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The influencing factors on the macroporous formation in polymer films by water droplet templating

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Abstract

Regular micrometer-size porous polystyrene film is prepared by water droplet templating, i.e. breath figures are stabilized by the polymer in solution and thermocapillary flow arranges them into ordered packing. The influences of polystyrene molecular weight, solvent properties, and the relative humidity of atmosphere on the pattern formation and hole sizes are investigated. Two different kinds of hole packing fashion are also observed and their formation mechanisms are discussed.

Keywords: Breath figures; Macroporous films; Water droplet templating

1. Introduction

Macroporous polymer films have received increasing interest in recent years because of their potential applications in photonic and opto-electronic devices, catalysis, and membranes, just name a few [1–3]. Usually, for species that do not self-assemble into the desired structures, a templating approach is beneficial, in which the architecture and the characteristic length scales of the system are determined by those of the template. These templating methods include using colloidal crystals [4,5], microphase-separated block copolymers [6,7], and polymers with rod-coil structure [8], etc. In these methods, the organic templates are eventually removed by calcinations or solvent extraction leaving behind the porous skeleton.

Recently, a simple method that utilizing the condensation of monodisperse water droplets on polymer solution was used to prepare honeycomb macroporous films as pioneered by François et al. [9–12]. The preparation method consisted in evaporating a layer of solution spread on a flat support under a flow of moist gas. When solvent and water droplets evaporated completely, an ordered honeycomb array of holes was formed in the solid polymer surface. They found the honeycomb morphologies were obtained with polystyrene block copolymers, star-like homopolystyrenes and linear polystyrenes with a polar terminal group. These polymers self-organized into spherical-shaped structure in carbon disulfide, which was believed to be a determinant element in the formation process. Subsequently, Srinivasarao et al. [13] further investigated this method and prepared 2D and 3D ordered macroporous layers depending on the solvent density with respect to the density of water. They also gave a vivid model for the formation of the regular structure based on thermocapillary convection. Shimomura et al. [14–20] photographed the dynamical movement of the rearrangement of water droplets during honeycomb pattern formation and used different kinds of compounds including organic–inorganic hybrid materials [15], amphiphilic copolymers [16–18], metalorganic [19], and saccharide-containing polymers [19] for patterning. Additionally, two kinds of substrates (solid glass slide and water surface) were used to prepare different porous films [20].

While many studies on the hole pattern formation have been proceeded, various influencing factors on the porous formation process are not studied schematically. In this paper, we try to investigate the influences of polymer molecular weight, solvent properties, and humidity etc. on the pattern formation and hole sizes and gain a better understanding of the formation mechanism. Polystyrene

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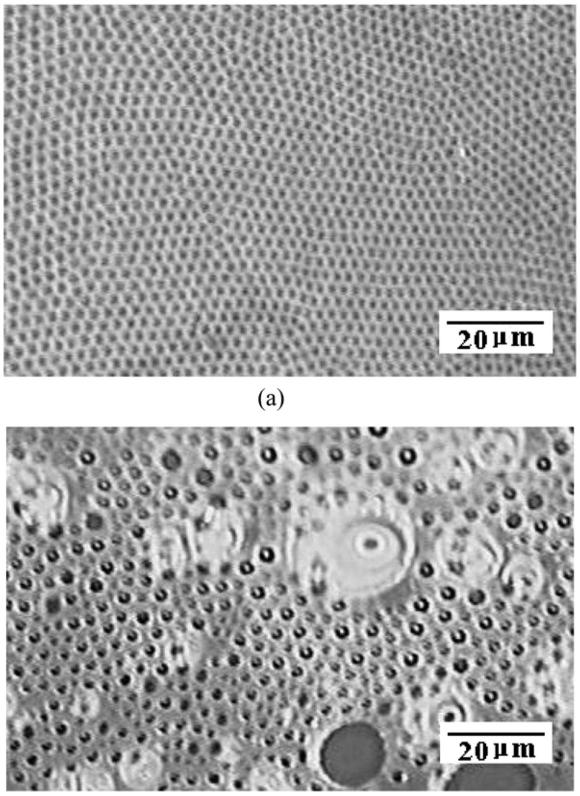
with different molecular weight and four different solvents are studied. The humidity of atmosphere is found to be the decisive factor to control the hole size. In addition, two different kinds of hole packing mode are observed after the water droplets templating process and their formation mechanisms are also discussed.

2. Experimental details

Polystyrene with three different molecular weight ($M_w = 1970$k, 223.2k, 29.3K) were purchased from Aldrich. It must be emphasized that all the used linear polystyrenes have no any polar end groups. To prepare ordered macroporous polymer film, several microliters of polymer solutions (1 wt%) were cast onto the glass substrate at room temperature. The carrier nitrogen gas was bubbled through distilled water and sent with water vapor onto the solution surface. The gas flow was controlled by a needle valve and measured with a flow meter. The relative humidity, which was controlled by changing gas velocity, was monitored with a hygrometer. The polymer solution started to evaporate and water vapor condensed onto the solution surface simultaneously. After complete evaporation of the solvent, the film morphology was investigated by optical microscopy (XJX-2, Nanjing, China) and atomic force microscopy (SPI3800N, Seiko Instruments Inc., Japan).



(a)

(b)

Fig. 1. Optical micrographs of hole patterns in PS films with different M_w. (a) Ordered honeycomb structures in PS ($M_w = 223.2$k) film. (b) Disordered holes with polydisperse sizes in PS ($M_w = 29.3$k) film. Both PS are dissolved in toluene with typical concentration 1 wt% in solution.

3. Results and discussion

3.1. Influence of molecular weight on the pattern formation

Polystyrene with three different molecular weight was dissolved in toluene respectively, with a typical concentration in solution 1% by weight upon casting a drop of PS toluene solution onto a glass slide in a humid atmosphere (about 50% r.h.) with nitrogen flow across the surface, all the three solution surface turned turbid due to emulsification while a little difference existed. The thickness of PS ($M_w = 1970$k) film was much thicker than the other two PS films. When viewed with optical microscopy (OM), the morphologies of three PS films were obviously different. Highly ordered honeycomb structures could be seen clearly in PS ($M_w = 223.2$k) film (Fig. 1(a)), which had a typical depth of 700 nm, an uniform diameter of ~2.0 μm and an interval of 2.6 μm between the adjacent holes further measured by atomic force microscopy (AFM). While for PS film with $M_w = 29.3$k, disordered holes with a relatively broad size distribution were produced (Fig. 1(b)). Almost no holes were observed in PS film with $M_w = 1970$k.

At this point, an obvious question arises: Why are the holes so ordered in PS with $M_w = 223.2$k film compared with the other two? It has been proved that polymer precipitation is a key element in producing regular hole pattern [14]. The M_w of polymers determines the solution viscosity upon other uniform conditions. When the M_w is comparably low, the solution viscosity is too low to encapsulate the droplets or prevent their coalescence, resulting in the formation of disordered membranes. While high M_w leads to highly viscous polymer solution and water droplets even cannot sink into it due to resistance before evaporating completely, resulting in few holes in PS films thereby. In addition, the convection is proved to locally arrange the droplets in well-ordered packing [13,21]. While as the solvent evaporates, the polymer solution becomes viscous which weakens the convection. With the increasing viscosity of the system, the convection patterns in thin polymer solutions disappear. Only appropriate viscosity like that of PS ($M_w = 223.2$k) toluene solution is achieved, monodisperse water droplets condense on the solution surface. Then polymer stabilizes the droplets by attractive interaction and inhibits their coalescence [10,18], resulting in highly uniform size of holes after water droplets evaporate completely. Therefore, the proper M_w of the polymer is believed to be an important factor in the process of regular hole formation, since disordered membranes or films without holes are obtained from low M_w or high M_w polystyrene solutions.

3.2. Influence of solvent properties on the pattern formation

In the second series of experiments, PS ($M_w = 223.2$k) was dissolved in four different solvents: toluene, chloroform ($CHCl_3$), carbon disulfide (CS_2), and tetrahydrofuran (THF) with a typical concentration 1% by weight. Fig. 2 shows a series of OM images of PS films prepared at different solvents (60% r.h.). Similar to the PS/toluene solution, regular hole patterns can be easily prepared from the PS/$CHCl_3$ solution (Fig. 2(a)). On the other hand, attempts to prepare ordered hole morphology from PS in CS_2 (Fig. 2(b)) and THF (Fig. 2(c)) solvents under other identical conditions were unsuccessful.

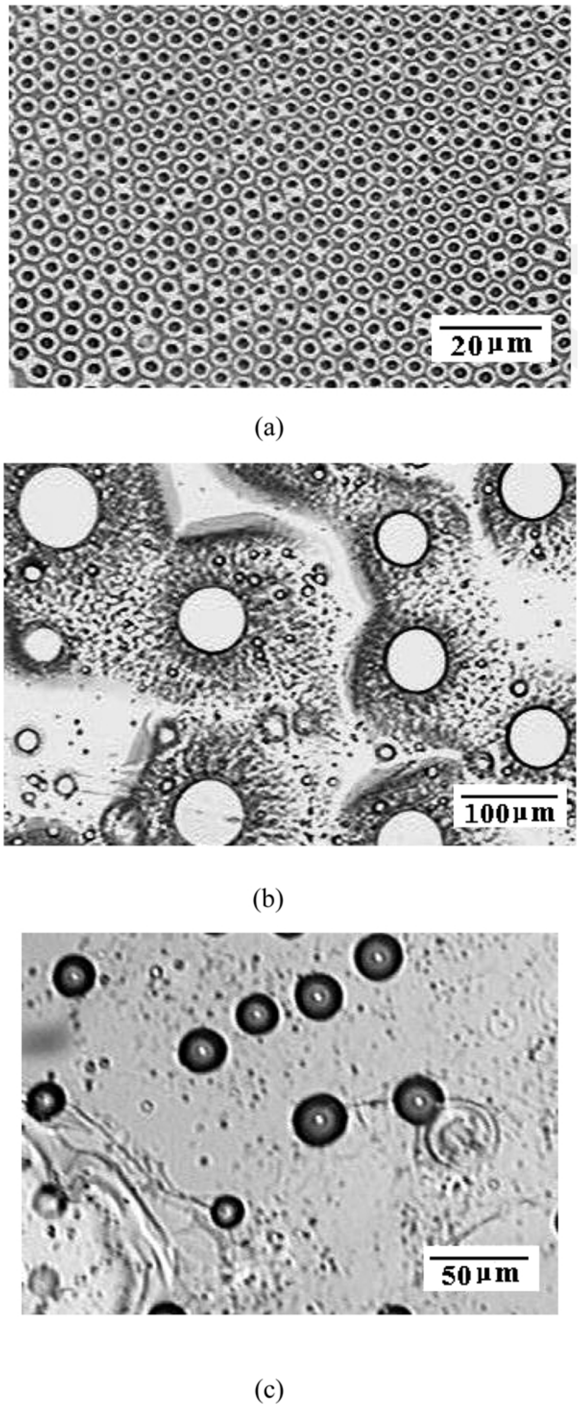


Fig. 2. A series of optical micrographs of PS ($M_w = 223.2$k, 1 wt%) from different solvents. (a) OM image of PS film from $CHCl_3$. (b) OM image of PS film from CS_2. (c) OM image of PS film from THF.

Another question then arises. What role does the solvent play in the process of pattern formation? To answer this question, the physical properties of solvents used are investigated (Table 1). The major differences between various solvents are their different evaporation rate and the droplets-solvent interactions. Because evaporation rates depend mostly on the vapor pressure above the liquid and next on the molecular weight of solvents, usually higher vapor pressure and lower molecular weight lead to faster evaporation. From Table 1, CS_2 evaporates fastest and the second is THF. In fact, during the experiments, we note that the evaporation of CS_2 and THF is indeed much faster than that of toluene and $CHCl_3$. Fast evaporation process induces a large perturbation of the system in a non-equilibrium state. In this case, the solvent may completely disappear from the system before water droplets form regular packing. In addition, water and THF are miscible with each other. When water droplets condense onto the PS/THF solution, they are soon dissolved into THF and thus no holes form after the complete evaporation of water and THF. François et al. also obtained disordered membranes from usual linear polystyrenes in CS_2, while regular hole structure were obtained in star-polystyrenes, associative polystyrenes (linear polystyrene chains with a polar terminal group able to associate in non-polar solvents such as CS_2) and polystyrene block copolymers. Therefore, polymers capable of association into spherical shape in used solvent were believed to be a determinant element in the formation of honeycomb structure [10,11]. Compared with their viewpoints, our results showed a little difference. Linear polystyrene without any polar end group also led to ordered structures in toluene and $CHCl_3$ solvents, in which polystyrene did not form aggregates like micelles. Accordingly, it was concluded that a special spherical shape of polymers in solvents was not necessary.

3.3. Influence of atmospheric humidity on the hole size

The PS ($M_w = 223.2$k, 1 wt%) toluene solution was used to investigate the influence of the relative humidity on pattern formation. To control the relative humidity above the polymer solution, nitrogen was passed through the flow

Table 1
Physical properties of the used solvents (20 °C)

	Toluene	$CHCl_3$	THF	CS_2
Density (g/cm^3)	0.867	1.489	0.889	1.248
Surface tension (mN/m)	28.53	27.14	26.4	32.25
Vapor pressure (KPa)	2.67	21.28	23.46(25 °C)	39.24
Molecular weight	92.13	119.38	72.11	76.14

meter with speeds varying from 0 to 1 l/min, resulting in the humidity ranging from 40 to 95% r.h. Ordered holes array could be found in PS films under controlled large range of relative humidity between 46 and 90% r.h. (Fig. 3(a)), beyond this range randomly distributed holes with broad size distribution were formed. The reason is at high humidity (>90% r.h.), too many water droplets condense onto the solution surface thus coalescence of some water droplets cannot be avoided, resulting in polydisperse hole size distribution. Size polydispersity disrupts order formation, and approximately 10% polydispersity is the upper limit for regular pattern formation [22]. While evaporation at lower humidity gives no turbid top layer and leads to transparent polymer films. In the range of 46–90% r.h., the regular hole sizes are found to linearly increase with increased humidity (Fig. 3(b)).

3.4. Mechanism of pattern formation

The formation process of this ordered morphology and its formation mechanisms have been widely investigated. It has been proved that the structures are formed by a templating mechanism, water droplets condense onto the solution surface and act as the vanishing honeycomb template after evaporation. The condensation phenomenon belongs to 'breath fingers', which represent the patterns form when a cold solid or a liquid surface is contacted with moist air [23, 24]. Compared with the solid surface, condensation onto a liquid surface can modify the interactions between droplets because the substrate is locally mobile and curved. Steyer et al. [25] have suggested the growth of breath figures on liquids evolves through three stages. In the initial stage, droplets grow as isolated objects with weak interdroplet interactions and the surface coverage is low. The average diameter D of droplets is increased with time t followed by the growth rule $D \sim t^a$, $a \approx 1/3$. The intermediate stage is characterized by maximal surface coverage. Water droplets are separated by liquid film, giving rise to a short ranged hard-sphere-like interaction. This interaction leads to uniformity in the size of droplets and the distance between them in some degree. The late stage is represented by constant surface coverage and coalescence between droplets dominates. The growth rule is $D \sim t^a$, $a \approx 1$. In our case, the breath figures were captured by the PS in solution thus coalescence was avoided. It can be proved from a comparative experiment that breath figures occurred on a surface of pure solvent without polymer, a turbid surface emerged too. However, nothing was left on the substrate when the solvent evaporated completely. Here, a typical initial stage of droplets condensation was given in Fig. 4, which was characterized after the evaporation of toluene solvent. The individual hole arrays formed at low coverage are well-ordered, but the randomly distributed neighboring arrays are not correlated. Since shape, periodicity and regularity of holes are determined by the corresponding water droplets structure, it is clear from these results that

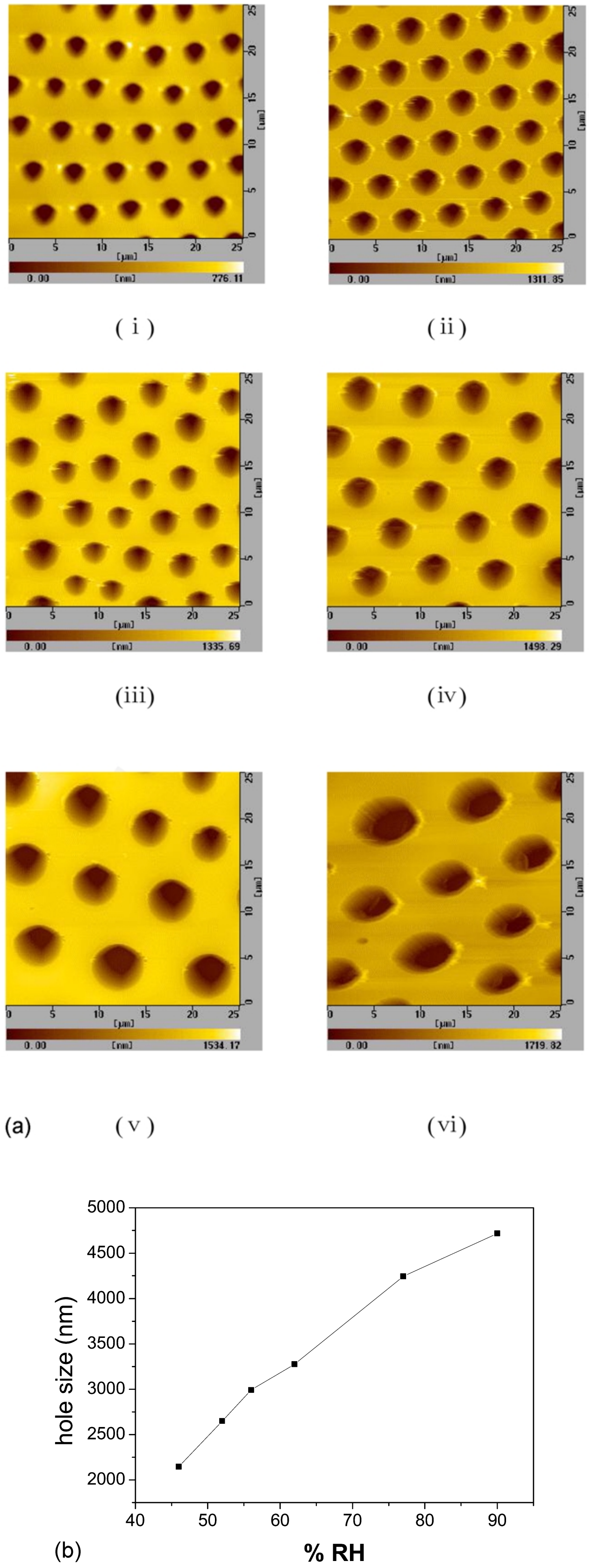


Fig. 3. (a) Relative humidity dependence of the hole sizes of PS toluene solution. Higher humidity leads to larger holes from the AFM images. The relative humidity is (i) 46%, (ii) 52%, (iii) 56%, (iv) 62%, (v) 77%, (vi) 90% r.h. (b) The hole sizes are found to linearly increase with increased humidity.

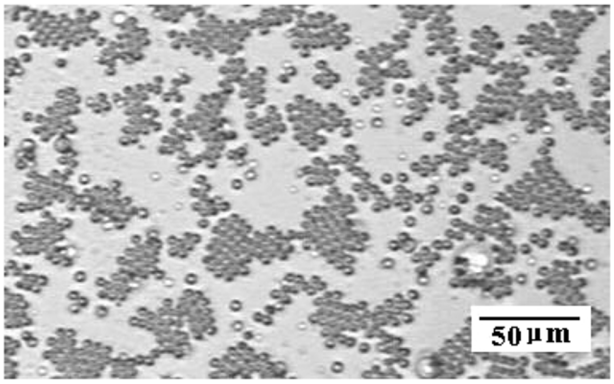


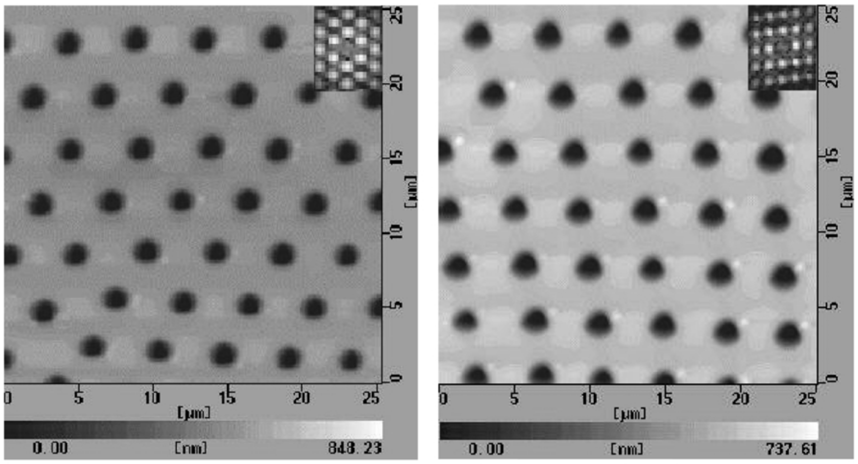
Fig. 4. Optical micrographs of the initial stage of water droplets condensation after the evaporation of water and toluene solvent. The floating monodisperse water droplets tend to aggregate and form ordered islands, resulting in well-ordered array separated from the others.

upon condensation, a few water droplets arrange themselves into islands with ordered structures. The presence of ordered structures at low coverage implies that the droplets are mobile on the solution surface and tend to aggregate to ordered packing due to the existent attractive surface forces between condensed water droplets. With more and more water droplets condense onto the solution surface, more and more islands form. The geometry of islands can be very different and the islands attract each other in a much stronger way than the single water droplets because the attractive force between the islands is proportional to the sixth power of their radii [26]. Due to evaporation, the layer of solution is subjected to a temperature gradient between the solution surface and the substrate that then induces a surface tension gradient. Because surface energy is minimized by decreasing the higher surface tension areas corresponding to cooler region, the solution with water droplets on its surface is then pulled from the hotter area to the cooler area, driving the thermocapillary flow through Marangoni [27–29] or Rayleigh [30,31] convection. In our case for films thinner than ca. 1 mm, Marangoni instabilities govern the convection and arrange the droplets in well-ordered packing.

In the process of hole pattern formation, although the hexagonal arrangement of holes is the usual packing mode, holes in square arrangement do occur sometimes. Fig. 5 shows two kinds of hole packing mode, which is proved by Fast Fourier Transform (FFT) pattern in the inset of the image. As we know, the preferred packing of the spherical microdomains at equilibrium will be that which corresponds to the lowest free energy. Based on calculations, the hexagonal arrangement is the most stabilized packing mode [32]. Therefore, the optimum-covering lattice is hexagonal. The close adjacent droplets are attracted to each other by the lateral capillary force that causes dense hexagonal packing. No obvious explanations can be given to explain the different square arrangement. However, due to the influences of environmental temperature, the convective flow between the solution surface and interior, etc., water droplets are disturbed sometimes and thus arrange into another square packing. Similar square pattern was also observed by Karthaus et al. [15] through flowing the solution over an inclined substrate during solvent evaporation and water condensation. It was then explained from another point of view that a 1D aggregation of the water droplets into straight strings was followed by a combination of those strings to a 2D array having a square symmetry.

4. Conclusions

We have shown a facile approach to highly ordered macroporous polymer films with a monodisperse pore size.



(a) (b)

Fig. 5. AFM images of the regular structures in PS films. (a) Hexagonal hole structures in PS film. FFT pattern is given in the inset of the image indicating a perfect hexagonal arrangement of the holes. (b) Square hole structure in PS film with FFT pattern in the inset.

The structure discussed here may be useful for potential photonic bandgaps and patterned LEDs for instance. The beauty of this approach is its simplicity and high regularity. This water droplets-templated process only occurs in investigated toluene and $CHCl_3$ solutions, indicating that the solvent effect plays an important role. Polystyrenes with appropriate M_w do favor to this behavior due to the proper viscosity of solutions. A strong linear correlation between the atmospheric humidity and pore sizes has been demonstrated and higher humidity leads to larger pores. Two different kinds of hole packing are also observed due to the influence of environmental conditions.

Acknowledgements

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