Inherently Conducting Polymers

Processing, Fabrication, Applications, Limitations

M. Aldissi

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INHERENTLY CONDUCTING POLYMERS

Processing, Fabrication, Applications, Limitations

by

M. Aldissi

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INHERENTLY CONDUCTING POLYMERS

Foreword

Processing, fabrication, applications, and limitations of inherently conducting polymers are covered in this book. Electrically conducting polymers have many potential applications and thus are a focus of research interest. Such polymers depend on a conjugated backbone that can be doped with highly reactive materials to increase conductivity, but this backbone is also the source of instability in these materials.

The work described concentrates on solving these instability problems, using various doping techniques to yield polymers more stable than polyacetylene, $(CH)_x$, the first extensively characterized covalent organic polymer. Several methods of synthesizing conjugated polymers and ways of doping the conjugated backbone are described. The stability of pristine and doped polymers is examined in ambient atmosphere and under thermal treatment, and several stabilization techniques are discussed, including chemical doping, ion implantation, plastification, copolymerization, antioxidative treatments, surface protection, and the use of crown ethers.

Although considerable progress has been made, a fully stable, highly conductive polymer still awaits development, Various possible uses of such a polymer and the conditions for successful applications are described, as are the relative advantages and disadvantages of currently available polymers.

The information in the book is from *Processing, Fabrication, Applications, and Limitations of Inherently Conducting Polymers* by M. Aldissi of the Los Alamos National Laboratory for the U.S. Department of Energy, November 1987.

The table of contents is organized in such a way as to serve as a subject index and provides easy access to the information contained in the book.

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I. Introduction

Electrically conducting polymers have been a center of scientific interest and active multidisciplinary research for the last decade. These materials have attracted academic and industrial research groups not only because of their theoretically interesting properties but also because of their technologically promising future.

Polymers as plastic materials have numerous technological applications because of their low cost, lightness, and flexibility. The discovery of electrical and optical activities in one class of polymers resulted in the development of one of today's exciting areas of condensed matter science.

The main characteristic of a conducting polymer is a conjugated backbone that can be subjected to oxidation or reduction by electron acceptors or donors, resulting in what are frequently termed *p-type* or *n-type* doped materials, respectively. The formation of a complex between the polymer and the dopant results in a considerable increase in electron mobility and, therefore, in electrical conductivity.

A large number of polymer synthesis techniques are available, and many of them are used daily by the polymer chemist. Among these are the stepwise synthesis routes, such as Wittig or Grignard reactions, polycondensation, oxidative coupling, and metal-catalyzed polymerization techniques. Some conducting polymers can also be obtained by using a doping agent, that is, by using anodic oxidation, a technique that leads directly to materials with a high conductivity.

The conjugation of the polymer backbones is necessary for conduction. However, this conjugation is also responsible for the instability of most of these materials to ambient atmosphere, and therein lies the research challenge.

Interest in the conducting polymers began in the mid-1960s, with Little.[1] (See chronology in Fig. 1.) He suggested in his theoretical studies that some organic materials could become superconductors. The first example that has been extensively studied is tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) and its derivatives. The first covalent polymer exhibiting the electronic properties of a metal, but containing no metal atoms, was polymeric sulfur nitride, $(SN)_x$, which was actively studied in the mid- to late 1970s. In 1977, the first covalent organic polymer, polyacetylene $(CH)_x$, which could be doped through the semiconducting to the metallic regime, was reported. This material has served as a prototype for the synthesis and study of other conjugated, dopable organic polymers, several of which have been discovered during the last four years. Polyacetylene has been investigated much more extensively than any other conducting polymer (Fig. 2). This fact is reflected in the discussion here.

II. Synthesis of Conjugated Polymers

A. Polyacetylene

1. Catalyst Categories. The following paragraphs describe the various catalytic systems known to polymerize acetylene.

- **Transition metal derivatives complexed with organometallic compounds.** A large number of transition metal derivatives can initiate polymerization when reduced by trialklyphosphines or trialkylaluminum. For example,

  NiX_2/R_3P (Ref. 2);

  $Ni(C_p)_2/AlEt_3$, $Ru(Cp)_2/AlEt_3$ (Ref. 3), where Cp = cyclopentadienyl;

  Fe dmg-2Py/$AlEt_3$ (Ref. 4), where Py = pyridine and dmg = dimethylglyoximate-2; and

  $NaBH_4$/Ni salt (Ref. 5).

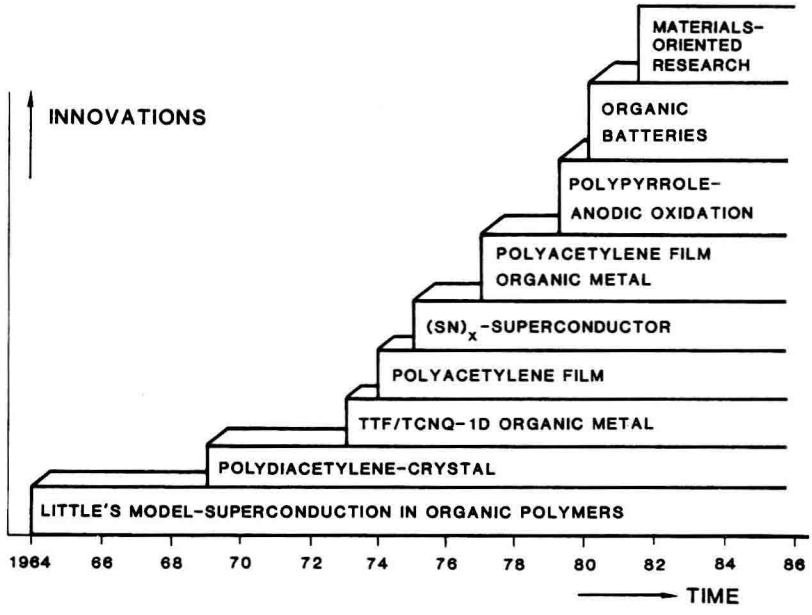

Fig. 1. Time chart of innovations in synthetic metals.

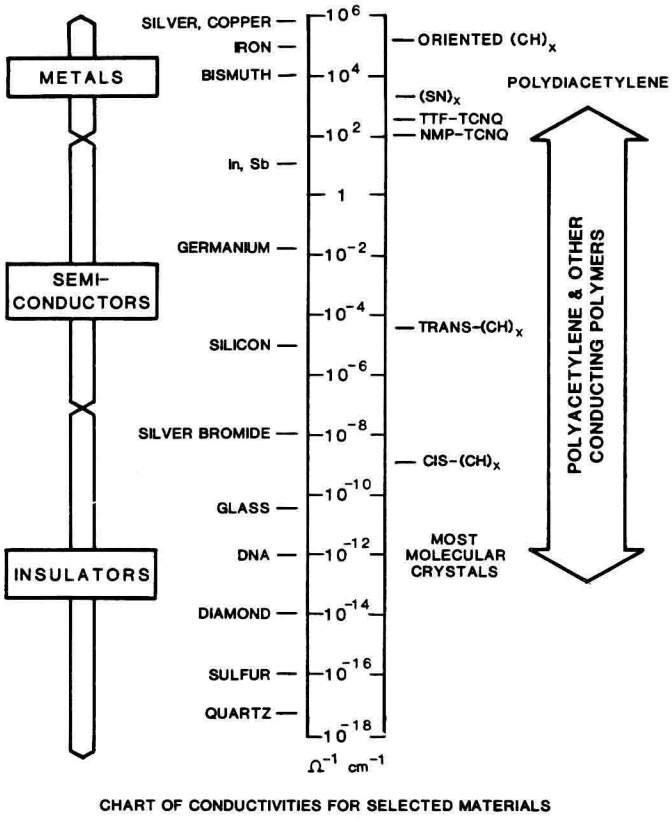

Fig. 2. Chart of conductivities for selected materials.

- **Transition metal derivatives that do not have to be complexed by an organometallic compound, such as tetrabenzyltitanium.** The intermolecular rearrangement during the aging of this catalyst leads to the reduction of Ti^{IV} to Ti^{III}, which could be determined from an electron spin resonance (ESR) study. The coupling of this catalyst with $AlEt_3$ increases its activity for the polymerization reaction.[6]

- **Ziegler-Natta catalyst.** This catalyst can be homogeneous,[7] heterogeneous,[8] or supported,[9] for example, on alumina, silica gel, or magnesium hydroxide.

- **Lanthanide derivatives complexed by organometallic compounds, such as $EuCl_3/AlEt_3$ (Ref. 3) and $Nd(Naph)_3/AlEt_3$.** These couples, when combined with a small amount of other reducing agents, such as acetone, become more active for the polymerization of acetylene.[10]

- **Metathesis catalysts.** These are materials such as $MoCl_5/Ph_4Sn$, WCl_6/Ph_4Sn (Ref. 6) and tricarbonylcyclopentadienylmolybdenum dimer/Ph_4Sn (Ref. 3).

- **Organometallic polymers.** Most of these polymers are prepared by linking a homogeneous catalyst to the polymer, which is functionalized to provide a ligand for linking the catalyst to another polymer chain. The majority of the systems use cross-linked polystyrene. In this process, one of the ligands of the homogeneous catalyst is replaced by the polymeric ligand, and the complex formed in this case retains its basic catalytic activity. However, the activity and the selectivity of the polymeric catalyst depend on the size and polarity of the polymer used as a substrate[11] and on the loading of that substrate.[12]

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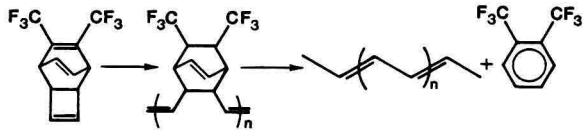
The main advantages of these catalysts are the possibilities of separating the catalyst in a reusable form and of modifying the catalytic activity by changing the substrate. The use of polymeric catalysts could be a method for varying the molecular weight of the desired polymer.

- **Anionic polymers combined with titanium derivatives.** The polymeric catalyst is prepared by alkylation of $Ti(OBu)_4$ with a lithiated polymer by means of an anionic-to-Ziegler-Natta transformation reaction. One of the butoxide groups is replaced by the polymeric chain, forming active sites for the polymerization of acetylene. It was reported[13,14] that styrene/acetylene copolymers could be prepared by alkylating $Ti(OBu)_4$ with polystyryllithium, with a low yield in copolymer.

- **The Durham route,[15] in which the monomer is 7,8-bis(trifluoromethyl) tricyclo[4,2,2,0] deca-3,7,9-triene (I).** The ring-opening polymerization of (I) by using WCl_6:$(C_6H_5)_4S_n$(1:2) and $TiCl_4$:$(C_2H_5)_3$ Al(1:2) involves only the cyclobutene ring, resulting in a soluble precursor polymer (II). This precursor undergoes an elimination reaction to lose hexafluoroxylene as a volatile fraction and to leave polyacetylene in a fully dense form as shown below:[15]



(1)

The synthesis of the polyacetylene powder has been known since the late 1950s, when Natta[7] used transition metal derivatives, which have since become known as Ziegler-Natta catalysts. The characterization of this powder was difficult until Shirakawa et al.[16] succeeded in synthesizing lustrous, silvery, polycrystalline films of $(CH)_x$ and in developing techniques for controlling the cis–trans content.

CIS TRANS

Because the most frequently used method for obtaining high-quality films of polyacetylene is the Ziegler-Natta method, the synthesis of these films and some of their interesting properties are described below.

Polyacetylene films may be prepared by simply wetting the inside walls of a glass reactor vessel with a toluene solution of $AlEt_3$ and $Ti(OBu)_4$ and then immediately admitting acetylene gas at any pressure from a few centimeters up to 1 atm. The cohesive film grows during a period of a few seconds to 1 hour, depending on the pressure of acetylene and the temperature used. The washed and dried film can be readily peeled from the glass surface. The films can therefore be made standing or on substrates, such as glass or metal, with thicknesses varying from 10^{-5} cm to 0.5 cm. If a polymerization temperature of −78°C is used, the film is formed completely as a cis–isomer; if a temperature of 150°C is used (decane solvent), the film is formed as the trans-isomer. With room temperature polymerization, the film is approximately 60% cis- and 40% trans-isomer. The cis-isomer may be conveniently converted to the trans-isomer (the thermodynamically stable form) by heating at 150°C for 30 min to 1 hour. The cis–trans content can be readily determined from the relative intensities of bands in the infrared (IR) spectra characteristics of a given isomer.

Electron microscopy studies show that the as-formed $(CH)_x$ films consist of randomly oriented fibrils, the diameter of which depends upon the experimental conditions used for their preparation. The density of the fibril is 1.2 g/cm^3, as determined by the flotation techniques, while the film density can be varied from 0.05 g/cm^3 to 1.0 g/cm^3; therefore, the active surface area can vary also (50 cm^2/g for a density equal to 0.4 g/cm^3 and a fibril diameter of 200Å). X-ray studies show that the films are polycrystalline, with principal interchain spacing in the cis-polymer of 4.39Å. Films of *cis*-$(CH)_x$ are

flexible and can be stretched easily at room temperature to more than three times their original length with partial alignment of the fibrils. The trans films can be stretched to a very small extent.[17]

The room temperature conductivity of films of polyacetylene depends on the cis-trans content, varying from 10^{-5} $(\Omega\ \text{cm})^{-1}$ for the trans material to 10^{-9} $(\Omega\ \text{cm})^{-1}$ for the cis-isomer. The intrinsic conductivity of pure polyacetylene is even lower. This fact is supported by the observation that exposing *trans*-$(CH)_x$ to the vapor of donor ammonia causes the conductivity to fall more than 4 orders of magnitude without detectable weight increase. This phenomenon may be due to the coordination of ammonia to traces of aluminum and titanium compounds, which can be detected by spark emission spectroscopy.

2. Kinetic Study and Polymerization Mechanism. The reactivity of the acetylene monomer and its derivatives is determined by the electronic density of its triple bond. This bond has a cylindrical symmetry distribution relative to the molecular axis. This decreases the polarizability of the molecule, especially in the acetylene molecule itself. Therefore, the only way to polymerize this monomer is by forming a π-complex involving an ionic or coordinative[7] mechanism (Fig. 3).

Although the ionic polymerization of acetylene is nonexistent, the coordinative method has been very widely used, particularly the Ziegler-Natta catalytic system, $Ti(OBu)_4$–$AlEt_3$, which is the most powerful way of forming polyacetylene powders, gels, or films.

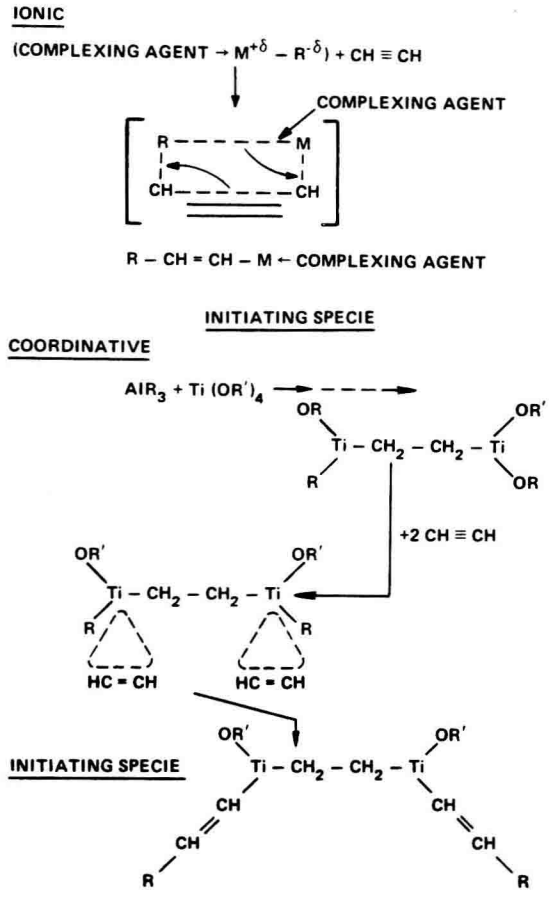


Fig. 3. Possible reaction mechanism for the polymerization of acetylene.

Acetylene consumption by a Ziegler-Natta catalyst solution shows a typical curve as a function of time: consumption is rapid in the beginning and then the rate slows with time as the polyacetylene film forms. To avoid the diffusion effect, the rate of reaction (initiation) is determined from the slope at the origin of the curve. The initiation rate is determined, and the polymers obtained are analyzed when the different parameters of the reaction vary. Such parameters include the aging time of the catalyst at room temperature, the concentration of the catalyst, and the pressure of acetylene.[18,19] Consumption data are shown in Fig. 4 for the various catalyst systems.

The initiation rate increases with the aging time (Fig. 5), reaches a maximum after 1 hour, and then decreases slowly. This decrease is due to the decomposition of the active centers of the catalyst, which are complexes of Ti^{III}, as seen by the electron paramagnetic resonance (EPR). The morphology as seen by a scanning electron microscope (SEM) is affected by this parameter (Fig. 6).

When the concentration of $Ti(OBu)_4$ is varied as other parameters are held constant, the rate of the reaction (Fig. 7) and the density of the polymer increase. The macroscopic morphology depends essentially on this parameter and varies from a gel to a film with variable densities. Below a concentration of $Ti(OBu)_4$ equal to 3 mmol/ℓ, a powder is obtained. By varying the concentration of the cocatalyst, an optimal ratio of Al/Ti equal to 4 is determined (Fig. 8). The morphology and the cis–trans composition of the $(CH)_x$ film may be varied (Fig. 9). The variation of the initiation rate is linear, with the acetylene pressure between 20 and 70 cm of mercury (Fig. 10). From the results obtained above, the initiation rate can be written as follows:

$$R_i = \frac{d(C_2H_2)}{dt} = K[Ti(OBu)_4]^{1/4}\ [Al(Et)_3]^{3/4}\ [C_2H_2]^1 . \tag{2}$$

Three molecules of $Al(Et)_3$ react with one molecule of $Ti(OBu)_4$ to form the active catalyst

$$Al(Et)_3 + Ti(OBu)_4 \xrightarrow{RT} \text{complexes of } Ti^{III} . \tag{3}$$

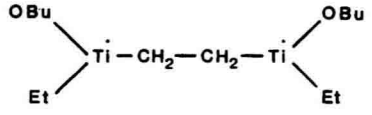
The rate of this reaction may be written as follows:

$$R_t = K_t[Ti(OBu)_4]\ [Al(Et)_3]^3 \tag{4}$$

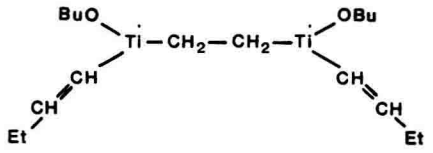
$$R_t = 9.6 \times 10^{-4}[Ti(OBu)_4][Al(Et)_3]^3. \tag{5}$$

From log R_t (aging) = f (aging time), k_t is determined. The EPR spectra at −78°C show two signals because of Ti^{III} ($g_1 = 1.934$, $g_2 = 1.950$).

The evolution of the EPR spectra suggests that the specie corresponding to the first signal ($g_1 = 1.934$) is responsible for the polymerization of acetylene in those conditions. The structure assigned to this signal is



The acetylene molecule forms a π-complex with this structure; then, by the insertion of acetylene into the titanium-carbon bond, it forms the new specie, as shown below:



which is responsible for the appearance of an additional signal ($g_3 = 1.984$) observed after *in situ* polymerization of acetylene.

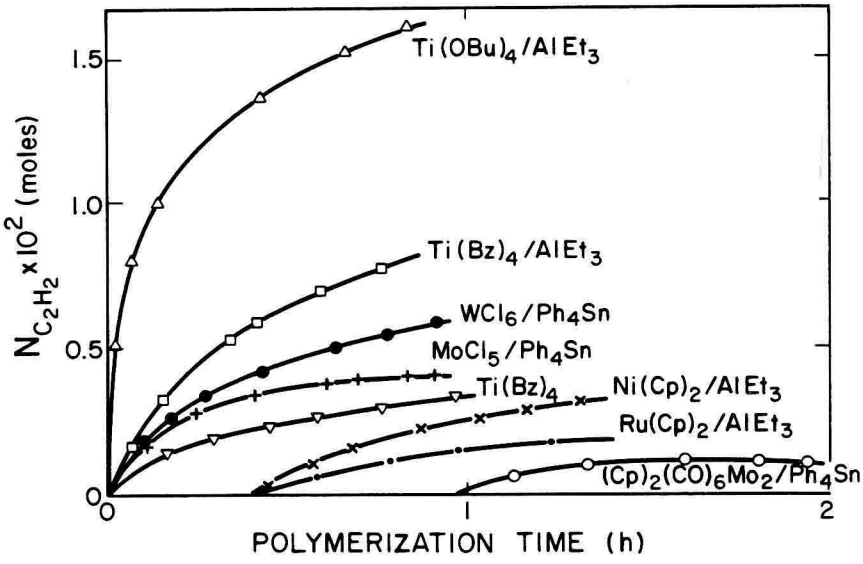


Fig. 4. Acetylene consumption for various catalyst systems.

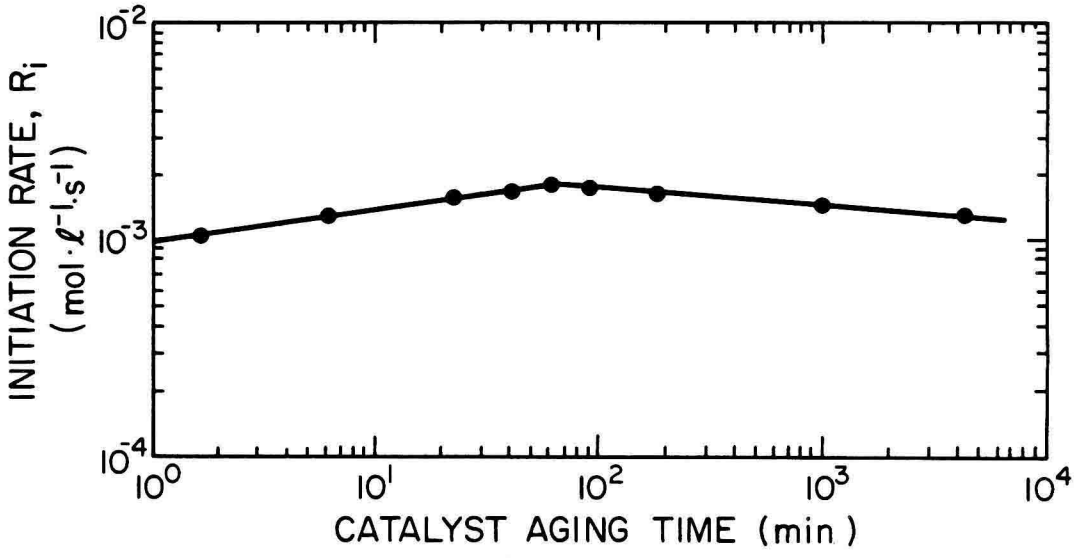


Fig. 5. Initiation rate as a function of aging time of the Ziegler-Natta catalyst at room temperature in toluene.

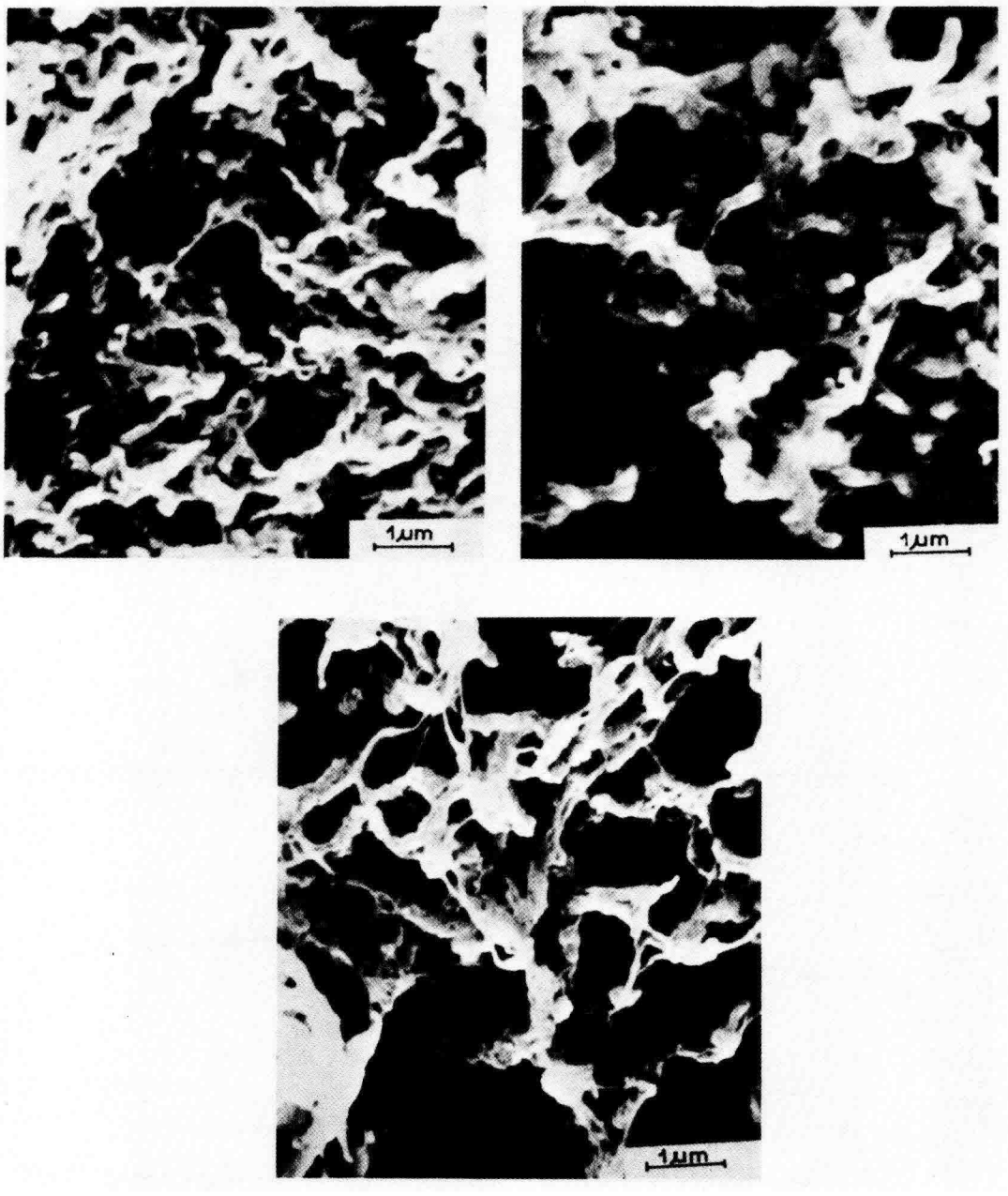


Fig. 6. Micrographs of polyacetylene obtained with the catalyst, shown for various times during the aging process.

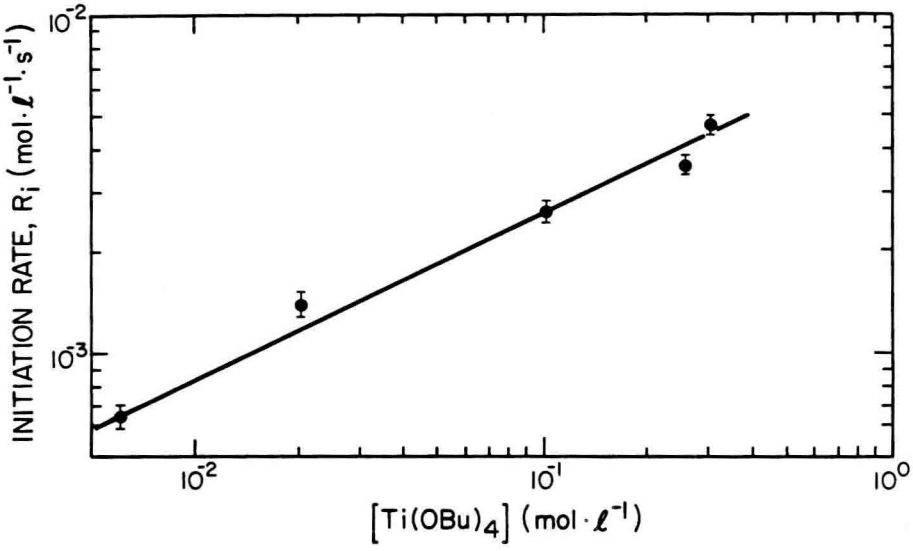


Fig. 7. Initiation rate as a function of [$Ti(OBu)_4$].

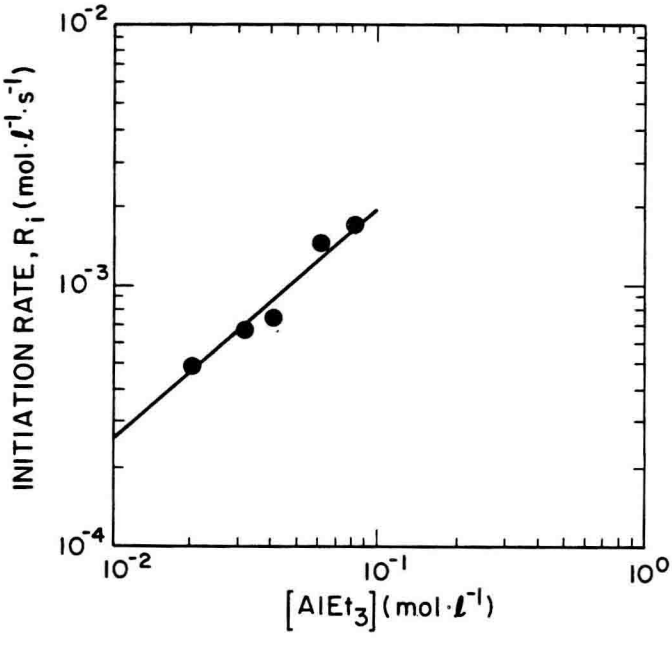


Fig. 8. Initiation rate as a function of [$AlEt_3$].

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