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Research News

Polymer Films with a Self-Organized Honeycomb Morphology**

By Bernard François,* Olivier Pitois, and Jeanne François

1. Introduction

Porous polymer films can be prepared with a large number of different morphologies depending on the nature of the polymers and on their applications. The pores may be open or closed. Their size (from some tens of Å to microns or more), their shape (spheres, more or less tortuous tubes, completely disordered spaces), and the thickness of their walls may be controlled, for an optimization of their membrane properties.^[1] Nevertheless until recently it was not possible to achieve regular spatial self-organization of these pores.

We succeeded in the preparation of porous polymer films with a regular arrangement of pores with a narrow size distribution.^[2] These films are made by one or several layers of empty spherical cells with similar size and organized upon an hexagonal network (Fig. 1). The cells of the upper layer are open so that the surface of the film is made by a regular arrangement of circular holes organized upon an 2-D hexagonal network (Fig. 2). The size of these cells was varied in a range 1–10 µm. Peeling off the superficial skin reveals a honeycomb morphology on the micron scale.

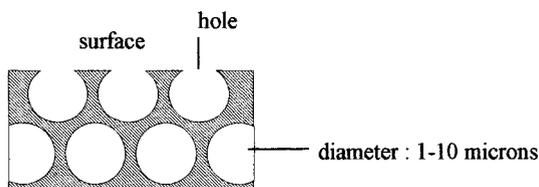


Fig. 1. Schematic cross-section of an auto-organized honeycomb film.

2. Materials

The honeycomb morphologies were obtained with polystyrene block copolymers, star-like homopolystyrenes and linear polystyrenes with a polar terminal group. Some examples of each group will be given on the following sections.

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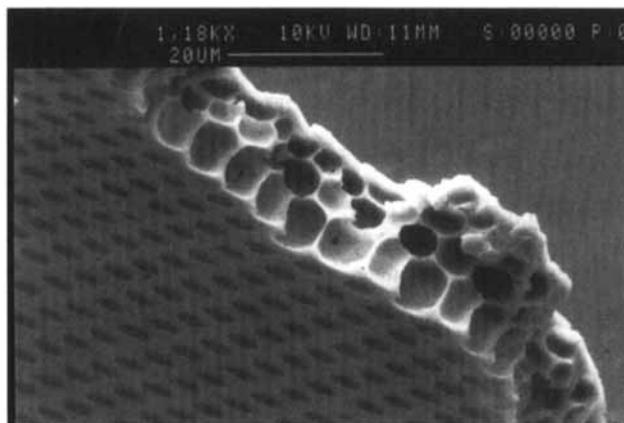


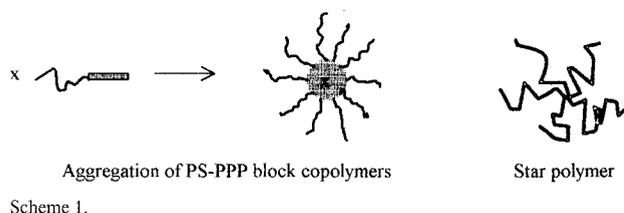
Fig. 2. Electron scanning micrograph (ESM) of an auto-organized honeycomb film made from a carbon disulfide solution of polystyrene-polyparaphenylene block copolymer [2].

In general, the materials were prepared as follows: Layers (0.1–1 mm thick) of polymer solutions, in a concentration range 0.5–10%, are spread on a flat support (generally glass) and rapidly evaporated by a flow of wet air. The nature of the solvent is very important. Among the studied solvents the carbon disulfide (CS₂) gives by far the most regular morphology. Nevertheless some organization has also been obtained with chloroform. The rate of evaporation and the composition of the evaporation atmosphere also play an important role. The presence of water vapor in the evaporation atmosphere is necessary. The evaporation conditions (temperature of the polymer solution and flow rate of humid air) have to be such that they produce water condensation at the surface of the evaporating solution layer: typically the initial solution temperature was 20 °C and the flow rate of water-saturated air 10 cm/s. It is remarkable that attempts to use vapors of other non-solvents of polystyrene in the evaporation atmosphere (methanol, ethanol, etc.) were, up to now, unsuccessful.

2.1. Block Copolymers

A quite unusual morphology was discovered during the casting of block copolymer films for neutron scattering studies. The aim of these studies was to examine the organization

of polystyrene-polyparaphenylene (PS-PPP) block copolymers in solution and in the solid state. Indeed, such copolymers^[3] have a soluble part (polystyrene sequences) and an insoluble part (the PPP sequence, which is also an electroactive polymer). They are organized, in solution and in the solid state, into quasi spherical micelles with a solid PPP core (30–150 Å) surrounded by a shell of polystyrene sequences (Scheme 1).^[4]



We obtained the same morphology with another block copolymer (polystyrene-polythiophene: PS-PT)^[5] which also contains an insoluble sequence of conducting polymer and aggregates as PS-PPP. It was moreover observed that a recently synthesized block copolymer polystyrene-poly-3-hexylthiophene (PS-P3HT)^[6] with a conjugated sequence soluble in CS₂, does not lead to any special morphology in its undoped state. But after a light doping of the P3HT sequence by FeCl₃ the regular porous morphology is observed. Neutron scattering data have shown that the electrically charged P3HT sequences associate with star-like micelles formation.^[7]

2.2. Star Polystyrenes

The structure of these copolymers is rather similar to that of star polystyrenes which can be prepared by reacting a reactive end of polystyrene chains with a multifunctional reactant. The honeycomb morphology was indeed obtained by evaporation of solutions of star-shape pure polystyrenes with different number of branches and different branch length (7 × 10 000, 70 × 6 000 for example). No special morphology was obtained with usual linear polystyrenes. The star shape of the polymer seems to be then a crucial condition.

2.3. Associative Polystyrenes

These observations were extended to linear polystyrene chains which carry at one of their ends a polar group able to associate in non-polar solvents^[8] such as CS₂. These polymers form micelle-like aggregates which behave as star-shape polystyrenes but in this case the association is due to dipole interactions and not to covalent bonding.

Porous film with a honeycomb morphology were prepared for example with CS₂ solutions of polystyrenes ($M_w = 5000$

and 15 000) capped at one end by the alkali salt of sulfonic (I) and carboxylic acid (II), or by alkaline alcoholate (III).

I was prepared by reaction of polystyryllithium (obtained by anionic polymerization of styrene by *sec*-butyllithium) on propanesultone. II was obtained by radical polymerization of styrene, in the presence of a transfer agent bearing a carboxylic acid group, and subsequent reaction with sodium. III was obtained by reaction of a polystyryl salt on ethylene oxide.

An example of the morphology obtained with the lithium salt of I is shown in Figure 3. The corresponding OH or COOH capped polystyrenes do not lead to the same special morphology. Preliminary viscosity measurements confirm that, under our experimental conditions, they are practically not associated into micelles, in contrast to their salts. This is further confirmation of the role of the polymer star shape.

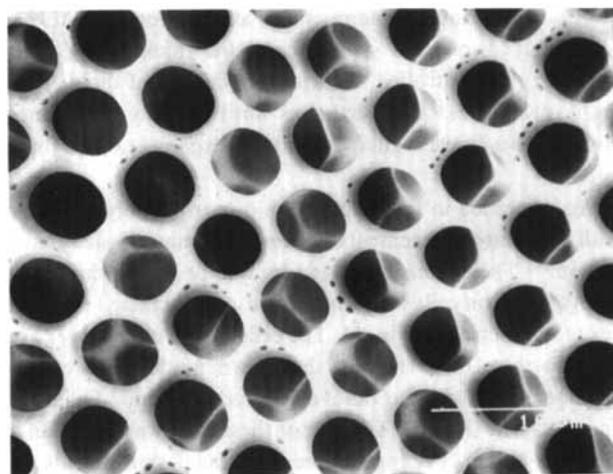


Fig. 3. ESM of an auto-organized film of polystyrene lithium sulfonate.

Chemical functionalities can be introduced in these membranes by a suitable choice of these associating ends. To what extent the polystyrene chain itself can be chemically modified without loss of organization is a question under study. It is interesting to note that polystyrene sulfonated at both chain ends does not lead to the honeycomb morphology.

2.4. Polymer Mixtures

By using CS₂ solutions of mixtures of star-like polystyrenes with other polymers it is possible to enhance some particular properties of the films while maintaining the organized morphology. For example, mixtures of star polystyrene (70 branches; Molar mass $M_w = 5000$ per branch) with up to 25% of linear polystyrene ($M_w = 300000$) lead to organized structures with improvement of their properties, particularly the suppression of cracks which are often observed to be formed during the drying step for pure star polymers.

Another new property is obtained by adding soluble "conducting polymers" in the CS₂ solution of the star polystyrene. For example, up to 50% of undoped poly-3-hexylthiophene (P3HT) has been added while maintaining the perfect organization of the morphology (Fig. 4). Such

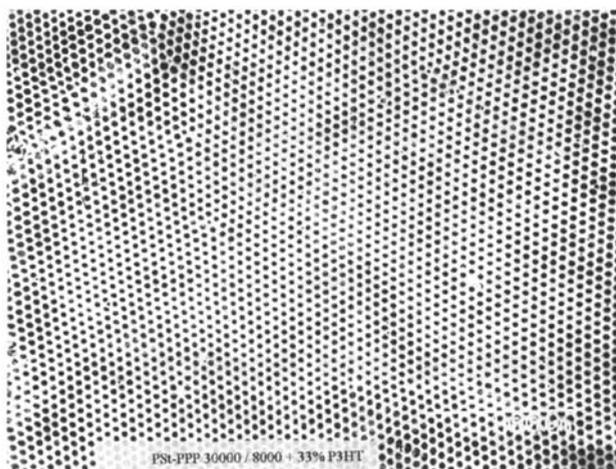


Fig. 4. ESM of an auto-organized film from a mixture of star polystyrene (7 branches with a molar weight = 10000 per branches) and 33% of poly-3-hexylthiophene.

films were easily doped by dipping in a solution of FeCl₃ in nitromethane. This p-type doping (an oxidation of the P3HT chain which becomes positively charged) is evidenced by a color change from red to black and a corresponding increase of the electrical conductivity from 10⁻⁹ S/cm to 10⁻³ S/cm.

3. Mechanism of Formation

The details of the formation process of this organized morphology are not yet perfectly clear but recent results have revealed some general trends. It is well known that the classical wet process for membrane preparation^[1] is the following: a non-solvent diffusing into a concentrated polymer solution induces a phase separation, the volatile solvent evaporates leaving a disordered mixture of polymer and non-solvent. The final evaporation creates the porous morphology in the dry polymer.

In our case a drastic difference comes from the fact that the non-solvent is introduced by a condensation process. Microscopic examination shows clearly the quick formation of a number of droplets, at the surface of the evaporating solution, due to water condensation. We have recorded the diffraction patterns produced, during this evaporation process, by illuminating the solution bottom with a laser (632 nm) perpendicular to the surface. A rapid sequence of moving diffraction rings and spots was observed. They have still to be interpreted in detail but the whole process is over in about 10 seconds.

Two special physical properties of the system "star-like PS/CS₂/water" are expected to play a crucial role:

- Solutions of atactic (non-stereoregular) polystyrene in CS₂ are known to gel readily upon cooling provided the concentration is high enough.^[9] This gelation is even more pronounced with star-shaped polystyrenes.^[10]
- Water is lighter than CS₂ (density = 1.26) and does not wet these carbon disulfide solutions so that water condensation occurs at the surface through droplets as observed in the "breath figures" obtained by blowing on a cold surface.^[11] The layer of polymer solution around the droplets of water and the observed formation of a polymer film at the interface prevents their coalescence, so that a hexagonal close packing of these spheres could take place leading to the observed morphology. It should be noted that the formation of this polymer film at the interface is instantaneous with block copolymers while nothing is visible with linear polystyrene.

These ideas are also supported by spreading experiments of linear polystyrene and CS₂ solutions of PS-PPP block copolymers on water and by interfacial tension measurements. A noticeable decrease of interfacial tension between CS₂ polymer solutions and water for sufficiently concentrated solutions of PS-PPP block copolymer has been observed while this effect is weaker with linear PS. This could be one of the key parameters which induces the size regulation of droplets and their organization.

4. Applications

The potential domain of applications of these films is very large and has still to be explored. The most obvious application is optimization and control of membrane geometry. For the moment some limitations may come from the limited mechanical properties of the films. Indeed, due to the compact star structure of the polymers, these films are rather brittle and they are hardly self-standing.

Another very interesting application concerns the potential optical properties of such structures, especially if the 3-D organization of cavities can be fully controlled. New properties can be expected, such as a "photonic band gap" (which is, to a first approximation, the equivalent in optics of the "electronic band gap", and represents one of the basic characteristics of semiconductors).^[12]

These films, with closed pores, could be used as thermally insulating materials on a microscopic scale. After improvement of mechanical properties the well known lightness and rigidity of the honeycomb structure could also be useful in acoustic devices (loud speakers etc.).

Specific applications are possible in cell biology as the size of the open superficial pores is in the range of that of biological cells. The electroconductive self-organized films prepared either from a block copolymer containing a conduct-

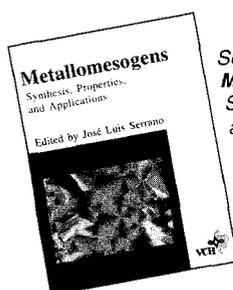
ing polymer sequence (PPP or PT) or by addition of soluble conducting polymer can be used, after doping, as electrodes for electrodeposits leading to new structured materials.

5. Conclusions

Self-organized honeycomb films can be now prepared from a variety of star polystyrenes, micellar polystyrenes and block copolymers, either pure or mixed with a suitable amount of other linear polymers. It is a challenge to find other "polymer/solvent/non-solvent" systems without polystyrene which lead to similar morphologies.

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Metallomesogens - Synthesis, Properties, and Applications



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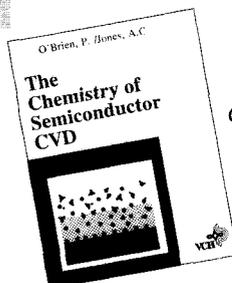
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