

## ORIGINAL ARTICLE

# Preparation of fractal-like structures of insoluble polythiophene via solvent vapor annealing of solid thermocleavable polythiophene films and subsequent thermal curing

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Polymer films with holes or fractal-like structures whose size is on the micron scale are of great interest. In this study, fractal-like structures of insoluble polythiophene were prepared via CS<sub>2</sub> vapor annealing of solid thermocleavable polythiophene films in the presence of high humidity and subsequent thermal curing. Atomic force microscope and transmission electron microscopy observations demonstrate that holes form during the initial stage of solvent vapor annealing (SVA), further developing into fractal-like structures with the coalescence of the individual holes. Meanwhile, the crystallinity of the films can also be improved. A mechanism that involves solvent-covered water droplets has been proposed to explain the formation of the holes and the fractal-like structures. This is the first report of the formation of holes and fractal-like structures from solid films of conjugated polymers via SVA. The fractal-like structures can be preserved during the conversion from thermocleavable polythiophene to insoluble polythiophene by thermal curing.

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**Keywords:** fractal-like structures; polythiophene; solvent vapor annealing

## INTRODUCTION

Solvent vapor annealing (SVA) is a widely used and promising method for controlling the morphology and structure of organic semiconductors and polymers,<sup>1–3</sup> as well as the phase separation between the donor and acceptor of the photoactive layers in organic optoelectronics.<sup>4–6</sup> The solvents absorbed via SVA may function as media for molecular motion and transport during the process of structural rearrangement and morphological evolution. The dependence of morphological evolution on time indicates that conjugated polymer microcrystals undergo Ostwald ripening during SVA.<sup>7</sup> Various organic solvents and processing conditions have been employed in the SVA treatment of poly(3-alkylthiophene) (P3AT).<sup>7–9</sup> Recently, Xiao *et al.*<sup>7,9,10</sup> obtained needle-like or rod-like single crystals of poly(3-hexylthiophene) (P3HT) and poly(3-octylthiophene) (P3OT) by the THF vapor annealing of polycrystalline films. The molecular weight and regioregularity of P3AT and the crystallization conditions determine the phase structures of the polymers upon SVA. In P3HT single crystals, the molecules are packed along the  $\pi$ - $\pi$  stacking direction perpendicular to the length axis of the crystals and the main chains parallel to the substrate, whereas in P3OT single crystals, the molecules are packed

along the  $\pi$ - $\pi$  stacking direction parallel to the length axis of the crystals and the main chains parallel to the substrate.<sup>9</sup> In another case, the CS<sub>2</sub> vapor annealing of a spin-coated poly(3-butylthiophene) (P3BT) film leads to the transformation of the backbones of regioregular P3BT from being oriented parallel to perpendicular to the substrate.<sup>8</sup>

SVA is also a widely used method for controlling the self-assembly and morphology of block copolymer thin films. During the morphological evolution of block copolymer thin films under SVA, the self-assembly of the block copolymers is controlled by the number of segments per polymer chain, block interactions, block volume fractions,<sup>11</sup> as well as the selected solvent type and the dynamics of controlling the solvent vapors.<sup>1,12</sup> Recently, Albert *et al.*<sup>13</sup> studied the effect of gradient SVA on the morphology of block copolymer thin films. The morphologies of poly(styrene-*b*-isoprene-*b*-styrene) could be subtly affected by applying discrete gradients of solvent vapor composition and/or concentration. Bang *et al.*<sup>14</sup> studied the effect of relative humidity on the ordering of thin films of PEO-based block copolymers such as poly(ethylene oxide-*b*-styrene) and poly(ethylene oxide-*b*-methyl methacrylate-*b*-styrene). The relative humidity of the vapor has been shown to play an important role in achieving ordered

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assembly during solvent annealing due to the humidity-induced swelling of the PEO fractions. In addition to controlling the self-assembly of block copolymer thin films on the nanoscale, SVA also generates fractal-like patterns in thin films of block copolymers, for example, poly(styrene)-block-poly(methyl methacrylate), under SVA using a PMMA-selective solvent (acetone). The heterogeneous stress induced by the residual solvent remaining in films after spin coating leads to anisotropic polymer mobility during the annealing process, resulting in the formation of fractal-like patterns.<sup>15</sup>

In this work, we developed a method for preparing fractal-like structures of a thermocleavable polythiophene (TCPT), poly(3-(2-methyl-2-hexylcarboxylate)thiophene-*co*-thiophene), using a dry solid film of the polymer via SVA. It was found that the formation of fractal-like structures is strongly dependent on the environmental humidity, and that holes and fractal-like structures can be formed on both polar and non-polar substrates. Thermal curing can transform the TCPT into an insoluble polythiophene (ISPT) that retains the fractal-like structures.

## EXPERIMENTAL PROCEDURE

### Synthesis of poly(3-(2-methyl-2-hexylcarboxylate)thiophene-*co*-thiophene)

Scheme 1 illustrates how poly(3-(2-methyl-2-hexylcarboxylate)thiophene-*co*-thiophene) was synthesized through a Stille coupling reaction of 2-methyl-2-hexyl-2,5-dibromothiophene-3-carboxylate (**2**) and 2,5-bis-trimethylstannanylthiophene (**3**) according to previous reports.<sup>16,17</sup> The details of the synthesis are included in the Supplementary Information. The TCPT can be converted to an ISPT upon thermal curing at 200 °C via cleavage of the tertiary ester groups.

### Preparation of fractal-like structures of the TCPT and ISPT

Indium tin oxide (ITO)-coated glass slides were sequentially cleaned by sonication in chloroform, acetone, deionized water, and isopropyl alcohol for 15 min in each solvent, followed by further cleaning with oxygen plasma. Amorphous TCPT thin films were coated on the surfaces of the ITO glass substrates by spin coating a TCPT solution in chlorobenzene (15 mg ml<sup>-1</sup>).

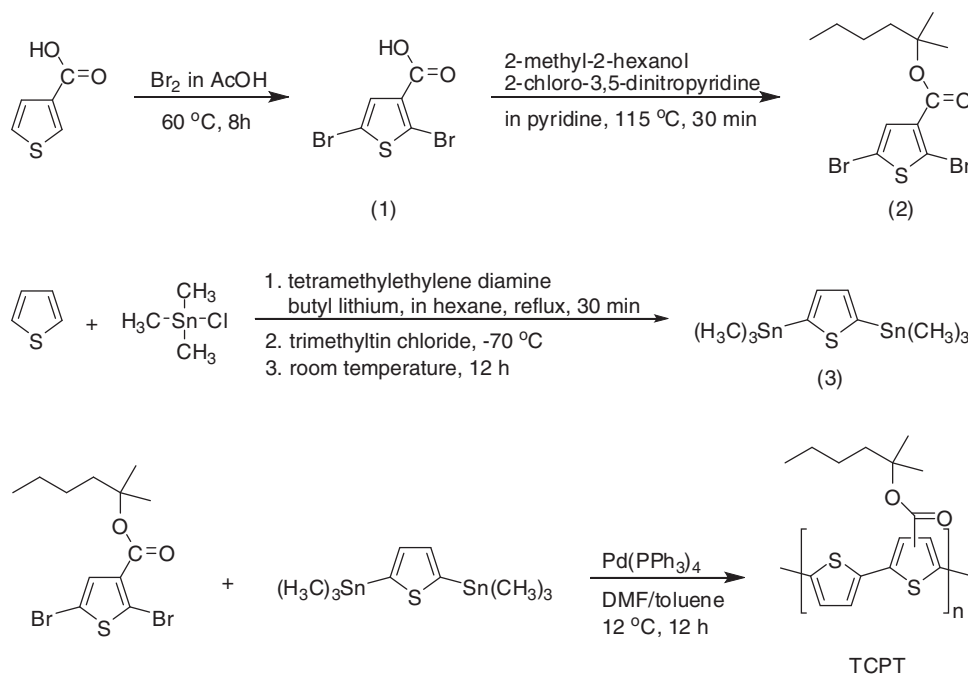
After fully drying, the amorphous TCPT thin films were annealed under a CS<sub>2</sub> vapor. SVA was completed by keeping the amorphous TCPT thin films in a covered Petri dish measuring ~10 cm diameter with ~2 ml CS<sub>2</sub>. The environmental conditions were a temperature of ~25 °C and a relative humidity of > 80%.

### Characterization

The molecular weight (Mw) and polydispersity index (PDI) of the TCPT were characterized by gel permeation chromatography (GPC, Polymer Laboratory GPC220) using a polystyrene standard in THF. The thermal stability of the TCPT was characterized using thermogravimetric analysis (TGA, TG 209 F3) under the protection of N<sub>2</sub> at a scanning rate of 5 °C min<sup>-1</sup>. FT-IR spectra were recorded on a JASCO FT/IR-470 Plus spectrometer (JASCO International Co., Ltd., Tokyo, Japan) using polymer films coated on silicon wafers. A Bruker AMX500 NMR (500 MHz), using TMS (0 p.p.m.) or the residual proton resonance of deuterated CDCl<sub>3</sub> (7.26 p.p.m.) as the internal standard, was used to characterize the products during the synthesis of the TCPT. Atomic force microscope (AFM) images were obtained using a SPA 3800N microscope with a SPA-400 scanner. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100F instrument operated at 200 kV. TEM samples were prepared as follows: TCPT thin films were prepared on the surfaces of amorphous carbon films coated on newly cleaved mica by spin coating a 5 mg ml<sup>-1</sup> TCPT solution in chlorobenzene. After drying, the TCPT films were annealed with CS<sub>2</sub> vapor using the same method used to anneal the TCPT films coated on ITO surfaces. Then, the mica substrates coated with the TCPT films and the amorphous carbon layer were immersed in water. The TCPT films and the amorphous carbon layer were picked up using 400 mesh Cu grids. After drying, the TEM specimens were kept for observation.

## RESULTS AND DISCUSSION

The TCPT was synthesized through a Stille coupling reaction of 2-methyl-2-hexyl-2,5-dibromothiophene-3-carboxylate (**2**) and 2,5-bis-trimethylstannanylthiophene (**3**) (Scheme 1). GPC measurements showed that the weight-averaged Mw of the TCPT was 47.6 K and the PDI was 2.28 (polystyrene standard in THF). NMR data showed that the TCPT had low regularity due to the random coupling



**Scheme 1** Synthesis of poly(3-(2-methyl-2-hexylcarboxylate)thiophene-*co*-thiophene).

of monomer 2 with monomer 3 during the polymerization (see Supplementary Figure S3).

In this study, amorphous TCPT films were annealed using CS<sub>2</sub> vapor in the presence of high relative humidity (relative humidity >80% and environmental temperature of ~25 °C). Figure 1a shows an AFM image of an annealed TCPT film containing individual holes, which were formed during the initial stage of the SVA (~15 min). It was observed that the individual holes have diameters that range from microns to tens of microns. Different holes have nearly the same depth, indicating that the holes penetrate to the surfaces of the substrate. Further evidence of the holes' depth reaching the substrate was obtained by a careful scanning of the insides of the holes (see Supplementary Figure S4). It was observed that the holes contain particles measuring ~0.4 μm, indicative of the surface features of the ITO substrates. This result solidly supports the notion that the holes penetrate to the substrate surface or, alternatively, that only a trace level of the TCPT material remains inside the holes. Therefore, the thickness of the film was measured to be ~90 nm by cross-sectional analysis. It is noteworthy that the hole edges are thicker than the film: ~140 nm for the edges vs ~90 nm for the film, which may be due to the specific mechanism of hole formation via SVA, as will be discussed later.

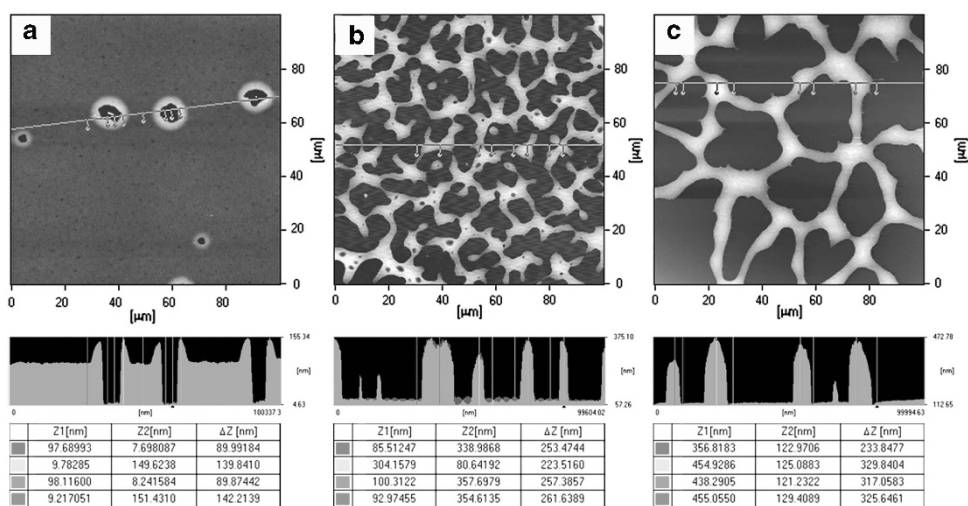
Figure 1b shows an AFM image of the annealed TCPT film that was obtained during the intermediate stage of the CS<sub>2</sub> vapor annealing (~2 h). The film shows fractal-like structures. We suspect that the fractal-like structures were formed via the coalescence of individual holes as the holes evolved. Furthermore, the fractal-like structures became thicker than the edges of the individual holes (Figure 1a): ~250 nm for the fractal-like structures vs 140 nm for the edges of the individual holes. This is due to the further deposition of the TCPT during the evolution of the fractal-like structures, as will be discussed later. Figure 1c shows an AFM image of the annealed TCPT film with further-developed fractal-like structures. One can see that the structures are larger than those formed at the intermediate stage (Figure 1b) and that the thickness of the fractal-like structures (>300 nm) is greater than that of the intermediate structures (~250 nm). In a control experiment, the hole and fractal-like structures could not be obtained at a lower humidity (see Supplementary Figure S5). The TCPT film used to obtain the AFM

image in Supplementary Figure S5 was annealed using CS<sub>2</sub> vapor at 25 °C and 60% relative humidity. This result indicates that the relative humidity plays a critical role in obtaining the hole and fractal-like structures.

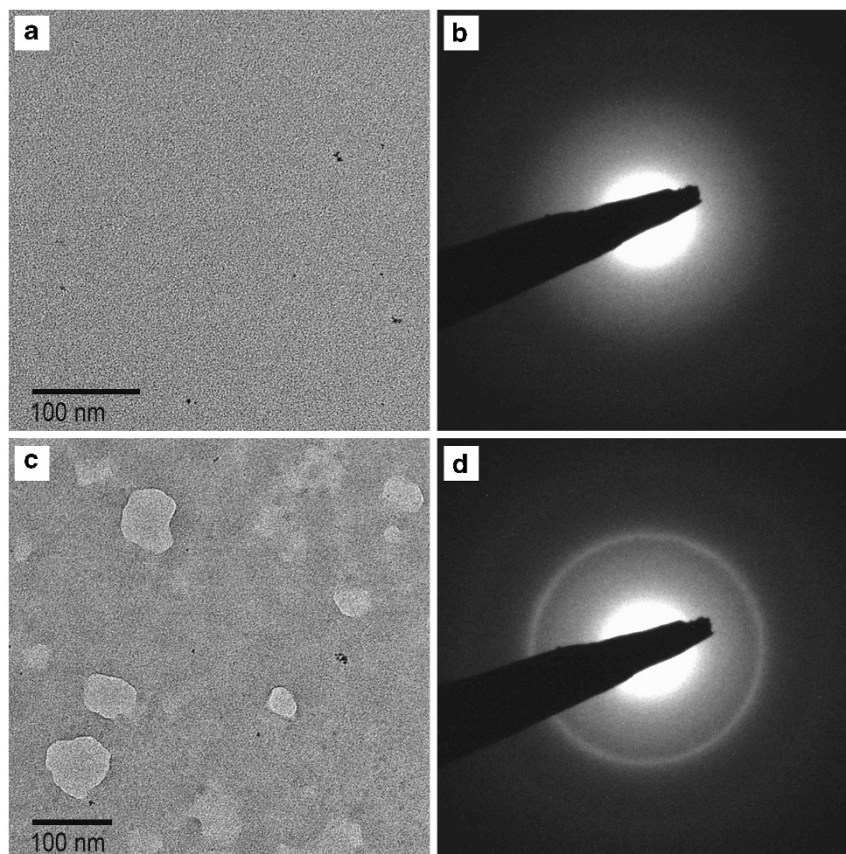
In addition to inducing morphological changes, SVA also enhances the crystallinity of the polymer films. The changes in the morphology and crystallinity of the TCPT films upon SVA were further investigated using TEM. Figure 2a shows the TEM image of an as-spin-coated TCPT film. The film is smooth and featureless. The ED pattern contains no diffraction spots, arcs, or rings (Figure 2b), indicating that the as-spin-coated TCPT film is amorphous. This structure might be due to the rapid evaporation of the solvent during spin coating, which hinders the ordered arrangement of TCPT chains. Figures 2c and d show the TEM image and ED pattern of the CS<sub>2</sub> vapor-annealed TCPT film. The holes have a shape similar to that of the holes observed in Figure 1a, but they are smaller than those observed in Figure 1a.

This finding may partially be due to the different thicknesses of the TCPT films prepared on the surfaces of ITO substrates and the amorphous carbon film: the concentration of the solution used to prepare films on ITO substrates was 15 mg ml<sup>-1</sup>, while the concentration of the solution used to prepare films on the amorphous carbon film (for TEM observation) was 5 mg ml<sup>-1</sup>. This difference in concentration resulted in a shorter time allowed for the formation of holes in the thinner films than in the thicker films; as a result, the holes formed in the thinner films were smaller than those formed in the thicker films. Additionally, because the amorphous carbon film is non-polar and the surface of the ITO substrate is polar, the difference in affinity between the polymer and the substrates may also play a certain role in the formation of holes. Nevertheless, the holes can be formed on both polar and non-polar substrates.

In contrast to the as-spin-coated TCPT film, the annealed TCPT film shows a sharp diffraction ring (Figure 2d) due to its enhanced crystallinity. This result is due to the rearrangement of polymer segments during the CS<sub>2</sub> vapor annealing. The sharp diffraction ring corresponds to the distance between TCPT chains along the π-π stacking direction and can be indexed as the diffraction of the (020) plane by referring to the well-studied diffraction pattern of poly(3-alkylthiophene).<sup>18</sup> SVA is a widely used method for treating



**Figure 1** Hole and fractal-like structures of the TCPT films annealed under CS<sub>2</sub> vapor during (a) the initial stage, (b) the intermediate stage, and (c) the final stage. A full color version of this figure is available at *Polymer Journal* online.

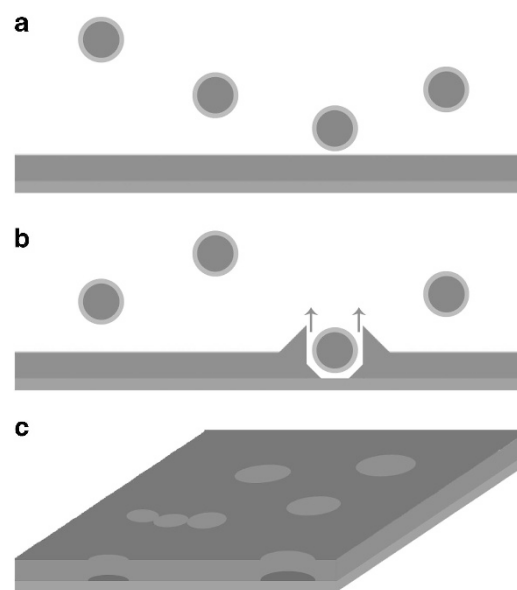


**Figure 2** (a) TEM image, (b) ED pattern of as-spin-coated TCPT film, (c) TEM image and (d) ED pattern of CS<sub>2</sub> vapor-annealed TCPT film at the initial stage.

polymer thin films. The absorbed solvents can improve the mobility of polymer chain segments, leading to enhanced crystallization, ordered self-assembly, the oriented arrangement of polymer chains, or intriguing structures. SVA shows advantages over thermal annealing in the following respects:<sup>12,19,20</sup> the absorbed solvent can markedly improve the mobility of polymer segments compared with that in the melt state; SVA does not destroy the molecular structures of polymers that are vulnerable at high temperature.

Compared with variation of the SVA method reported previously, our method is different in the following respects: (1) a high relative humidity is required to obtain holes and fractal-like structures, although water is not the solvent for the TCPT; (2) the size of fractal-like structures is on the micron scale, whereas the reported size of self-assembled structures of block copolymers is usually on the nanoscale. Based on these differences, we speculate that the formation of fractal-like structures in this study involves three steps (Figure 3): (a) the formation of a CS<sub>2</sub> layer on the surfaces of the water droplets created in the humid environment, (b) the formation of individual holes as the CS<sub>2</sub>-covered water droplets fall to the surface of the TCPT film, and (c) the formation of fractal-like structures through the coalescence of individual holes.

In detail, the evaporation of CS<sub>2</sub> cools the temperature in the covered Petri dish, leading to the formation of water droplets through condensation under the humid conditions. Then, a layer of CS<sub>2</sub> can form on the surfaces of the water droplets (Figure 3a). This process is possible because a monolayer of hexagonally arranged water droplets



**Figure 3** Formation of fractal-like structures by annealing the TCPT films using CS<sub>2</sub> vapor: (a) formation of a CS<sub>2</sub> layer on the surfaces of water droplets created under the humid conditions, (b) formation of individual holes as the CS<sub>2</sub>-covered water droplets fall to the surface of the TCPT film, and (c) formation of fractal-like structures due to the coalescence of individual holes. A full color version of this figure is available at *Polymer Journal* online.

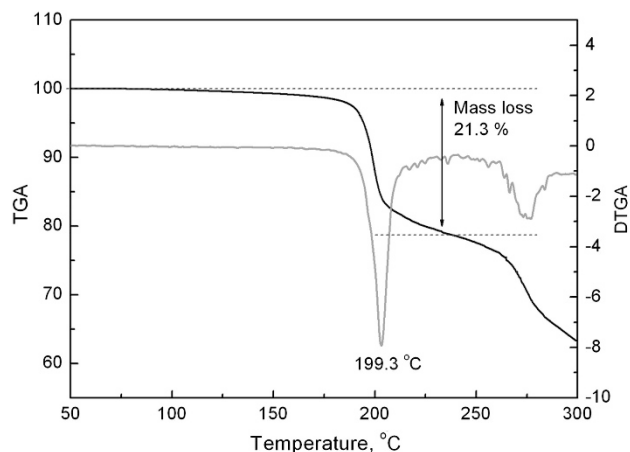


can form on the surface of an immiscible solvent and gradually sink into solution through a breath figure process.<sup>21</sup> Figure 3b shows that the CS<sub>2</sub>-covered water droplets fall toward the surface of the TCPT film. As soon as the water droplets contact the surface of the TCPT film, the CS<sub>2</sub> on the surfaces of the water droplets can swell the TCPT, leading to the release of heat of solution. In turn, the heat drives the evaporation of the CS<sub>2</sub>, elevating the swelled TCPT with the evaporation of the solvent. Consequently, the TCPT deposits on the edges of the holes. The water droplets continue to sink into the film as the swelled TCPT is elevated with the evaporation of the solvent until they reach the surface of the substrate.

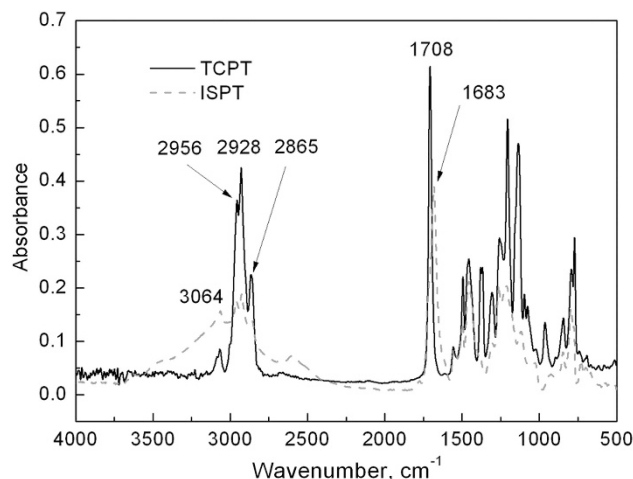
This process is feasible and is supported by two facts: (1) the average size of the water droplets formed under the humid conditions is  $\sim 10\ \mu\text{m}$ , which is in agreement with the size of the individual holes formed during the initial stage of the SVA performed in this study (Figure 1a); (2) the size of some holes (Figure 1a) is on the scale of microns, which is similar to the size of the holes formed by the breath figure process.<sup>22</sup> Finally, as the holes grow, they coalesce to form the fractal-like structures (Figure 3c).

The 4-tert-heptyl ester groups in thiophene rings are less thermally stable than the TCPT backbones. Figure 4 shows the TGA and DTGA curves of the TCPT. It was observed that the TCPT undergoes a marked mass loss at  $\sim 200\ ^\circ\text{C}$  (21.3%), which is due to the cleavage of the 4-tert-heptyl groups (Scheme 1). Furthermore, the TCPT continues to lose mass at  $\sim 275\ ^\circ\text{C}$  due to the removal of the resulting carboxylic acid groups.<sup>17</sup> Because the backbones of polythiophene and its derivatives are also susceptible to thermal treatment, it is safe to thermally treat the TCPT films at  $200\ ^\circ\text{C}$  to convert the TCPT into an ISPT derivative.

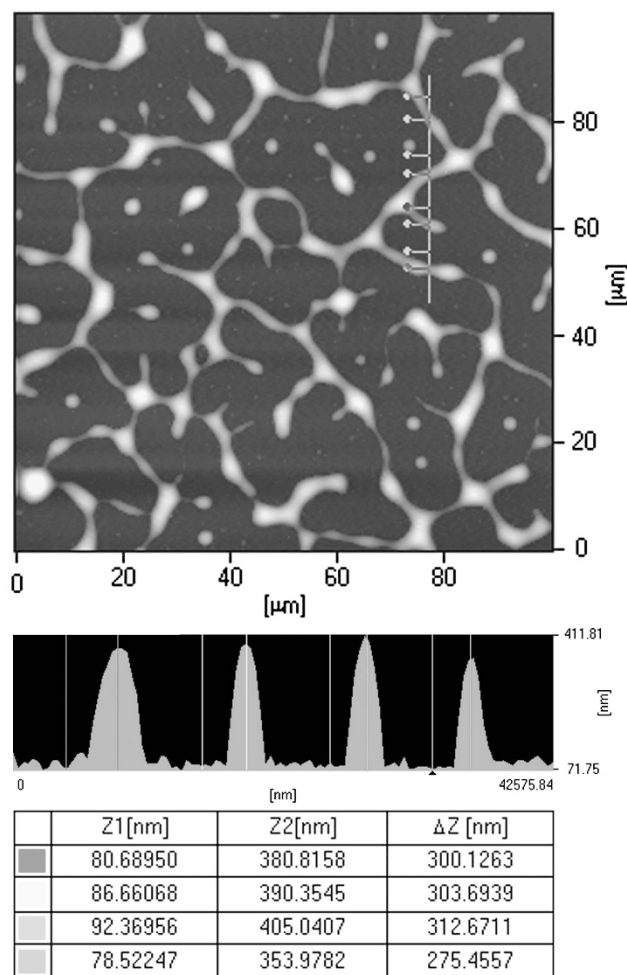
The thermal stability of the TCPT was also investigated using FT-IR. Figure 5 shows the FT-IR spectra of the TCPT and the ISPT. The TCPT shows a spectrum containing characteristic peaks at 3064, 2928, and  $1708\ \text{cm}^{-1}$ , which correspond to the vibrations of the C–H bonds of the thiophene rings, the C–H bonds on the aliphatic chains, and the carbonyl groups of the 4-tert-heptyl esters, respectively. In contrast, in the spectrum of the ISPT, the peak at  $2928\ \text{cm}^{-1}$  was reduced, and a broad peak ranging from  $\sim 2500\text{--}3500\ \text{cm}^{-1}$  appeared. Additionally, the vibration peak at  $1708\ \text{cm}^{-1}$  shifted to  $1683\ \text{cm}^{-1}$ , which corresponds to the carbonyl moieties of carboxylic acid groups. Therefore, the FT-IR data also support the conversion of the TCPT into ISPT upon thermal treatment at  $200\ ^\circ\text{C}$ .



**Figure 4** TGA and DTGA curves of the TCPT. A full color version of this figure is available at *Polymer Journal* online.



**Figure 5** FT-IR spectra of the TCPT and the ISPT. A full color version of this figure is available at *Polymer Journal* online.



**Figure 6** Fractal-like structures of the ISPT film obtained by thermally curing the TCPT film. A full color version of this figure is available at *Polymer Journal* online.

Polymer films with holes or fractal-like structures whose size is on the micron scale are of great interest because they are widely used in medicine and pharmacology for the separation and concentration of particles, proteins, and enzymes.<sup>23–25</sup> Insoluble films with holes or fractal-like structures are convenient for solution-based applications. An ISPT film with fractal-like structures was obtained by thermally curing the fractal-like structures of TCPT films. Figure 6 shows an AFM image of the fractal-like structures of the ISPT film. It was observed that the fractal-like structures of the ISPT film are similar to those of the TCPT film, indicating that the fractal-like structures can be retained during the conversion of TCPT to ISPT. The fractal-like structures of the ISPT film are not soluble in common organic solvents such as chloroform, THF, toluene, acetone, providing an approach for the infiltration of guest materials into the fractal-like structures for the fabrication of host-guest composite materials.<sup>26,27</sup>

## CONCLUSIONS

In this study, we developed a method for preparing holes and fractal-like structures using solid dry films of conjugated polymers via SVA. A mechanism that involves the formation of solvent-covered water droplets has been proposed to explain the formation of holes and fractal-like structures based on the fact that a high level of environmental humidity is crucial to the fabrication process. The holes and the fractal-like structures can be formed on both polar and non-polar substrates. The fractal-like structures can be retained upon the conversion of the TCPT films to ISPT films. We expect this work to open an avenue for the application of fractal-like structures of conjugated polymers in areas such as organic optoelectronics.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)