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Hyperbranched Polymer Structures via Flexible Blade Flow Coating

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ABSTRACT: Evaporative self-assembly has been shown to be a scalable method for organizing nonvolatile solutes, for example, nanoparticles; however, the influence of substrate surface energy on this technique has not been studied extensively. In this work, we utilized an evaporative self-assembly process based upon flexible blade flow coating to fabricate organized structures that have been modified to systematically vary surface energy. We focused on patterning of polystyrene. We observed a variety of polystyrene structures including dots, hyperbranched patterns, stripes, and lines that can be deposited on substrates with a range of wet-

ting properties. We explained the mechanism for these structural formations based on the competition between Marangoni flow, friction, and viscosity. The development of this fundamental knowledge is important for controlling hierarchical manufacturing of nanoscale objects with different surface chemistries and compositions. © 2015 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2015**, 00, 000–000

KEYWORDS: evaporation; polystyrene; structure patterning; surface modification; wetting

INTRODUCTION Evaporative self-assembly techniques have been developed to create ordered structures on nanometer-to-micron scales for a range of potential applications from electronics^{1,2} to printing.^{3,4} Several methods that use evaporative assembly have been reported, including dip-coating,^{5–7} Marangoni flow-induced self-assembly,^{8,9} constraining solutions in a sphere-on-flat geometry,¹⁰ and oscillating flow-coating.^{11,12} In particular, flow-coating is a simple and an inexpensive method to controllably deposit uniform or gradient polymer thin films, as well as stripe or grid patterns of polymer or nanoparticles.^{11–13}

For many of these methods, silicon-based substrates are commonly used. However, this material choice has presented problems for certain solutes. For example, polystyrene (PS) has been observed to form rings with fingers and rings with hole-punch-like structures on hydrophilic silicon wafers, rather than the typical, well-defined rings from a sphere-on-flat evaporative assembly process.^{10,14} For PS on hydrophobic silicon wafers, dewetting in PS thin films, forming discontinuous films with holes, are widely observed.^{15,16} Although considerable understanding has been provided for the formation of patterns on both hydrophilic and hydrophobic substrates, a systematic study of substrate properties on patterns developed with flow coating has not been conducted.

In this article, we investigate the effect of surface energy on structure formation during flexible blade flow coating¹² by tuning the substrate surface and varying flow-coating parameters with PS in toluene as a model solute. Upon modifying the surface energy of a silanized substrate with ultraviolet/ozone (UVO) exposure (which provides a range of water advancing contact angles from 112° to 34° as shown in Fig. 1), we find that a variety of structures (such as hyperbranched structures and lines perpendicular or parallel to the flow receding direction) may be fabricated with flow-coating. In particular, our findings lead to the description of a mechanism for the formation of regular, centimeter-scale hyperbranched structures due to the interplay between Marangoni flow and solute deposition on the surface.

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EXPERIMENTAL

Sample Fabrication

Polished silicon wafer (100 mm diameter, ~500 μm thickness, 100 orientation, P/B doped, University Wafers) substrates (typically cut into 1.2 × 1.2 cm) were prepared by rinsing with toluene, acetone, and deionized water, drying under nitrogen, and then treating with Harrick oxygen plasma at 250 mTorr for 20 min. The oxide layer thickness was measured with ellipsometry (refractive index, $n_1 = 1.46$ -setting by

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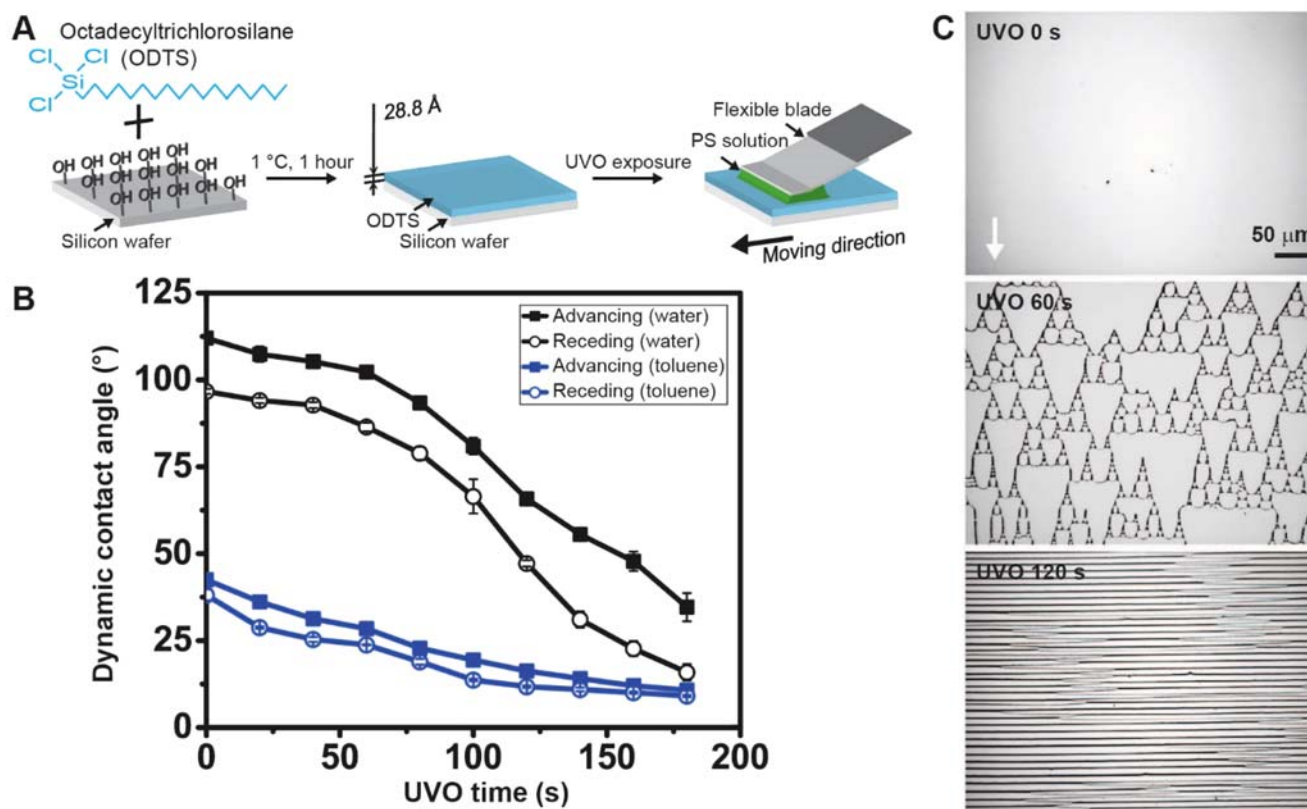


FIGURE 1 (A) Schematic of preparing substrates with tunable surface energy and then applying flow-coating process. (B) Dynamic contact angles including advancing (solid data points) and receding (open data points) of substrates as a function of UVO time. Liquid of water (black data points) and toluene (blue data points) are used. The error bars denote standard deviation for three independent samples. (C) Structures fabricated on substrates with tunable surface energy, varying from no deposition, hyperbranched structures to horizontal lines via flow coating. Other flow-coating parameters used here are initial concentration, c_0 , as 0.5 mg/mL, stopping time, t , as 100 ms, and set distance, d , as 5 μm.

LSE Stokes ellipsometer, Gaertner, Inc.). Surface-modified substrates were transferred to sealed 20 mL scintillation vials containing 1 μL *n*-octadecyltrichlorosilane (ODTS) (95%, Gelest, Inc.) and 999 μL toluene (use as received from Fisher Scientific) (0.1% ODTS by volume). Each vial was placed in an ice water bath for 1 h to regulate the temperature to 1 °C. After 1 h, the modified silicon wafer in each vial was rinsed and dried following the same pretreatment process, but excluding the 20 min oxygen plasma treatment. The wafers were then baked in a 120 °C oven for 2 h, allowed to cool to room temperature, and sonicated in toluene for 60 s. The wafers were again rinsed and dried. The thickness of the ODTS layer was measured with ellipsometry (ODTS, refractive index, $n_2 = 1.457$, Gelest, Inc.) as 28.8 ± 0.83 Å (averaged by 20 samples) [Fig. 1(A)]. To control surface energy, the modified ODTS layers were treated with UVO (Jelight 342 UVO system) for different exposure times. Immediately thereafter, the substrates were used for measuring dynamic contact angle or flow-coating.

Dynamic Contact Angle Measurement

Advancing and receding contact angles for ODTS treated substrates were determined using deionized water and toluene at room temperature (VCA-optima TM, AST, Inc.).

Flexible Blade Flow-Coating of Polystyrene

Flow-coating was conducted with programmed velocity (v) (velocity the substrate moved), set distance (d) (distance the substrate moved), and stopping time (t) (time the substrate paused) under move-stop alternating steps (Supporting Information, Fig. S1). In this work, the programmed velocity, v , is kept constant at 1 mm/s. The flow-coating technique is discussed in detail in Refs 11 and 12. An improvement in the flow-coating technique has recently been reported,¹² where a flexible polyethylene terephthalate (PET) blade is used as the top confining boundary. A flexible PET blade (75 μm × 2 cm × 4 cm) will be used in this work. A solvent region was made by scoring the PET blade 1 mm from the meniscus edge. The solution used for flow coating experiments reported here was polystyrene 0.0115 wt % to 0.1721 wt % in toluene solution (polystyrene, $M_n = 1100$ kg/mol, PDI = 1.15, Polymer Source, Inc.). *In situ* observation of structure formation was performed with an upright optical microscope (Zeiss Axio Tech Vario, Pixel Link CCD camera).

RESULTS AND DISCUSSION

Various flow-coating parameters are used to form different structures, such as hyperbranched structures, lines perpendicular to

the flow direction (which we will denote as “horizontal lines”), or lines parallel to the flow direction (which we will denote as “vertical stripes”). To explore the formation of these structures, we control the following parameters: UVO exposure time (to control the substrate surface energy), initial PS solution concentration (c_0), stopping time of flow-coating (t), and set distance of flow-coating (d).

Importance of Substrate Surface Energy

UVO exposure time induces bond breaking and cross-linking in the ODTS layer to cause a change in surface energy of the ODTS-modified substrate.¹⁷ The increase in UVO exposure time leads to the decrease in the contact angle of water and toluene [Fig. 1(B)]. In our study, flow-coating a PS solution on UVO-treated ODTS substrates with UVO exposure times between 0 and 20 s resulted in no PS deposition [Fig. 1(C)]. As UVO exposure time increased between 70 and 180 s, horizontal lines of PS were deposited with spacing determined by the slip distance (the distance between pinning and depinning of the contact line).¹² However, interestingly at 60 s of UVO exposure, hyperbranched structures were observed as well-aligned, self-similar triangles [Fig. 1(C)].

One of the significant results of our work here is the formation of these hyperbranched structures on 60 s UVO-exposed ODTS substrates via flow-coating. Importantly, these structures were created via flow-coating, which introduces controlled “stick-slip” motion into the contact line where PS deposition occurs. Without flow-coating, in a droplet of PS solution, for example, vertical stripes were (Supporting Information, Fig. S2) deposited.

Solutal Marangoni Flow

To our knowledge, arrays of hyperbranched structures have not previously been obtained via confined evaporative assembly; however, similar periodic patterns have been created by adding surfactant to an evaporative drop containing microspheres¹⁸ on neat silicon wafers. Stebe et al. speculated that Deegan’s periodical patterns result from Benard cells, driven by thermal Marangoni stresses.^{19–21} As the droplet evaporates, the surface of the droplet cools and creates temperature gradients as a function of depth and radius. These temperature gradients create surface tension gradients which induce the thermal Marangoni stresses.^{22,23} Besides thermal Marangoni stress, surface tension gradients can also be generated from solute concentration gradient,²⁴ as was observed and predicted for polymer solutions.^{25,26} This effect is referred to as a solutal Marangoni effect. One noteworthy example of solutal Marangoni stresses is “Tears of Wine,” in which fluid from an area of lower surface tension is drawn to an area of higher surface tension due to a tension gradient^{27,28} (Marangoni force). In our work, friction induced by the moving substrate occurs in the direction of the edge front to the bulk solution,²⁹ a direction that is opposite to that of the Marangoni force in flow-coating. These opposing forces induce the periodic formation of vertical stripes, parallel to the flow direction. Consequently, we speculate that these stripes give rise to hyperbranched structures.

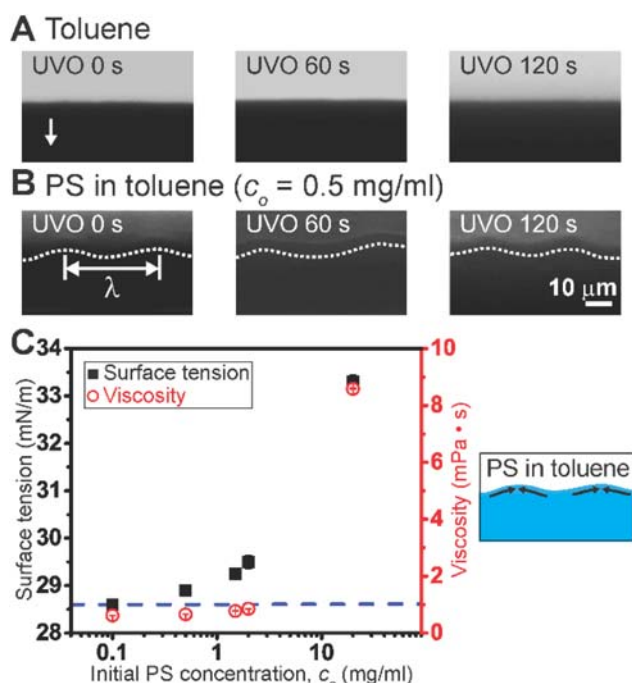


FIGURE 2 (A) Meniscus front of toluene only via flow coating. The arrow indicates the flow receding direction. (B) Meniscus front of polystyrene (PS) in toluene via flow coating. The white dash lines are guides to the eye and the meniscus front follows periodic wavelength of λ . (C) Surface tension and viscosity as a function of initial PS concentration. The blue dash line indicates the surface tension of toluene. The schematic illustrates possible flows caused by surface tension gradient (induced by concentration gradient) for PS in toluene at the meniscus evaporating front.

While the thermal Marangoni effect is of minor importance for our process, as illustrated by the stability of the toluene meniscus in the absence of PS in Figure 2(A), we believe that the solutal Marangoni effects play a large role in the formation of hyperbranched structures (Fig. 2B). In support of this hypothesis, we note that the meniscus fronts, shown in Figure 2(A,B), display a straight line for toluene only and a sinusoidal wave for PS in toluene suggesting that the solutal Marangoni effect is more important than the thermal Marangoni effect. The solutal Marangoni effect, which is generated by a concentration gradient induced surface tension gradient,²⁴ results from the local fluctuation of the concentration of polystyrene [Fig. 2(C)].

To quantify the solutal Marangoni effect,^{25,26,30,31} we estimate the Marangoni number (M_a) and Marangoni wavelength (λ).³²

$$M_a = \left(\frac{d\gamma}{dc} \right) \frac{\Delta c \cdot h}{\eta D} \quad (1)$$

$$\lambda = \frac{2\pi h}{\sqrt{M_a/8}} \quad (2)$$

Here, $(d\gamma/dc) \cdot \Delta c$ is the surface tension difference caused by concentration gradient, h is the size of the gap height beneath

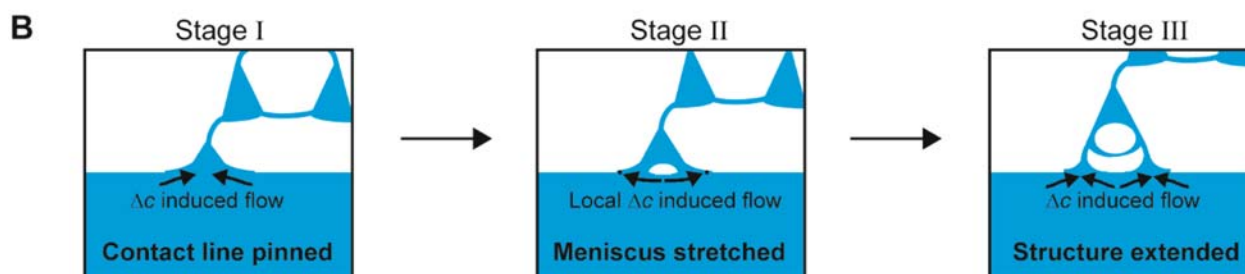
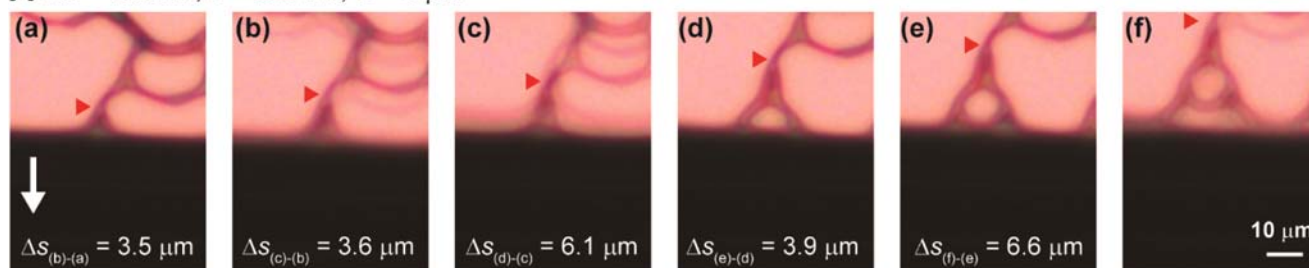
A $\Delta t = 100$ ms, $t = 100$ ms, $d = 5$ μm 

FIGURE 3 (A) *In situ* video images of hyperbranched structure formation with stopping time, $t = 100$ ms and set distance, $d = 5$ μm . The interval time (Δt) is 100 ms between snapshots, and the step distance (Δs) is measured from the red triangle marker. The white arrow indicates the flow receding direction. (B) Schematic of evolution in hyperbranched structures.

the flexible flow coating blade,¹² η is the viscosity, and D is the diffusion coefficient. The viscosity of the PS in toluene solution increases as the PS concentration increases.³³ The change in surface tension changes corresponding to various levels of initial PS concentration [Fig. 2(C)] was measured with the Wilhelmy method using Micro Trough XS (Kibron, Inc.). From this data, we determine $(d\gamma/dc) \cdot \Delta c$. In addition, the changes in viscosity corresponding to various levels of initial PS concentration [Fig. 2(C)] was measured, using TA Instruments AR2000 Rheometer with standard concentric cylinders at 20 °C under shear rate of 200 s^{-1} . Using measured values, assuming $D = 2.1 \times 10^{-11}$ m^2/s (comparable to Ref. 34) (see Supporting Information for calculation), and assuming that the solution concentration changes near the evaporating meniscus (see Supporting Information for calculation), we find the Marangoni number to be on the order of 10^5 – 10^6 , which indicates a major contribution at the meniscus front by the solutal Marangoni effect. Therefore, the local Marangoni flow [schematic in Fig. 2(C)] results in a sinusoidal shape for the meniscus, whose wavelength is given by the characteristic wavelength of Marangoni flow (see Supporting Information for calculation). Thus, this Marangoni effect sets the periodicity of the vertical stripes and dots in Figure 3. Although the magnitude of the Marangoni wavelength is predicted to be between 1.3 and 3.1 μm , which is smaller than the measured 30 μm , it remains nearly constant regardless of UVO exposure time. This discrepancy in predicted and measured Marangoni wavelength is most likely due to the unmeasurable increase in viscosity at the evaporating meniscus front.^{25,30}

Hyperbranched Structure Formation

To reveal the details of spontaneous structure formation of hyperbranched structures, we employed *in situ* microscopy

[Fig. 3(A)]. The video images revealed that hyperbranched structures are generally formed in three stages [Fig. 3(B)]. We note that due to the dynamics of the meniscus in our process, we have difficulty measuring the wavelength of the dynamic meniscus. In the first stage, fingers parallel to the flow direction appeared as a result of Marangoni instability and friction. Importantly, a triangle-shaped meniscus connects the fingers to the meniscus front. Since the fingers are more highly concentrated with PS than the bulk solution, the surface tension of a finger is relatively higher, drawing in the bulk solution, which has a lower surface tension. This step is shown schematically in Figure 3(B) (a).

In the second stage, one finger divides into two, thereby creating a branch. This division is associated with sufficient thinning of the triangularly shaped meniscus as it is stretched to a length determined by the flow coating set distance. If the set distance is sufficiently small, then thinning does not occur and PS solution continues to feed the vertical stripe. For thinned triangular meniscus, we hypothesize that the evaporation process at the two edges [two dots in Fig. 3(B) (b)] evaporate at a faster rate due to the geometry of the meniscus at this location, that is, proximity to the blade which causes a steeper angle. Therefore, the edges become more concentrated, increasing the surface tension, which in turn draws in a lower level of solution [curved arrows of flows in Fig. 3(B) (b)]. The outward flow in the stretched triangular meniscus results in a lower height profile in the middle as characterized by atomic force microscopy (Supporting Information, Fig. S3).

The branching continues until the third stage [Fig. 3(B) (c)] when the programmed set distance is reached. At this time, the substrate stops moving, and the triangular meniscus fingers

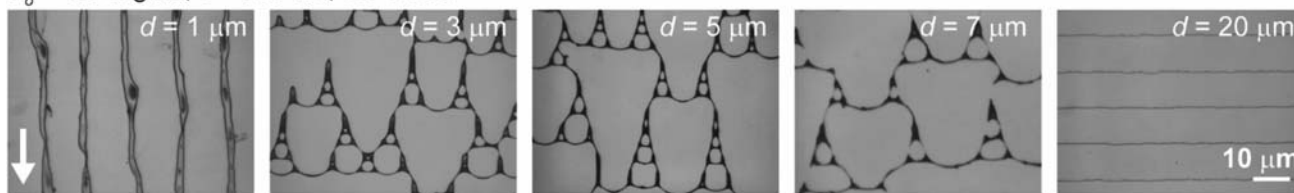
$c_0 = 0.5 \text{ mg/ml}$, $t = 100 \text{ ms}$, UVO 60s

FIGURE 4 PS patterns as a function of set distance d with constant c_0 ($c_0 = 0.5 \text{ mg/mL}$), t ($t = 100 \text{ ms}$), and UVO exposure time (60 s). The white arrow indicates the flow receding direction.

again form, and the process repeats to form an extended hyperbranched structure [same as in Fig. 3(B) (a)].

Importance of Set Distance

To understand the controlling parameter of the hyperbranch geometry, we examined the effect of set distance d (Fig. 4), while holding c_0 , stopping time, and UVO exposure time constant. When d was small, for example, $d = 1$ or $2 \mu\text{m}$, vertical stripes parallel to the flow direction were formed. The spacing of these vertical stripes is set by the Marangoni wavelength; however, as the set distance was increased, structures changed from stripes to hyperbranched structures. Furthermore, when d was greater than the slip distance, for example, $d = 20 \mu\text{m}$ or greater, horizontal lines perpendicular to the flow receding direction were deposited. This transition is associated with the development of a critical stress at the meniscus contact line to cause destabilization. At small d , while the Marangoni flow drives material to the contact line, the blade movement drags

the polymer material away from the contact line; therefore, vertical stripes are deposited. When the meniscus is stretched between 3 and $7 \mu\text{m}$, hyperbranched structures are formed. For sufficiently large d , the meniscus is strongly stretched and destabilizes. The concentrated materials at the pinned contact line are deposited and form a horizontal line while the other part of the stretched film moves along with the blade.

Importance of Solute Deposition

Although surface energy does not influence the Marangoni flow, it does play a role in the deposition of polymer during coating,^{15,16,35} including flow-coating of hyperbranched structures [Fig. 1(C)]. As reported previously,^{26,36,37} evaporation is faster when contact angle is lower, thus outward flow of solute is increased, resulting in more deposition. This effect was confirmed in our method by observing the quantity of PS deposited at the initial contact line with controlled stopping time [Fig. 5(A)]. The quantity of PS adsorption increased as UVO exposure time increased, due to the increased solvent evaporation at lower contact angles for the meniscus. Future studies on controlled evaporation rate effects on pattern formations^{6,38} with flow-coating can be carried out, for example, by forced air convection to vary evaporation rate.⁶ Furthermore, larger contact angles are known to favor dewetting,^{15,16} and therefore, the destabilization of the stretched meniscus, explaining why hyperbranched structures tend to appear on substrates with larger contact angles.

Importance of Initial Solution Concentration and Stopping Time

To further explore the variables influencing hyperbranched structure formation, we kept the UVO exposure time and set distance, d , constant, 60 s, and $5 \mu\text{m}$ respectively, and varied the flow-coating parameters, initial solution concentration, c_0 , and stopping time, t . Figure 5(B) shows the typical morphological features of deposited PS as a function of c_0 and t . For deposition of the PS solute at the contact line, to some extent, stopping time is equivalent to concentration. Longer stopping times facilitate more evaporation,³⁹ thus creating a more concentrated region at the contact line, compared to shorter stopping times with the same c_0 . This similarity was revealed by increasing c_0 or by increasing stopping times, showing the same transition from hyperbranched structures to vertical stripes. Transitions were achieved by lower c_0 with longer stopping times or by shorter stopping times with higher c_0 . At low c_0 ($c_0 = 0.1 \text{ mg/mL}$), no deposition was observed at shorter stopping times ($t = 70 \text{ ms}$), or dots with vertical tails

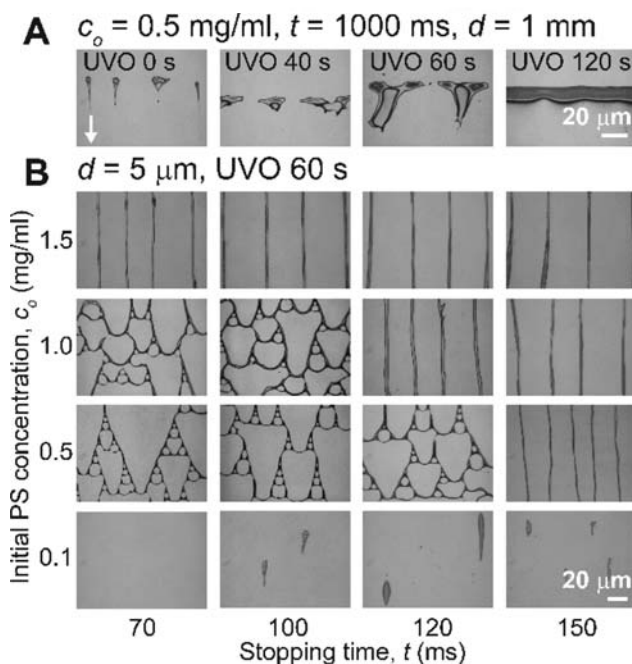


FIGURE 5 (A) PS patterns as a function of UVO exposure time with constant initial PS concentration ($c_0 = 0.5 \text{ mg/mL}$), stopping time ($t = 1000 \text{ ms}$), and set distance ($d = 1 \text{ mm}$). The white arrow indicates the flow receding direction. (B) PS patterns as functions of c_0 and t while keeping constant set distance ($d = 5 \mu\text{m}$) and UVO exposure time at 60 s.

were produced at longer stopping times ($t = 100\sim 150$ ms). For these lower c_0 , it is anticipated that even longer stopping times would be required for sufficient viscosity increases to be achieved for PS deposition. At higher c_0 or longer stopping times, more polymer material is available close to the contact line, preventing the destabilization of the stretched meniscus into the branched structure. The periodicity (wavelength) between vertical stripes was determined by the Marangoni instability and the periodicity increased as c_0 increased [vertical columns at $t = 120$ and 150 ms in Fig. 5(B)]. This increase in periodicity was observed because the viscosity, η , increase [Fig. 2(C) demonstrated the η increase as c_0 increased] results in a decrease in M_a and an increase in λ (eqs 1 and 2).

CONCLUSIONS

In conclusion, we have described the formation of hyperbranched structures of polystyrene solutions via flow-coating. The geometry of the hyperbranched structure is affected by the surface energy of substrates (i.e., UVO exposure time), concentration or stopping time, and set distance. The patterns are a result of competition between Marangoni flow and friction in the stretched meniscus created during subsequent oscillations in the programmed flow-coating process. Understanding this balance of fluid mechanics and flow instabilities may lead to new fabrication methods for creating structurally integrated assemblies.

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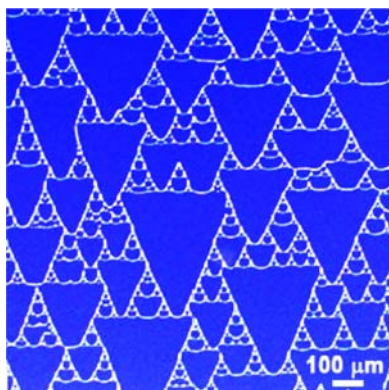
We thank Dr Joseph W. Krumpfer and Professor Thomas McCarthy for help in silane surface modification and Lang Chen for help in surface tension measurement. We thank the Center for Hierarchical Manufacturing (CMMI-1025020) at the University of Massachusetts for financial support. The authors declare no competing financial interest.

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Controlled patterning of nanoscale structures has been proposed to impact technologies, including electronic devices and coatings. In this article, we apply the flexible blade flow coating method, to fabricate organized polymer structures and characterize this structure formation mechanism as the wetting property of the substrate is varied. We find that for a specific substrate surface energy, hyper-branched polymer structures are formed. We explain this novel pattern formation through a relationship between Marangoni flow, friction, and viscosity.

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Center for Hierarchical Manufacturing (CMMI-1025020) at the University of Massachusetts	Division of Civil, Mechanical and Manufacturing Innovation	10.13039/100000147	

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