

# Film-Forming Process from Globular Polytetrafluoroethylene Latex Particles

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**ABSTRACT:** Film formation from an aqueous polytetrafluoroethylene (p-TFE) latex dispersion on glass tissues was studied. The p-TFE particles were of globular shape, had a diameter of  $220 \pm 20$  nm, and were of high crystallinity ( $\sim 100\%$ ). The melting point of the material was  $332^\circ\text{C}$ . For the study of the film formation, stripes of glass tissues were dipped in a concentrated p-TFE latex dispersion and then removed. The samples were then dried in an oven at well-defined temperatures below and above the melting temperature  $T_m$  of the p-TFE latex. The film formation from the particles was then studied by taking SEM micrographs of the surface of the samples at various times and conditions. It was observed that the globular particles kept their globular shape and did not coalesce to a film as long as the temperature of the sample was kept below  $T_m$ . When the samples were tempered with  $T > T_m$  the film formation started. The neighboring globular particles coalesced into wormlike par-

ticles that grew in length with time. During the growth of the particles the thickness of the particles remained constant. In the first stages the film can be imagined as a porous network from short wormlike objects. It is concluded that the coalescence begins above  $T_m$  when the polymer chains become mobile along their axis. The chains of neighboring particles can therefore interdigitate into each other along their main axis and crosslink the particles. The proposed mechanism of film formation is confirmed by AFM micrographs on which the individual particles from the dispersion are still visible in the wormlike objects. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 733–742, 2004

**Key words:** polytetrafluoroethylene (p-TFE); coatings; differential scanning calorimetry; scanning electron microscopy (SEM); latices

## INTRODUCTION

Polytetrafluoroethylene (p-TFE) is widely used as a material for both one-component and composite coatings.<sup>1–6</sup> The interest in p-TFE as a coating material is mainly caused by its very low surface energy, which gives it excellent water-repellent and lubricating properties. In addition, p-TFE is chemically and thermally inert and therefore it is more stable against environmental influences than other polymers. On the other hand, serious restrictions on the applicability of p-TFE as a coating material are caused by its lack of solubility in any common solvent as well as by its high melting temperature of approximately  $327^\circ\text{C}$ .<sup>4</sup> The former reason makes it necessary to formulate aqueous dispersions containing p-TFE particles. These dispersions are applied to the substrate at rather high temperatures, above the melting point of p-TFE, to ensure the formation of a homogeneous p-TFE film on the surface. Overcoming of the problems associated with such a procedure were tried by designing low-melting

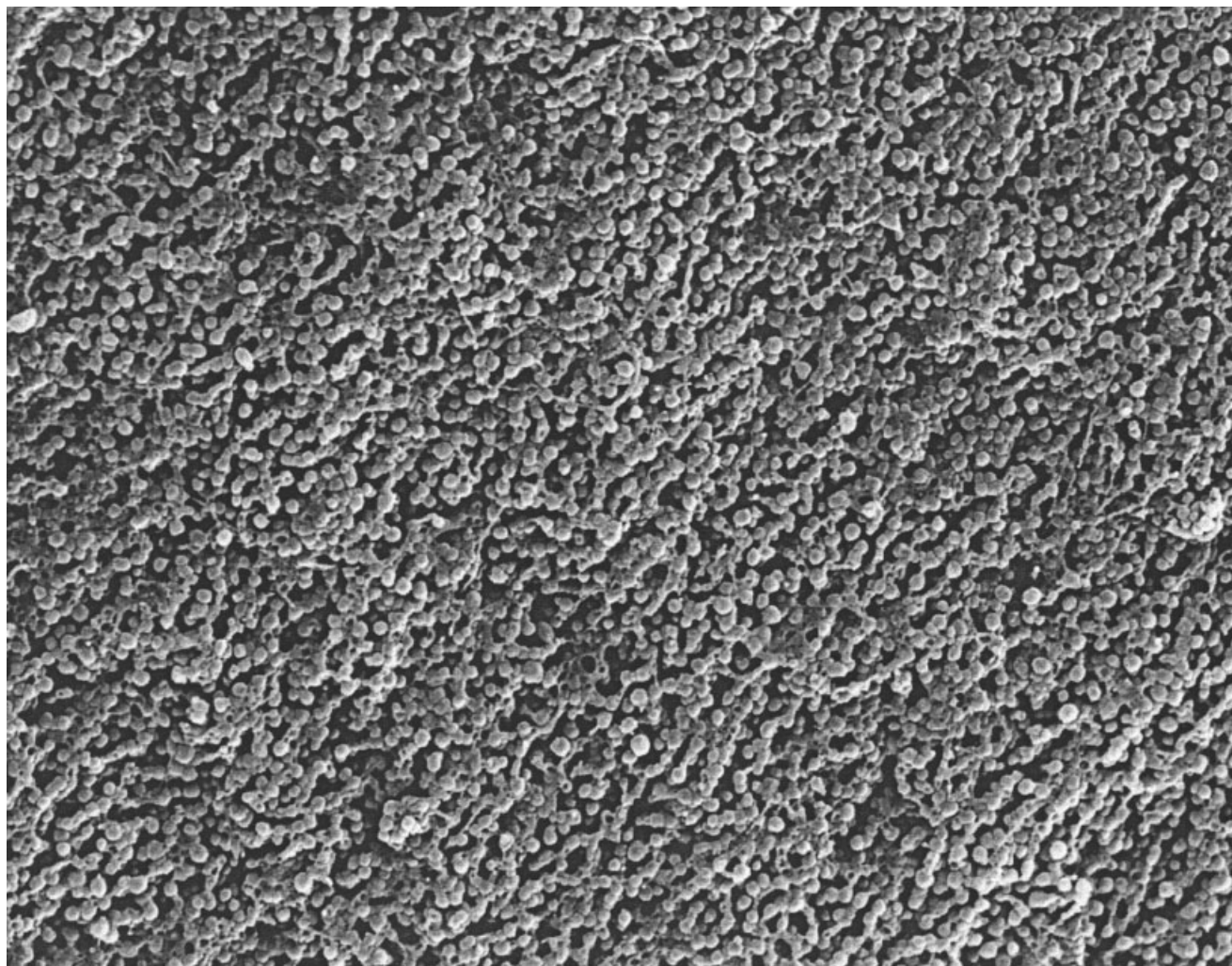
TFE copolymers<sup>4</sup> or better soluble fluorinated compounds.<sup>2</sup>

p-TFE crystals grown from solution,<sup>7</sup> from melt,<sup>8,9</sup> or obtained from latex dispersions<sup>10</sup> were investigated since the late 1950s. Symons<sup>7</sup> reported the growth of star-shaped or dendritic crystals from solutions in perfluorokerosene. The positive birefringence of these crystals indicates that the polymer chains are oriented perpendicularly to the lateral elements of the dendrites. Crystallization of p-TFE from melt resulted in striated bandlike structures on fractured surfaces<sup>8</sup> and in plate- or needle-like single crystals with the polymer chains being folded and oriented perpendicularly to the basal plane of the crystals.<sup>9</sup> Ribbon- and rodlike single crystals obtained from p-TFE latex dispersions consist of extended polymer molecules aligned parallel to the long axis of the ribbons or rods.<sup>10</sup> The described morphologies are in accordance with the observation that p-TFE crystallizes one-dimensionally from preexisting nuclei.<sup>11,12</sup> This conclusion was drawn from investigations of both nonisothermal<sup>11</sup> and isothermal<sup>12</sup> crystallization of p-TFE, the latter being rather difficult to observe because of the very rapid crystallization of p-TFE.

The formation of rodlike p-TFE particles in suspension by a special polymerization method was described in Folda et al.<sup>13</sup> The width of the rods was

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**Figure 1** SEM micrograph of the p-TFE dispersion (60 wt % p-TFE; 3 wt % Triton X-100).

approximately 20 nm, whereas their length ranged from one to several tens of micrometers. These suspensions display liquid-crystalline properties. From electron diffraction investigations it was concluded that the rods consist of fully extended p-TFE chains with their molecular axis oriented parallel to that of the rods.

In this article we report on the process of film formation from an aqueous p-TFE latex dispersion. The focus of the work was the investigation of the industrially relevant process of the coating of a glass tissue with a p-TFE dispersion stabilized by the nonionic surfactant Triton X-100. The original dispersion and films that were tempered under different conditions were studied using a scanning electron microscope. Additionally, we examined the thermal properties of the dispersion and of the pure p-TFE received thereof by means of calorimetry and thermogravimetry. Finally, we propose a mechanism of the film-formation process.

## EXPERIMENTAL

An aqueous p-TFE dispersion was received from Dyneon GmbH (Gendorf, Germany). The content of p-TFE is 60% by weight and the diameter of the globular particles is  $220 \pm 20$  nm. The dispersion was stabilized by a nonionic surfactant (Triton X-100; 3% by weight, Dyneon GmbH, Gendorf, Germany).

To determine the dry solid content, the dispersion was freeze-dried using a Christ Alpha 1-4 device (Osterode, Germany).

For calorimetry measurements of the dispersions we used a micro DSC III (Setaram, Lyon, France), which works in a temperature range from 0 to 120°C. For the dried samples that had to be examined in an extended temperature range a CCA7 apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT) was used. The thermogravimetric investigations were performed with a STA 409 (Netzsch-Gerätebau GmbH, Bavaria, Germany).



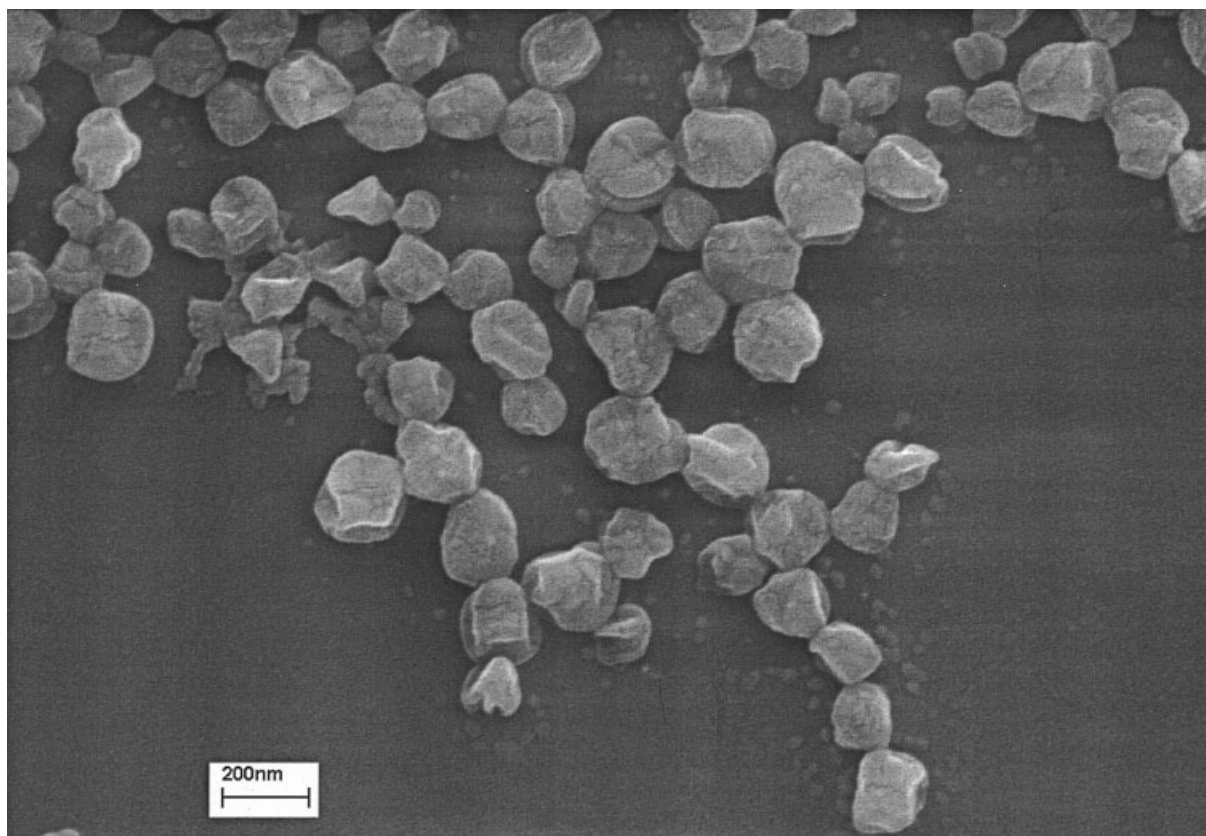


Figure 2 SEM micrograph of the diluted p-TFE dispersion.

The surface tension was measured with a TE 1C tensiometer of Lauda (Königshofen, Germany).

Coating experiments were performed in the following manner: stripes, approximately  $2 \times 5$  cm in size, were cut from a glass tissue (supplied by Dyneon GmbH) and put in the dispersion for approximately 2 h. The samples were then dried at room temperature and tempered using a Nabertherm L15 oven with program controller S 27 (Lilienthal, Germany).

Scanning electron microscope (SEM) images were obtained with a field-emission microscope 1530 (Leo Co., Oberkochen, Germany).

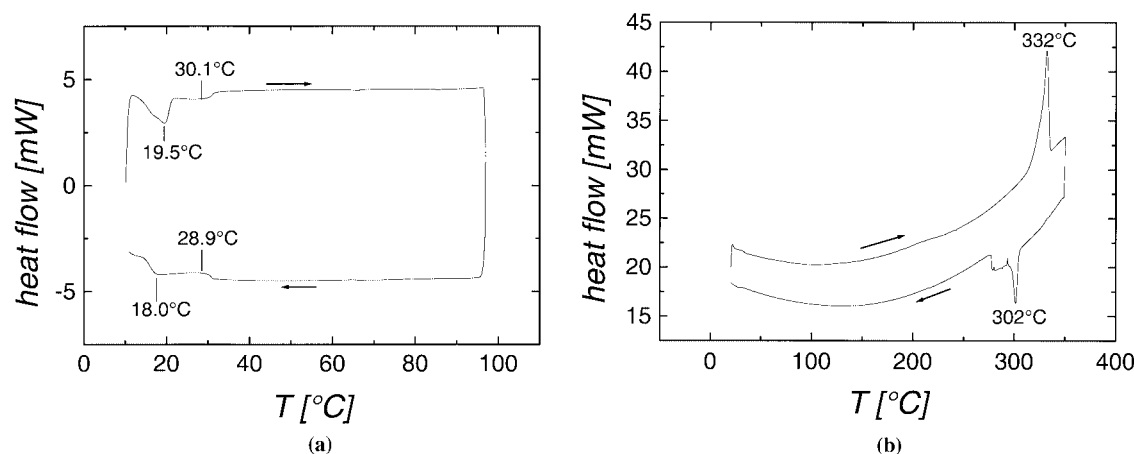
Atomic force microscopy (AFM) images were made using a Dimension 3100 M Metrology (Digital Instruments, Santa Barbara, CA) device.

## RESULTS AND DISCUSSION

### The p-TFE particles in the dispersion

The p-TFE latex dispersion was received from Dyneon GmbH. The dispersion contained 60 wt % of p-TFE. The dispersion was stabilized by a nonionic surfactant (3 wt % of Triton X-100) and was stable for extended times. To characterize the particles a few measurements were made to determine the exact shape of the particles, their size distribution, and their crystallinity.

In Figure 1 a freeze-fracture SEM micrograph of the dispersion is shown. The micrograph was prepared by temperature quenching a thin liquid film of the sample to 77 K. The frozen sample was then fractured at a low temperature, the fractured surface was sputtered with metal and the fracture plane was then monitored with SEM. The micrograph clearly shows the individual latex particles of the dispersion. The particles are well dispersed in the aqueous fluid. Practically no aggregated particles are present. The particles are of globular shape, have a mean diameter of 220 nm, and have a low polydispersity. To have a good idea on the statistics of the sample, the micrograph of Figure 1 shows a large area of the sample. The exact shape of the particles, however, is not so clear. A higher magnification of the individual particles of a more diluted dispersion is shown in Figure 2. This micrograph shows clearly that the particles are not of perfect spherical shape but they are polygons. Some of the flat surfaces of the particles are clearly visible on the micrograph. It should be mentioned here that the electron beam of the SEM can change the morphology of the p-TFE surfaces if they are exposed to the beam for long times at high magnifications. Therefore it was necessary to scan the pictures rapidly and to avoid very high magnifications. The morphologies of the



**Figure 3** (a) DSC curve for the p-TFE dispersion (60 wt % p-TFE; 3 wt % Triton X-100); heating rate: 0.2 K/min. (b) DSC curve for the solid content of the p-TFE dispersion obtained after freeze-drying the dispersion; heating rate: 10 K/min.

p-TFE particles obtained by SEM were also confirmed by AFM measurements. The polygon shape obviously is a result of the crystalline nature of the particles. The crystalline nature of the particles is documented by the results of DSC [the measurements are shown in Fig. 3(a) and (b)]. The crystalline nature of the particles obviously has consequences for the film-forming process. Because it is unlikely that each particle consists of a single domain and is actually a single crystal, the particles must have an internal three-dimensional topology, the exact structure of which is not known.

### DSC results

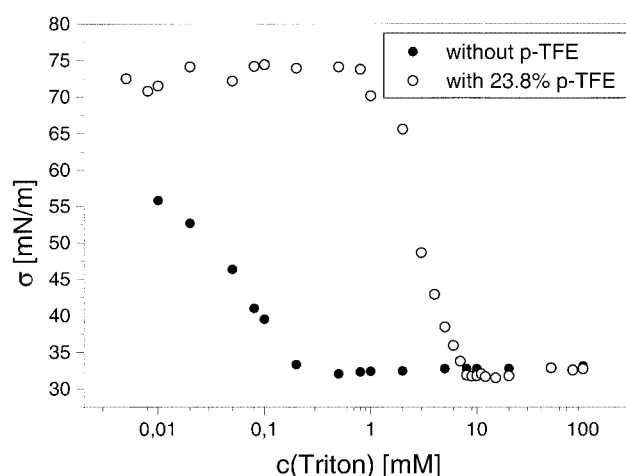
The DSC signals in Figure 3(a) and (b) were obtained when the dispersion [Fig. 3(a)] and dried samples of the dispersion [Fig. 3(b)] were heated at rates of 0.2 and 10 K/min, respectively. We observed two small transitions at 19.5 and 30.1°C [Fig. 3(a)] and a large transition at 332°C [Fig. 3(b)]. All the transitions appear on cooling whereby the exact temperatures are somewhat lower because of undercooling. The first peak in Figure 3(a), located at 19.5°C in the heating curve and at 18°C in the cooling curve, is well known in the literature.<sup>14,15</sup> This first-order transition is caused by a slight untwisting from 13 to 15 CF<sub>2</sub> groups per 180° twist as well as by a change of the unit cell

from triclinic to hexagonal.<sup>16</sup> The second transition in Figure 3(a) that can be found at 30.1°C in the heating curve and at 28.9°C in the cooling curve is attributed to a crystal disordering. In the temperature range between the two peaks (i.e., between 19 and 30°C), the nearly perfect three-dimensional order of the polymer chains that exists below 19°C disappears, as well as the hexagonal unit cell.<sup>17</sup> The peaks in Figure 3(b) show the melting and recrystallization of the p-TFE.

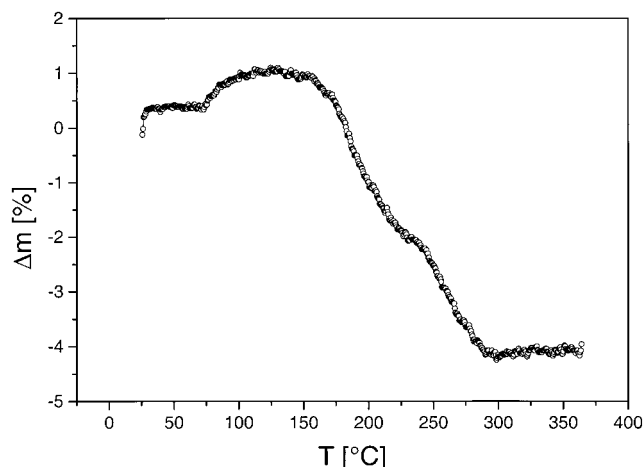
The integral heats of transformation are given in Table I. The table also contains some results from references from the literature. It is a well-known fact that the heat of melting that can be determined from the first heating cycle is larger than the value obtained from the cooling cycle because not all of the material recrystallizes again after the sample was in the molten state. Given that the heat of melting for a perfect crystalline state is known, we actually can determine a

**TABLE I**  
Thermal Transitions and Integral Heats of p-TFE from Figure 3(a) and (b)

$T_{\text{Peak}}$ (°C)		$\Delta H$ (J/g)		Ref. 18
Heating	Cooling	Heating	Cooling	
19.5	18.0	1.72	0.64	13.4
30.1	28.9			~ 1
332	302	60	15.8	58



**Figure 4** Surface tension of Triton X-100 in the presence and in the absence of p-TFE.



**Figure 5** Thermogram of the solid content of the p-TFE dispersion after freeze-drying.

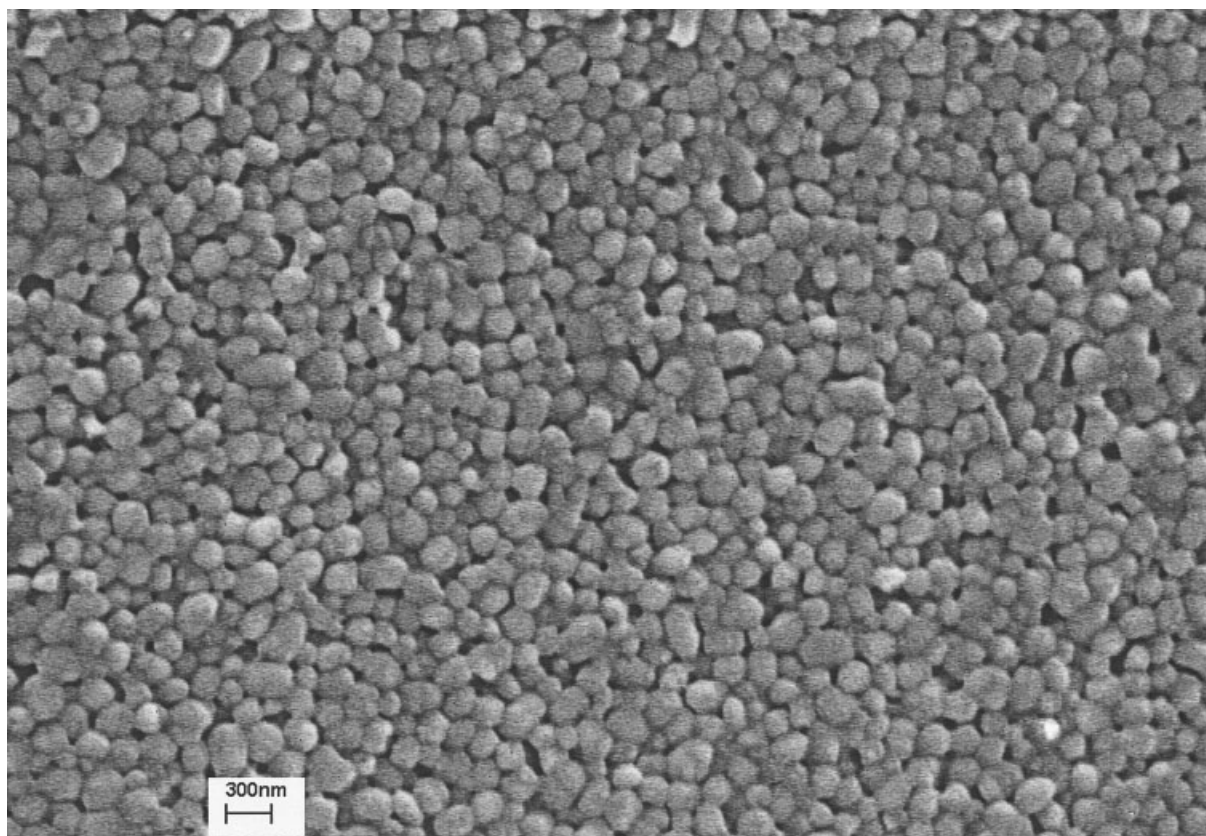
degree of crystallinity for our samples from the determined heat of melting. Comparison of the data given in Table I reveals that the freeze-dried material that was not in the molten state before is nearly 100% crystalline. After cooling from  $T > T_m$ , only about 30% of the crystallinity remains.

#### Thermogram of the latex dispersion

The p-TFE latex dispersion was stabilized with the nonionic surfactant Triton X-100. It was likely that part

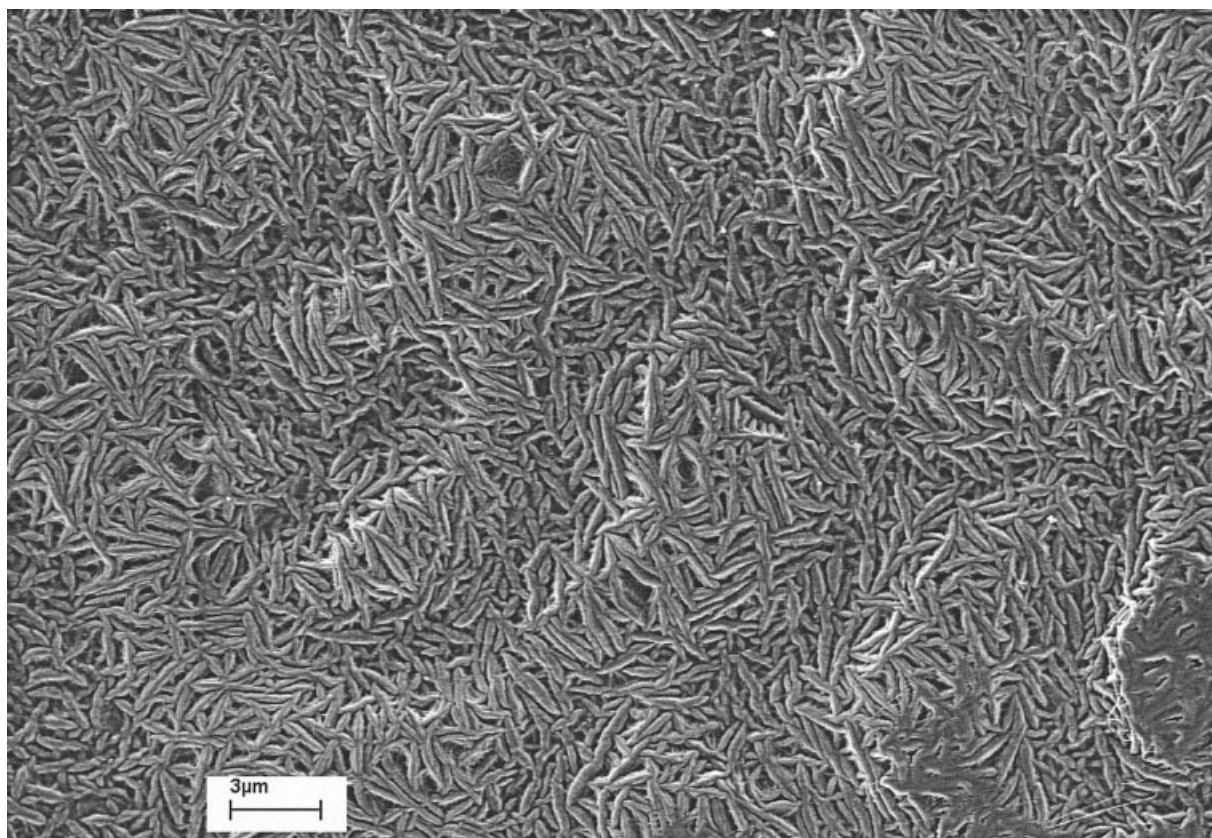
of the surfactant was adsorbed onto the particles and part of it was dissolved as micelles in the bulk phase. To find out the fraction that was in the bulk and in the adsorbed state we made surface tension measurements as a function of the dilution. The results are shown in Figure 4. The surface tension of Triton X-100 in water and in a 23.8 wt % p-TFE dispersion is plotted versus the surfactant concentration. The critical micelle concentration of the surfactant was shifted from 0.25 to 8 mM in the presence of 23.8 wt % p-TFE. This means that 7.75 mM Triton X-100 was adsorbed by the p-TFE particles. Assuming a density of p-TFE of 2.3 g/mL it can be calculated that the concentration of p-TFE in the system is 275 g/L and thus 0.028 mmol of Triton X-100 were adsorbed per gram of p-TFE. From this result it can be further deduced that in the original dispersion containing 60 wt % p-TFE 1.68 mmol (1.05 g if the molecular weight of 624 g/mol for Triton X-100 is taken into account) of Triton X-100 are adsorbed per 100 g of dispersion. Therefore it can be said that in the original dispersion with 3 wt % Triton X-100 1 wt % of the surfactant was in the adsorbed state and 2 wt % was in the bulk phase. The adsorbed and the micellized surfactants could play a role in the film-forming process. For this reason it is important to know what happens to the surfactant when samples are heated to the melting temperature of p-TFE.

In Figure 5 we show therefore a thermogram of a



**Figure 6** SEM micrograph of a glass tissue that was coated with the p-TFE dispersion and tempered at 320°C for 5 h.





**Figure 7** SEM micrograph of a glass tissue that was coated with the p-TFE dispersion and tempered at 350°C for 5 h.

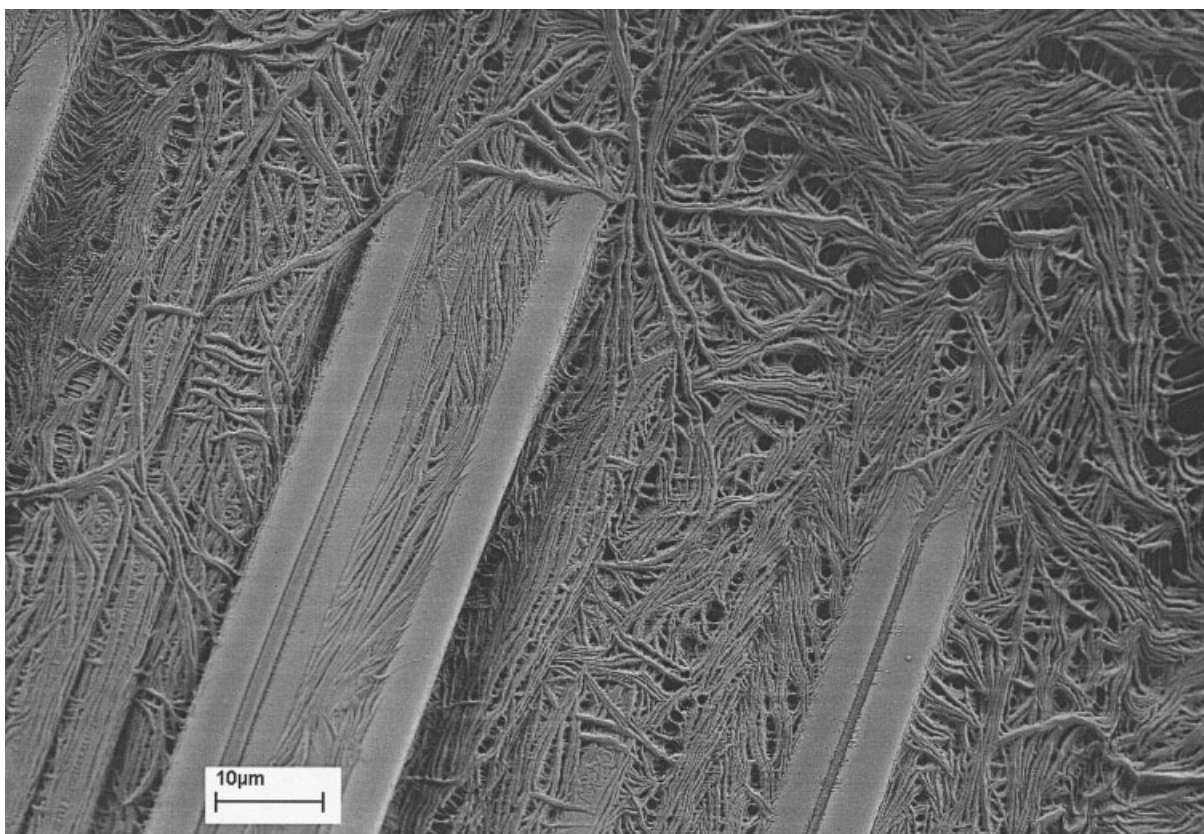
dried sample containing approximately 5 wt % of Triton X-100. It shows that the sample loses weight between 150 and 300°C. It is likely that the weight loss is attributable to the decomposition of the nonionic surfactant. The thermogram thus shows that all the surfactant has been decomposed by the time the melting point of p-TFE is reached. It is unlikely that some material is left on the p-TFE particles when the film formation starts because the melting point of p-TFE is significantly higher than the decomposition temperature of Triton X-100. Furthermore, the same structures as described below were also found when a surfactant-free raw dispersion was used as the coating material. The thermogram in Figure 5 also shows that p-TFE does not begin to decompose at temperatures below 380°C. From the literature it is known that thermal degradation of p-TFE starts at about 440°C.<sup>19</sup> We can thus conclude that the film-forming process cannot be influenced by the surfactant film.

The next step tested at which temperature the film-forming process starts. For that purpose a dried sample of the dispersion was heated to 320°C and tempered at this temperature, just 10° below the beginning of the melting point. The sample was then cooled to room temperature and a micrograph taken by SEM (Fig. 6). The micrograph clearly shows that the p-TFE particles were not changed by this procedure. All par-

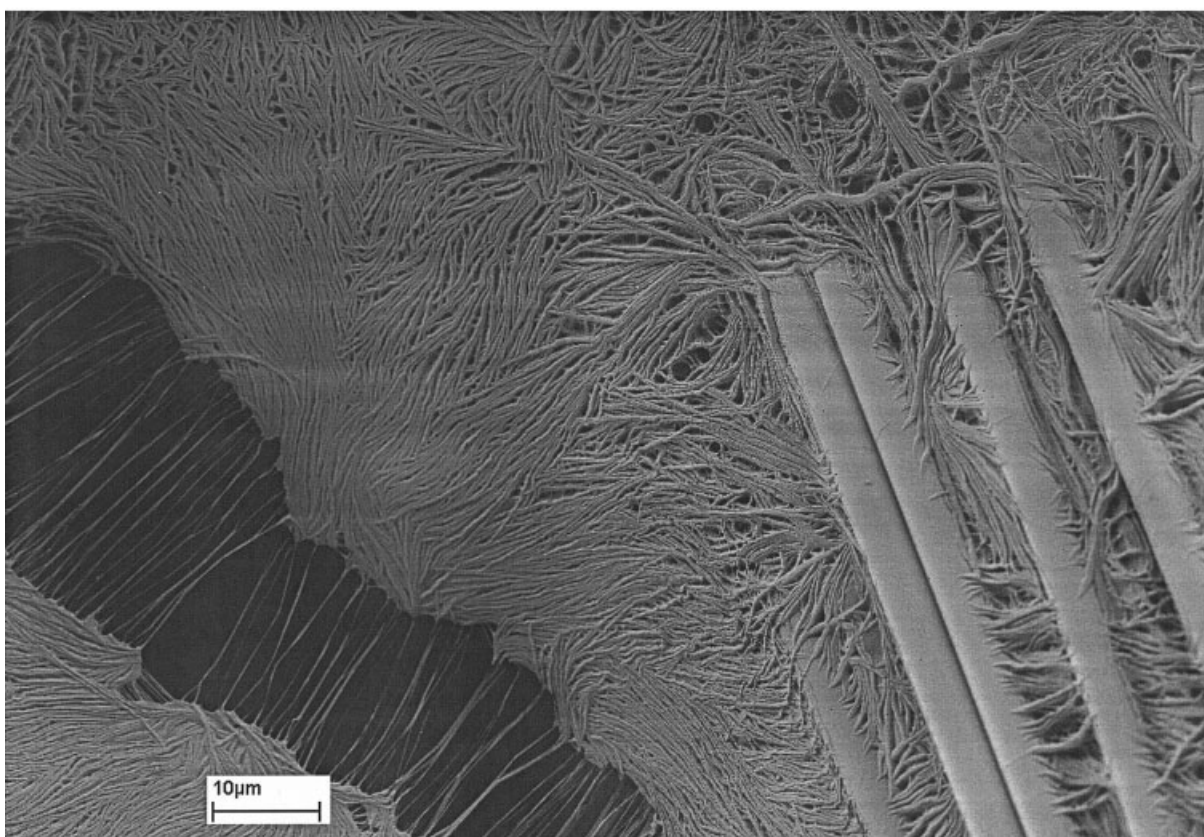
ticles still have the same size and shape and no coalescence occurred.

The situation is completely different if the samples are heated above  $T_m$  and the sample is kept for some time at this temperature (Fig. 7). Now one notices that all globular particles have been transformed to wormlike objects of about the same size. On closer inspection one realizes that the thickness of the wormlike particles is about the same as the diameter of the globular particles in the dispersion. The lengths of the particles vary widely. The axial ratio varies between 2 and at least 10. The shape and the size of the wormlike particles make it likely that they have been formed by a one-dimensional aggregation process of the primary particles. It is not completely clear from the micrograph whether the individual worms are connected with each other or whether they are individual particles. On closer inspection of details of the micrographs one notices situations in which several worms seem to originate in a starlike arrangement from the same point. Such a configuration makes it likely that some worms are really connected with each other and that the center of such a star is a globular particle, which is connected to several worms. It should be noted here that the same wormlike structures were found when plane-metal sheets were used as substrate. The texture





(a)



(b)

**Figure 8** (a) SEM micrograph of a glass tissue that was coated with the p-TFE dispersion and tempered at 400°C for 5 h. (b) SEM micrograph of a glass tissue that was coated with the p-TFE dispersion and tempered at 420°C for 5 h.

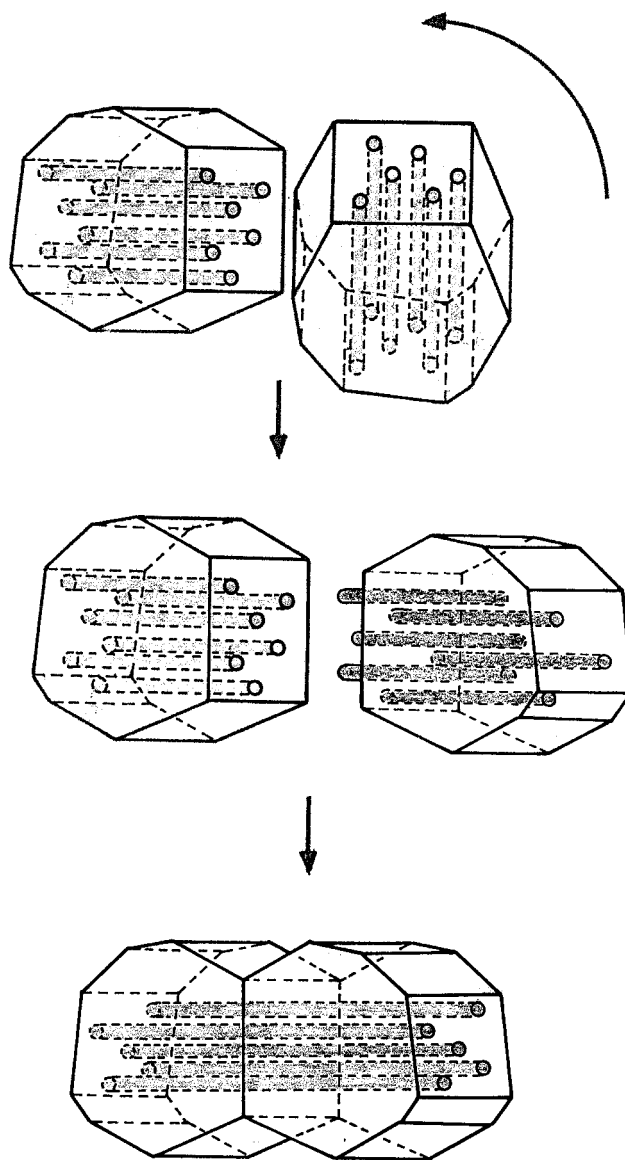
seems to be independent on the material that is coated with p-TFE.

Figure 8 shows the temperature dependency of the structure. The different samples were exposed to increasing temperatures above  $T_m$  for 5 h each. It can be noted that the wormlike particles grow in length when the temperature is increased.

### Proposal for the film-forming mechanism

One particle with a radius of 100 nm has a weight according to  $m = 4\pi/3r^3\rho = 9.34 \times 10^{-15}$  g. That corresponds to a MG of  $5.63 \times 10^9$  g/mol. Because the molecular weight of the p-TFE polymer is, according to Dyneon GmbH, only about  $7 \times 10^6$  g/mol it has to be concluded that one particle contains about 800 polymers. Although the exact structure of the polymer particle is not known, it is likely that the whole particle is built from smaller crystallites. Because the fluorine atoms in p-TFE are rather large, the chains are in an all-*trans* configuration and they are rigid.<sup>20</sup> Electron diffraction studies on ribbon- and rodlike particles in emulsion-grade p-TFE revealed that these particles are single crystals with the chain axis parallel to the long axis of the ribbons or rods.<sup>10</sup> Similar studies on rodlike p-TFE dispersion particles showed that they are composed of fully extended chain crystals with only a few defects.<sup>21</sup> The rodlike entities thus formed can arrange randomly and build up spherical particles. Taking into account this experimental evidence and the results presented here, it is likely that some of the faces of the globular particles are formed from the front faces of the polymer chains, whereas some other side faces contain no ends and the chains lie parallel to the faces. It is evident that in such a situation two neighboring particles cannot coalesce into each other when two unlike faces come into contact, but can melt into a single particle only when two like faces come into contact. The particles therefore first have to undergo a rotational diffusion until two like faces have contact and then the interdigitation process can start. This idea is supported by the observation that the original globular particles of the dispersion are still present if the system is tempered at 350°C for up to 2 min. The wormlike structures appear only if the system is kept for longer times ( $\sim 5$  min) at 350°C. If most of the particles have only two phases with free front ends and these faces are on opposite sides of the globular particles the result would be the unidimensional growth of the wormlike particles to long fibers. This situation is shown in a sketch in Figure 9.

The proposed mechanism is supported by the AFM micrograph shown in Figure 10, which displays the surface of a glass tissue that was coated with the p-TFE dispersion and tempered at 350°C for several



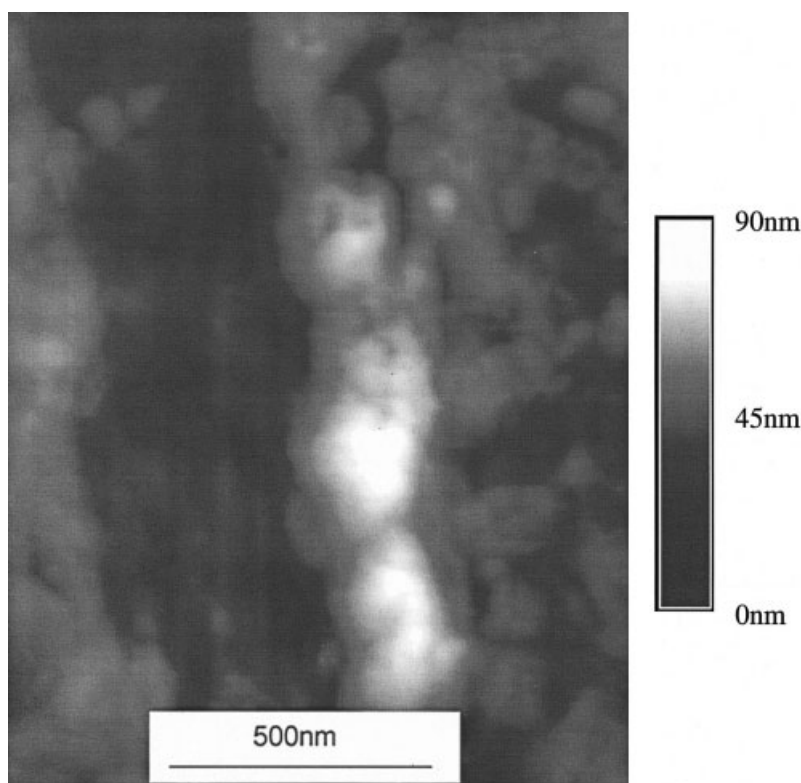
**Figure 9** Sketch of the growth process of p-TFE particles: fully extended polymer chains (shadowed), present in the globular p-TFE particles, can interdigitate and thus fuse two neighboring particles when two like faces of the particles come into contact.

hours. The elongated object in the middle represents one "worm." Obviously, it consists of five globular particles connected with each other. The diameters of the particles are between 180 and 230 nm; that is, they are in the same range as those of the original particles in the dispersion.

### CONCLUSIONS

The process of film formation from aqueous p-TFE dispersions was investigated. Scanning electron micrographs clearly showed that the p-TFE particles in the dispersion, which have a mean diameter of 220





**Figure 10** AFM micrograph of a glass tissue that was coated with the p-TFE dispersion and tempered at 350°C for 5 h.

nm, are not of perfect spherical shape but they are polyhedrons. This is a consequence of the high crystallinity of the p-TFE. Differential scanning calorimetry investigations of the freeze-dried material confirmed that the crystallinity is nearly 100%. However, only 30% of the crystallinity remained when the p-TFE had been in the molten state. The change in crystallinity was accompanied by a shift of the melting point to lower temperatures.

The morphology of glass tissues coated with the p-TFE dispersion and tempered at various temperatures was studied using a scanning electron microscope. The investigations showed that the size and shape of the original particles in the dispersion are not changed as long as the temperature was kept below the melting point of p-TFE. Exceeding this temperature, however, resulted in the formation of wormlike objects which seem to be formed by the one-dimensional aggregation of several p-TFE particles. This suggestion was confirmed when the worms were investigated with an atomic force microscope that could resolve the fine structure of the aggregates. The formation of the wormlike objects was not influenced by the surfactant used to stabilize the p-TFE dispersion because this surfactant is decomposed at significantly lower temperatures than the melting point of p-TFE and the same worm structure was also observed when a surfactant-free raw dispersion was used in the coating process. A further increase in the temperature at

which the coated samples were kept again changed the morphology of the coating: the wormlike particles grew in length with increasing temperature. The uni-dimensional growth of the original globular particles to wormlike aggregates and to long fibers can be explained if it is taken into account that p-TFE chains are rigid and fully extended in the crystallites. Two particles can coalesce to one aggregate only if two "like" faces come into contact, that is, if the polymer chains are perpendicular to the faces in both particles. Only in this case the chains can interdigitate, resulting in the fusion of the particles.

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