green, and finally to bright green, which most probably corresponds to Cp_3Ti . Practically neither of these systems catalyzed the polymerization of acetylene.

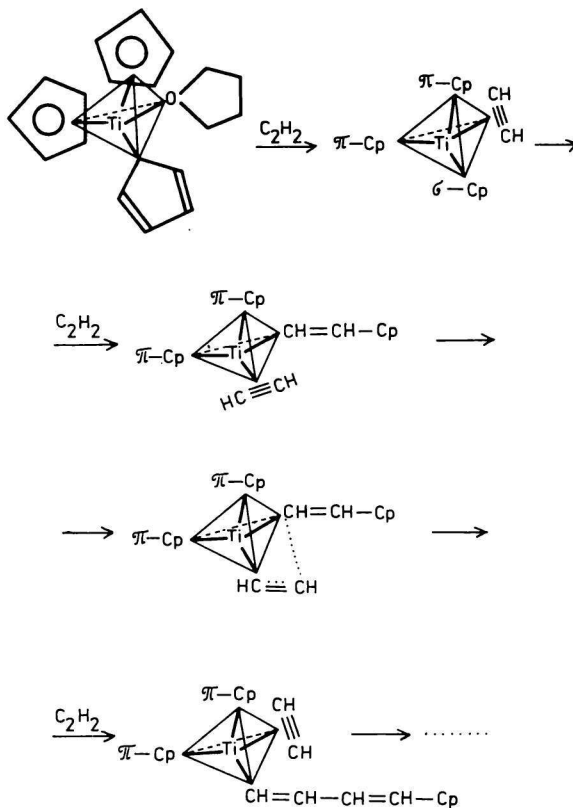
When, however, aprotic donor solvent (e.g. tetrahydrofuran, 1,4-dioxane, acetonitrile, etc.) was added in excess into a system in which the mole ratio of $\text{TiCl}_3\cdot 2\text{C}_4\text{H}_8\text{O}:(\text{C}_5\text{H}_5)_2\text{Mg}$ was approximately 1:7 or more, then almost immediately the polymerization of acetylene to black insoluble polyacetylene $(\text{CH})_x$ set in. For this reason solutions of the following complexes in tetrahydrofuran, and partly in acetonitrile, were examined as regards their catalytic activity for acetylenic polymerization: $\text{TiCl}_3\cdot 3\text{C}_4\text{H}_8\text{O}$, nitrilo complexes $\text{TiCl}_3\cdot 3\text{C}_5\text{H}_5\text{N}$, $\text{TiCl}_3\cdot 4\text{CH}_3\text{CN}$, $\text{TiCl}_3\cdot 3\text{CH}_2:\text{CHCN}$, alcoholates $\text{TiCl}_3\cdot 3(1-\text{C}_3\text{H}_7\text{OH})$, $\text{TiCl}_3\cdot 3(1-\text{C}_4\text{H}_9\text{OH})$, alkoxo complexes $\text{TiCl}_{1.74}(\text{OCH}_3)_{1.26}$, $\text{TiCl}_{1.60}(1-\text{OC}_3\text{H}_7)_{1.40}$, $\text{TiCl}_{1.40}(2-\text{OC}_3\text{H}_7)_{1.60}$, and $\text{TiCl}_{1.70}(2-\text{OC}_4\text{H}_9)_{1.30}$ (see [33]). In all cases catalytic formation of polyacetylene took place. Polyacetylene separated from the solution as a black, in organic solvents (tetrahydrofuran, acetonitrile, benzene, hexane) insoluble precipitate. The solutions of titanium(III) complexes were catalytically active over a broad range of concentrations (approximately from 10^{-5} M higher).

Comparative experiments were made with the aim to find whether magnesium bis(cyclopentadienide) can be replaced by sodium cyclopentadienide. The polymerization of acetylene was found to take place also in presence of CpNa , the yields, however, were much smaller.

Further the possibility of replacing $\text{TiCl}_3\cdot 3\text{C}_4\text{H}_8\text{O}$ and similar titanium(III) complexes by the tetrahedral dimeric titanium(III) bis(cyclopentadienyl) chloride (in absence of Cp_2Mg), dissolved in benzene (green solution), in tetrahydrofuran (bright yellow solution), in pyridine (brick-reddish brown solution), in acetonitrile (grass green solution), and in dimethylformamide (bright green solution) was

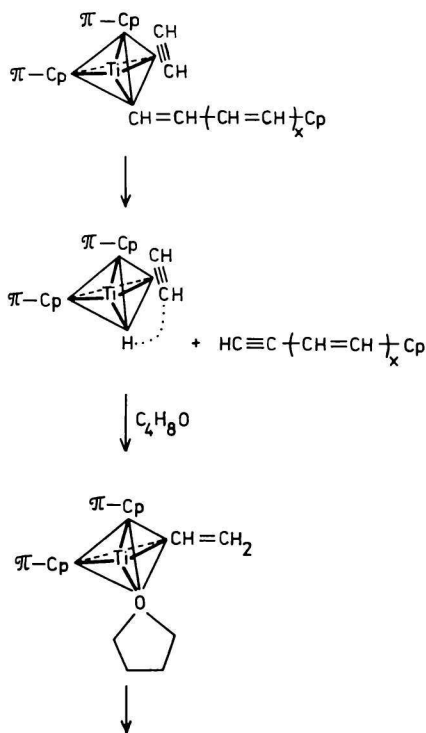
checked. In neither of these cases polymerization took place as long as magnesium bis(cyclopentadienide) in mole ratio 1Ti:6Mg or more was not added in the system. Bis(cyclopentadienyl)titanium(IV) dichloride Cp_2TiCl_2 did not catalyze the polymerization of acetylene, not even in the presence of Cp_2Mg .

The experimental results can be interpreted in the following way: By the action of magnesium bis(cyclopentadienide) on titanium(III) chloro complexes, a successive replacement of terminal chloride ligands by cyclopentadienyl ligands takes place. Since tetrahedral distorted coordination is typical for titanium(III) cyclopentadienyl complexes (if the composition of the complex makes it possible), from the original distorted octahedral or trigonal bipyramidal titanium(III) chloro complexes in a noncoordinating medium, first the tetrahedral dimer $\text{Cp}_2\text{TiCl}_2\text{TiCp}_2$ is formed, from which with further excess of Cp_2Mg only with difficulties Cp_3Ti is formed as this reaction requires an exchange of bridging chloride ligands by terminal Cp ligands. On the other hand, in the presence of a coordinating solvent (tetrahy-



drofuran), by the action of Cp_2Mg the monomeric tetrahedral complex Cp_2TiClL is formed, from which, in consequence of the excess of Cp_2Mg , by replacement of terminal chloride ligand, the catalytically active $(\pi\text{-Cp})_2\text{Ti}(\sigma\text{-Cp})\text{L}$ can arise more readily. Its catalytic activity depends on the strength of the Ti-L bond, which affects the capability of the ligand L to be replaced by acetylene in the course of the reaction.

The catalytic polymerization comprises, most probably, in agreement with recent notions on mechanism of catalytic polymerization of nonpolar olefins by Ziegler—Natta type catalysts [34—36], several consecutive elementary reaction steps, especially replacement of the ligand L by acetylene in the coordination sphere of titanium(III) complex, π coordination and subsequent insertion of the coordinated acetylene molecule, by which conditions for chain growth are formed (Scheme 1) and finally termination of the chain in the consequence of the β elimination reaction (Scheme 2).



Scheme 2

The relative molecular mass of polyacetylene is not known and it cannot be determined by the usual methods since without degradation the polyacetylene does not dissolve in any known solvent. The degree of polymerization can be estimated by indirect methods from the absorption of light in the visible spectral region (*i.e.* from their yellow, red, violet, brown, and black colour in dependence on the increasing length of the conjugated chain). The content of the polyacetylene isomers can be determined from their characteristic absorption in infrared spectrum. The preferred content of isomers can be influenced by adjusting temperature of the reaction system during polymerization: *cis*-polyacetylene is formed mainly at low temperatures (round -78°C), *trans*-isomer at elevated temperature (above 150°C) [16].

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