# Polymerization of acetylene by soluble Ziegler–Natta catalyst. Kinetic studies

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(*Received* 11 *May* 1981)

In the present work some preliminary studies on the kinetics and the optimum conditions for the preparation of polyacetylene films are reported using the soluble Ti $(OC_4H_9)_4$–$Al(C_2H_5)_3$ system, as well as the observation of the morphology of the films by electron microscopy. The kinetic curves obtained show two distinct parts: a rapid consumption of acetylene, followed by a retarding of the rate due to the polyacetylene film formed. If the rate of polymerization is plotted as a function of ageing time of the catalyst for a ratio Al/Ti = 4, a maximum is found for about one hour.

**Keywords** Polymerization; kinetics; acetylene; catalyst; morphology; electron microscopy

## INTRODUCTION

The semi-conducting polyacetylene film denoted as $(CH)_x$ prepared by the polymerization of acetylene with various soluble Ziegler–Natta type catalysts exhibits a dramatic increase in electrical conductivity, over twelve orders of magnitude, when chemically doped with various donors and acceptors[1–9].

Electron microscope and X-ray studies indicate that the films consist of a random accumulation of fibrils with ca. 200 Å diameter[10]. The bulk density of the film is in the range of 0.3–0.6 g $cm^{-3}$ compared with the 1.15 g $cm^{-3}$ obtained by the flotation technique, indicating that the fibrils fill only a part of the total volume[11]. The macroscopic morphology of the films depends on the concentration of the catalyst system. At high catalyst concentration, polymerization occurs on the free surface of the catalyst solution to form a polyacetylene film.

At low concentration, the polymerization yield a gelatinous mass. At extremely low concentration, the product obtained is a powder[11].

In the present work, some preliminary studies on the kinetics and the optimum conditions for the preparation of polyacetylene films using the soluble $Ti(OC_4H_4)_4$–$Al(C_2H_5)_3$ system and the observation of the morphology of the films by electron microscopy are reported.

## EXPERIMENTAL

The high reactivity of the Ziegler–Natta type catalyst requires the use of high vacuum technique and all glass apparatus.

### *Materials*

Acetylene and acetylene-$d_2$ were purified before use by successively passing through a sodium hydrogen sulphite solution, a dry ice-methanol trap, a calcium chloride column, a phosphorous pentoxide column, and finally a molecular sieve column.

Toluene was treated by sulphuric acid, then distilled onto potassium and finally stored under vacuum over *n*-butyllithium. Tetrabutoxytitanium and triethylaluminium were used as purchased.

### *Polymerization procedure* (see *Figure 1*)

In a typical experiment, $6.10^{-4}$ moles of tetrabutoxytitanium and $24.10^{-4}$ moles of triethylaluminiun, in that order, were added to 30 ml of toluene in the reaction vessel (A) using hypodermic syringes through the serum cap (B). After the mixture was stirred for one hour at room temperature, the reaction vessel was connected through tap (C) to the vacuum line, cooled by a dry ice-methanol mixture and evacuated. After the system was allowed to reach constant temperature ($T = -78°C$) acetylene was rapidly introduced into the flask until a pressure of 700 mm of Hg was reached. The consumption of acetylene was measured at constant pressure by using the compression tube (D). The polymerization was interrupted by evacuating the

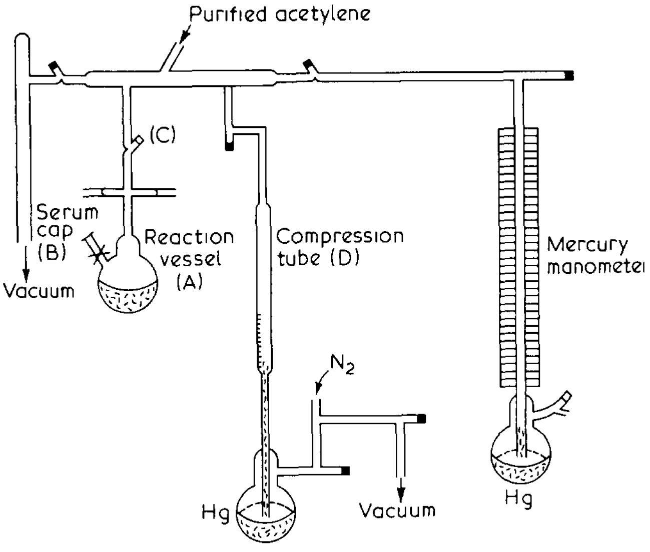

*Figure 1* Kinetic apparatus

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0032-3861/82/020246-05$03.00

system. Purification of the film formed was performed by washing it repeatedly with toluene, until the solution became colourless. This was carried out at the same temperature as the polymerization temperature in order to prevent *cis–trans* isomerization of the polymers. The purified films were dried under vacuum. All the processes were carried out under high vacuum techniques.

### *Measurements*

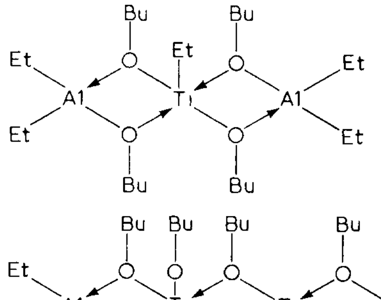
The morphology of the films was characterized by *SEM* (JEOL JSM 35 apparatus). The residual catalyst containing (Al,Ti) was measured through the film thickness by mean of CASTAING micropobe (CAMECA M460). Infra-red spectra were performed on 577 Perkin–Elmer apparatus.

## RESULTS AND DISCUSSION

Important factors affecting the formation of polyacetylene film are the state of the catalyst in the system, catalytic activity for acetylene polymerization of the system, and its concentration. The most effective catalyst system which gave a uniform film with good physical properties was $Ti(OC_4H_9)_4$–$Al(C_2H_5)_3$ (Al/Ti = 3–4) which is known to give a highly crystalline polyacetylene.

The minimum concentration at which the film was formed was Ca $3.10^{-3}$ mol $l^{-1}$ of $Ti(OC_4H_9)_4$ in case of Al/Ti = 4. Below the critical concentration, although the formation of polyacetylene was observed, the product was a powder. It has also been reported that polyacetylene obtained with a ratio Al/Ti = 4 and at low temperature contained mainly *cis* polymer. But, at lower Al/Ti ratios of the system, *trans*-rich polymer was obtained at low temperature[10].

Addition of triethylaluminium to tetrabutoxytitanium solution in toluene produces an instantaneous change of colour and an evolution of gas[12]. The observed colour changes with ratio Al/Ti. The gas evolution concerns essentially ethane[13,14] and ethylene[15]. According to an infra-red study, Takeda *et al.* have concluded to a ligands exchange between the catalyst and the cocatalyst, with formation of $AlEt_2OBu$[16]. Together with this exchange, reduced organometallic species are detected by electron spin resonance (e.s.r.) and polarography[13,17,18]. It seems reasonable actually to conclude that $Ti^{III}$ compounds are responsible for the polymerization. E.s.r. absorption provides a powerful tool for investigating the structure of complexes involving transition metal atoms. According to different authors[16,19–21], several spectra are obtained depending on the ratio Al/Ti and structures like the following were proposed.



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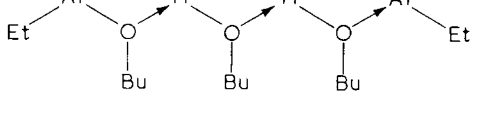
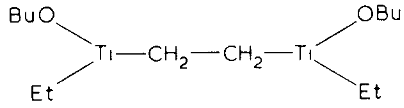


More recently, Clement[22] has studied the polymerization of pentadiene by this catalyst for a ratio Al/Ti = 6. He first showed that the concentration of the active species was one thousand the initial concentration of Ti and proposed the following $Ti^{III}$ product as precursor.



Many experimental results support such assumptions. It is not very easy in those conditions to correlate the concentration of the catalyst and our kinetic results.

*Figure 2* represents a typical curve of consumption of acetylene on quiescent surface of toluene as a function of time. The curve obtained shows two distinct parts:

(1) A rapid consumption of acetylene, the slope of the tangent to the curve at time $t = 0$ corresponding to the rate of initiation ($R_i$) at the surface of the solution.

(2) The first part is followed by a retarding of the rate due to the polyacetylene film formed. This film retards further polymerization because of the limited diffusion of acetylene monomer through the films and the limited diffusion of the catalyst to the surface of the film at contact with acetylene. The diffusion becomes the rate determining step for the polymerization[11].

Three experiments support these arguments. In a first experiment, $2.9 \times 10^{-3}$ moles of tetrabutoxytitanium and $11.8 \times 10^{-3}$ moles of triethylaluminium, in that order, were added without solvent in the reaction vessel according to the polymerization procedure described previously. The mixture was stirred for one hour at room temperature. After the system was allowed to reach constant temperature ($T = -78°C$), acetylene was introduced until a pressure of 690 mm of Hg was reached. *Figure 3* represents the curve of consumption of acetylene on the surface of the catalyst as a function of time. The curve obtained shows a rapid consumption of acetylene followed by a plateau reached after 25 min of reaction.

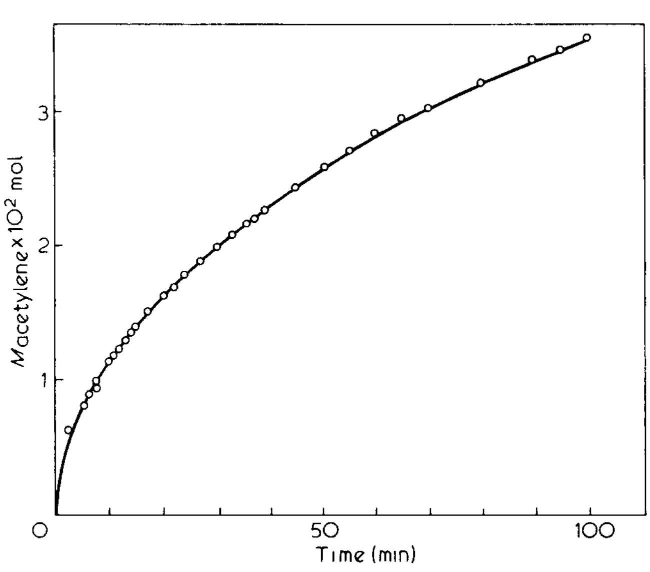


*Figure 2* Consumption of acetylene on a quiescent surface of toluene as a function of time. $[Ti(OBu)_4] = 2.10^{-2}$ mol $l^{-1}$; $P_{acetylene}$ = 69 cm Hg; $T^0 = -78°C$; aging time of catalyst = 60 min; $V_{toluene}$ = 30 ml; Al/Ti = 4

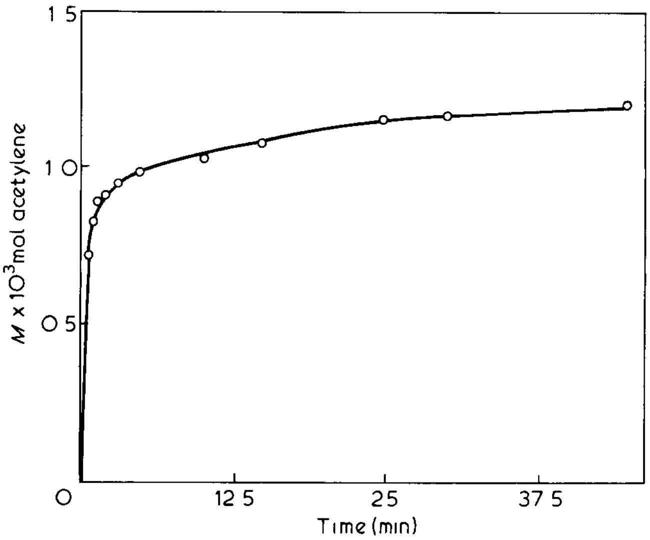


***Figure 3*** Consumption of acetylene on a Ziegler–Natta catalyst without solvent as a function of time. $Ti(OBu)_4$ → 1 ml (2.94 mmol); $Al(Et)_3$ → 1.64 ml (11.76 mmol); $T$ °C = −78°C; $P_{AC}$ = 69 cm Hg; aging time of catalyst = 60 min

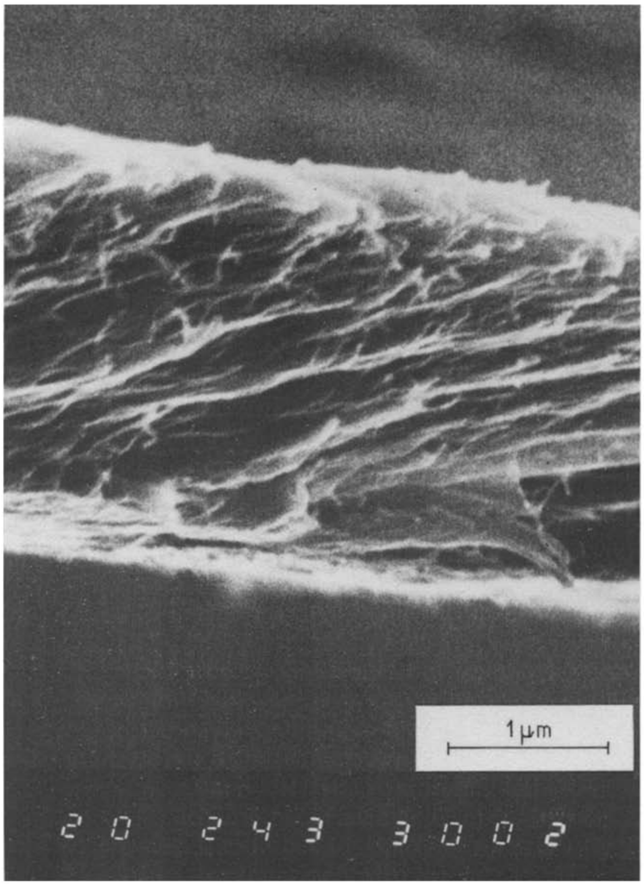
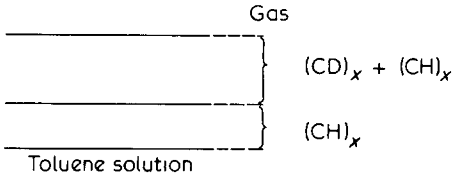


***Figure 4*** Scanning electron micrograph of the surface of a $(CH)_x$ film synthesized on the Ziegler–Natta catalyst without solvent

Indeed, the density of the film is so high that diffusion of acetylene monomer through the film becomes impossible. In *Figure 4* observation by a scanning electron microscope shows that the fibril structure is not visible at the surface of the film due to this high density.

In a second experiment we first polymerize $^2D$ acetylene on a toluene solution of catalyst in the same condition as described previously. After the film was formed, the polymerization was interrupted by evacuating the system and then, we add $^1H$ acetylene. The polymerization goes on indicating some living character of the initiating and/or the propagating species. A study of the cross section, as shown below, of the film by infra-red spectroscopy[23] indicates that, when $^1H$ acetylene is added, it polymerizes in the existing $(CD)_x$ film and also diffuses through in order to polymerize at the contact of the toluene solution.



In a third experiment, observations by a scanning electron microscope show that the surface which was in contact with the gas during the polymerization gives quite a different morphology as shown in *Figure 5* although it retains the fibril morphology. The fibrils are flattened to 400 Å and packed more tightly than on the solution surface (*Figure 6*). Indeed, the last Figure shows typical fibrils (800 Å in diameter) whose packing is less dense than previously observed.

The result is confirmed by a study of the cross section of the film by microprobe analysis. A special carbon profile is given on *Figure 7*.

If now, we plot $R_i$ as a function of ageing time of the catalyst for a ratio Al/Ti = 4 (*Figure 8*), we find a

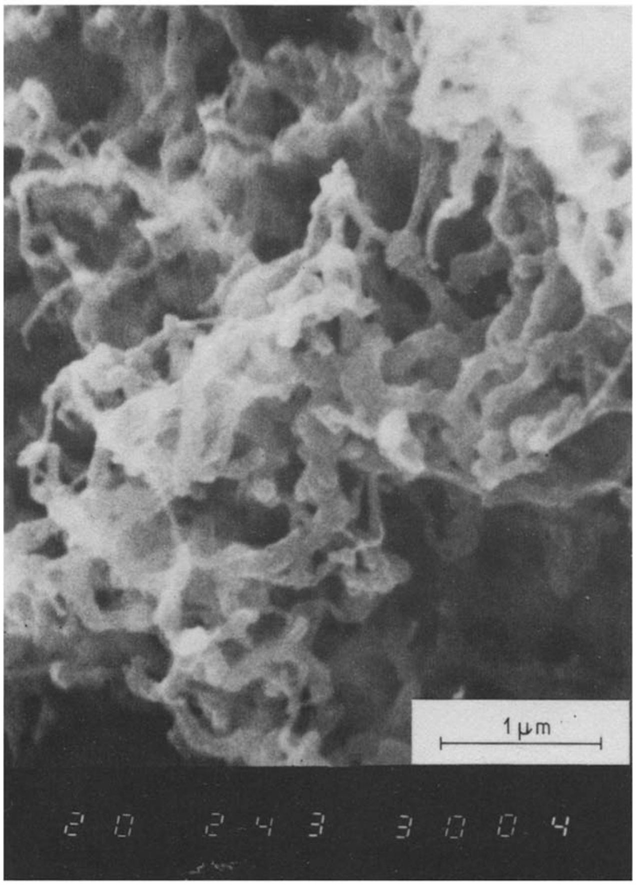


***Figure 5*** Scanning electron micrograph of the surface of a $(CH)_x$ film in contact with acetylene gas during the polymerization on a quiescent surface of catalyst in solution in toluene

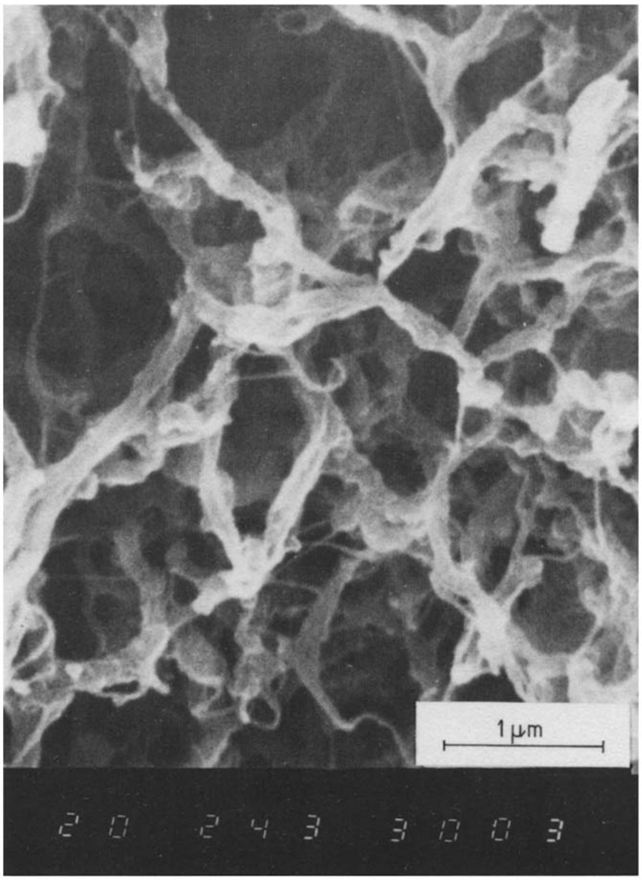


*Figure 6* Scanning electron micrograph of the surface of a $(CH)_x$ film in contact with the quiescent surface of catalyst in solution in toluene

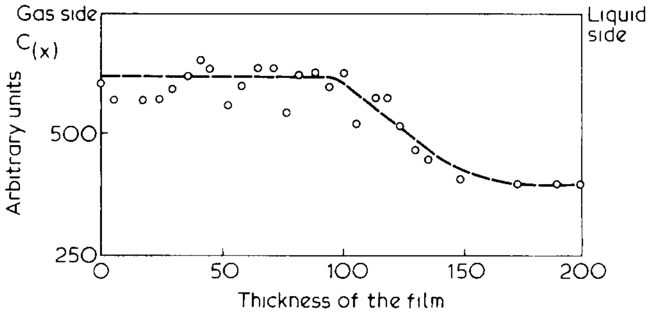


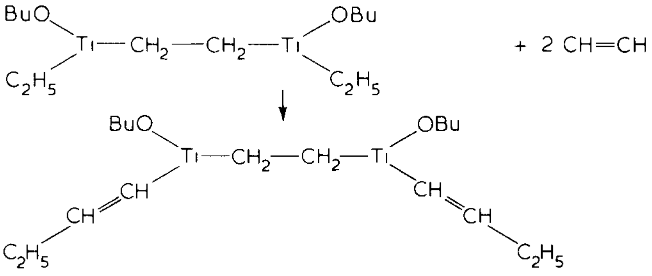
*Figure 7* Carbon profil of the cross section of a $(CH)_x$ film by microprobe analysis

maximum for about one hour. Similar results have been found by Clement[22], when studying the polymerization of pentadiene. The highest concentration of precursor is only reached after a given time of ageing after which a very low degradation of the precursor is observed. This result confirms the stability of the precursor and agrees with the preceding result obtained for the polymerization of $^2$D acetylene. The macroscopic morphologies of products observed by scanning electron microscope are shown as a function of ageing time of the catalyst. (*Figures 9* and *10*). For a short time of ageing (about one minute at room temperature), the packing of the fibrils whose diameter is ~200 Å is less dense compared to the one for an ageing time of about one hour in the same condition and for which the fibrils have a diameter of ~800 Å.

When we plot $R_i$ as a function of the ratio Al/Ti for an ageing time of the catalyst of 60 min, (*Figure 11*), we find a maximum for a ratio Al/Ti equal to ~4.

Several other experiments at different pressures of acetylene (*Figure 12*) show a linear dependance of $R_i$ as a function of P acetylene above a pressure of ~20 cm of Hg.

According to our preliminary results and to the ones of the literature, we can assume that the monomer is coordinated with the precursor and then inserted into the titanium–carbon bond indicated as follows:



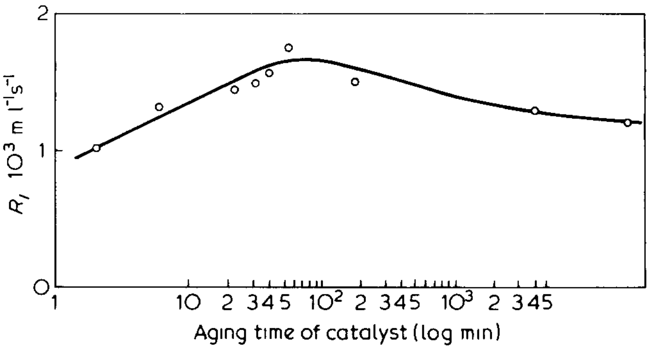


*Figure 8* $R_i$ as a function of aging time of the catalyst. $r$ = Al/Ti = 4 $t$ = −75°C; $P_{AC}$ = 69 cm Hg; [Ti(OBu)$_4$] = 2.10$^{-2}$ m l$^{-1}$

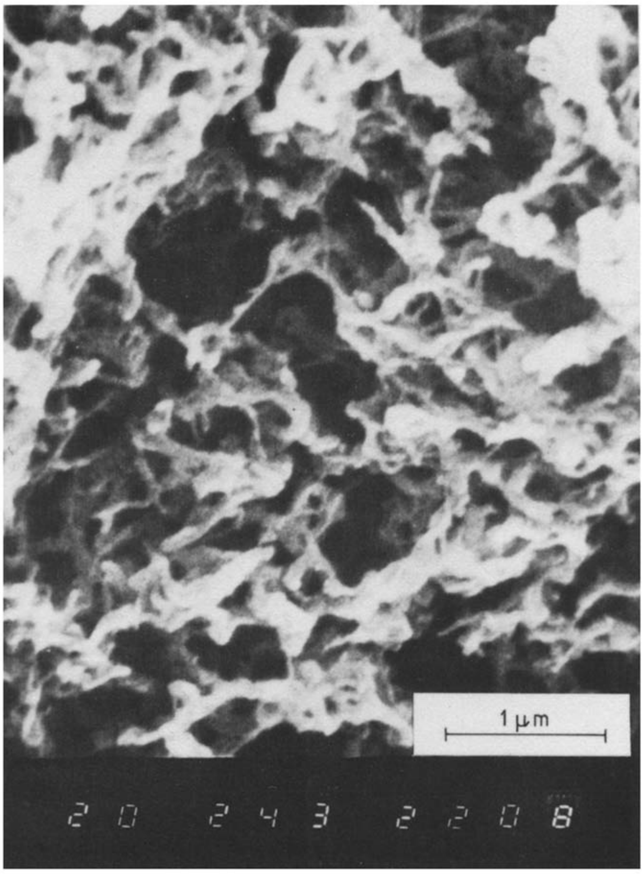


*Figure 9* Scanning electron micrograph of a $(CH)_x$ film synthesized on a catalyst prepared with a short time of aging (one minute)

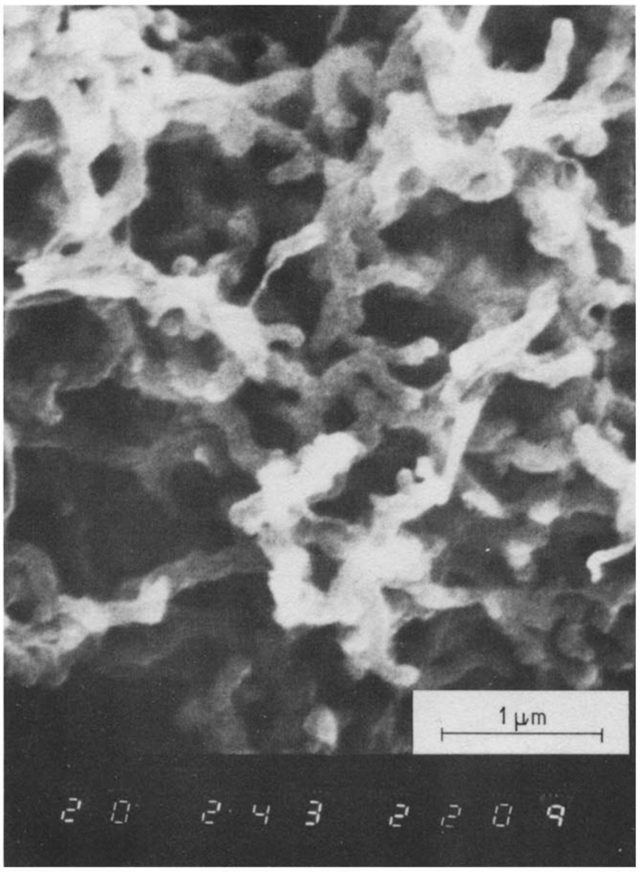


***Figure 10*** Scanning electron micrograph of a $(CH)_x$ film synthesized on a catalyst prepared with a long time of aging (one hour)

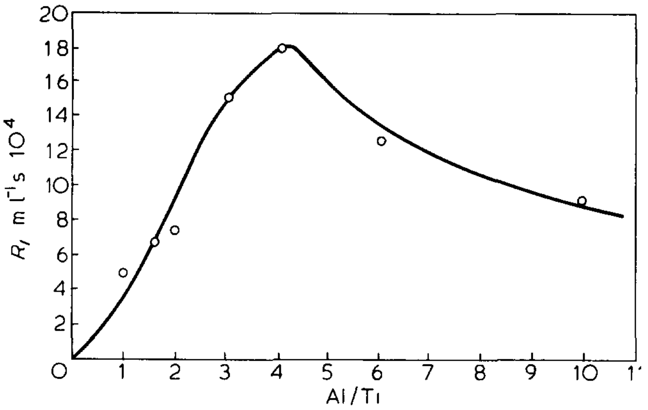


***Figure 11*** $R_i$ as a function of the ratio Al/Ti for an aging time of the catalyst of 60 min. $[Ti(OBu)_4] = 2.10^{-2}$ ml$^{-1}$; $T^0 = -78°C$; aging time of catalyst = 60 min; $P_{AC}$ = 69 cm Hg

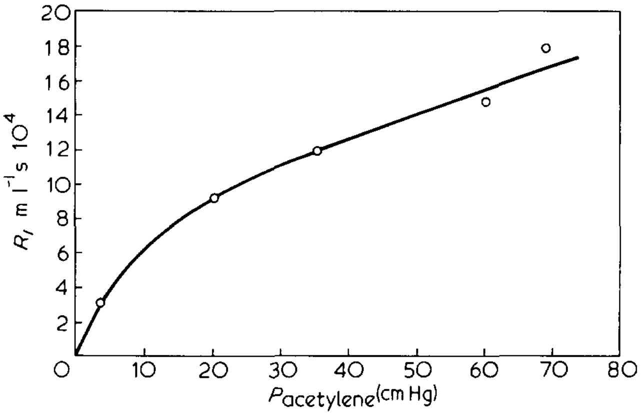


***Figure 12*** $R_i$ as a function of the pressure of acetylene. $[Ti(OBu)_4] = 2.10^{-2}$ m l$^{-1}$; $T^0 = -78°C$; aging time of catalyst = 60 min; Al/Ti = 4

The new species formed has to be stable enough in order to allow the formation of a film of polyacetylene. More work has to be done in the field in order to establish a better knowledge of this mechanism of polymerization.

## ACKNOWLEDGEMENTS

Financial support from Direction des Recherches Etudes et Techniques under contract number 78/259 is greatly acknowledged.

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