Mesoscopic Patterning in Thin Polymer Films Formed under the Fast Dip-Coating Process

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Summary

Mesoscopically ordered self-assembled polystyrene, polycarbonate and polymethylmethacrylate films were obtained when polymer solutions were deposited on vertical plates and dried with hot air. It was shown that characteristic size ($\sim 50 \mu\text{m}$) of the mesoscopic cell is practically insensitive to the polymer or substrate kind, while the thickness of the substrate plays a decisive role in the mesoscopic patterning. Junction angles of 120° and 90° were observed. Marangoni instability plays an important role in the cell's structure formation. A semi-quantitative model explaining the phenomenon of mesoscopic cell formation is proposed.

Keywords: dip-coating, mesoscopic, self-organization, instability, surfaces.

Introduction

Micrometric (i.e., mesoscopic) polymer structures attracted considerable interest recently^[1-3]. It was shown that processes of self-assembling and self-organization bring into existence strictly ordered, periodic mesoscopically scaled patterns, thus allowing various optical applications, including photonic molecules and full dielectric

long period gratings (LPG) - a new class of dielectric media that can provide novel ways to manipulate and control light. Photonic molecules are mesoscopic hierarchical structures, constructed from units with typical dimensions of 1-10 μm , which function as coupled optical resonators⁴. LPGs with a grating period of 50-1000 μm have been effectively employed as spectral-selective filters in various optical devices⁵.

We developed a new method of formation of mesoscopically patterned thin polymer films through a fast dip-coating process. Thin polymer films were obtained under drying of the polymer solution falling vertically along a metal, glass or polymer substrate. Mesoscopic patterning of the evaporated polymer films was observed by various groups and studied very thoroughly recently [6-11]. At the same time, the mechanism of the evaporation-induced mesoscopic self-assembly is still not clearly understood. Several mechanisms of mesoscopic self-organization were discussed. Srinivasarao, Shimomura and Pitois have related the phenomenon to atmospheric humidity, which can favor the formation of the honeycomb films^[8-10, 12-14]. L. Weh related self-organization to mass and heat transfer processes, which take place in the thin polymer film under the dewetting procedure. He supposed that overcritical concentration or temperature gradients perpendicular to the surface and the consequent periodic changes in the surface tension are responsible for the structure formation. In the overcritical unstable case, cellular vorticity in the layer (the so-called Marangoni instability) arises. The simplest forms of this surface tension – induced instability are patterns similar to the well-known hexagonal Bénard-Rayleigh cells. On the other hand, De Gennes related mesoscopic self-organization to another kind of instability. He has shown that in an evaporating film, a “plume” of solvent-rich fluid induces a local depression in surface tension, and the surface forces tend to strengthen the plume. His calculations led to the conclusion that this kind of

instability should dominate over the classic Bénard-Marangoni instabilities^[15-16]. It has to be emphasized that describing physical processes occurring in evaporating films turns out to be very challenging since couplings between the microstructure and hydrodynamic flow are highly non-linear^[17-18]. Within recent years there were several attempts to work out the mathematical model describing a flow of evaporated liquid layers, considering strong non-linearities inherent to such flows^[19-24]. At the same time the comprehensive understanding of the mesoscopic structuring occurring under the evaporation of polymer liquids has still not been achieved. We propose semi-quantitative model explaining the phenomenon of mesoscopic patterning.

Experimental Part

Three kinds of polymers: polystyrene (PS) 143 E (supplied by BASF), polycarbonate (PC) Lexan 141 (supplied by GE Plastics) and polymethylmethacrylate (PMMA) Acrylex CM 205 (supplied by Chi Mei Corp) were dissolved in two kinds of solvents: dichloromethane CH_2Cl_2 and chloroform CHCl_3 pure for analysis supplied by Karlo Erba Reagenti, the concentration of solution was 5% wt for all kinds of polymers and solvents. Physical properties of these solvents important for our investigation are summarized in Table 1^[24-27]. Three types of substrates (quartz glass, chrome steel and polypropylene (PP)) were coated under conditions of the fast dip-coating process. Substrates were cleaned thoroughly with acetone and ethyl alcohol and rinsed with a big amount of distilled water. The thickness of quartz glass and polypropylene substrates was varied in the range 40-4000 μm . The thickness of the chrome steel substrates was varied in the range 10-350 μm .

When the substrate is dip-coated, the liquid film runs out from the polymer solution, adheres to the substrate surface and solidifies during the evaporation of the

solvent (see Fig. 1). Dip-coating was carried out with an unusually high pulling speed $V = 47$ cm/min (the traditional speed of the dip-coating process is about 0.1-1 cm/min); thus we called this process fast dip-coating. Pulling direction was vertical in all our experiments. Films were immediately dried with an air current or dried nitrogen ($v = 3\text{ m/s}$), under isothermal conditions. Gas current velocity was measured with anemometer PROVA AVM 03. Gas stream was stabilized with 0.5 m length tube preventing formation of air vortices. The drying temperatures were varied in the range $t_d = 20-100^\circ\text{C}$. The structure of the dry film was studied by means of optical and scanning electron microscopy.

Results and discussion

Optical and SEM microscopy study of the structure of self-assembled mesoscopic patterns

Optical microscopy study of deposited films led to the conclusion that all polymers produced mesoscopic patterns, such as presented in Fig 2-3, when deposited under the above mentioned conditions. All kinds of substrates and solvents brought into existence self-assembled mesoscopically structured films. The orientation of the mesoscopic structure is vertical and is obviously due to gravity. Pulling direction (vertical) and longitudinal direction of the structures depicted in Fig. 2-3 are identical. It is important to note that characteristic size of the mesoscopic cell was 30-50 μm , and it was only slightly sensitive to the kind of polymer, substrate or solvent.

Closer SEM inspection revealed that various structures of the mesoscopic cells can be observed. Fig. 3 depicts mesoscopic patterning typical to the films deposited on the metal substrates. The SEM image displayed in Fig. 3 B-C presents PC domains separated by relatively broad ($\sim 10\text{-}20\ \mu\text{m}$) highly porous areas, which may of interest in a view of membrane applications of the films. The detailed makeup of the porous

boundary separating mesoscopic cells is presented in Fig. 3 D-E. The average size of pores is 1 μm . SEM study of the internal area of the mesoscopic cell also indicated the presence of small pores with a diameter even less than 1 μm (Fig. 2C, 3 F).

However, Fig 4-5 present mesoscopic patterns separated by relatively thin ($\sim 1\text{-}2\ \mu\text{m}$) porous boundaries, typical to the crack patterns, studied experimentally by Weh and theoretically treated by De Gennes^[2, 15]. It seems that these structures have a potential as photonic molecules. Polycarbonate, when dissolved in chloroform, formed cells containing highly porous areas located at the center of the film (Fig. 6). Junction angles of 120° (Fig. 4) and 90° (Fig. 6) were observed, whereas disordered mesoscopic structures occurred as well (Fig. 5).

2. Influence of the parameters of the dip-coating process on the mesoscopic patterning.

Experimental data led us to the conclusion that atmospheric humidity does not play a considerable role in the pattern formation. We varied the atmospheric humidity in our experiments over a wide range and did not observe any evidence of the humidity having impact on mesoscopic pattern formation. We want to emphasize that we deposited our films on vertical plates, whereas other groups worked with horizontal substrates; hence, the sinking of water droplets, discussed by Srinivasarao^[12-14] et al, cannot be invoked for the explanation of the phenomenon.

The low boiling temperatures of both dichloromethane and chloroform, which are 39.6°C and 60°C correspondingly, are noteworthy; hence, the drying takes place at a temperature which is close or higher to the boiling point, thus drying is accompanied by intensive formation of bubbles filled with the solvent vapor. Migration of the bubbles towards the cell boundaries (see Fig. 3) or centers (see Fig. 6) could be explained in the framework of the concept developed by Weh, who

related the effect to the Marangoni instability, which induced spreading motions of the solution^[2]. However, insensitivity of the mesoscopic cell size to the kind of polymer or used solvent calls for an explanation, which will be proposed below.

3. The impact of the substrate thickness on pattern formation.

The most surprising results were obtained when both organic and non organic substrates of various thicknesses (varied from 40 to 4000 μm) were coated under the fast dip-coating process. A strong impact of the substrate thickness on the mesoscopic self-assembling was revealed. Self-assembling was observed exclusively on relatively thin quartz glass and PP substrates, with a thickness of less than 150 μm (Fig. 2). We deposited PC films on the chromium steel substrates with thicknesses of 10, 20, 30, 40, 60, 70, 80, 100, 150 and 350 μm . Mesoscopic self-organization was revealed on the metal substrates with a thickness of less than 100 μm only (see Fig. 3).

4. Mechanism of mesoscopic patterning

Formation of the mesoscopic structures may be described with the help of the considerations presented below. Due to fast external drying, all solvent which leaves the solution is immediately removed from the system. Then, at an early stage of the evaporation process, a polymer – rich layer is formed¹⁶. According to earlier results, the characteristic thickness of such layer may be of order 50-70 nm, about 20 times less than characteristic thickness of the film in the end of drying¹⁶. This boundary layer has essentially lower diffusion coefficient than the bulk solution; therefore, the evaporation of the solvent is primarily governed by diffusion through this layer. Formation of such boundary layer seemingly has been considered in the first time in paper²⁸.

In order to provide crude estimation for characteristic size of the mesoscopic pattern we propose semi – qualitative model. The solvent flux through the boundary layer is determined by the equation

$$J = D \frac{\Delta c}{s} \quad (1)$$

where J is the volume flux per second through the unit area (number of molecules $\times$ cube of characteristic solvent molecule size), s is the boundary layer thickness, Δc is the dimensionless concentration jump at the boundary layer and D is the characteristic diffusion coefficient (see Fig. 7). Due to the evaporation, the upper boundary of the system moves. Rather roughly, it is possible to estimate the velocity of motion of the upper boundary as

$$v_0 = -J = -D \frac{\Delta c}{s} \quad (2)$$

Estimation (2) describes the steady evaporation process with almost constant velocity. Still, similarly to other hydrodynamic instabilities such as Marangoni or Bénard instabilities^[19, 21-22, 29], there exists a possibility for instability of a fixed – thickness boundary layer. The physical mechanism of this instability is based on the observation that the local trough from outside the boundary layer has a tendency to grow as the reduced thickness facilitates the diffusion of the solvent in this place. Consequently, a local crest outside the boundary layer has a trend to grow as it suppresses the diffusion. Small – wavelength perturbations of this sort are suppressed by surface tension, and therefore there exists some critical scale for development of the layer instabilities.

It should be stressed that classic Marangoni instability driven by temperature dependence of the surface tension hardly may be responsible for the pattern formation in our case. The reason is that the film is very thin and characteristic time of thermal

conduction (estimated as $\tau \sim Cx/\kappa$, where C is heat capacity, x – the characteristic film thickness and κ - heat conduction coefficient) is of order 10^{-2} s – at least two orders of magnitude less than the characteristic time of the process. Therefore the whole process may be considered as isothermal.

In order to evaluate this critical scale, we pass to the frame system moving with the constant velocity v_0 together with the upper boundary of the layer. $\chi(x,y,z,t)$ is a local coordinate of the upper-layer boundary. The thickening of the layer leads to a decrease of the local velocity:

$$\delta v = +v_0 - D \frac{\Delta c}{s + \chi} \quad (3)$$

Consequently, the local perturbation equation for the χ variable with respect to viscosity and surface tension may be written as follows³⁰:

$$\frac{\partial^2 \chi}{\partial t^2} \sim \frac{\eta}{\rho} \frac{\partial}{\partial t} \left(\frac{\partial^2 \chi}{\partial x^2} + \frac{\partial^2 \chi}{\partial y^2} \right) + \frac{\sigma}{\rho} \frac{\partial}{\partial z} \left(\frac{\partial^2 \chi}{\partial x^2} + \frac{\partial^2 \chi}{\partial y^2} \right) + \frac{(D\Delta c)^2}{s^4} \chi \quad (4)$$

where η is the viscosity coefficient, ρ is the density of the solution, σ is the coefficient of the surface tension. Standard linear stability analysis invokes the following characteristic shape of the perturbation:

$$\chi = \psi(t) \exp(kz) \sin(kx) \sin(ky) \quad (5)$$

Substituting (5) to (4), one gets

$$\frac{d^2 \psi}{dt^2} \sim -\frac{2\eta}{\rho} k^2 \frac{d\psi}{dt} + \psi \left(\frac{(D\Delta c)^2}{s^4} - \frac{2\sigma}{\rho} k^3 \right) \quad (6)$$

The critical wavenumber for stability thus may be estimated as

$$k_{crit} \sim \sqrt[3]{\frac{(D\Delta c)^2 \rho}{s^4 \sigma}} \quad (7)$$

For the sake of numeric evaluation we take $s \sim 70$ nm (this estimation for the thickness of the boundary layer has been obtained in paper¹⁶.) Physical parameters of the solvents are given in Table 1 (self-diffusion coefficient of the solvents were

calculated by Dang³¹ and they are in a satisfactory accordance to the experimental data obtained by Prielmeier and Lüdemann²⁶), resulting on $k_{\text{crit}} \sim 6 \cdot 10^5 \text{ m}^{-1}$. This estimation corresponds to the typical scale for the loss of stability equal to $2\pi/k_{\text{crit}} \sim 10 \text{ } \mu\text{m}$. This figure qualitatively coincides with experimental findings. It could be seen that our estimation does not contain physical parameters of polymer, but parameters of the solvent only, which are actually rather similar for different kinds of organic solvents. It should be mentioned that the above approximation is very crude. No attention has been paid to interaction with the underlying surface in the final stages of the evaporation process and other important issues, like dependence of the surface tension on the solvent concentration. The latter effect may intensify the process described above, as well as bring about different mechanism of instability (Marangoni concentration – driven instability)²⁹. Possible role of this mechanism should be a scope of special investigation.

Let us discuss the influence of the substrate thickness. We have shown experimentally that heat transfer in the substrate plays a decisive role in the process of self-organization. It is necessary to compare the typical drying time τ_d (determined experimentally as $\tau_d \approx 10 \text{ s}$) with the characteristic time necessary for the establishment of thermal equilibrium in the substrate τ^* , given by $\tau^* \approx \Delta^2/\alpha$, where Δ and α are the thickness and thermal diffusivity of the substrate respectively (see Table 2).

We observed mesoscopic patterning at all substrates only if the condition $\tau_d \gg \tau^*$ was fulfilled. In other terms, a cooling due to the evaporation has been rapidly compensated by the heat flux from outside the system. Srinivasarao has shown that high vapor pressure of the solvent and the velocity of air across the surface drive solvent evaporation, rapidly cooling the surface, this cooling to be as much as 25°C ¹²

It is possible to suggest that in the absence of such compensation the evaporation cooling would lead to a decrease of the diffusion coefficient and increase of the viscosity. Both of these factors are able to prevent formation of nontrivial mesoscopic structures.

Conclusions

The process of self-assembling of thin polymer (PS, PC and PPMA) films deposited on vertical organic and non-organic substrates under conditions of fast dip-coating was studied first. The phenomenon of self-assembling was observed on the mesoscopic scale. It was established that the characteristic size ($\sim 50\text{ }\mu\text{m}$) of the mesoscopic cell is practically insensitive to the kind of polymer or substrate, while the thickness of the substrate plays a decisive role in the mesoscopic patterning. Typical crack patterns were observed with junction angles of 120° and 90° . Migration of the solvent vapor bubbles plays an important role in the cell structure formation. A semi-quantitative model based on the analysis of instability of the evaporated surface layer was proposed. The model explains the insensitivity of the mesoscopic cell characteristic size to the type of polymer and substrate. The fast dip-coating process presented in the paper, is simple, highly reproducible and permits fabrication of large areas (up to 100 cm^2) of mesoscopically structured films, which have a potential as membranes, long period gratings and photonic molecules.

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Table 1. Physical Properties of Solvents

Solvent	Density, g/cm ³	Boiling point °C	Surface Tension, J/m ²	Diffusion Coefficient, m ² /s
Dichloromethane	1.326	40	$27 \cdot 10^{-3}$	$3.9 \cdot 10^{-9}$
Chloroform	1.47	60	$20 \cdot 10^{-3}$	$4.0 \cdot 10^{-9}$

Table 2. Thermal diffusivity of the substrates used in the experiment.

Substrate	($10^{-7} \text{ m}^2/\text{s}$)
Polypropylene	0.95
Quartz glass	4.4
Chrome steel	40

Fig. 1. Scheme of the dip-coating process.

Fig. 2. Optical microscopy image of self-organized mesoscopic structures. A mesoscopically patterned PS film deposited on the quartz glass substrates (thickness of the substrate 130 μm, solvent - chloroform), B PC deposited on the polypropylene substrate (thickness of the substrate 25 μm, solvent – dichloromethane). The drying temperature – 25°C, C SEM image of the typical boundary separating PS mesoscopic cells.

Fig. 3. Optical microscopy and SEM images of self-organized mesoscopic and nanoscaled structures obtained under fast dip-coating deposition of PC films on the chrome steel substrate (thickness of the substrate 60 μm). Solvent - dichloromethane. The drying temperature – 25°C. A – Optical microscopy reveals ordered mesoscopic structure. B-C – SEM images of the same sample show domains of PC separated by porous areas. D - Magnified SEM image of the porous area demonstrates honeycomb nanoscaled structure of the boundary (area B in Fig. 3 B). E – internal area of the boundary. F – SEM image of the interior area of the cell (area A in Fig. 3 B-C).

Fig. 4. Optical microscopy and SEM images of self-organized mesoscopic structures obtained under fast dip-coating deposition of PMMA films on the quartz glass substrate (thickness of the substrate 100 μm). Solvent - dichloromethane. The drying temperature – 90 °C. A, B – Optical microscopy reveals ordered mesoscopic structure. C – SEM image of the mesoscopic cell. D – SEM image of the cell boundary.

Fig. 5. SEM images of mesoscopic patterns obtained under fast dip-coating deposition of PMMA film on the quartz glass substrate (thickness of the substrate 100 μm). Solvent - chloroform. The drying temperature – 60°C. A, B - SEM images of mesoscopic cells. C – SEM image of the boundary.

Fig. 6. Optical microscopy and SEM images of self-organized mesoscopic structures obtained under fast dip-coating deposition of PC film on the quartz glass substrate (thickness of the substrate 100 μm). Solvent - chloroform. The drying temperature – 50 °C. A – Optical microscopy shows ordered mesoscopic structure. B – SEM image of the mesoscopic cells. C – SEM image of the internal area of the cell (framed in Fig A-B).

Fig. 7. Scheme of the evaporation process.