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POLYMERIZATION OF ACETYLENE WITH NEW CATALYTIC SYSTEMS AND OPTIMIZATION OF THE PROPERTIES OF THE POLYMERS

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ABSTRACT

This paper reports a comparative study of different catalytic systems for the synthesis of novel polyacetylene films. That the morphology could be optimized by the use of a highly viscous complexing solvent together with thermal treatment [1, 2] encouraged us to study the catalytic systems with the aid of ESR spectroscopy. The different samples were characterized with the aid of IR and ESR spectroscopic methods, conductivity measurements, and scanning electron microscopy before and after doping.

INTRODUCTION

The metallic conductivity of doped polyacetylene (PA) has generated considerable interest in this simplest of all conjugated polymers. Nevertheless, its crosslinking and degradation in air, which decrease the conductivity, affect its possible applications.

EXPERIMENTAL

The high reactivity of Ziegler-Natta initiators necessitates high-vacuum techniques and glass apparatus. Purification of the materials and details of the polymerization procedure have been described in previous publications [3, 4]. Infrared studies were performed with a Bruker IFS 85 spectrometer, and the catalytic systems and PA films were measured with a double-cavity Bruker ER200D ESR instrument. Doping of the PA was carried out in 0.2 *M* ferric chloride solution, and conductivities were measured by means of the four-probe technique.

The morphology of the undoped and doped films was characterized by means of scanning electron microscopy (SEM) (Cambridge Stereoscan 100). In the scanning electron mode, this instrument is capable of resolving images to 70 Å. The beam currents were kept sufficiently low to preclude sample damage ($\sim 10^{-11}$ A).

In the micrographs shown in the figures, the digits signify the conditions at the time the micrograph was taken. The first three digits on the left represent the magnification factor (e.g., 10.3 KX = 10 300). The next two digits give the accelerating voltage in kilovolts, and WD (working distance) indicates the distance in millimeters between the last diaphragm and the sample. The following digits are the sample (s) and photo (p) numbers. The remaining digits indicate the length of the white bar in micrometers. Evaporation sputtering (cathodic pulverization) was used to provide conductive coatings (Au) in order to reduce charging effects. To study the interior morphology of the film, samples were submerged in liquid nitrogen and fractured to expose the cross-sectional area.

RESULTS AND DISCUSSION

Table 1 contains the conditions for the polymerization of acetylene in the presence of different catalysts. The content of *cis* isomer, which was calculated by means of IR spectroscopy, and the densities of the PA films are given in Table 2. Symmetrical ESR signals were observed at $G = 2.0026$ for all the films and, together with the corresponding linewidths, are also given in Table 2.

Three catalyst systems were used: (a) $Ti(OBu)_4/AlEt_3$, (b) $Ti(OBu)_4/n\text{-}BuLi$, and (c) $TiBz_4/AlEt_3$, each with two solvents, toluene and silicone oil. Having made use of SEM to observe that the compactness of the films increases, relative to those synthesized in toluene at -78°C, when a combina-

TABLE 1. Conditions for the Polymerization of Acetylene by Different Catalyst Systems

System	$Ti(OBu)_4/AlEt_3$ [11]		$Ti(OBu)_4/n\text{-}BuLi$ [12]		$TiBz_4/AlEt_3$ [11]	
	I	II	III	IV	V	VI
Solvent	Toluene	Silicone oil	Toluene	Silicone oil	Toluene	Silicone oil
Concentration of catalyst, mol/l	0.3		0.3		0.3	
Ratio $\frac{\text{cocatalyst}}{\text{catalyst}}$	4		2		4	
Catalyst aging time, min	60 (22°C)	10 (120°C)	45 (22°C)	10 (100°C)	40 (22°C)	10 (95°C)
Pressure of C_2H_2, torr	670		670		670	
Polymerization time, min	15 (-78°C)	15 (22°C)	15 (-78°C)	15 (22°C)	15 (-78°C)	15 (22°C)

TABLE 2. Properties of Polyacetylene Films Obtained by the Different Catalyst Systems

System	$Ti(OBu)_4/AlEt_3$ [11]		$Ti(OBu)_4/n\text{-}BuLi$ [12]		$TiBz_4/AlEt_3$ [11]	
	I	II	III	IV	V	VI
% of *cis* isomer	90	60	85	40	63	86
ESR linewidth ΔHpp, *G*	6.8	4.4	6.1	3.5	4.7	6.14
$(CH)_x$ density, g/cm^3	0.4	0.55	0.53	0.58	0.61	1.00
Conductivity after doping with $FeCl_3$, S/cm	900	2200	1000	1600	—	—
Critical doping level Y, %	8	5	4.5	4.2	—	—

tion of silicone oil and thermal treatment (95-120°C) is used, we were encouraged to study Systems II, IV, and VI by ESR. Ti^{3+} complexes are the active species in the polymerization of olefins. especially acetylene [2, 5, 6a], and they are produced by the reduction of organometallic compounds. The Ti^{3+} complexes are paramagnetic and yield complicated ESR spectra, with four signals (G values of G_1 = 1.977, G_2 = 1.972, G_3 = 1.954, and G_4 = 1.986, and respective line widths of 5.0 ± 0.5, 5.0 ± 0.5, 20 ± 2, and 5.0 ± 0.5 G (System II)) that are in agreement with those given by Chien [6a].

We observed no change in intensity during aging at 22°C. However, when the catalyst was aged at 100°C for 10 min, we observed an increase in the intensity of the species G_3 = 1.954, which can be attributed to the trimer [2, 6a] complex and a decrease in the intensity of the other three species (which seem to be unstable at high temperatures). The catalyst is most active immediately after ambient (22°C) temperatures have been reached. Heating to 120°C, followed by cooling to ambient temperatures shows that the most important signal is that with G_3 = 1.954.

Similar observations were made with Systems IV and VI (increase in G_3 = 1.954 and decrease in other species).

We conclude that the increase in density of PA is due to the higher efficiency of the systems in G_3 species as a result of heating, which transforms inactive Ti^{4+} species to active Ti^{3+} (trimers). Similarly, Ti^{3+} species of low activity are reduced. The maximum conductivities reached by Systems II and IV (Fig. 1) are not due solely to a simple increase in the density of PA but also to the decrease in the amount of sp^3 defects [2], a fact confirmed also by comparison of Curves II and IV with I and III, respectively (Fig. 1, Table 2). Curves II and IV show a shift in the critical doping level (Y corresponds to the optimum conductivity) toward lower values, and this corresponds to a lower number of defects (Fig. 1, Table 2). The inverse proportionality between conductivity and sp^3 fraction has been pointed out by other authors [8].

It seems that a stereospecific polymerization mechanism might be involved, and, indeed, the presence of only one major active species (G_3 = 1.954) in the catalytic solution after heating and during the polymerization, supports this hypothesis.

On studying the morphology of PA synthesized at -78°C in toluene (System I) by Shirakawa's [7] method, we observed in the cross section of the film that the average diameter of the fibrils of the undoped sample is 850 Å, whereas the dull surface of the side of the film facing away from the reactor wall (gas side) consists of fibrils of a smaller diameter, 280 Å, called "microfibrils."

As has already been recorded by Chien [6], a fibril consists of several microfibrils joined together by weak bonds. One effect of the solution used

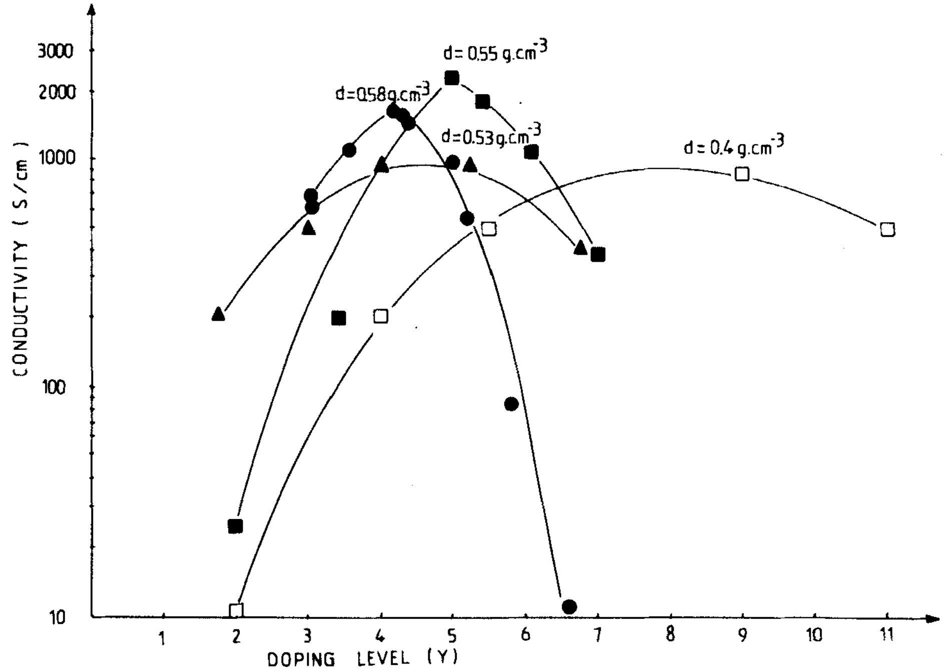

FIG. 1. Conductivity of $(CH)_x$ films obtained by the different catalyst systems: (□) I, $Ti(OBu)_4/AlEt_3$/toluene; (■) II, $Ti(OBu)_4/AlEt_3$/silicone oil; (▲) III, $Ti(OBu)_4$/*n*-BuLi/toluene; (●) IV, $Ti(OBu)_4$/*n*-BuLi/silicone oil.

to eliminate the catalytic residue is to diminish the interbond forces and thus cause the fibrils to separate into microfibrils. On the highly reflecting side of the film (the side facing the reactor wall, glass side) we observe flattened, uniformly oriented fibrils. After heating the catalyst ($Ti(OBu)_4$-$AlEt_3$) in silicone oil at 120°C (System II), we observed an increase in fibrillar density in the cross section of the PA films near the glass side (Fig. 2a). Near the gas side (Fig. 2b) we observed thin fibrils of an average diameter of 170 Å. The surfaces of the films are also compacted (Figs. 2c and 2d). The increase in the apparent fibrillar density is due to the high efficiency of this system in G_3 active species after heating.

Another catalyst ($Ti(OBu)_4$-*n*-BuLi, System III) in toluene [12] yields a PA that has very thin fibrils (100-120 Å) and good mechanical properties (Figs. 3a and 3b). System IV ($Ti(OBu)_4$-*n*-BuLi in silicone oil) has a singular morphology in which parallel stacks of long, thin fibrils are observed in the film cross section (Fig. 4a).

The white arrow on the right side of Fig. 4a indicates the surface of the film, while the three on the left side show the parallel stacks of fibrils in the film's cross section. The possibility that the cross-sectional morphology has been caused by tearing can be excluded because the samples were fractured under liquid nitrogen. Higher magnification of the same section shows oriented fibrils of 180-200 Å diameter (Fig. 4b). Both surfaces of the PA film are compacted and have the same closed appearance. System VI ($TiBz_4$-$AlEt_3$ in silicone oil [11]) yields very unusual, shiny, transparent films with a thickness of 800-1000 Å (Fig. 5a) and a film density as high as 1.0 g/cm^3.

Magnification of 30 000 (Fig. 5b) produces a very dense micrograph. Thus, the film is thin because it is exceptionally dense and does not allow acetylene to diffuse through it. The same catalyst in toluene [11] (System V) affords distinct fibrillar structure with fibril diameters of 120-140 Å.

All the polyacetylene films show that doping does not significantly change the fibrillar morphology, and this is in agreement with the results reported by another [10]. We only observe swelling of the fibrils on the surface (gas side) of the film (System II) (Fig. 6a), which is accounted for by intrafibrillar diffusion of the dopant anion $FeCl_4^-$ [9]. Higher magnification reveals that the diameter of the fibrils is 10 times the initial value (Fig. 6b). The cross section and the glass side of the film are less affected by intrafibrillar penetration of the dopant. This result corroborates the Castaing microprobe studies [13], where an inhomogeneous repartition of the dopant on the cross section of the film was recorded. With Systems III (Fig. 7a) and IV (Fig. 7b), there is no swelling of the fibrils but only an intercalation of the dopant between the parallel stacks of fibrils.

The influence of the method of preparation of the polyacetylenes on their morphology, stability, and other properties will be published in detail shortly.

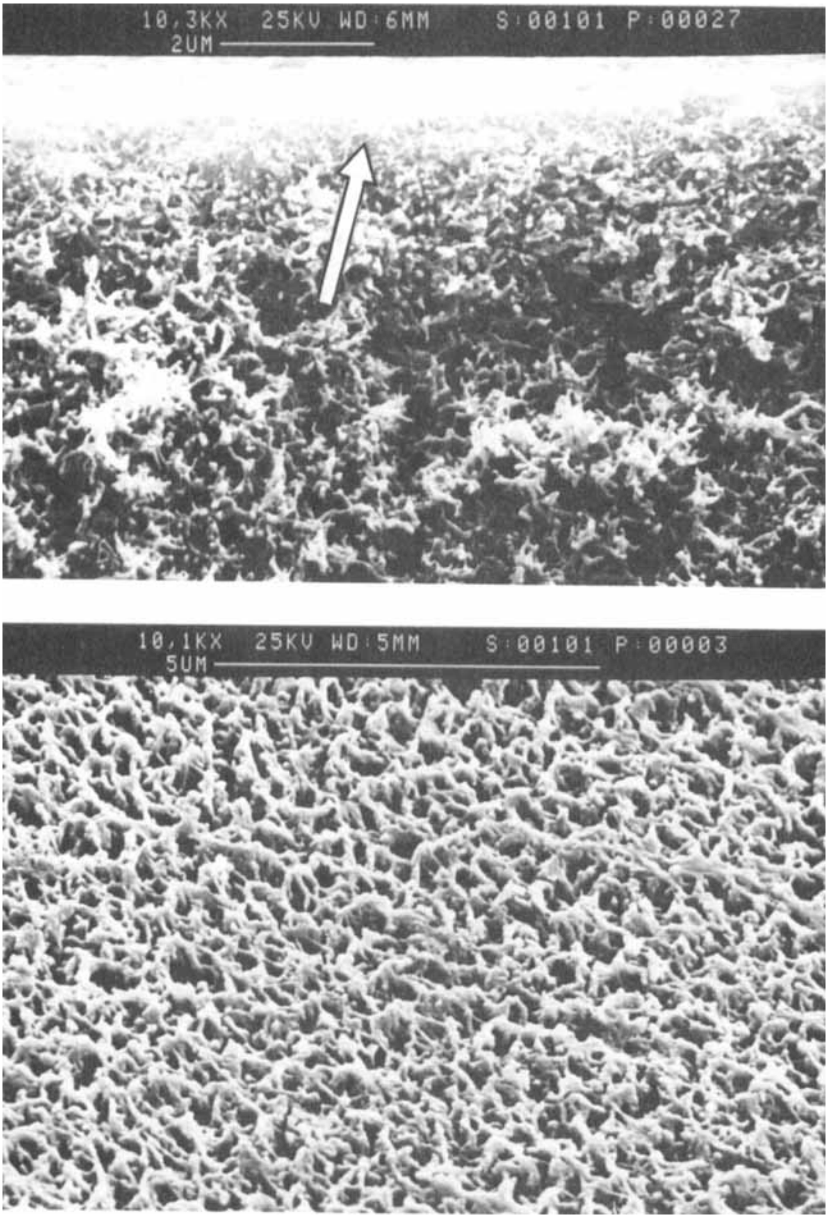

FIG. 2. SEM of (top left, a) cross section near the highly reflecting surface (glass side); (top right, b) cross section near the dull surface (gas side); (bottom left, c) dull surface; and (bottom right, d) highly reflecting surface of $(CH)_x$ undoped film, synthesized with System II ($Ti(OBu)_4/AlEt_3$/silicone oil).

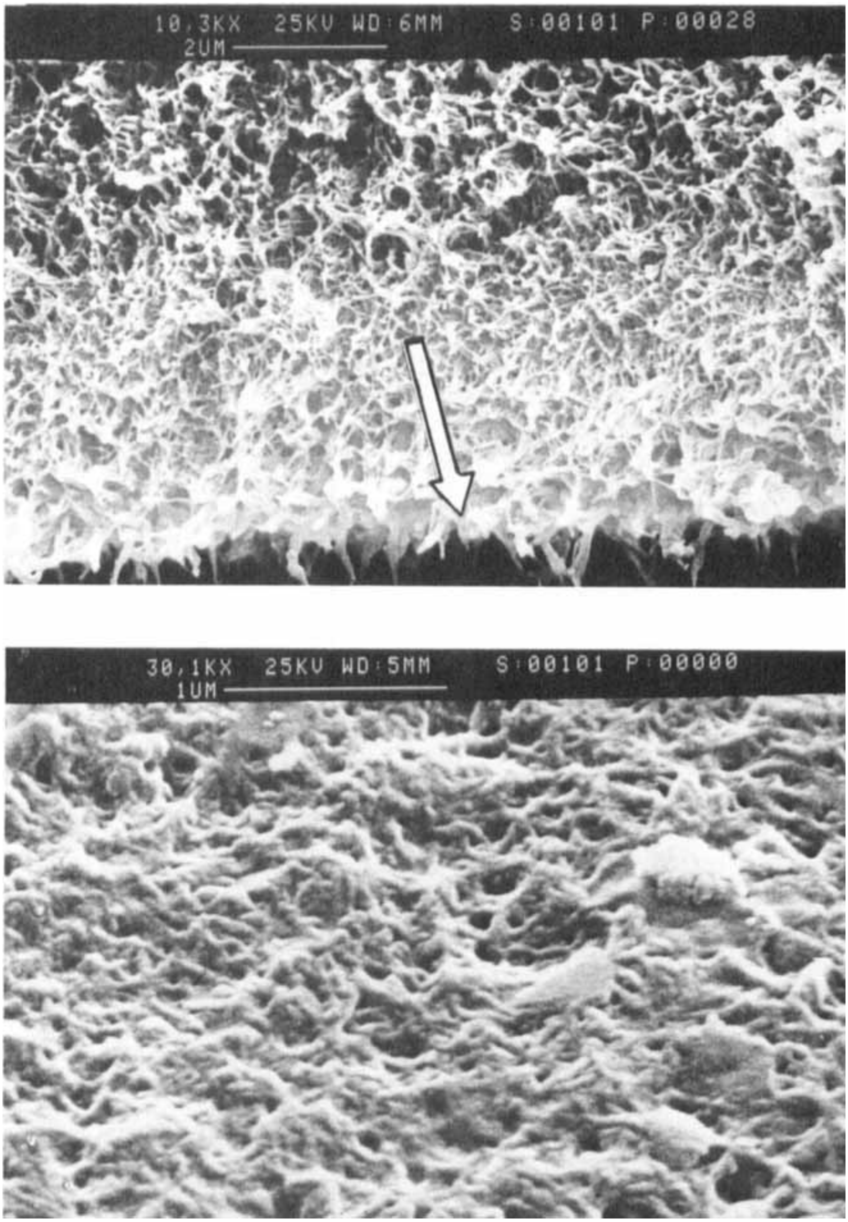

FIG. 2. (continued)

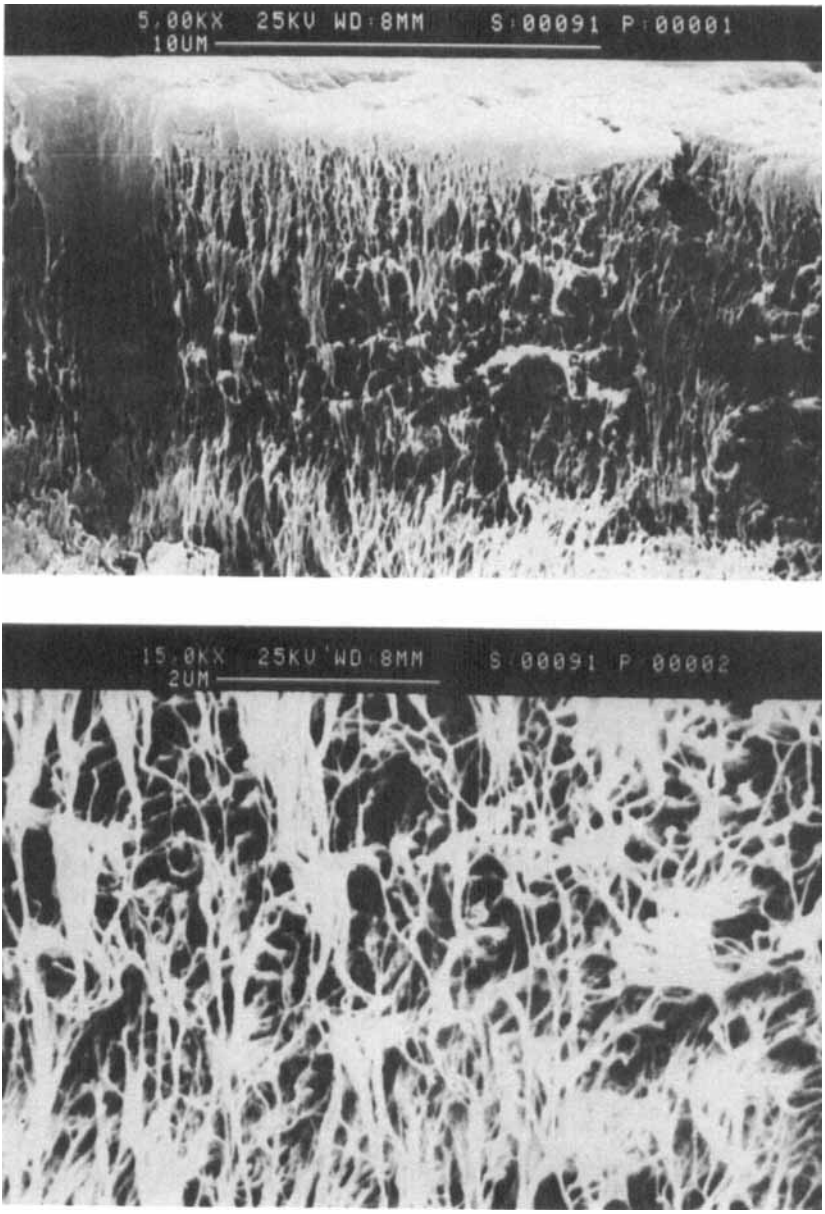

FIG. 3. SEM of a cross section (low magnification top and high magnification bottom) of undoped $(CH)_x$ film, synthesized with System III ($Ti(OBu)_4$/*n*-BuLi/toluene).

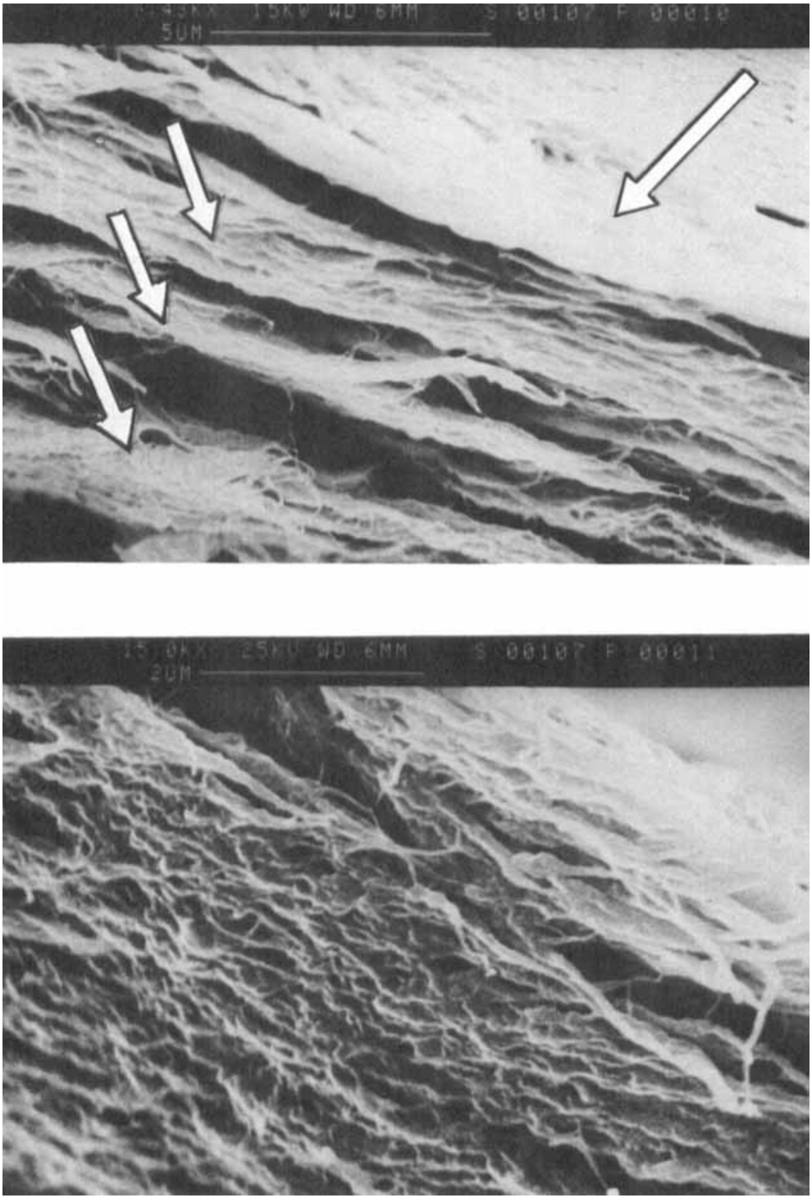

FIG. 4. SEM of a cross section (low magnification top and high magnification bottom) and surface of undoped $(CH)_x$ film, synthesized with System IV ($Ti(OBu)_4$/*n*-BuLi/silicone oil).

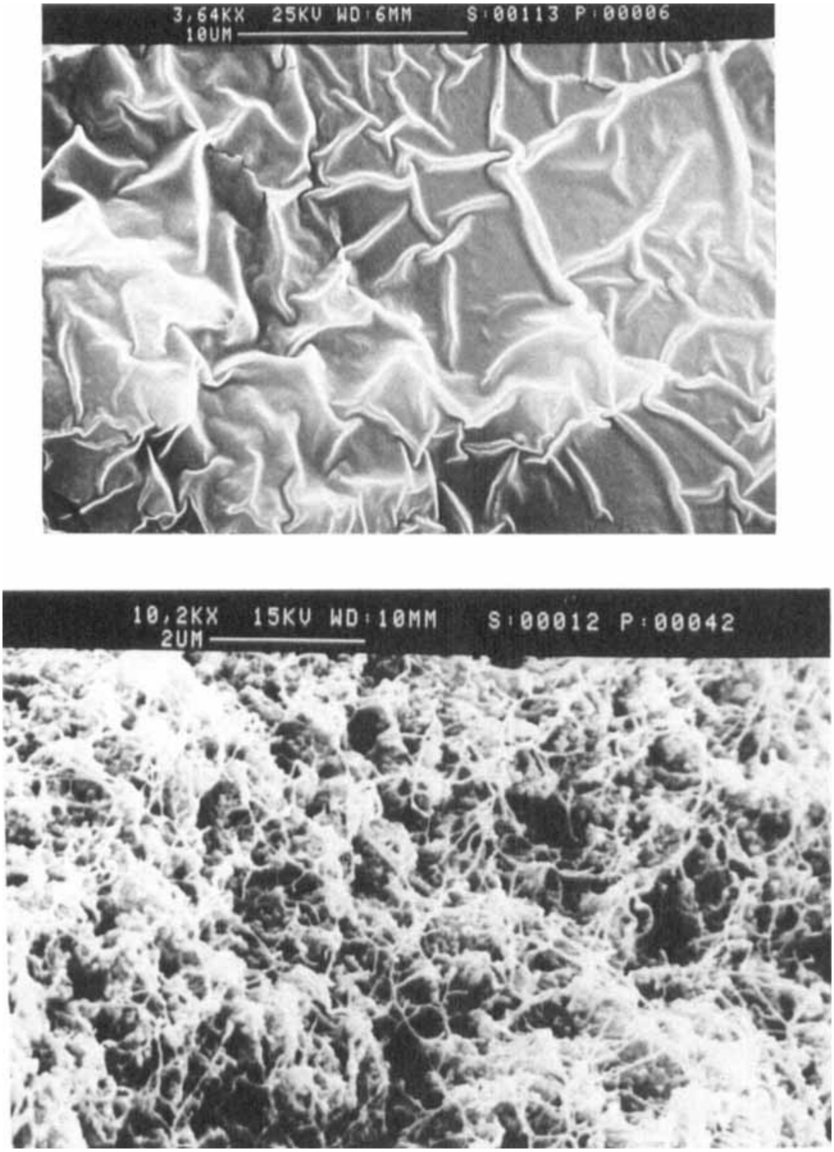

FIG. 5. SEM of a surface (low magnification (a) at top left and very high magnification (b) at top right) of an undoped $(CH)_x$ film synthesized with System VI $(TiBz_4)AlEt_3$/silicone oil) and section (low magnification (c) at bottom left and high magnification (d) at bottom right) of an undoped $(CH)_x$ film synthesized with System V $(TiBz_4/AlEt_3$/toluene).

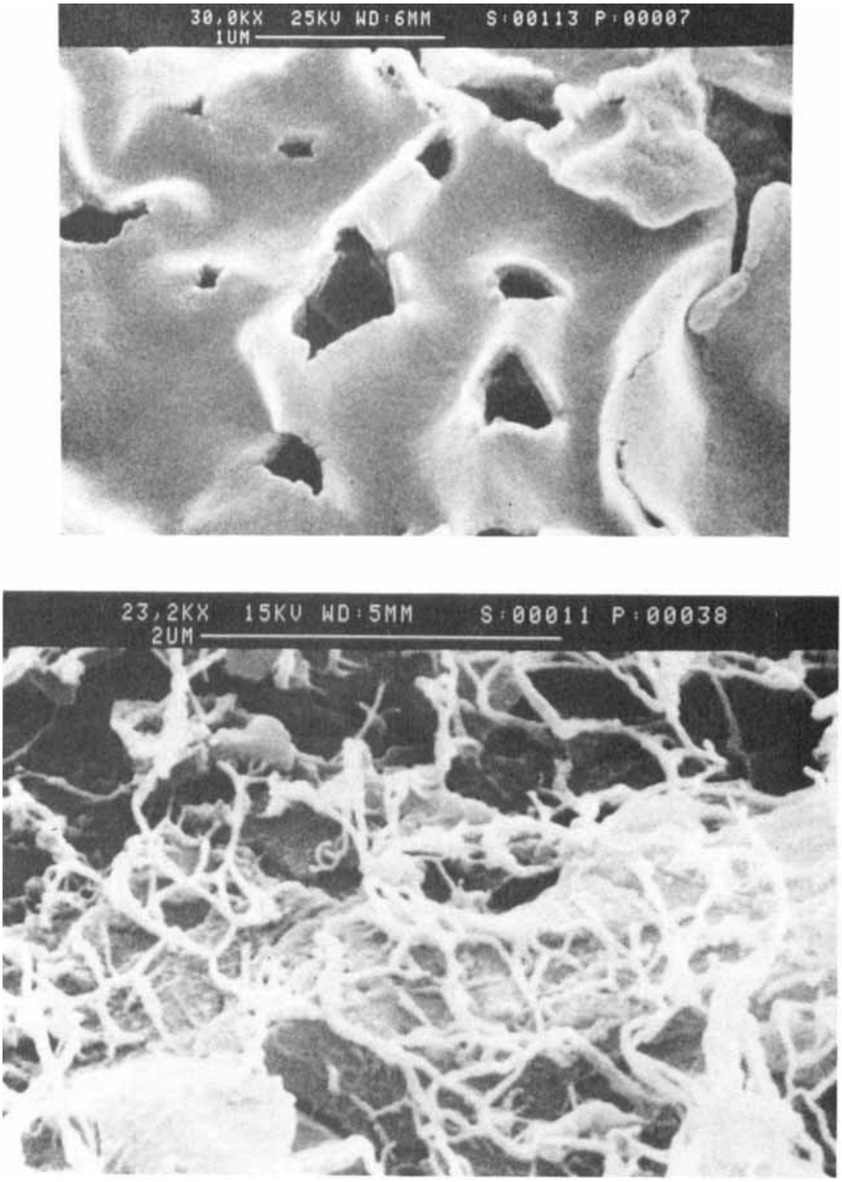

FIG. 5. (continued)

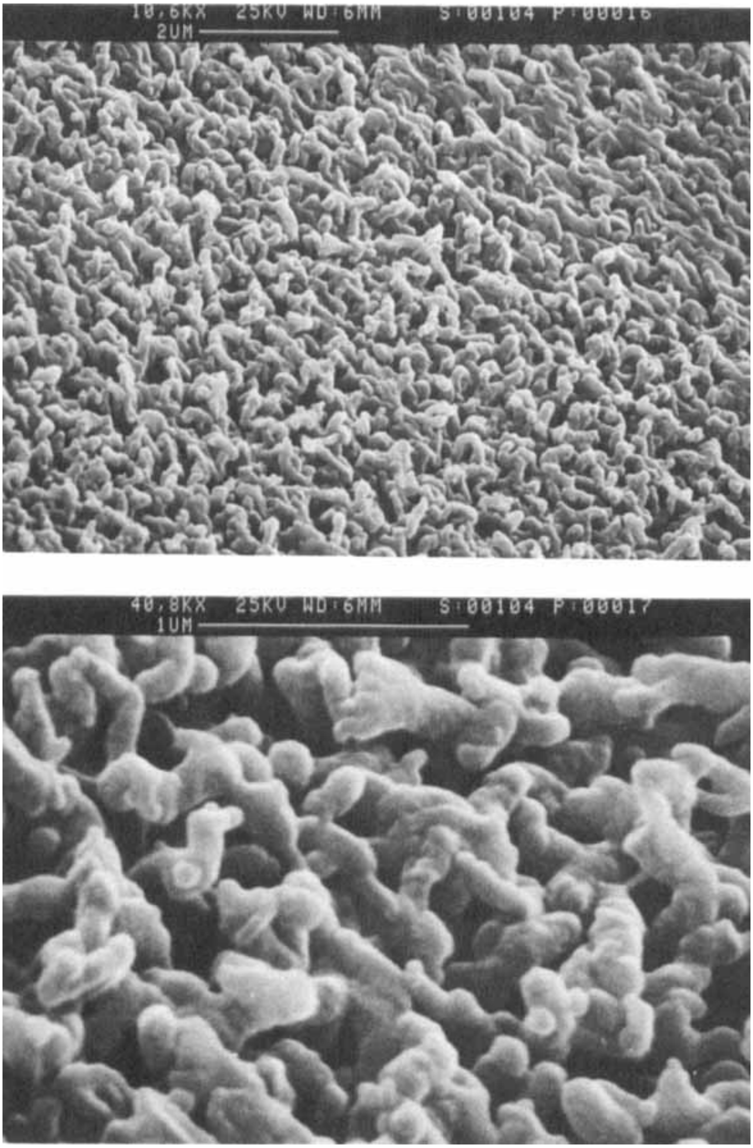

FIG. 6. SEM of dull surface (gas side, low magnification top and very high magnification bottom) of a $(CH)_x$ film synthesized with System II ($Ti(OBu)_4/AlEt_3$/silicone oil) and doped with $FeCl_3$/nitromethane solution.

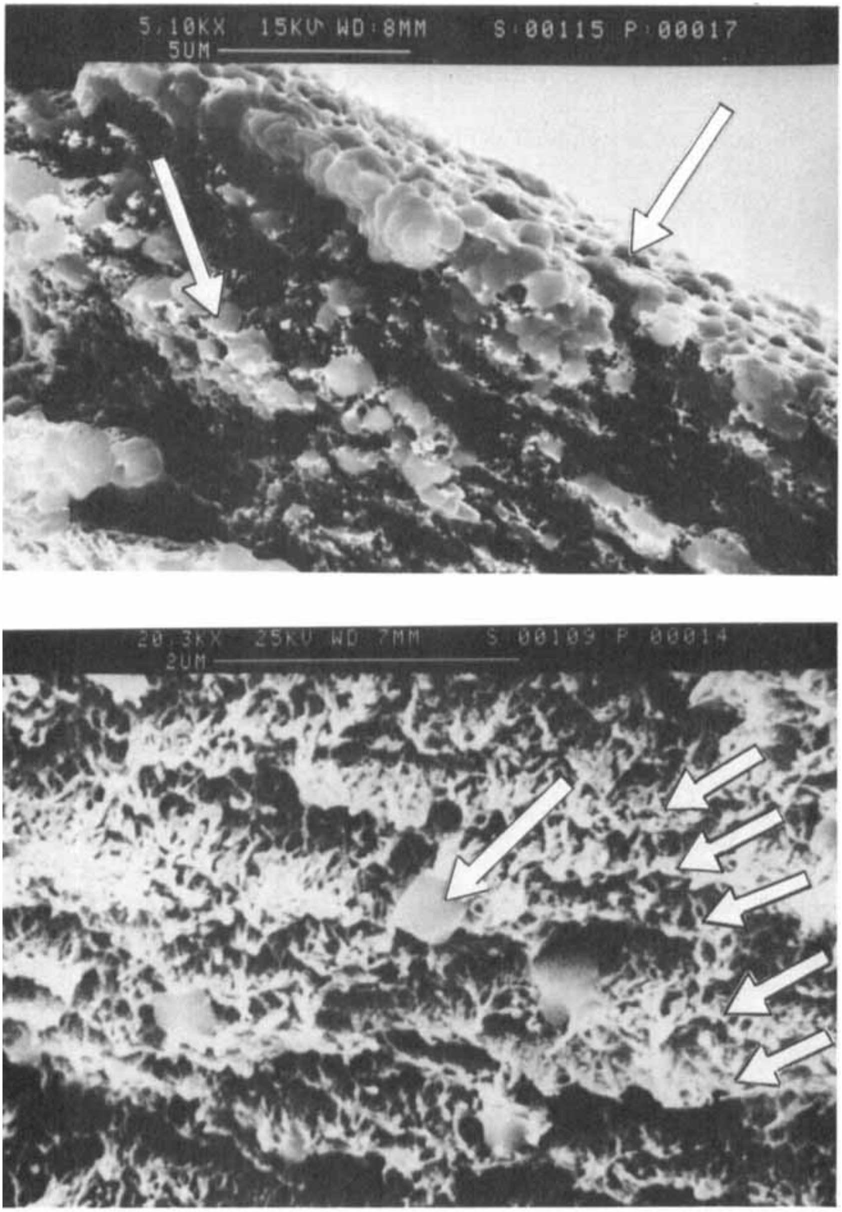

FIG. 7. SEM of a section of $(CH)_x$ films doped with $FeCl_3$/nitromethane solution and synthesized with System III ($Ti(OBu)_4$/*n*-BuLi/toluene (a) and System IV ($Ti(OBu)_4$/*n*-BuLi/silicone oil (b).

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