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Morphology evolution in polytetrafluoroethylene as a function of melt time and temperature. Part III. Effect of prior deformation

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Abstract

In parts I and II the effect of melt time and temperature on dispersed dispersion particles of various molecular weights was described: substantial molecular motion on the substrate occurs with the development of both planar folded chain single crystals, and single molecule single crystals and banded structures with parallel double-striations oriented along the long axis of the crystal or band. The molecules in the single molecule single crystals and bands are parallel to the substrate, an individual double-striation appearing to consist of a ‘double edge’, folded chain, lamella more or less normal to the substrate. In this paper, the effect of deformation and subsequent heat treatment of the nascent particles is described. Similar to the known effect of deformation of compacted nascent PTFE dispersion particles, large scale shear of dispersed dispersion particles can lead to nano-fibrils of indefinite length for both standard size resins and nano-emulsions, of both high and low molecular weight. Sintering of the nano-fibrils in contact with the substrate leads to the development of shish–kebab structures with the nano-fibril as a core and epitaxially nucleated, ‘double edge’, folded chain single crystal kebabs oriented perpendicular to the fibril axis and the substrate. No change is seen in similar fibrils remaining suspended between the dispersion particles. The molecules forming the ‘kebabs’ have ‘wandered’ individually on the substrate (glass) before attaching to the growing kebabs.

Keywords: Polytetrafluoroethylene; Nano-fibrils; Shish–kebabs

1. Introduction

Nearly 40 years ago it was shown that heating of dispersed high molecular weight PTFE dispersion[1] particles for 2 h at 350 °C led, during crystallization, to the growth of folded chain, lamellar single crystals and banded structures resembling those observed on free surfaces of bulk samples treated similarly [1,2]. In parts I [3] and II [4], following a discussion of the morphology of the nascent particles of several resins of various molecular weight, we discuss the evolution of the morphology of these particles as a function of time and temperature in the melt. Substantial molecular motion occurs on the substrate; large, angular particles form first for short melt times, followed by development of both planar, folded, multi-chain, lamellar single crystals and single molecule single crystals and banded structures with parallel double-striations oriented along the long axis of the crystal or band. The molecules in the single molecule single crystals and bands are parallel to the substrate, an individual double-striation appearing to consist of a ‘double edge’, folded chain, lamella more or less normal to the substrate. These observations are summarized below relative to Fig. 1. During the time in the melt individual molecules apparently ‘wander’ away from the dispersion particles, wandering on the substrate and forming the folded chain crystals when cooled. Similar double edge crystals also form epitaxially on the nascent particles. It was suggested that the morphology develops in a mesomorphic ‘melt’, the morphology depending primarily on the melt time and temperature rather than the rate of cooling.

For a similar time period it has been known that fracture of cold compacted nascent PTFE dispersion particles or by uniaxial or biaxial deformation of paste extruded structures (sheets or tubes consisting of mixtures of the PTFE particles and lubricants) can lead to the formation of nano-fibrils of

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[1] Also known as emulsion particles; prepared by an emulsion polymerization process.

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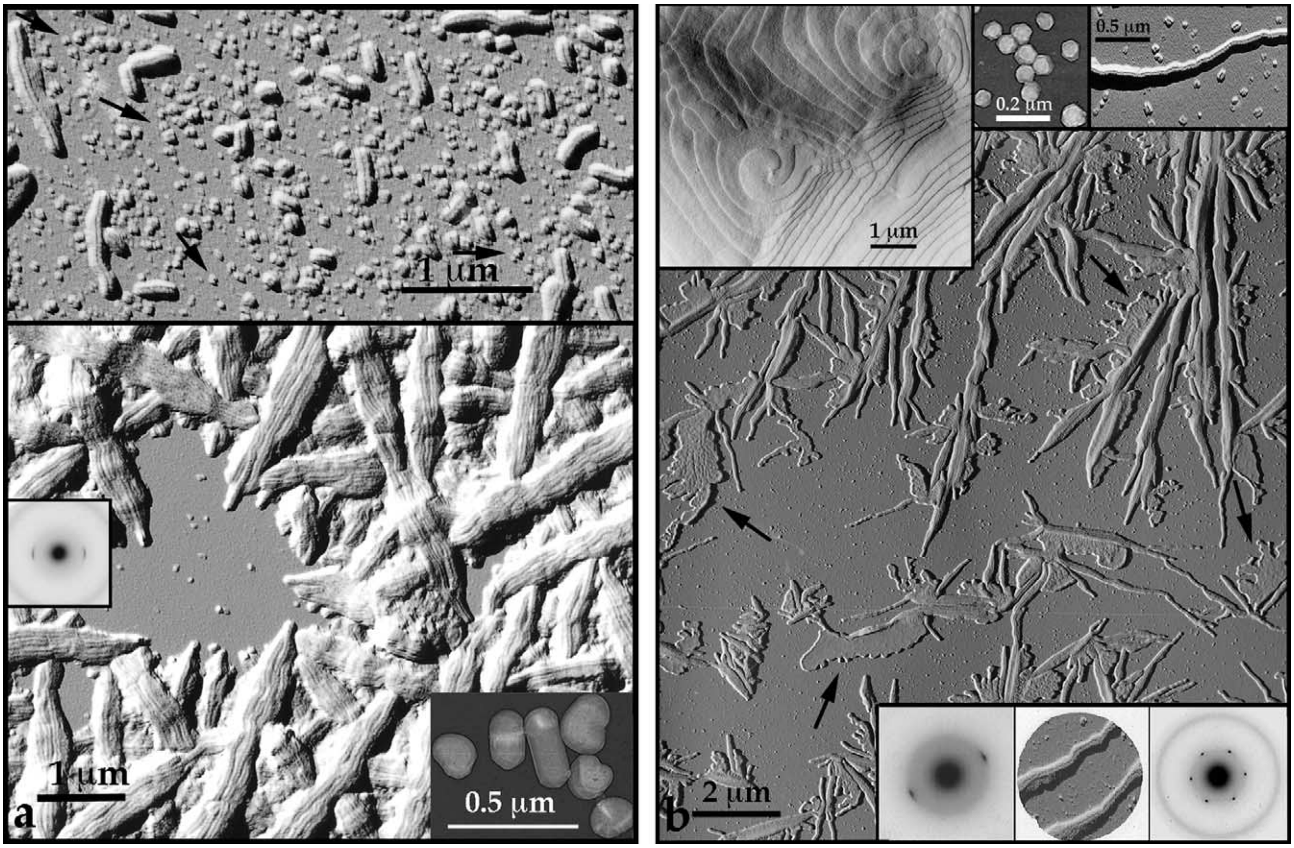

Fig. 1. Sintered (a) standard size resin (TE-30) and (b) nano-emulsions. Sintering times, temperatures and details of the insets are given in the text.

indefinite length [5,6]. Similar fibrils can even be produced by molding another polymer between PTFE coated Al foil and then removing the foil [7]. Here, we show that large scale shear of dispersed dispersion particles can lead to apparently similar nano-fibrils, whereas small scale compression/shear [3] or shear on the surface of water [8] of the nascent particles has been suggested to result in an unfolding of the folded rods proposed to be involved in their development. The effect of sintering (annealing) the nano-fibrils at temperatures at and above the melting point (T_m) is also described. Further details of the nascent particle structure, and effects of sintering and deformation, are described in Ref. [9].

2. Experimental

Diluted suspensions of dispersion particles were dried on glass cover slips, sheared by drawing another slide across the surface and then heated, if desired, between the platens of a molding press; temperature control was no better than ±5 °C. Resulting samples were shadowed with Pt/C, coated with C, floated on dilute HF and picked up on transmission electron microscopy (TEM) grids. Nascent diluted dispersion was dried on C coated glass slides, shadowed if desired, and treated similarly. Bright field diffraction contrast (BFDC) images were taken with low beam intensity, after focusing on a nearby area. The sintering temperatures and times before cooling, by turning off the heat of the press (i.e. slow cooling), unless specified, are given in the text and captions. A Phillips CM-12 was used for the TEM images and electron diffraction (ED) patterns, with most figures printed as negatives by scanning the original negatives with a Microtek ArtixScan 1800f scanner, adjusting contrast and brightness and sharpening with Adobe Photoshop. Scanning electron microscope (SEM) images were taken at 2 kV on a field emission Hitachi 4700 (SEM) using Cr coated samples.

Results for two types of 'standard size' resins and two 'nano-emulsions' are described here. Standard resin G (supplied by W. L. Gore and Assoc., Inc.) has a $\bar{M}_w$ of 50×10^6 Da (extended chain length (ecl) $=1.3\times 10^6$ Å $=$ **0.13** mm); Teflon 30 (DuPont, TE-30) has $\bar{M}_w = 15–20\times 10^6$ Da (ecl $=0.4–0.5\times 10^6$ Å). Nano-emulsion 18749/26 (Ausimont, A18749) has $\bar{M}_n = 2\times 10^5$, $\bar{M}_w = 49\times 10^6$ Da, number average ecl $=5200$ Å, weight average ecl $=$ **0.13** mm; nano-emulsion TE 5070 (Teflon 5070, DuPont) has $\bar{M}_n = 50,000$ Da, corresponding to a DP of 500, ecl $=$ 1300 Å. Molecular weights were measured by zero shear melt viscosity. For characterization of ecl and molecular volume, in form IV (19–35 °C) PTFE has 38.5 Da/Å ecl, 1.3 Da/Å^3 [10].

3. Results and discussion

3.1. Summary of effect of sintering non-sheared particles

Fig. 1(a) and (b) summarizes observations of the effect of sintering dispersed standard-size resins (here TE-30, Fig. 1(a)) and both nano-emulsions (Fig. 1(b)). Further details are given in Refs. [3,4,9]. The 'standard-size' resins (dark-field diffraction contrast micrograph inset at lower right in Fig. 1(a)) consist of more or less elliptical particles or rods of various lengths with all dimensions larger than 1000 Å. The dispersed dispersion particles were sintered for 20 min (upper) and 30 min (lower) at 380 °C on glass and then slow cooled. In the upper portion of the figure 'double-striation' structures, suggested to be folded chain lamellae (ribbons) on-edge, of various length are present, with the arrows indicating short double-striations with a volume corresponding to ca. one $\bar{M}_w$ molecule; i.e. they are single molecule, single crystals. It is suggested these particles correspond to individual molecules 'wandering' on the substrate after 'disentangling' from the original nascent particle and becoming trapped when the sample was cooled. A common observation, as for the long double-striation at the left of the upper portion, is that the base of the double-striation is considerably wider than the striation spacing. In the lower portion of the figure, from a region with more concentrated particles initially, numerous 'bands' are present, each with several double-striations on their surface, running the length of the band. The inset diffraction pattern with two 100 arcs, from another region but set in with the proper orientation for the band directly beneath it, indicates the molecular axes are perpendicular to the long axes of the bands. Apparently related bands observed on fracture surfaces of long time (1–2 h) sintered bulk samples have striations perpendicular to the long axis [2] resembling the fracture surfaces of extended chain polyethylene [11].

The main area of Fig. 1(b) is a sample of dispersed A18749 sintered at 350 °C, 60 min on glass. A micrograph of the nascent A18749 is inset in Fig. 3. As shown in Refs. [3,9], the rod-like particles are single crystals, with the molecular axes parallel to the rod axis and folded; the ca. 200 Å diameter particle indicated by the arrow corresponds in volume to one $\bar{M}_w$ molecule. In Fig. 1(b) there are a number of narrow bands primarily extending downwards from the top, with poorly resolved double-striations one of which often extends out from the end of the band. The selected area and ED pattern inset at the center bottom of the figure (from another area) better resolves the double striations, with the ED pattern indicating the molecules are perpendicular to the long axis of the double-striations; with the $\bar{M}_n$ molecules being an order of magnitude larger than the width of the striations; i.e. they are folded. There are

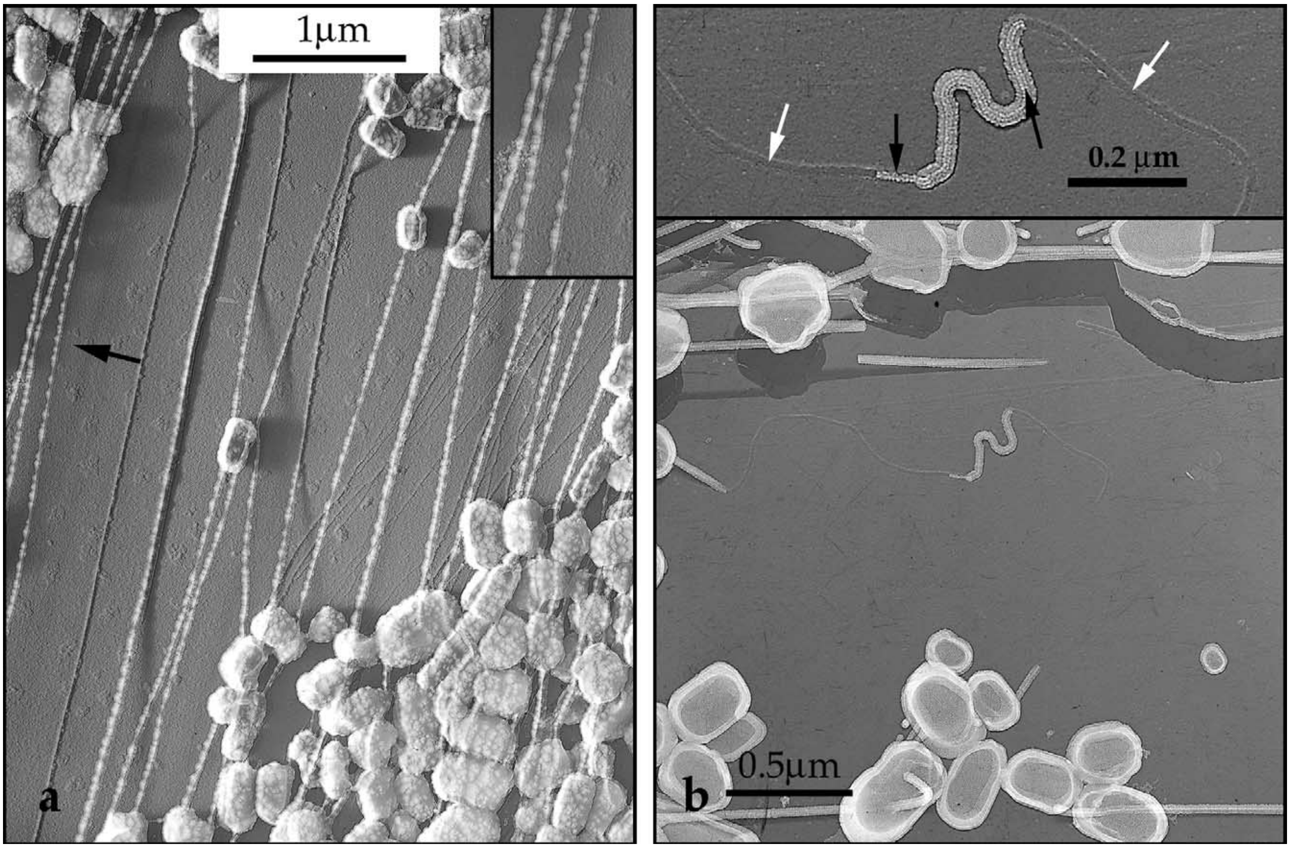

Fig. 2. Sheared resin G (a) Pt/C shadowed and (b) coated with ca. 50 Å of Cr. The insert in A (and many subsequent figures) is from the area indicated by the arrow. As shown in the figures the Pt/C 'beads' on both the fibrils and the particles whereas Cr produces a more uniform coating.

also numerous areas with ca. 500 Å thick lamellae lying parallel to the substrate (arrows). The inset [001] ED pattern at lower right is from a similar area, the molecules again being folded. The inset at upper right, from a A18749 sample sintered at 350 °C, 30 min on mica consists of a single, long double-striation, ca. 500 Å wide and a number of short double-striations. The ones indicated by the arrows correspond in volume to ca. 4/5 of a single $\bar{M}_w$ molecule; i.e. they again are single molecule, single crystals; whether they correspond to the original location of the nascent particle or were trapped at the present location while 'wandering' on the substrate is not known. The upper left inset shows the folded chain, ca. 100 Å thick lamellae that developed in a TE 5070 sample sintered at 350 °C for 30 min, slow cooled, reheated at 350 °C, 30 min and then quenched into water; similar micrographs were obtained from the slow cooled samples before reheating. The nascent TE 5070 particles consist of ca. 750 Å diameter, 750 Å thick, hexagonal single crystals; i.e. ca. 1/2 the thickness of the number average ecl.

All four of the samples examined here, when sintered in the bulk for sufficient time and temperature, developed the typical banded structure in their interior, as revealed on fracture surfaces; except for TE 5070, the thickness of the bands was considerably less than the ecl [3,4,9]. With the molecular axes being parallel to the striations, i.e. perpendicular to the band axis, the chains must be folded. On the basis of micrographs taken as a function of sintering time it was suggested that folding occurs first with a short fold period (e.g. ca. 2100 Å for T 5070), and then extends with increasing sintering time, similar to the development of the extended chain crystals in linear polyethylene when crystallized under pressure (e.g. Ref. [12]).

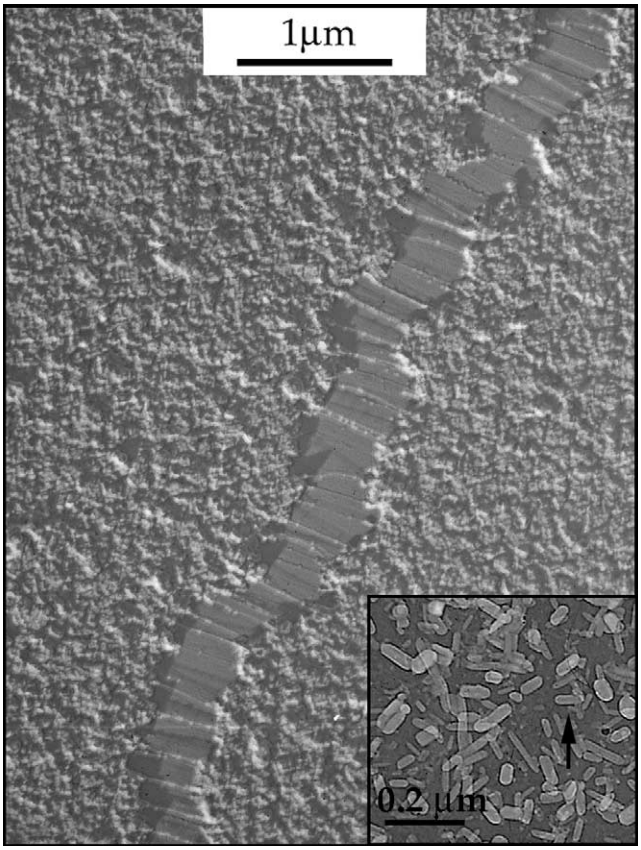

Fig. 3. Nano-fibrils of A18749 spanning a crack formed while drying a relatively thick film of the resin. The inset is an unshadowed micrograph of the nascent resin particles; the particle indicated by the arrow has a volume corresponding to one $\bar{M}_w$ molecule.

3.2. Fibril formation

Fig. 2(a) and (b) are of (a) Pt/C shadowed and (b) Cr coated sheared samples of resin G. Similar fibrils are shown for other resins below. For the 'standard size' resins the fibrils are of indefinite (TEM) length with neither the starting or ending point having been clearly identified. The Pt/C aggregates as isolated particles on the suspended fibrils on the side facing the shadowing source (as well as the PTFE particles) but not on fibrils lying on the substrate. Coating with C alone also results in aggregation, although to a lesser extent [9]. These materials must be mobile on the fibrils, but whether this mobility occurs during the shadowing or during beam irradiation is not yet clear. Cr coating, however, results in uniform coatings despite the normally expected larger grain size. When the fibrils are Cr coated, the fibril itself appears to be visible (inset), unexpectedly, as a more highly scattering structure in the core of the coating (black arrows), with a diameter of <150 Å; the Cr coating appears to have a similar thickness although the coating was supposed to be only 50 Å thick. As shown in the inset the core fibril, that was lying on the substrate when coated, appears to have been removed during subsequent handling (white arrows), only a rim surrounding its original position remains. The core fibril, only, is present at the position of the left black arrow. The sample in Fig. 2(a) was annealed at 275 °C, 5 min; at this temperature there is no visible effect on the nascent PTFE particles or fibrils of the sintering. The mechanism of development of the nano-fibrils by shear is still unknown. They presumably have no relationship to the rods suggested to develop initially during polymerization and fold back on themselves to form the standard size particles as the suspension agent is used up (e.g. Ref. [11]). The rods are much shorter than these nano-fibrils (discussion in Refs. [3,9]).

While we have not attempted to observe fibrils in non-annealed, sheared samples of the other resins, evidence for similar, long initial fibrils was seen in sintered, sheared samples of all of them, including, despite its low molecular weight, TE 5070. In addition, as shown in Fig. 3, sufficient cohesion can be developed in the nano-emulsion A18749 by simply drying a thick film of the PTFE particles that fibrils will form spanning a crack developing during drying. This is despite the fact these particles (inset) are presumably each a folded single molecule lying parallel to the long axis of the rod-like single crystals [3]. Therefore, an individual fibril

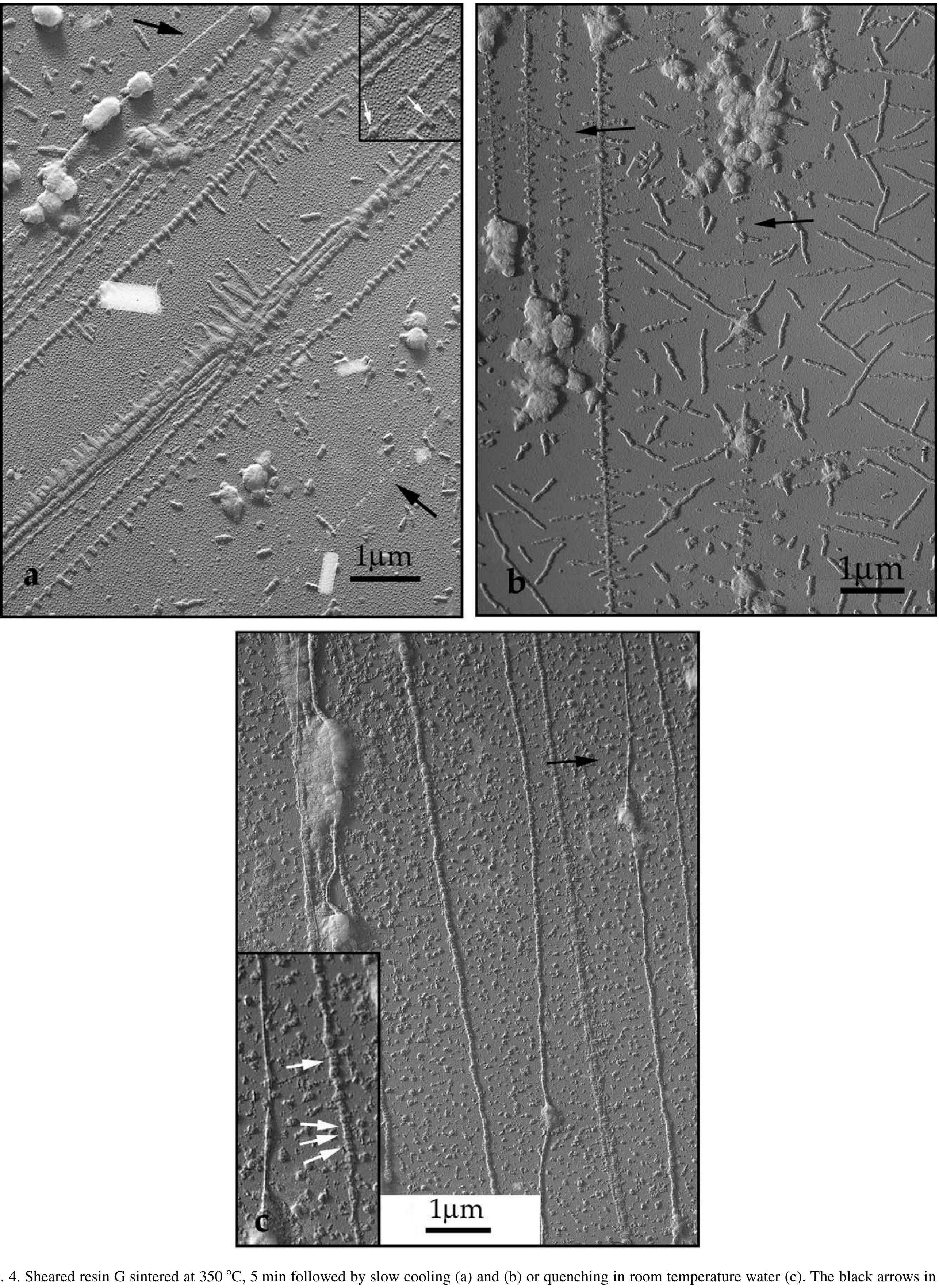

Fig. 4. Sheared resin G sintered at 350 °C, 5 min followed by slow cooling (a) and (b) or quenching in room temperature water (c). The black arrows in (a) indicate suspended nano-fibrils, in (b) regions in which the ‘nucleating’ shish has apparently retracted, and in (c) the region shown enlarged in the inset. The white arrows in the insets indicate representative double-striations.

must involve cooperative unfolding and drawing out of molecules from several particles.

3.3. Effect of sintering

Resin G was the subject of the broadest range of sintering conditions. As shown in Fig. 4(a) and (b), annealing for only 5 min at 350 °C results in substantial rearrangement of the morphology. Slow cooling results in shish–kebab formation on any fibril in contact with the substrate, with the kebabs consisting, in general, of single double-striations (see below; they are not well resolved in Fig. 4(a) and (b); the white arrows in the inset in Fig. 4(a) indicating several relatively well resolved). In addition there are isolated double-striation structures of varying length, as described in more detail in Refs [3,4,9], and, in Fig. 4(a), a granular background. The granule volume (ca. 10^6 Å^3), if PTFE, corresponds to $<1.5\times10^6$ Da. On the other hand, the substrate in Fig. 3(b), sintered under the same conditions, is clean. The suspended fibrils (black arrows in Fig. 4(a) remain unaffected. In Fig. 4(b) some of the nano-fibrils on the substrate (shish) have apparently retracted (arrows)).

Quenching the sample in water after 5 min annealing results in only incipient double-striation kebab formation (white arrows in inset) and numerous irregular particles (Fig. 4(c)). As in parts I and II, we suggest the latter are ‘wandering molecules’ that were trapped on the surface individually or as ‘few molecule’ aggregates during the quench [3,4,9]. In general these do not have a double-striation structure, possibly because of their irregularity as a result of the quenching.

Longer times at 350 °C (Fig. 5(a)) can result in considerably wider kebabs, each with a single, double-striation on its upper surface (upper white arrow in inset). The large kebabs resemble the bands in well dispersed, annealed, undrawn samples (e.g. Fig. 1(a)) in the base on the substrate being wider than the striations on the top. The lower white arrows in the inset indicate ‘incipient’ kebabs, each again with a single, double-striation on its surface and a wider base; the shish fibril can be seen between the kebabs in the upper shish–kebab. The granular background here is similar to that in Fig. 3(a); whether it is PTFE (molecules) is not known. In the inset the shish can still be seen between the separated kebabs.

Air quenching of the 30 min, 350 °C resin G sample (Fig. 5(b)) resulted in narrower, more closely spaced kebabs and a background with larger small particles that were more isolated. As shown by the white arrow in the inset (from the region indicated by the black arrow in the main part of the figure) some of the larger particles have double-striations;

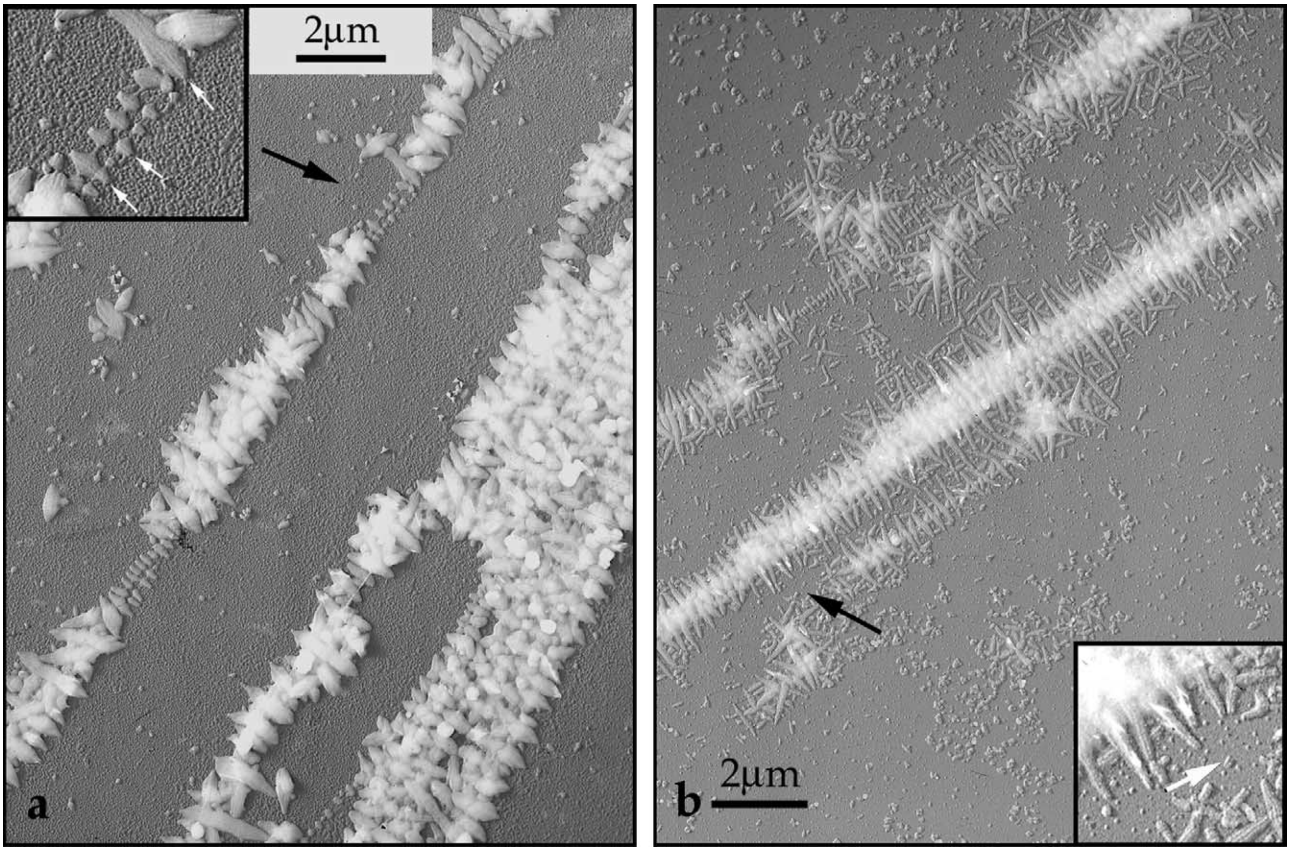

Fig. 5. Sheared resin G sintered at 350 °C, 30 min and (a) slow cooled or (b) quenched in air. The particles indicated by the arrows in the insets have double-striations; in (b) the particle volume is less than that corresponding to one $\bar{M}_w$ molecule.

we suggest, again, that these are PTFE molecules trapped on the substrate during quenching. The BFDC image in the inset is discussed below.

Sintering at 375 °C, 10 min results in finger-like double-striation out-growths from the nascent particles, and closely spaced kebabs, but still leaves the suspended fibrils unaffected (Fig. 6). This type of outgrowth was also observed for samples without shear, both from individual nascent particles (e.g. Fig. 6(a) part I [3]) and from the ends of the bands (Fig. 1(a), lower and Fig. 1(b), main portion). As shown in Fig. 1(a) and (b) the molecular axis is normal to the axis of the individual double-striations and the long axes of the bands. Isolated double-striations are also present on the substrate. The Pt/C beads are widely spaced on the suspended fibrils but it is not known if this is a sintering temperature effect.

Similar shish–kebabs were also grown by sintering sheared TE-30 (Fig. 7(a)–(d)). As for resin G the spacing and width of the kebabs has no relationship with the time of sintering; we suggest it is related to the amount of nearby material from which the shish 'draws' molecules during kebab growth. In Fig. 7(a) (350 °C, 5 min) the kebab spacing in the insets is about 1500 Å and the single double-striations are only slightly wider at their base than top. The particle indicated by the arrow in the left center inset has a volume, including the thickness of the shadowing, that corresponds to ca. 5 $\bar{M}_\mathrm{w}$ molecules. In Fig. 7(b), for a similarly treated TE-30 sample, a number of the original particles remain, with some of the suspended fibrils having widely separated Pt beads (black arrows), short shish on the shish–kebabs where the fibril was in contact with the substrate and double-striation outgrowths from and on the particles (white arrows). The smaller particles on the substrate, with double-striations, are considerably smaller than that in Fig. 7(a); they likely are single molecules.

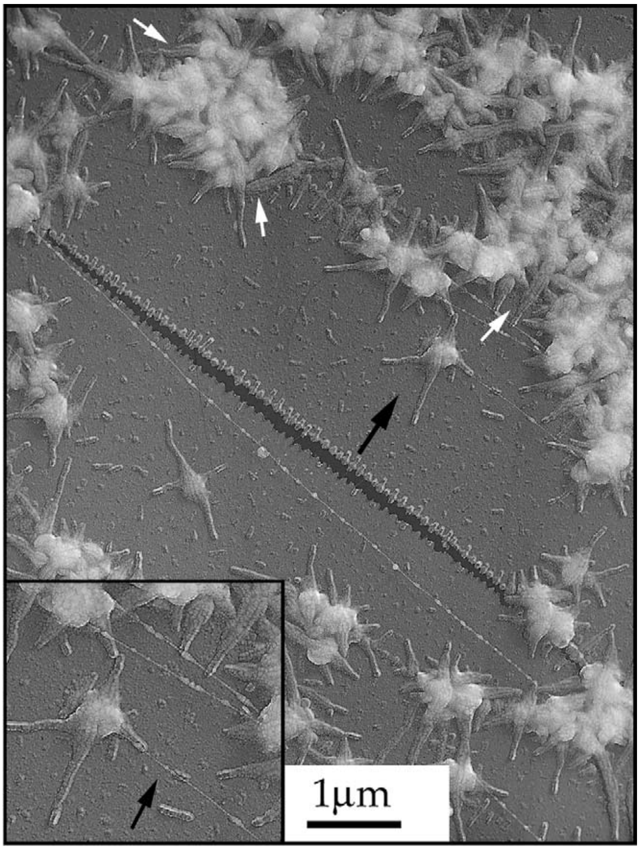

Fig. 6. Sheared resin G sintered at 375 °C, 10 min. Individual particles have double-striation outgrowths with single- and few-molecule double-striations on the substrate. The carbon substrate cracked at the edge of the shish–kebab, the kebabs each consisting of a double-striation.

After 10 min sinter (Fig. 7(c)) many of the kebabs contain several double-striations and are more randomly oriented relative to the shish core (which, in most cases, has retracted), with similar bands also grown from the dispersed particles. These bands closely resemble the bands for TE 30 shown in Fig. 1(a) and part I, Fig. 5 (380 °C, 30 min) [3]. Air cooling after 20 min sinter at 350 °C results in similar band kebabs and randomly oriented bands, as well as isolated single- to few-molecule, double-striation particles (Fig. 7(d)). As shown here for both resin G and TE-30, considerably faster band development seems to occur in the sheared samples than occurs when sintering the nascent particles; [3] further evaluation, however, is needed both because the remaining particles in the above micrographs do not appear to have been affected by the shearing and because of the general variability of the results due, at least in part, to the cooling conditions.

The insets in Fig. 7(c) are examples of BFDC from the kebabs (bands); the diffracting regions appear to consist of lines about the width of a single striation with crystal registry extending diagonally (arrow in lower inset) from striation to striation in places. This would appear to contradict our suggestion in Ref. [3] and in Section 1 above that the double-striations correspond to a single folded chain lamella, the striations being the pt nucleated on the folds; possibly the diffraction contrast image is shifted relative to the shadowing image or is due to an underlying structure. The BFDC is discussed further below, relative to similar observations for sheared, sintered A-18749 and TE-5070.

As-sheared samples of the nano-emulsion were not examined with only limited studies of sheared, sintered samples; that nano-fibrils could form is shown in Fig. 3 where they span a crack in a coalesced film of A18749 nascent particles and several of the micrographs of sintered samples below. Sintering of sheared films of A18749 at 350 °C, 30 min, followed by slow cooling, (Fig. 8(a)) produced rows of bands similar to those of TE-30 in Fig. 7(c); many of the bands lie at angles to the presumed shish. The BFDC again consists of lines ca. the width of a single striation, often lying at an angle to the striations. Unless the BFDC is due to an underlying structure we have no explanation as to how the lattice orientation propagates across the presumed fold surface of the double-striation lamellae (ribbons) to give rise to the diagonal lines. Thus,

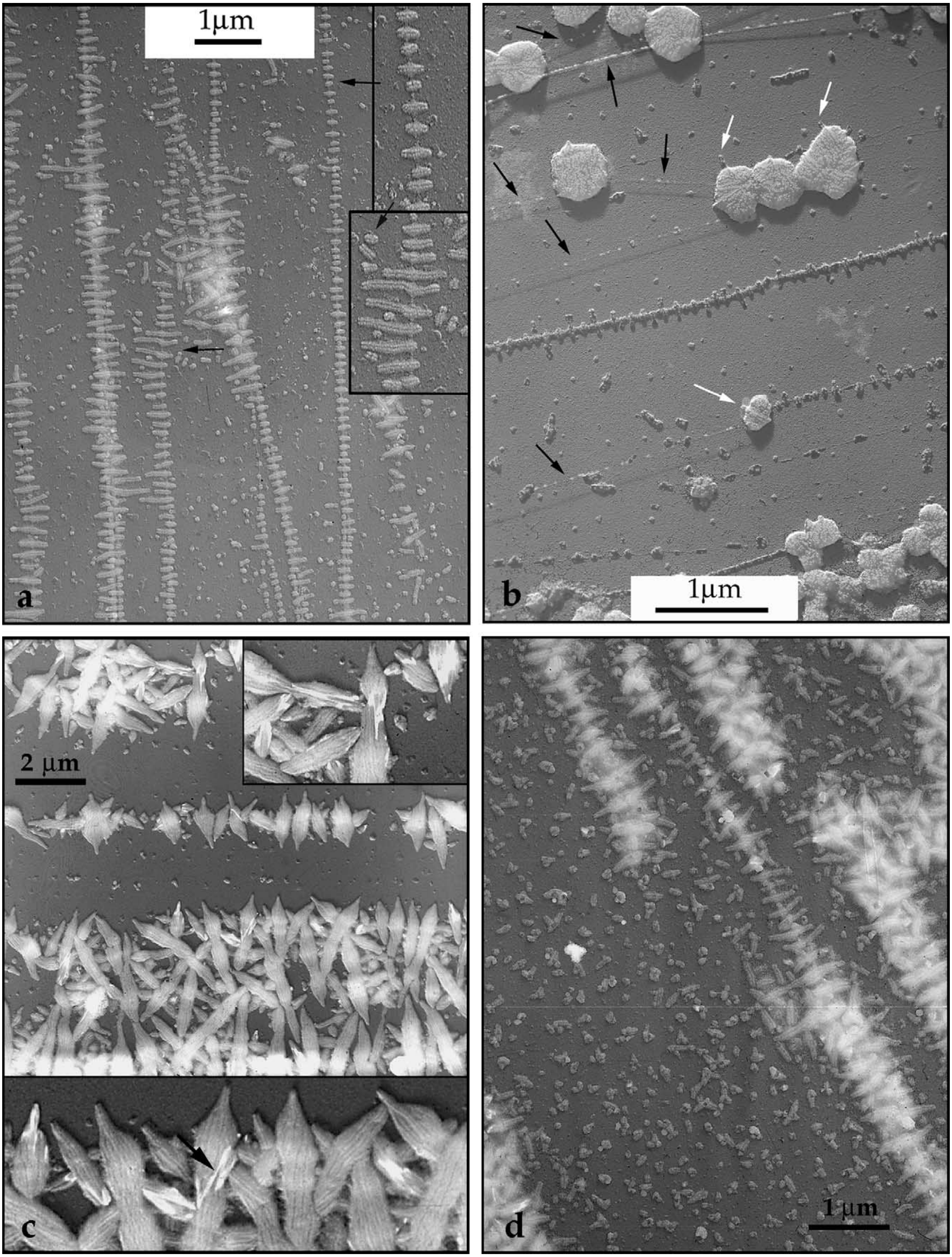

Fig. 7. Sheared TE 30 sintered at 350 °C for (a) and (b) 5 min, (c) 10 min, all slow cooled, and (d) 20 min followed by air quenching. See text for description of arrows. The insets in (c) are enlargements of arrows showing BFDC.

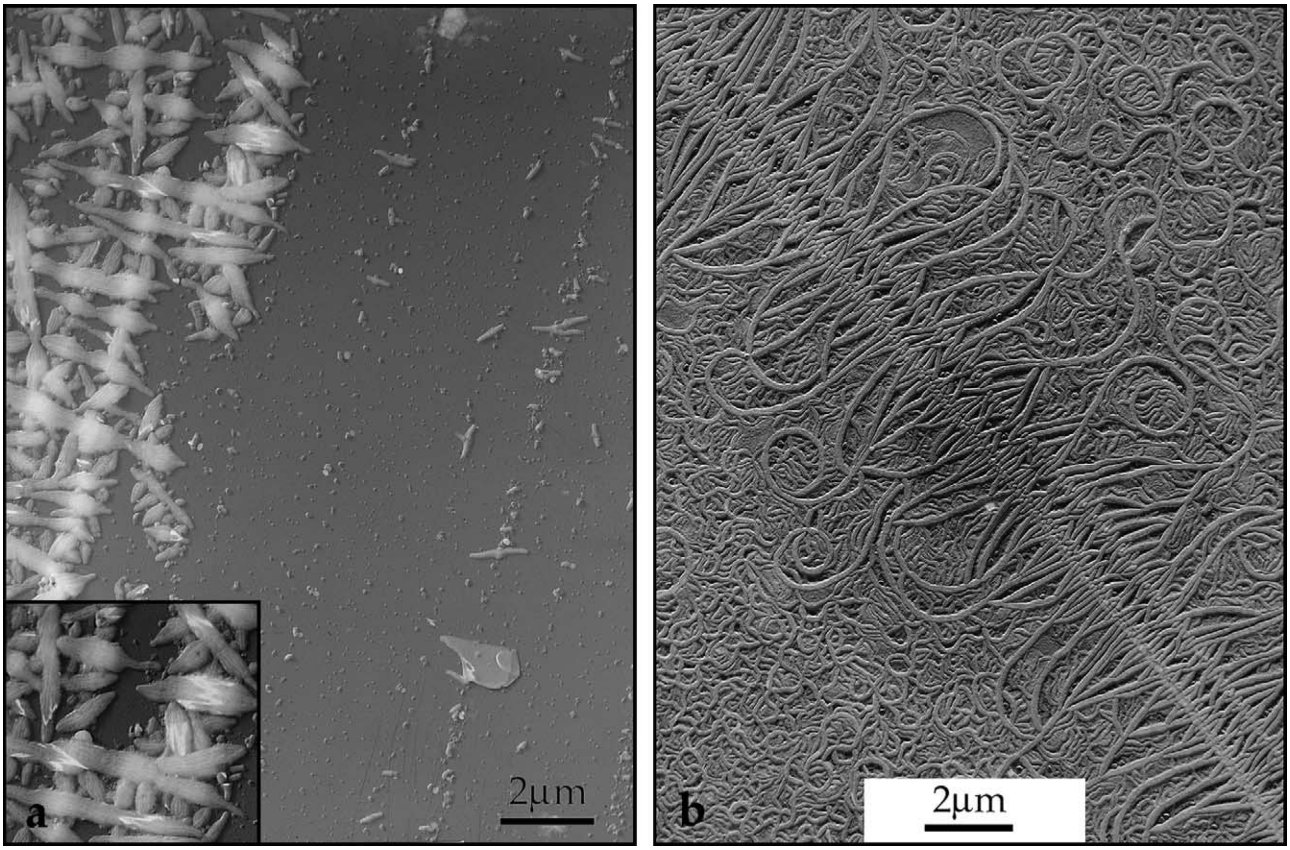

Fig. 8. Sheared A18749 sintered at 350 °C, 30 min followed by (a) slow cooling and (b) air quenching.

we tentatively suggest the contrast is due to an underlying lamella lying parallel to the surface. An individual, flat-on lamella is present in the lower right of Fig. 8(a) with several sharp diffraction contrast lines.

No shish are present in Fig. 8(a). Indeed there is some question as to whether the oriented rows of bands are shish–kebabs since many of the kebab-bands lie at an oblique angle to the apparent shear direction. On the right side of the figure rows of small particles and double-striations may have resulted from shish–kebab growth with subsequent retraction of the shish. Fig. 8(b), however, shows unmistakable shish–kebabs (350 °C, 30 min, followed by air quenching). In the shish on the left nearly all of the kebabs are nucleated at the sides of the apparent fiber, a split being present between the kebabs growing in opposite directions. On the right shish, however, many of the kebabs extend across the centerline as on the previous figures. Nucleation may have occurred on top of the underlying fibril, with the nucleated lamella then growing in both directions. Interestingly the on-edge double-striation ribbons all curl, apparently randomly relative to direction. The kebabs consist of both short and long ribbons, with additional curled ribbons forming the matrix; some of the ribbons make complete circles. Similar curling was also observed for non-sheared samples (Fig. 11, part I [3]). Based on discussions at PP-04 [13] relative to these results and that in Ref. [14], it is suggested that they are related to the twisted lamellae in banded spherulites (Fig. IV-64 in Ref. [2]), curling instead of twisting when the film is thin; possibly thin enough that twisting would require twisting out of the thickness of the film.

Sintering of sheared TE 5070 also gives rise to ‘shish-less’ shish–kebabs (Fig. 9(a), 320 °C, 5 min). The low molecular weight of TE 5070 results in a lower melting temperature and, apparently, retraction of the shish material during the sintering. The kebabs consist of a short, single, double-striation on a nearly circular or elliptical mound, as do all of the individual particles as well (inset). That fibrils can form, despite the low molecular weight and a number average ecl of only 1300 Å, is shown by the suspended nano-fibrils in Fig. 9(b) of a water quenched TE-5070 sample (350 °C, 5 min). In addition, as shown in the inset, nano-fibrils were drawn out across the gap between the particles, possibly as the sample cooled. The individual short, double-striation particles have a volume of ca. 5×10^6 Å^3 corresponding to a molecular weight of ca. 6×10^6 Da, much larger than the molecular weight of the TE-5070; they thus consist of many molecules.

6. Conclusions

Shearing of both standard size dispersion particles and

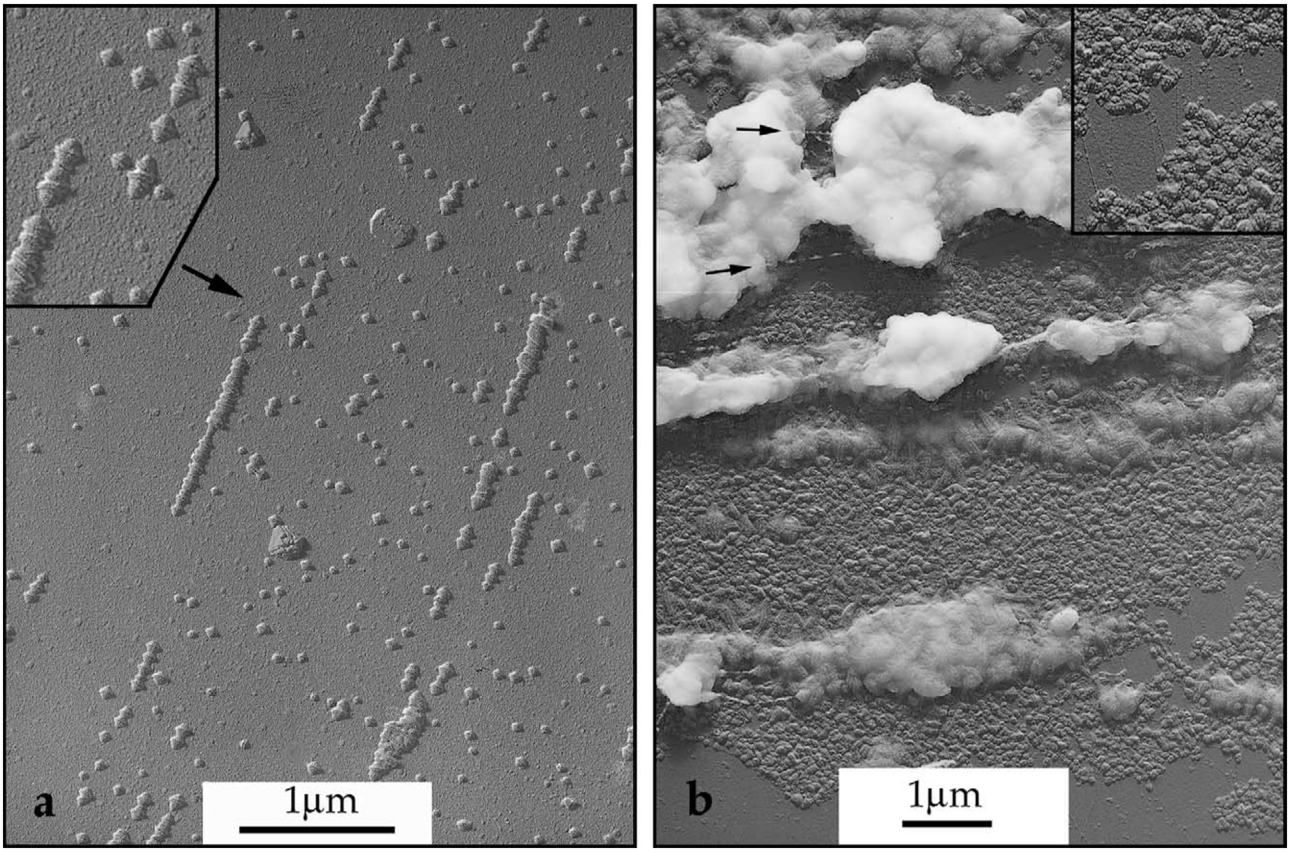

Fig. 9. Sheared TE 5070 sintered at (a) 320 °C, 5 min, slow cooled and (b) 350 °C, 5 min, water quenched. In (b) there are both suspended nano-fibrils and, enlarged in the inset, barely visible nano-fibrils on the substrate between the two films of particles. Most of the particles in (b) are 'double-striations, but are considerably larger in size than would correspond to a single molecule.

the nano-emulsion particles yields nano-fibrils of ca. 100 Å diameter and indefinite length. To date we have not been able to identify, with certainty, the ends of the fibrils or the mechanism by which they are formed. Of particular interest is the ability of TE 5070 to form fibrils significantly longer than its ecl, despite its low molecular weight.

Sintering of suspended nano-fibrils, for temperatures up to 375 °C and times as long as 2 h (not shown) produced no visible change. On the other hand, nano-fibrils lying on the substrate served as nuclei for molecules 'wandering' on the substrate, resulting in formation of shish–kebabs. The kebabs appear to be identical to the double-striation on-edge ribbons growing out from the bands and the single- and few-molecule crystals described in Fig. 1(a) and (b) and, in more detail, in parts I and II; [3,4,9] the molecular axes are normal to the kebabs (parallel to the fibril (shish) axis), with the molecules folded. Extended sintering time, with the presence of sufficient material, resulted in the kebabs becoming (or growing as) bands.

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