Communications to the Editor

Polyacetylene Fibril Growth in Soluble Ziegler–Natta Catalysts

Free-standing polyacetylene films prepared by using the soluble Ziegler–Natta catalyst $Ti(OBu)_4/AlEt_3$[1] are of great interest for they exhibit an electrical conductivity in the metallic regime, 10^3 $(\Omega\ cm)^{-1}$, when doped with various donors or acceptors.[2,3] Scanning electron microscopy shows that the as-formed films consist of randomly oriented fibrils with a diameter and an interfibrillar distance depending upon the polymerization conditions.

A detailed mechanistic study[5,6] of the polymerization at −78 °C showed that the number of active centers for polymerization of acetylene, which consists of Ti^{III} species, is only one part per thousand of the total amount of catalyst. The same study showed also that the kinetic equation of the reaction can be written as

$$R_i = d(C_2H_2)/dt = K[Ti(OBu)_4]^{0.25}[AlEt]^{0.75}[C_2H_2]^1$$

where R_i is the initial reaction rate (i.e., initiation) and K is the reaction constant.[7] The morphology of the films and the fibril dimensions have a great effect on the properties of the polymer when it is doped with electron donors or acceptors, chemically or electrochemically.[8] The doping process consists of the diffusion of the doping ion into the film and its fibrils with known diffusion rates under well-defined conditions. The homogeneity of the material is consequently affected by the diffusion factor, and therefore it is important to study the nature of the host polymer.

The polymerization of acetylene using a concentrated solution of $Ti(OBu)_4/AlEt_3$ in toluene ($[Ti(OBu)_4] > 3$ mmol·L^{-1}) is a surface reaction in which the thickness of the film and the fibril diameter increase with the polymerization time.

The polymerization reactions are performed under vacuum at −78 °C in toluene. The concentration of $Ti(OBu)_4$ is in the range 0.005–0.3 mol·L^{-1} and the Al/Ti ratio is 4. The acetylene pressure is kept constant at 69 cmHg. The polymer films are washed repeatedly with toluene and dried under vacuum. The analysis of the polymer's morphology is performed by using scanning electron microscopy. The film thickness is measured with a micrometer with a very good reproducibility.

This paper discusses the growth of the fibrils, the evolution of their size, and the interfibrillar distance in the films formed on the surface of the catalyst solution. The values given in Figures 1–3 are average values and a good reproducibility of these results is obtained only when the experimental conditions are kept constant during the polymerization reaction.

Figure 1 shows the evolution of the film thickness with time with an error in the range of 1–5%. A rapid increase is obtained at the beginning of the polymerization, and then a slowing in the film growth is observed due to the diffusion of the acetylene gas through the film. A plateau is obtained after a given time, at a given thickness depending upon the concentration of the catalyst. During the growth of the film the fibrils grow and their diameter increases as the polymerization proceeds.

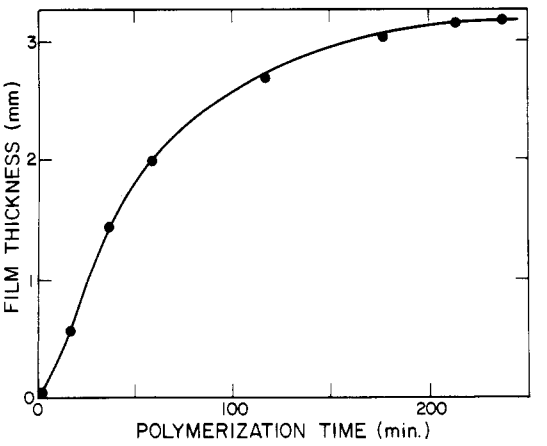

Figure 1. Polyacetylene film thickness as a function of the polymerization time (catalyst aging time at rm = 1 h, $[Ti(OBu)_4]$ = 0.02 mol·L^{-1}, Al/Ti = 4, P_{AC} = 69 cmHg, t_p = −78 °C).

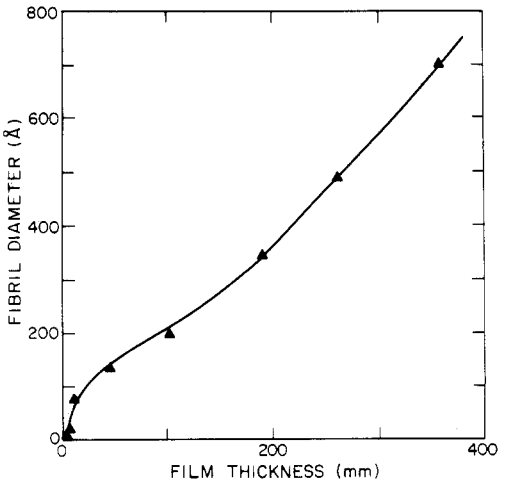

Figure 2. Polyacetylene fibril diameter as a function of the polymer film thickness (catalyst aging time at rm = 1 h, $[Ti(OBu)_4]$ = 0.02 mol·L^{-1}, Al/Ti = 4, P_{AC} = 69 cmHg, t_p = −78 °C).

It was reported[4] that the fibril diameter is not a constant throughout the film's cross section; the fibrils existing in the part of the film that is formed at the beginning of the polymerization are larger than the ones existing in the part formed at the end of the polymerization.

The variation of the *cylindrical* fibril diameter as a function of the film thickness is examined very closely as shown in Figure 2 by using scanning electron microscopy and transmission electron microscopy (for the first two values). From these results and those reported,[4] the increase in the fibril diameter can be explained by the aggregation of catalytic active centers onto the preformed fibrils by diffusion of the catalyst solution through the film. The growth of other chains on existing fibrils leads to the

Table I
Variation of Polyacetylene Film Density with the Concentration of $Ti(OBu)_4$

$[Ti(OBu)_4]$, mol·L^{-1}	0.006	0.02	0.1	0.25	0.3	10
density, g·cm^{-3}	0.05 ± 0.01	0.22 ± 0.02	0.28 ± 0.02	0.38 ± 0.05	0.55 ± 0.05	1.00 ± 0.05

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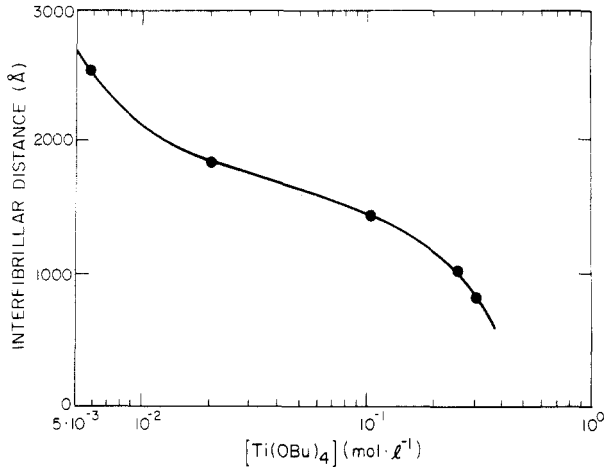

Figure 3. Interfibrillar distance in polyacetylene films as a function of $[Ti(OBu)_4]$ (catalyst aging time at rm = 1 h, Al/Ti = 4, P_{AC} = 69 cmHg, t_p = -78 °C).

formation of larger fibrils. This process is mainly affected by the concentration of the catalyst solution, its aging time, and the polymerization temperature.

An important characteristic in polyacetylene films is the variation of its interfibrillar distance with the experimental conditions of the reaction. The average distance[9] between the fibrils throughout the film is measured on two-dimensional micrographs assuming that the three-dimensional fibril growth on the surface of the Ziegler–Natta catalyst solution is homogeneous. A slight decrease in the interfibrillar distance is observed when the fibril diameter increases. The decrease in this parameter becomes significant when the catalyst concentration is increased as shown in Figure 3. These results can be explained by the increase in the number of the active centers on the surface of the catalyst solution which gives closer fibrils when the polymerization occurs. The data shown in Figure 3 are consistent with the density measurements performed on the same films (Table I).

The last parameter is of importance, particularly when electrochemical doping of the polymer is involved. The surface area, which varies with the interfibrillar distance, is the main factor in determining the current density of polyacetylene batteries that have been studied and developed for few years.[10]

In conclusion, the kinetics of growth of polyacetylene film and fibrils show that the experimental conditions of the polymerization are very important in the determination of the polymer density, porosity, and fibril diameter and have to be taken into account when it is doped and characterized.

Registry No. $Ti(OBu)_4$, 5593-70-4; $AlEt_3$, 97-93-8; polyacetylene (homopolymer), 25067-58-7; acetylene, 74-86-2.

References and Notes

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Kinetics of the Cooperative Complex Formation and Dissociation of Poly(acrylic acid) and Poly(oxyethylene)

The formation of complexes between poly(carboxylic acids) and polymeric hydrogen bond acceptors such as poly(oxyethylene) or poly(vinylpyrrolidone) in aqueous solution has been investigated over a number of years.[1] The association is a cooperative process; since there is only a small *difference* between the stability of hydrogen bonds of these polymers with the aqueous medium and the stability of the interpolymer hydrogen bonds, a large number of the interpolymer bonds must form to yield a stable complex. Complex stability is thus a steep function of the length of the shorter of the interacting chains.

In 1977, Anufrieva et al.[2] showed that if one of the interacting polymers carries a fluorescent label, its displacement from the polymer complex by an unlabeled polymer can be monitored by the change in the depolarization of fluorescence. More recently, Chen and Morawetz[3] studied the kinetics of such a "complex interchange" using poly(acrylic acid) (PAA) labeled with the dansyl chromophore, which fluoresces very weakly in water but strongly in organic media.[4] It was found that complexation of labeled PAA with poly(oxyethylene) (POE) leads to a large increase in fluorescence intensity. Displacement of labeled PAA from the complex by the unlabeled polymer could, therefore, be followed by the decay in the emission.

We have now found that the change in fluorescence intensity of dansyl-labeled PAA when it participates in complex formation can also be used to follow the kinetics of complexation and of complex decomposition. Since these are relatively fast processes, a stopped-flow apparatus had to be used for their study. Unless stated otherwise, experiments were carried out at 25 °C, at pH 2.7, and in the presence of 1 M NaCl. Polymer complexation was studied by mixing 4×10^{-4} N PAA labeled with 1.8 mol % of dansyl groups[3] with an equal volume of a POE solution. Complex decompositions were followed after solutions of the dansyl-labeled complex were mixed with a buffer at a pH at which the complex is known to be unstable.

Complexation of PAA with an excess of POE (molecular weight ~20 000) was found to be biphasic with the fluorescence intensity I varying with time t as

$$\ln [(I - I_\infty)/(I_0 - I_\infty)] = \alpha \exp(-k_{obsd}t) + (1 - \alpha) \exp(-k'_{obsd}t)$$

Table I lists the parameters obtained at various concentrations of POE and at various temperatures. Assuming that the fast process can be represented by a simple scheme

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB$$

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