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Self-assembly of nano-sized arrays on highly oriented thin films of poly(tetrafluoroethylene)

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Abstract

Self-assembly of nano-sized arrays by casting a dilute solution of a guest material on the friction-transferred poly(tetrafluoroethylene) (FT-PTFE) substrate was newly discovered. Long axis of the rod-like structures forming the arrays is aligned perpendicular to the chain direction of FT-PTFE, and accordingly, the arrays are highly anisotropic. This phenomenon was observed for aqueous or organic solutions of polymers or organic materials. Each rod-like structure forming the arrays is composed of small grains. The arrays in question are formed regardless to the crystallinity of the guest materials. The formation mechanism of the nano-sized arrays is still unclear. However, we guess that they are formed as a result of microscopic flow pattern at the edge of the solution film. The arrays in question may be a new type of dissipative structure.

Keywords: Convection; Fingering; Dissipative structure

1. Introduction

Oriented thin layers of poly(tetrafluoroethylene) (PTFE) prepared by the friction-transfer technique (namely, FT-PTFE) have been studied as substrates for orienting a wide variety of crystalline and liquid crystalline materials, including polymers, monomers and small organic and inorganic molecules from vapor, solution and melt phases [1]. In the previous studies for crystalline polymers, also solution casting onto the FT-PTFE substrate has led to oriented growth of crystalline phase [1–9]. Resulting lamellae stacking, namely 'hetero–shish–kebabs', has been a measure of successful oriented growth [2].

Here, we report a new type of structure formation that occurs on the FT-PTFE. In this case, nano-sized arrays of guest material are formed spontaneously by casting a dilute solution of the guest material regardless to crystallization. In this communication, our finding of this phenomenon is briefly reported.

2. Experimental

2.1. Materials

The PTFE rod used in this study was a soft one before sintering, which was kindly supplied by Daikin Industries, Ltd. In our preliminary study, no essential difference was found between this soft PTFE rod and other commercial sintered PTFE rods, except for the better continuity of the final FT-PTFE layers prepared with the former. Two types of atactic polystyrene (a-PS; $M_w = 280{,}000$ and 45,000 g/mol) were purchased from Scientific Polymer Product Inc. Two types of polyethylene (PE; $M_w = 36{,}500$ and 115,500 g/mol) were purchased from Fluka Chemie AG. Potassium hydroxide (KOH), sodium stearate, 1,6-di-(*N*-carbazolyl)-2,4-hexadiyne (DCHD), ethanol, acetone, methyl ethyl ketone (MEK) and *p*-xylene were purchased from Wako Pure Chemical Ind. Ltd. All the materials were used without further purification.

2.2. Preparation of FT-PTFE substrate

Glass slides were cleaned in a 1 wt% solution of KOH to a mixed solvent of 10 wt% water and 90 wt% ethanol for at least 1 h, rinsed with distilled water, and dried [10]. Then each glass slide was heated up to ca. 300 °C and rubbed with the PTFE

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rod at 0.8 MPa, 2.7 cm/min using a custom-made instrument. In this way, the thin layers of FT-PTFE were prepared on the glass slides.

2.3. Preparation of the nano-sized arrays

Dilute solutions of guest materials were cast onto the FT-PTFE/glass slide substrates in one of several ways (hereafter, the phrase, 'the substrates', denotes the FT-PTFE/glass slide substrates). Typically, a drop of the dilute solution was put directly onto the substrate. In other cases, the dilute solution was atomized onto the substrate, or the substrate was dipped into the solution and drawn up. Subsequently the solution on the substrate was dried at room temperature or at prefixed temperature using a hot plate. The nano-sized arrays in question are formed on the substrate with this simple operation. Detailed conditions for preparation of each sample will be described when the corresponding results are presented.

2.4. Measurements

The structure formed on the substrate was metal shadowed if necessary. Then the sample was carbon-coated and transferred from the glass slide to a copper grid for transmission electron microscopy (TEM) by a conventional method [11].

For TEM observation, two types of instruments were used. One was a conventional JEOL JEM-200CS operated at 200 kV. The other was a phase-contrast electron microscope [12–14] customized from a JEOL JEM-3100FFC. The objective lens was specially designed to insert phase plates accurately on the back focal plane. The accelerating voltage was 300 kV and the phase-contrast images were taken at 4.2 K using an energy filter (zero loss).

Dynamic observation of the drying solution on the substrate was performed by differential interference contrast optical microscopy (DICM). A Nikon ECLIPSE E600 equipped with a CCD camera was used for the optical observation. In this case, a drop of 4.2×10^{-3} wt% MEK solution of a-PS ($M_w=45{,}000$ g/mol) was put onto the substrate, and the edge of the solution film was observed by the transmission mode.

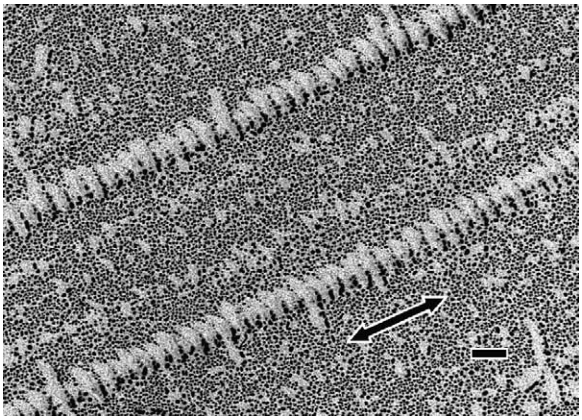

Fig. 2. Conventional TEM image of the nano-sized arrays formed from a 3.3×10^{-4} wt% *p*-xylene solution of PE ($M_w=36{,}500$ g/mol) atomized onto the substrate maintained at 80 °C using a hot plate. The sample was shadowed with Au. Scale bar, 200 nm. The arrow indicates the chain axis of PTFE.

3. Results and discussion

When we carefully observe the specimen by TEM, we can find sporadic regions where the nano-sized arrays are formed. Fig. 1 shows an example prepared from a dilute MEK solution of a-PS. These structures look like 'hetero–shish–kebabs' composed of PTFE fibrils (the 'shish') and lamellae crystals (the 'kebab') of the guest material [2]. Because a-PS is not a crystalline polymer, however, they can never be the 'hetero–shish–kebabs'. The arrays in question are found along the ridge of the PTFE layer. They are composed of rod-like entities, which are roughly parallel with each other and elongated mostly from the PTFE fibrils toward regions where the glass

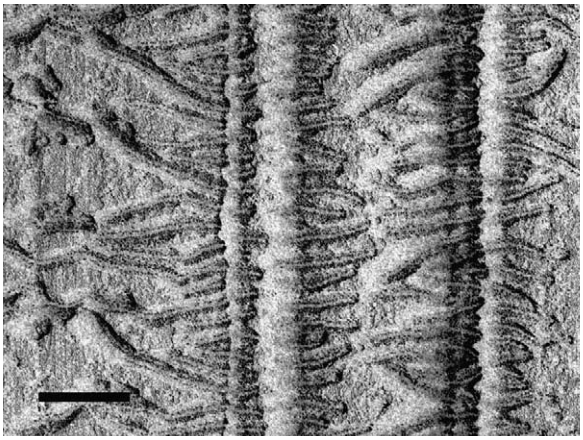

Fig. 1. Conventional TEM image of the nano-sized arrays formed from a 2.0×10^{-3} wt% MEK solution of a-PS ($M_w=280{,}000$ g/mol). A drop of the solution was dried on the substrate maintained at 70 °C. The sample was shadowed with Pt–Pd. Scale bar, 500 nm. The molecular chains of PTFE are oriented vertically.

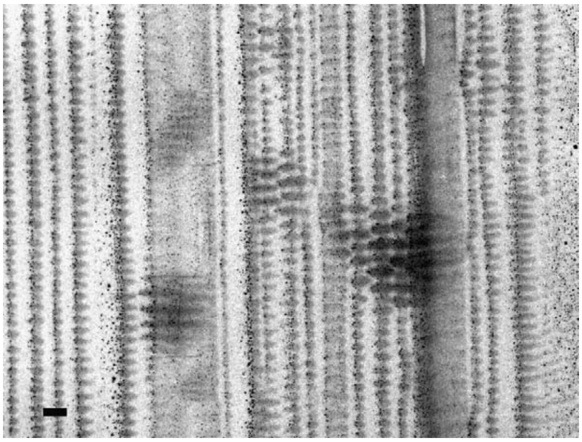

Fig. 3. Conventional TEM image of the nano-sized array formed from a 6.3×10^{-4} wt% acetone solution of DCHD. The substrate was dipped into the solution (containing small amount of water for precipitation of DCHD), picked up and dried. The sample was shadowed with Au. The molecular chains of PTFE are oriented vertically. Scale bar, 500 nm.

Table 1
Examples of materials forming the nano-sized arrays on the FT-PTFE layers

Species	Solvent	Conditions[a]
Polyethylene	*p*-Xylene	3.3×10^{-4}–1.0×10^{-2} wt%, 80–110 °C
Atactic polystyrene	Methyl ethyl ketone	3.3×10^{-4}–4.2×10^{-3} wt%, 25–110 °C
Atactic poly(vinyl alcohol)	Water	3.8×10^{-3} wt%, 80 °C
Poly(acrylic acid)	Water	3.7×10^{-3} wt%, 80 °C
1,6-Di(*N*-carbazolyl)-2,4-hexadiyne	Acetone	0.05–0.25 wt%, 10–30 °C
Sodium stearate	Water	2.5×10^{-3} wt%, 80 °C[b]

[a] Conditions refer to the concentration and temperature.

[b] The solution contains an immeasurably small amount of carbon nanotubes. Originally, the experiment was planed to align the carbon nanotubes. Sodium stearate was added as dispersing agent. However, carbon nanotubes were not observed in the resulted arrays.

surface is exposed. The periodicity of the arrays is about 100 nm. Close inspection of Fig. 1 reveals that the core of each rod has a dent, judging from the absence of Pt-Pd particles. Similar structures are formed from other solution systems. For example, Figs. 2 and 3 show the nano-sized arrays prepared from a *p*-xylene solution of PE and an acetone solution of DCHD, respectively. We have so far observed the nano-sized arrays using the systems listed in Table 1. As the table shows, the nano-sized arrays are formed from a variety of solute–solvent systems. As their occurrence is not limited to specific material, an unidentified self-assembly phenomenon in the nanometer-scale must be concerned.

Even the structure of PE in Fig. 2 is not the 'hetero–shish–kebabs'. Because there are different features, we can distinguish the 'hetero–shish–kebabs' and the novel nano-sized arrays by TEM. First, the nano-sized arrays are mostly consisted of amorphous phase, though they are prepared from PE, namely, highly crystalline polymer. In the selected-area electron diffraction (SAED) patterns, though the reflections from PTFE crystals were observed, crystalline reflections of PE were mostly not observed from the nano-sized arrays. The reason for this peculiarity is still under study.

The second feature to differentiate the nano-sized arrays from 'hetero–shish–kebabs' is the internal fine structure of the rod-like entities. Fig. 4 shows 'hetero–shish–kebabs', namely the edge-on lamellae crystals, of PE formed on the FT-PTFE. In the SAED pattern containing this structure, we could observe the oriented crystalline reflections of PE. In Fig. 4, we can recognize the stacked lamellae in each 'kebab'. The top faces of the 'kebabs' are flat, contrasted to the existence of the dents for the nano-sized arrays. On the other hand, by Zernike phase contrast TEM (ZPC-TEM) [12,14], we could observe different features for the arrays in question. (ZPC-TEM is a new technique, which can provide high contrast for unstained specimens.) Fig. 5 shows the ZPC-TEM image of the arrays of PE. The rods are composed of grains smaller than ca. 30 nm. The same feature is observed also for the arrays prepared from an MEK solution of a-PS (Fig. 6) and from an aqueous solution of sodium stearate. Accordingly, the granular feature is thought to be common for the nano-sized arrays. The dent at the center of each rod-like structure is visualized as a region of sparse grains.

Now, how are the nano-sized arrays formed? As the features of the arrays appear to be far from the thermodynamic equilibrium, they should be formed due to dynamical reasons. In this case, evaporation and convection are plausible causes. Therefore, as a first step, we observed the dynamic structure in the drying solution by optical microscopy. Fig. 7 shows a time series of a drying film of an MEK solution of a-PS on the substrate. Just after the solution was put onto the substrate, at first, we could observe no special feature, probably because the solution was too dilute to induce enough contrast for DICM. After ca. 40 s, the solution became concentrated and the internal features could be visualized. In Fig. 7, the meniscus is pinned due to the surface texture of the FT-PTFE. Along the meniscus, finger-like fluctuations (namely fingerings) elongated perpendicular to the edge appeared and disappeared repeatedly. Because of the similarity between the arrays and the fingerings, we can guess that the fingerings would be the origin of the arrays.

According to previous studies [15,16], capillary flows toward the pinned edge are induced in the drying solution film. At the same time, the thermal and concentration gradients caused by evaporation can lead to circulating flows driven by surface-tension gradients (that is, the Marangoni convection). Thus parallel swirls aligned perpendicular to the meniscus may have formed as a result of the two types of flows (Fig. 8).

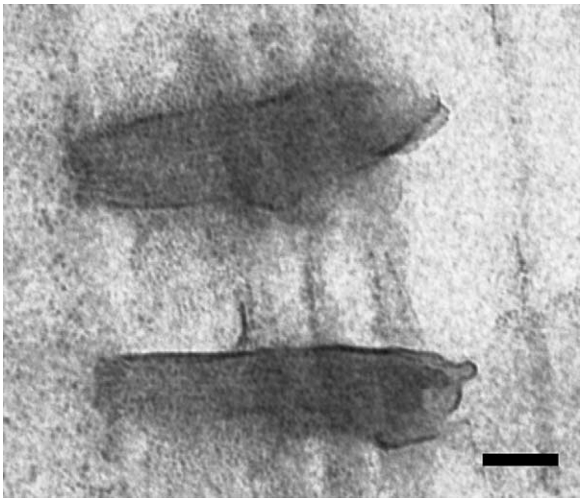

Fig. 4. Conventional TEM image of the 'hetero–shish–kebab' structure from a 1×10^{-3}wt% *p*-xylene solution of PE ($M_w = 11{,}550$ g/mol). A drop of the solution was dried on the substrate maintained at 80 °C. The sample was shadowed with Pt–Pd. Scale bar, 100 nm. The molecular chains of PTFE are oriented vertically.

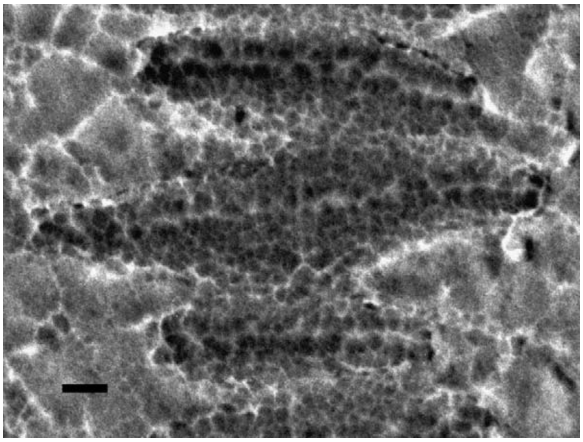

Fig. 5. ZPC-TEM image of the nano-sized array formed from a 3.3×10^{-4} wt% *p*-xylene solution of PE ($M_w=36{,}500$ g/mol) atomized onto the substrate maintained at 80 °C using a hot plate. The sample was not metal-shadowed. The molecular chains of PTFE are oriented vertically. Scale bar, 50 nm.

Similar fingerings are widely observed [17–20] and categorized as dissipative structures.

During the dynamic observation by DICM, the minimum periodicity of the fingerings reached to the resolution limit of the CCD camera (ca. 1 μm), which was observed at early stages. As time passed and the solution became concentrated, the periodicity of the fingerings increased. Conversely, when the solution was much dilute, smaller fingerings corresponding to the periodicity of the arrays in question may have occurred. By the small fingerings, the solute would be aligned in the arrays forming the particulate features, and the structures would be fixed after complete evaporation of the solvent. As such a process may occur only within a certain limited condition, when the condition is not fulfilled, another competitive result will be obtained. For example, the edge-on lamellae in Fig. 4 was observed on the same sample with the novel nano-sized arrays at different location. Because the condition (e.g. concentration) changed during drying of the relatively large drop of the PE solution, these two types of structures might have appeared at different locations as the meniscus moved.

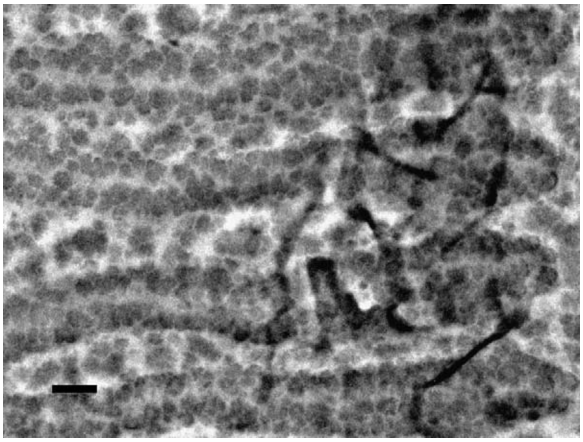

Fig. 6. ZPC-TEM image of the nano-sized arrays formed from a 4.2×10^{-3} wt% MEK solution of a-PS ($M_w=45{,}000$ g/mol) atomized onto the substrate maintained at 80 °C using a hot plate. The sample was not metal-shadowed. The molecular chains of PTFE are oriented vertically. Scale bar, 50 nm.

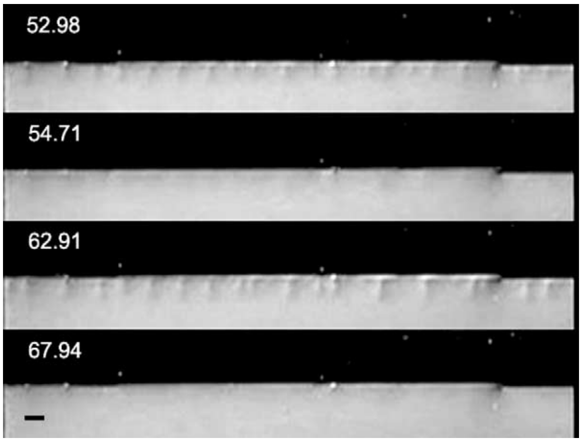

Fig. 7. Time series of a drying film of a 4.2×10^{-3} wt% MEK solution of a-PS ($M_w=45{,}000$ g/mol). A drop of the solution was put onto the substrate at room temperature, and a pinned edge was observed by DICM. Elapsed time (sec) is indicated at the left side of each part. The FT-PTFE/glass surface is exposed in the upper dark area, while the lower bright area is covered by the solution. The molecular chains of PTFE are oriented horizontally. Scale bar, 10 μm.

Though we can guess as above, we have not yet obtained conclusive evidences for this formation mechanism. It is desirable to perform dynamic observation of the drying solution film to detect the structures smaller than 100 nm, though such an experimental method is currently not available. Thus there still remain many questions about the detailed mechanism and requirements for the formation of the nano-sized array. A great deal of further study is necessary for detailed understanding of this phenomenon.

4. Concluding remarks

We found that nano-sized arrays are spontaneously formed on FT-PTFE/glass slide substrates by casting a dilute solution of guest material. Long axis of the rod-like structures forming the arrays is aligned perpendicular to the chain direction of FT-PTFE. This phenomenon was observed for aqueous or organic solutions of polymers and organic materials. Each rod-like structure forming the arrays has a dent at the center, which is composed of small grains. The arrays in question are formed

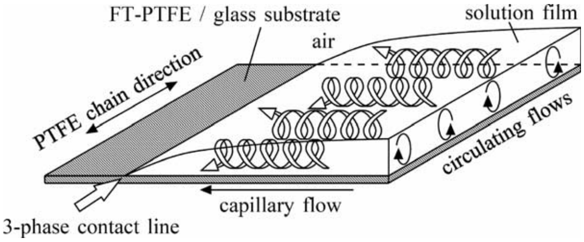

Fig. 8. Schematic drawing of the parallel swirls along the edge of the solution film. In order for better visibility, each swirl is spaced. The real swirls may be tightly packed with each other.

regardless to the crystallinity of the guest material. The detailed formation mechanism of the nano-sized arrays is still unclear. However, we assume that they are formed as a result of microscopic flow pattern at the meniscus.

In recent years, self-assembly of ordered structures in nanometer scale is enthusiastically studied [19,21–23]. If formation of the nano-sized arrays can be controlled, this phenomenon may be applicable to fabrication of, e.g. optical devices. The unique features of the novel nano-sized arrays are the smaller periodicity and the high anisotropy, compared to the previous studies on the self-assembly of ordered structures. We have indeed found an interesting optical anisotropy of a nano-sized structure prepared by using this phenomenon, which will be reported in the near future.

Acknowledgements

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