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Formation of honeycomb patterns in evaporated polymer solutions: Influence of the molecular weight

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Abstract

The influence of polymer molecular weight on the formation of honeycomb patterns obtained by evaporation of polystyrene solutions was investigated. Pattern structure was studied with scanning electron and atomic force microscopy. It was determined that molecular weight exerts a decisive influence on the patterns makeup. Pore size and depth, distance between pores and specific porosity depend strongly on the polymer's molecular weight.

Keywords: Polymer solution; Evaporation; Molecular weight; Honeycomb pattern

1. Introduction

The evaporation-induced formation of honeycomb patterns in polymer solutions was under intensive investigation recently [1–12]. Nanoscaled self-assembling, allowed formation of strictly ordered honeycomb patterns comprised of air holes dispersed in the polymer matrix. These structures allow various applications, including photonic crystals, membranes, biofunctional interfaces and templates intended for the growth of colloid crystals [13–15].

At the same time, the mechanism of the evaporation-induced self-assembly is still not clearly understood. Srinivasarao, Shimomura, Matsuyama, Xu and Pitois have related the phenomenon to atmospheric humidity, which can favor the formation of the honeycomb films [1–3,5,6,9,12]. We have reported recently self-assembled patterns produced under conditions of relatively low humidity, in a fast dip-coating process, under intensive evaporation of chlorinated solvents [17–19]. Self-assembly was observed on two scales: mesoscopic (characteristic dimension ~50 μm), and micrometric. We have shown already that patterning depends strongly on the solvents' make up, and the mixture of chloroform $CHCl_3$ (8 wt.%) and dichloromethane CH_2Cl_2 (92 wt.%) promotes formation of the micrometrically scaled honeycomb patterns only [19]. 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 et al., cannot be invoked for the explanation of honeycomb pattern formation.

It is clear that in view of the possible applications, it is extremely important to control the size and depth of the pores. Our work will show that the pore diameter and depth are significantly influenced by the polymer's molecular weight. The impact of polymer molecular weight on these patterns' parameters was reported and discussed first by Matsuyama and Xu [9,12]. However Matsuyama and Xu obtained their patterns under conditions of high humidity (80% r.h.), and related the phenomenon to the behavior of water droplets. In addition to that results reported by Xu were obtained within the narrow range of molecular weights $44{,}000 < M_w < 75{,}000$. We will show that molecular weight exerts a decisive influence on the patterning processes over a broad range of molecular weights under conditions of

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much lower humidity, and is most likely associated with nucleation of the polymer under evaporation.

2. Experimental

Five kinds of polystyrene with different molecular weights of M_w=4800, polydispersity index PDI=M_w/M_n=1.34; M_w=42,500, PDI=1.52, M_w=227,100, PDI=2.23, M_w=1,000,000, PDI=2.0, M_w=2,800,000, PDI=1.4 were supplied by Polymer Source Inc. All polymers were dissolved in a mixture of chloroform $CHCl_3$ (8 wt.%) and dichloromethane CH_2Cl_2 (92 wt.%). Solvents (pure for analysis) were supplied by Karlo Erba Reagenti; the concentrations of the solutions were 2.5 and 5 wt.%.

Polypropylene substrates (50 μm thickness) were coated with the solutions using fast dip-coating experimental techniques, described in detail previously [17,18], with only one modification: drying was carried out with IR lamps in a slow air current (v=0.1 m/s). Use of IR lamps instead of intensive hot air drying avoided problems connected with undesirable air vortexes, exerting an influence on the pattern formation. The drying temperature was 60 °C, humidity was 30%–40% r. h. Air current velocity and humidity were measured with a precise hygro-thermo-anemometer from Extech Instruments 407412.

Samples were studied with SEM (JSM 6300, JEOL) and AFM (Park 5 M, scanning probe microscope, Scientific Park Instruments) microscopy. SEM images were processed with SIAMS 600 software.

3. Results and discussion

It has to be noted that the drying procedure was carried out at a drying temperature, which was higher than the boiling point of dichloromethane (39.6 °C) and close to that of chloroform (60 °C). Thus drying was accompanied by intensive formation of solvent vapor bubbles, which produced honeycomb patterns under intensive evaporation of the solvent [16,17].

We used in our investigation solutions with concentrations c of 2.5 and 5 wt.% Solutions with the lower concentration allowed us to obtain homogenous films at all molecular weights, whereas 5 wt.% solutions did not form a homogenous film when the molecular weight of the polymer was M_w=2,800,000 (the solution was too viscous). However, at both concentrations the patterning tendency was the same. First of all, low molecular weight (M_w=4800 and M_w=42,500) polystyrene promoted formation of the bi-modal pore size distribution, illustrated by SEM images displayed in Fig. 1A-B.

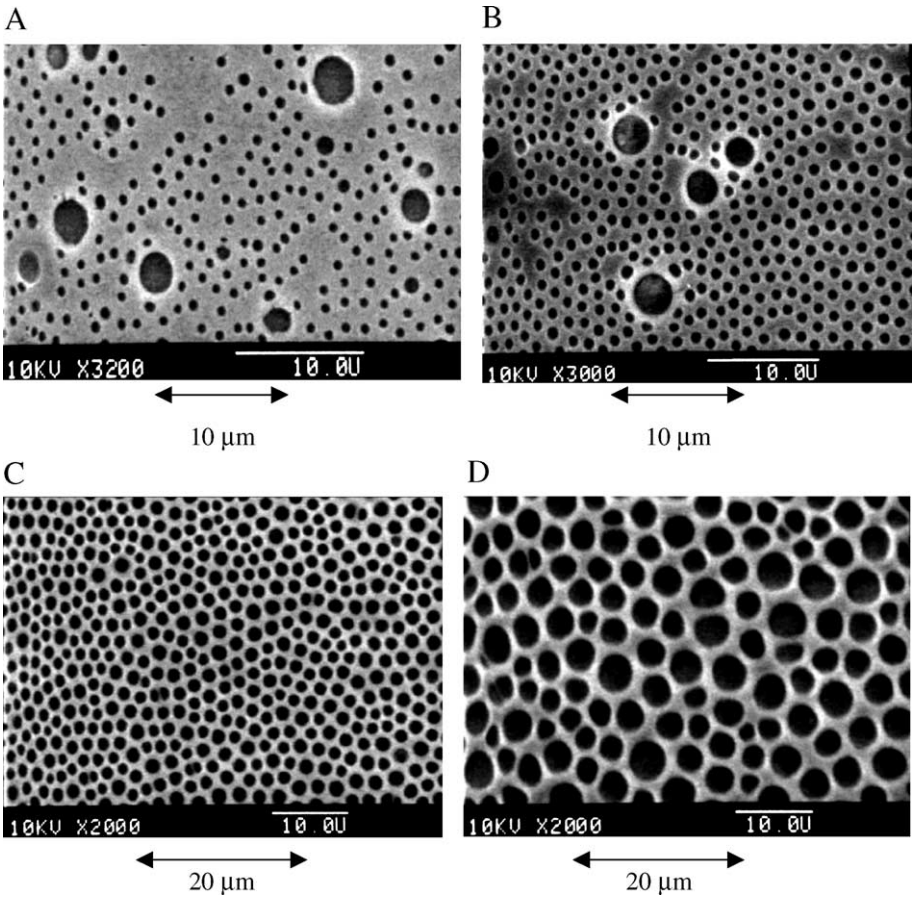

Fig. 1. SEM images of patterned films, concentration of the solution 5 wt.%. A–M_w=4800, B–M_w=42500, C–M_w=227100, D–M_w=1,000,000.