Effect of polymerization conditions on polyacetylene morphology

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In an effort to optimize the synthesis of polyacetylene we have studied the evolution of its morphology by scanning electron microscopy (SEM) and also determined the density of the polymer. Both results are correlated and discussed.

(Keywords: polyacetylene; morphology; electronic microscopy; density; scanning electron microscopy)

INTRODUCTION

The discovery in 1974 by Shirakawa and coworkers[1] of the synthesis of silvery flexible films of polyacetylene was the origin of a tremendous interest in this particular polymeric material. By now more than 500 papers have been written conerning its synthesis, morphology, kinetics, electrical and mechanical properties. Recently a book published by J. C. W. Chien[2] was entirely concerned with this conductive polymer.

It is well known that polyacetylene may act as a conductor when suitably doped with a variety of donors or acceptors (n or p) and exhibits the properties of a synthetic metal. Its morphology has also been widely described, constituting mainly, in standard conditions, of randomly oriented and entangled fibrils, interspaced with voids. The bulk density is $\sim 0.4\,g\,cm^{-3}$ compared with $1.2\,g\,cm^{-3}$ as obtained by flotation techniques, indicating that the fibrils fill only *ca.* 1/3 of the total volume.

Although polyacetylene has focussed the attention of researchers, only a few studies correlate the morphology of the polymer[3-11] with the differing parameters of polymerization kinetics. In particular it is still not known exactly what experimental conditions are required to lead to large, wide and compact fibrils which might then be expected to exhibit conductivity.

The first to identify the relationships between the structure of polyacetylene and polymerization conditions was Aldissi[12]. We have continued this study in more detail[13,14] by looking systematically at the influence of the following parameters:

(i) ageing time of the catalytic solution, t_a;
(ii) ageing time temperature of the catalytic solution T_a;
(iii) polymerization temperature of acetylene, T_P;
(iv) catalyst concentration, $Ti(OBu)_4$;
(v) ratio cocatalyst $AlEt_3$/catalyst $Ti(OBu)_4$;
(vi) acetylene pressure, P_a;

on the morphology and density of polyacetylene films obtained under various experimental conditions.

EXPERIMENTAL

Materials

The polyacetylene films were synthesized, according to Shirakawa's technique, directly on the horizontal surface of the catalytic system $Ti(OBu)_4 + AlEt_3$ in presence of toluene as solvent. The different parameters were varied widely[13,14]:

(1) ageing time of the catalytic solution from $t_a = 1$ min to 860 min;
(2) ageing time temperature from $T_a = -78°C$ to $+75°C$;
(3) catalyst concentration from $Ti(OBu)_4 = 3 \times 10^{-3}$ mol dm^{-3} to 1.14 mol dm^{-3};
(4) ratio $AlEt_3/Ti(OBu)_4$ from 0.5 to 10;
(5) acetylene pressure from $P_a = 3.5$ cm Hg to 61 cm Hg;
(6) polymerization temperature T_P from $-78°C$ to $+50°C$.

After synthesis, the films were washed 8 to 10 times with pentane, sealed under vacuum and stored at low temperature ($-30°C$).

Electronic micrography

The SEM micrographs presented here were obtained using a JEOL JSM-35 apparatus used under conditions that preclude sample damage at an accelerating voltage of 20 kV and a current of 1 mA. Samples studied were embedded in Electrodag 502. A gold film of thickness ~ 80 Å was obtained by sputtering. We observed the middle of the section of the films (thickness $\sim 150\,\mu m$) to avoid any boundary effects.

Density

The bulk density is obtained from the dimensions and weight of the films.

RESULTS AND DISCUSSION

Different samples of polyacetylene have been investigated with respect to the experimental conditions used in their

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preparation. Our goal was to correlate the morphology of polyacetylene with the conditions of its preparation.

Ageing time effect

Kinetic studies show a maximum consumption of acetylene for an ageing time of 45 min[13,14] of the catalytic solution $AlEt_3 + Ti(OBu)_4$. This results in a modification of the morphology of the polymer (*Figures 1*, *2* and *3*) particularly in the fibril dimensions. Therefore a catalyst of weak activity in terms of slow consumption of acetylene (after short or long ageing time) leads to a similar morphology: short and thin fibrils joined by globular clusters *Figure 1* ($t_a = 5$ min) and *Figure 3* ($t_a = 860$ min).

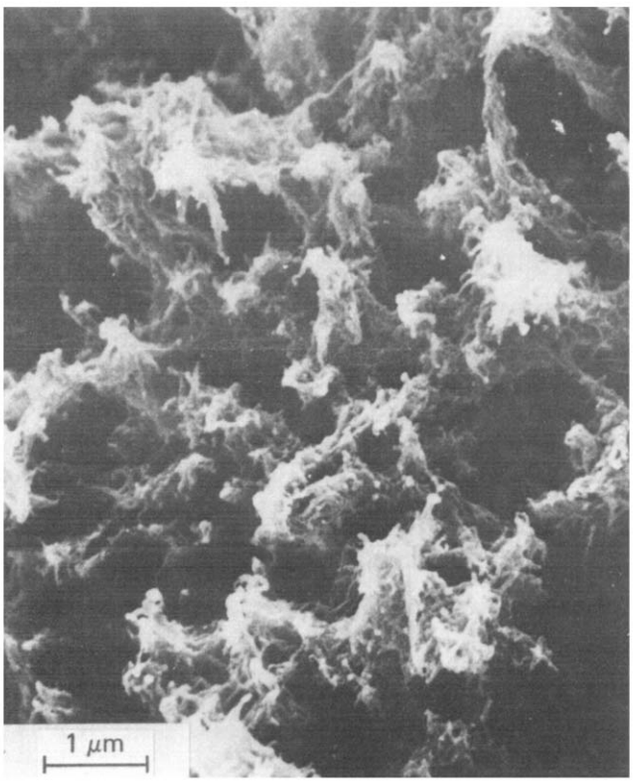

Figure 1 Polyacetylene morphology, $t_a = 5$ min

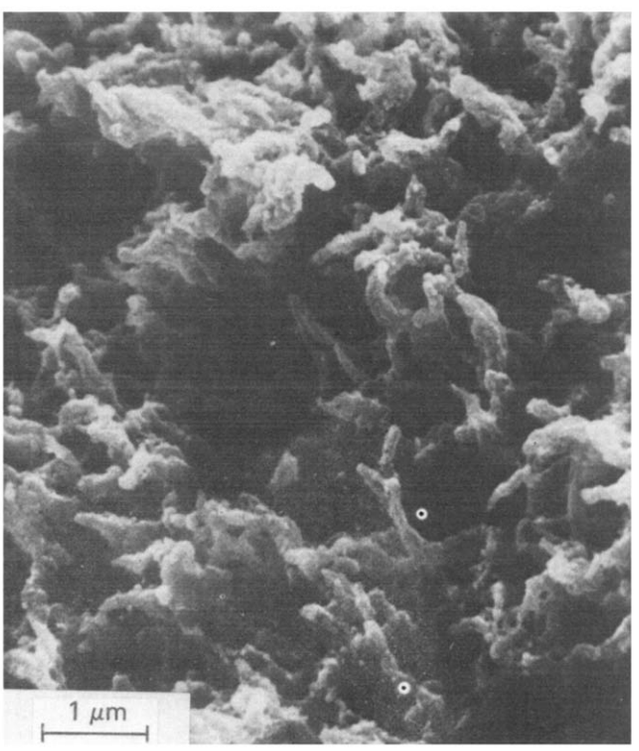

Figure 2 Polyacetylene morphology, $t_a = 180$ min

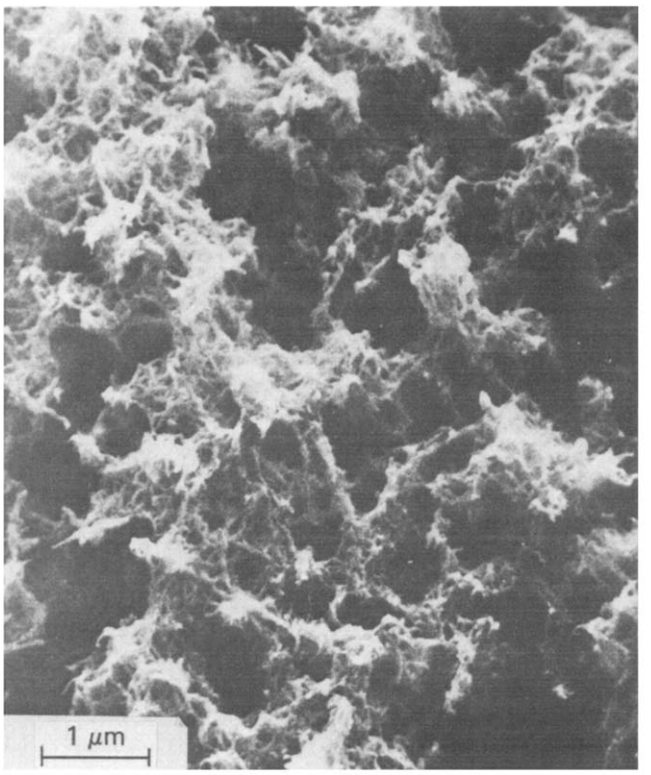

Figure 3 Polyacetylene morphology, $t_a = 860$ min

Table 1 Variation of density *versus* ageing time for:polyacetylene pressure, $P_{AC} = 12$ cm Hg and 61 cm Hg, $Ti(OBu)_4 = 0.1$ mol dm^{-3}, $T_a = 20°C$, $T_P = -78°C$, Al/Ti = 4

	P_{AC} (cm Hg)	
	12	61
t_a (minutes)	ρ (g cm^{-3})	ρ (g cm^{-3})
1	0.11	0.20
30	0.20	0.32
45	0.26	0.36
60	0.23	0.34
90	0.24	0.37
120	–	0.41
180	–	0.43
240	–	0.41
270	0.30	–
860	–	0.45
960	0.32	–

On the other hand with a moderate ageing time, $t_a \sim 45$ to 180 min, the fibrils are more differentiated, well formed, larger and with a greater diameter.

However, the progressive evolution in the size of the fibrils which is noticed, except for the extreme values of ageing time, does not agree with the kinetic results. We observe the same contradiction with the density which increases slowly with ageing time at both low pressure and high pressure to the same degree (see *Table 1*).

Temperature effect on ageing time

Kinetic studies[13,14] show a maximum acetylene consumption between 0°C and 20°C. At −78°C and

$-40°C$ (see *Figure 4*) we observe a similar morphology with very large thin fibrils similar to the network of a spider's web. For $T_a = 0°C$ (see *Figure 5*) the polymer has higher compactness with larger and wider fibrils. Finally for $T_a = 75°C$ (see *Figure 6*) we observe larger fibrils with big voids. These observations are in agreement with the density being at a maximum at room temperature (see *Table 2*).

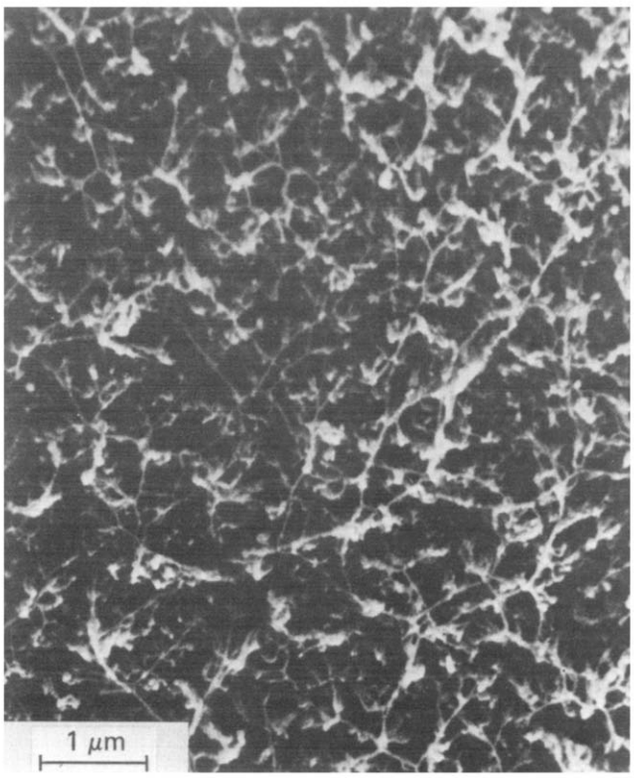

Figure 4 Polyacetylene morphology, $T_a = -40°C$

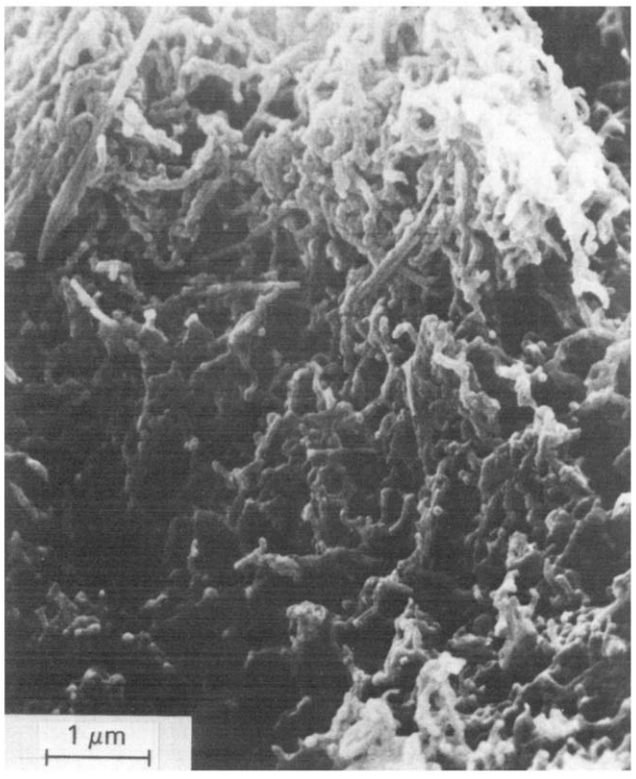

Figure 5 Polyacetylene morphology, $T_a = 0°C$

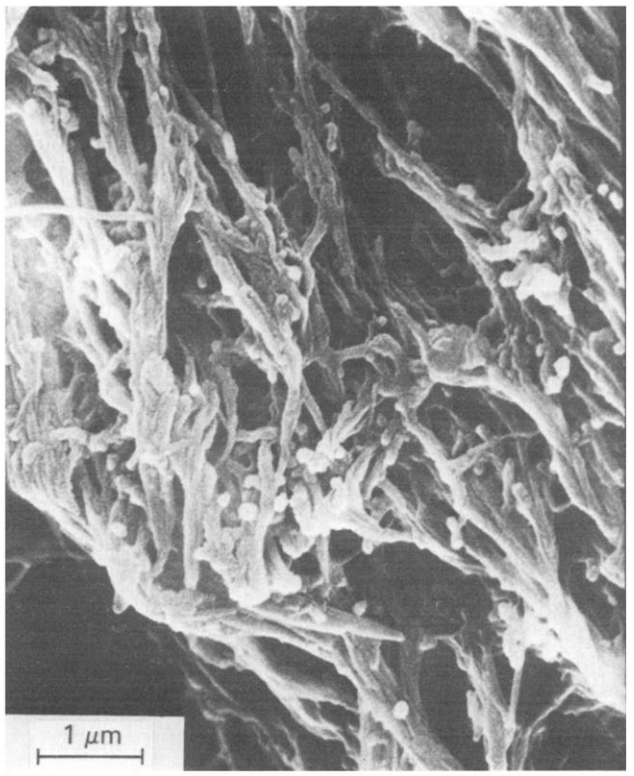

Figure 6 Polyacetylene morphology, $T_a = 75°C$

Table 2 Variation of density *versus* ageing time temperature: $Ti(OBu)_4 = 0.1\ mol\ dm^{-3}$, $P_{AC} = 61\ cm\ Hg$, $t_a = 45\ min$, $T_P = -78°C$, $Al/Ti = 4$

T_a (°C)	ρ (g cm^{-3})
−78	–
−40	–
0	0.30
20	0.36
30	0.27
50	–
75	0.22

Catalyst concentration

Figure 7 shows the usual morphology obtained under standard conditions while in *Figure 8* there is no longer a fibrillar structure but a high density of short sticks which appear for the catalyst ($Ti(OBu)_4 = 1.14\ mol\ dm^{-3}$ (see *Table 3*).

Al/Ti effect

Figures 9 and *10* show polyacetylene obtained with the ratio $Al/Ti = 7$ and 10, respectively. When Al/Ti increases, the size of fibrils decreases. In borderline cases, we have globular clusters. The density values agree with these observations (see *Table 4*).

Acetylene pressure

We do not observe any noticeable modification in the morphology with acetylene pressure. Only the diameter of the fibrils increases with the acetylene pressure. The density increases slightly with pressure (see *Table 5*).

Polymerization temperature

Figures 11, *12* and *13* show a progressive transformation in the fibril morphology. When the temperature increases, the length, particularly of the

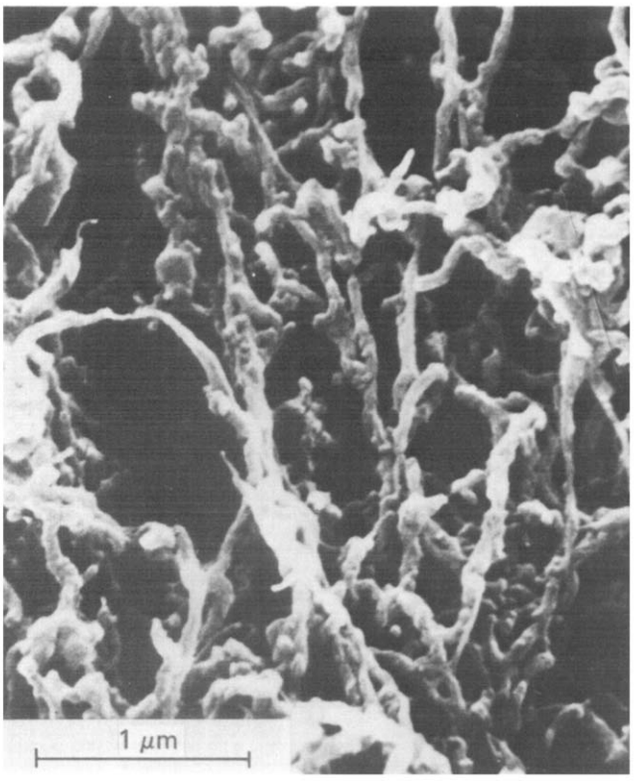

Figure 7 Polyacetylene morphology, $Ti(OBu)_4 = 0.1$ mol cm^{-3}

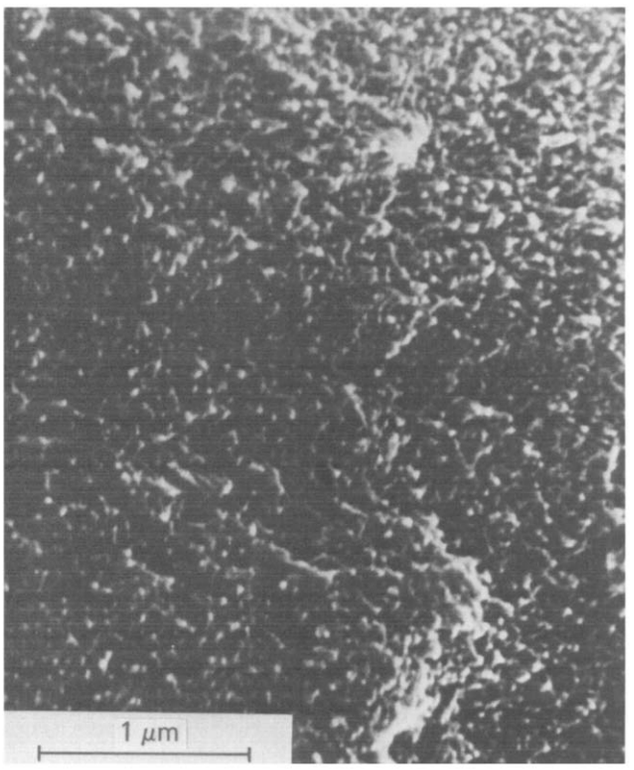

Figure 8 Polyacetylene morphology, $Ti(OBu)_4 = 1.14$ mol dm^{-3}

Table 3 Variation of density *versus* catalyst concentration. $t_a = 45$ min, $T_a = 20°C$, $T_P = -78°C$, $P_{AC} = 61$ cm Hg, Al/Ti = 4

$Ti(Obu)_4$ (mol dm^{-3})	ρ (g cm^{-3})
10^{-1}	0.36
0.4	0.53
1	0.68
1.14	1.1

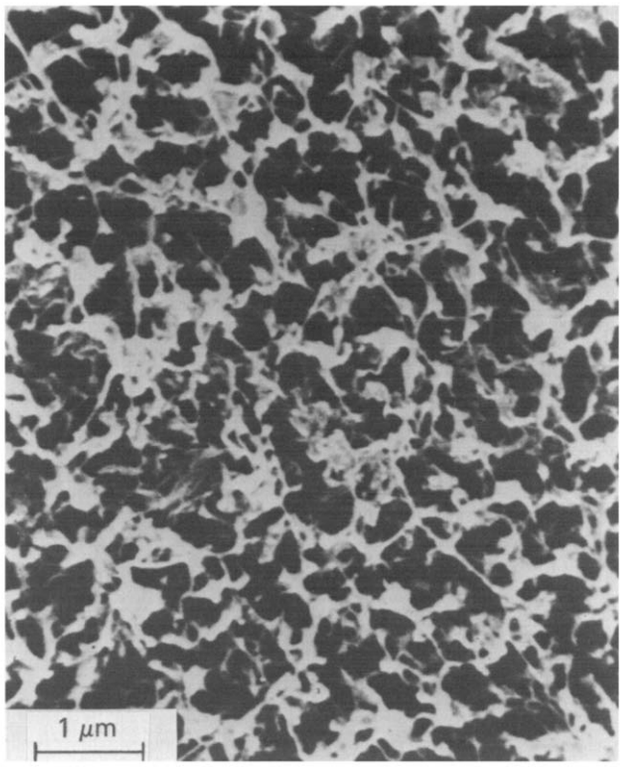

Figure 9 Polyacetylene morphology, Al/Ti = 7

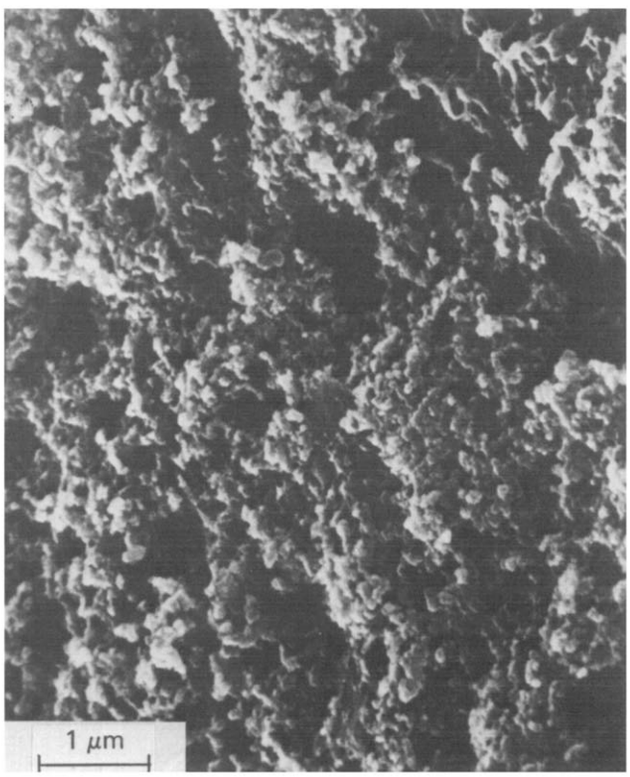

Figure 10 Polyacetylene morphology, Al/Ti = 10

Table 4 Variation of density *versus* Al/Ti ratio: $t_a = 45$ min, $T_a = 20°C$, $T_P = -78°C$, $Ti(OBu)_4 = 0.1$ mol dm^{-3}, $P_{AC} = 61$ cm Hg

[Al/Ti]	2	4	7	10
ρ (g cm^{-3})	0.21	0.36	0.50	0.81

Table 5 Variation of density *versus* acetylene pressure: $Ti(OBu)_4 = 0.1\ mol\ dm^{-3}$, $t_a = 45\ min$, $T_a = 20°C$, $T_P = -78°C$, Al/Ti = 4

P_{AC}	12	35	61
ρ (g cm^{-3})	0.26	0.32	0.36

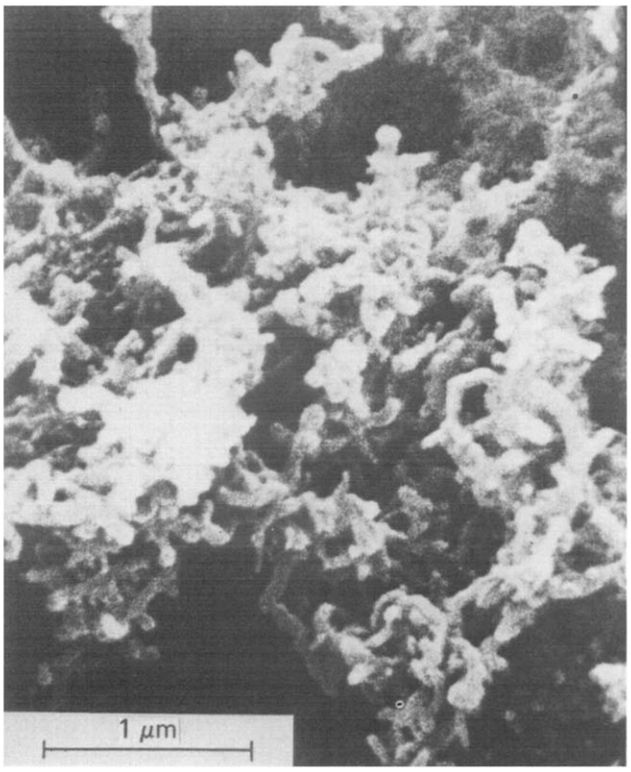

Figure 11 Polyacetylene morphology, $T_P = -40°C$

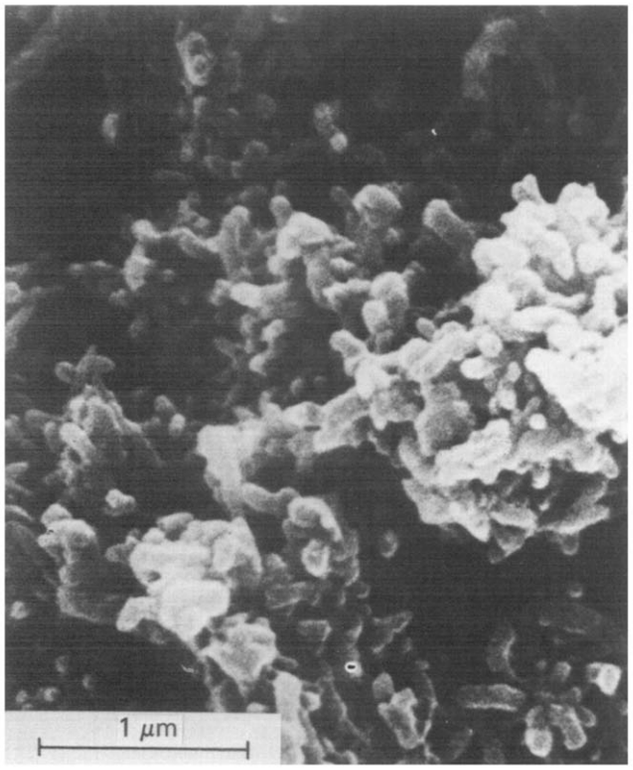

Figure 12 Polyacetylene morphology, $T_P = 0°C$

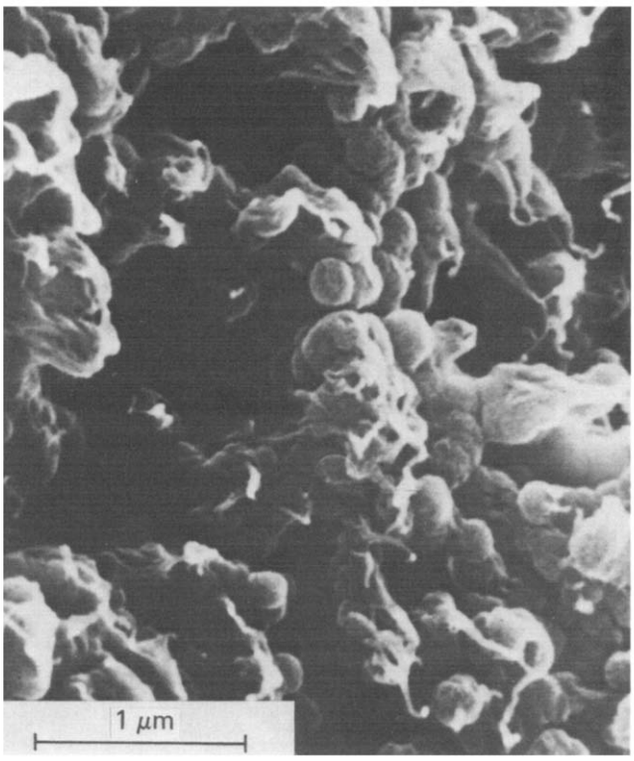

Figure 13 Polyacetylene morphology, $T_P = 20°C$

Table 6 Variation of density *versus* polymerization temperature: $Ti(OBu)_4 = 0.1\ mol\ dm^{-3}$, $t_a = 45\ min$, $T_a = 20°C$, $P_{AC} = 61\ cm\ Hg$, Al/Ti = 4

T_P	−78	−40	20	50
ρ (g cm^{-3})	0.36	0.44	0.91	1.04

fibril, decreases but the diameter increases. Finally we observe rods and globules. The density also increases with temperature (see *Table* 6).

CONCLUSION

The use of scanning electron microscopy allows the evolution of morphology of polyacetylene films prepared under various conditions to be followed. We have determined the experimental conditions required to obtain a well-tailored morphology, i.e. long or short fibrils, large or small diameter, rod or globular forms. This should help in the correlation of morphology with conductivity in further research with polyacetylene.

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