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Self-assembly fabrication of ordered microporous films from a soluble polyimide modified by methyl groups based on Breath Figures

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ABSTRACT

A kind of soluble and low-molecular polyimide was obtained from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 3,3′-dimethyl-4,4′-diaminodiphenylmethane (DMMDA) with *N*,*N*-dimethylformamide (DMF) as solvent by a two-step method, and it could be dissolved both in strong polar solvents and in common low-boiling-point solvents. The ordered porous films were prepared by spreading the solution on solid substrate using water droplets as templates, and the pore size was about 1 μm. Furthermore, several influencing factors on the morphologies of the ordered pores, such as the concentration of the solution, solvents, and the solid substrates, were investigated. Fabrication of ordered microporous films from a kind of low-molecular polymer, with the number-average molecular mass (M_n) of 50433, was reported for the first time in this study. The results showed that the best-ordered pattern with strong periodicity, regularity, and a large, defect-free area could be formed from the polyimide with concentration of 50 mg/mL using dichloromethane as solvent and silicon as substrate.

Keywords: Polyimide; Soluble; Ordered micropores; Breath Figures; Self-assembly

1. Introduction

During the last few years, the scientific community has witnessed great interest in the study of microporous films due to their good prospects for application in the field of chemistry, biology, and life science, for example, they can be used as optical apparatus [1], chemical sensors [2], scaffolds in catalysis [3], and filters in separation [4]. However, the traditional methods, such as photolithography [5], microcontact printing [6], and selective etching [7], of fabricating microporous structure will be at the expense of destroying the templates, and the size of pore depends on the template so that it cannot be adjusted dynamically. A new method, named "Breath Figure," utilizing water droplets as templates to form ordered porous films, first described by François [8] aroused much attention. They cast the solution of

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polyparaphenylene in carbon disulfide onto a substrate in a high humid atmosphere, and after the solvent and water droplets evaporated completely, a film with regular honeycomb pores was obtained, and they believed that the water droplets condensed at the surface of the solution acted as the templates. This method is simple, economy and does not require additional removal of the template of water droplets.

Many polymer materials [9–11] have been used to prepare microporous films, all of which contain hydrophilic structures in their molecules to stabilize the water droplets that condense on the surface of the polymer solution. Polyimide materials have been widely researched for the past decade for their excellent thermal stability, mechanical, electrical, and solvent-resistant properties and are being widely used in the aerospace and electronic industries in the forms of films and moldings, whereas most polyimide are insoluble in volatile organic solvents and this limits their extensive applications, for example, in the film fabricating with water droplets as templates. In this study, we prepared a kind of low-molecular and soluble polyimide derived from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA)-and 3,3′-dimethyl-4,4′-diaminodiphenylmethane (DMMDA) and its intrinsic viscosity was 0.48 dl/g. BTDA contained carbonyl group and DMMDA had methyl in aromatic groups, both of which could increase the flexibility of the polyimide and ensured its solubility. Its physical properties were characterized. The porous films were simply fabricated by casting the polyimide solution onto a substrate under the humid atmosphere. Several influencing factors on the morphologies of the orderly pores, such as the concentration of the solution, solvents, and the solid substrates, were investigated.

2. Experimental

2.1. Materials

BTDA was purchased from J and K and dried before use. DMMDA was synthesized from our laboratory. *N*,*N*-Dimethylformamide (DMF) was supplied by Beijing Chemical Reagents Company and was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 Å). Water was purified by a Millipore system (Milli-Q, Millipore). *N*-Methylpyrrolidone (NMP), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), toluene, tetrahydrofuran (THF), acetic anhydride, and triethylamine (TEA) were analysis grade.

2.2. Polymer synthesis and characterization

The BTDA–DMMDA polyimide was synthesized by a two-step solution-imidization technique [12]. The number-average molecular weight and its distribution were determined by gel permeation chromatography (GPC2695, Waters, Milford) using THF as solvent. The glass-transition temperature (T_g) and melting temperature (T_m) were analyzed by differential scanning calorimeter (DSC200, Seiko, Japan) from 100 to 400˚C at a heating rate of 10 K/min. The loss 10 wt.% temperature and residue of this polymer were determined by Thermogravimetric analysis (TGA) performed on a TGA-2050 thermal analyzer (TA Instruments, New Castle, DE) at a heating rate of 10 K/min in 20 mL/min of N_2.

The solubility was determined with 1 g of BTDA–DMMDA in 9 g of solvent (10 wt.%) and put at room temperature for 24 h.

2.3. Film preparation and characterization

BTDA–DMMDA was first dissolved in the volatile organic solvents, and then, 50 μL of the solution was directly cast onto a substrate at room temperature in a chamber whose relative humidity was controlled at 90%. With the evaporation of the solvent and the condensation and final evaporation of the water droplets, the casting solution gradually turned milky, and a few minutes later, the porous film was formed. The surface morphology of the microporous films was characterized using scanning electron microscopy (JSM-6700F, JEOL, Tokyo, Japan) operated at 3 kV and 10 μA. The water contact angles of the substrates were tested on a contact angle meter (FACE CA-D, Kyowa, Kaimenkagaku Co.).

3. Results and discussion

3.1. Polymer characterization

The properties of BTDA–DMMDA are listed in Table 1. Its M_n of 50,433 indicates that this polymer has a relatively low molecular weight, so it is proved in this study that not only high-molecular polymers that are widely reported [13–16] but also the polyimide with low molecular weight can form ordered microporous films via Breath Figures method; moreover, it has a narrow distribution of 1.35. Its thermal properties were characterized with DSC and TGA. A glass transition was observed at 278˚C (glass-transition temperature, T_g), demonstrating the admirable rigidity of BTDA–DMMDA. TGA provided the decomposition temperature (T_d) of 512˚C and a 10 wt.% loss at 520˚C, showing its good thermal stability.

Table 1
Physical properties of BTDA–DMMDA

Polymer	M_n	M_w/M_n	T_g (℃)	T_m (℃)	T_d (in N_2/℃)	Loss 10 wt/% T (℃)	Residue (wt.%)
BTDA–DMMDA	50,433	1.35	278	380	512	520	49.5

The solubility was determined with 1 g of BTDA–DMMDA dissolved in 9 g of solvent (10 wt.%) at room temperature. The data are listed in Table 2. BTDA–DMMDA exhibits good solubility not only in polar organic solvents such as NMP, DMAc, DMF, and DMSO but also in common low-boiling-point solvents such as THF, CH_2Cl_2, and $CHCl_3$, which is attributed to the introduction of flexible methyl and carbonyl groups. So that it can be used in Breath Figures.

Table 2
Solubility of BTDA–DMMDA

Solvent	BTDA–DMMDA
NMP	S
DMAc	S
DMF	S
DMSO	S
THF	S
$CHCl_3$	S
CH_2Cl_2	S
m-Cresol	S
Toluene	I

S = soluble; I = insoluble.

3.2. Influence of solution concentration

The polymer concentration varied from 10 to 70 mg/mL to investigate the influence of the polymer concentration on pattern morphology. Fig. 1 shows the SEM images of the films prepared by BTDA–DMMDA/$CHCl_3$ solution using glass as substrate at a RH of 90%. It can be seen that ordered pores can be obtained when the concentrations ranges from 10 to 70 g/L and that the average diameter of pores has a slight decrease with the increase in concentration. It is reported that the pore size is inversely proportional to the concentration [17], that is $R = K/c$, in which K is a constant. But this theory is limited in an appropriate concentration range. When the concentration is excessively low, the solution viscosity is too low to

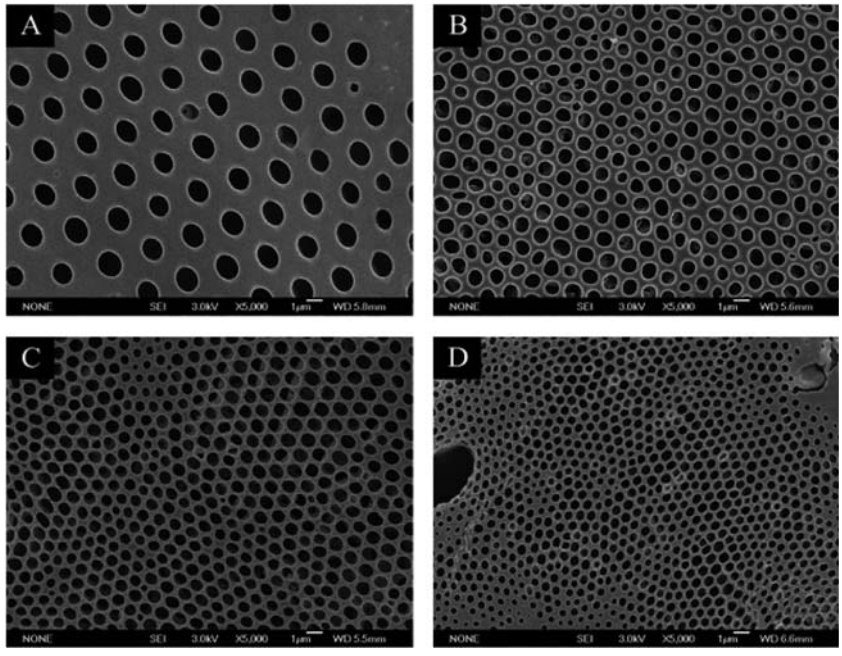


Fig. 1. SEM images of the porous structure in BTDA–DMMDA films prepared from different solution concentrations: (A) 10 mg/mL; (B) 30 mg/mL; (C) 50 mg/mL; (D) 70 mg/mL. Other conditions: spreading volume, 50 μL; substrate, glass plate; solvent, $CHCl_3$; relative humidity, 90%; temperature, 20 ℃.

encapsulate the droplets or prevent their coalescence, consequently resulting in the formation of disordered membranes (data not shown), as described by Shimomura [18]. While excessively high concentration leads to a highly viscous polymer solution, and water droplets can not even sink into it due to resistance before evaporating completely, thereby resulting in few holes in the films.

Table 3
Measurement results of contact angles of different substrates

Substrates	Oxide-coated Al	PE	Al	Si	Glass
Contact angles	112.3°	98.7°	80.4°	53.6°	25.3°

3.3. Influence of substrates

Mica, glass, and metal-coated glass slides and so on are all used as the substrates to fabricate porous polymer films, but how the substrates affect the pattern formation is still inconclusive. In this study, we select glass, aluminum, oxide-coated aluminum, silicon, and PE membrane to investigate the influence of substrates on pattern formation. Their contact angles of spreading water are tested and listed in Table 3, and it is clear that their hydrophilicity were different. Fig. 2 shows SEM images of the films

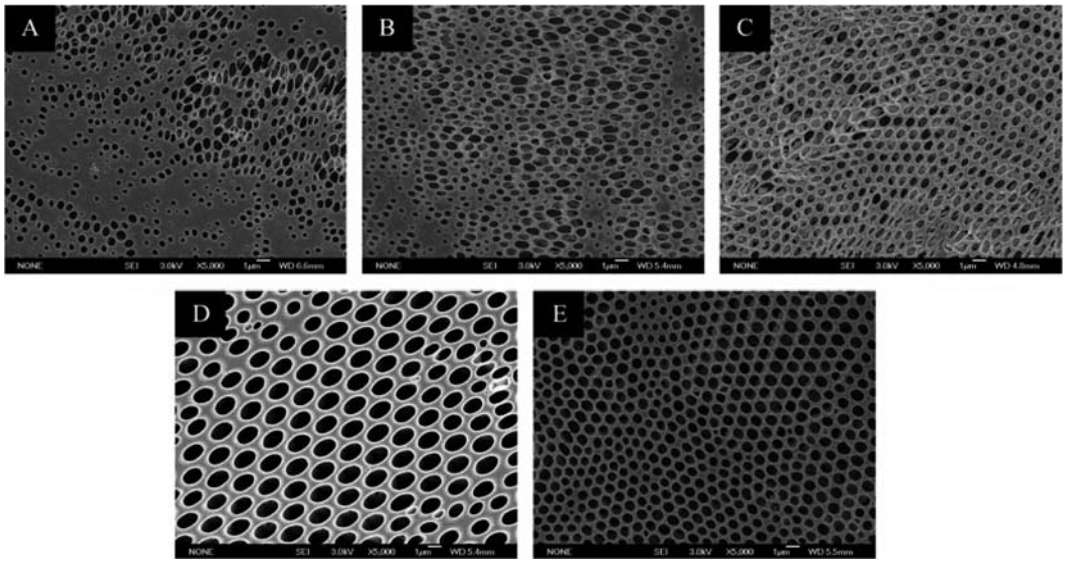


Fig. 2. SEM images of the porous structure in BTDA–DMMDA films prepared on different substrates: (A) oxide-coated Al, (B) PE, (C) Al, (D) Si, and (E) glass plates. Other conditions: polymer concentration, 50 mg/mL; spreading volume, 50 μL; solvent, $CHCl_3$; relative humidity, 90%; temperature, 20˚C.

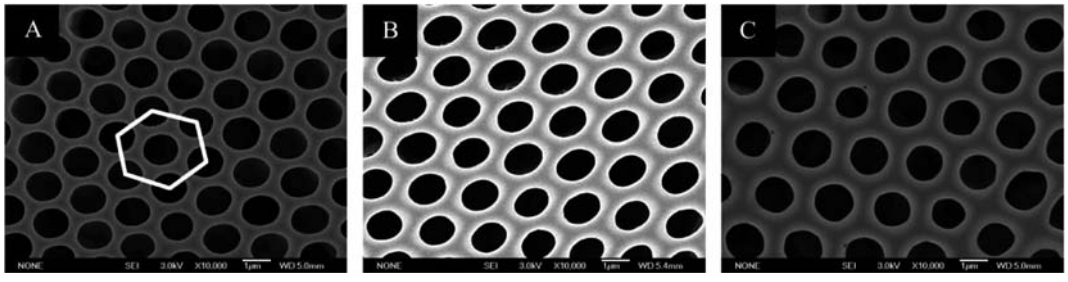
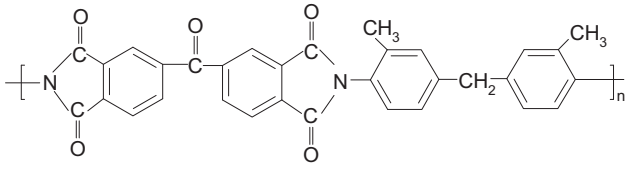


Fig. 3. SEM images of the porous structure in BTDA–DMMDA films prepared with different solvents: (A) CH_2Cl_2, (B) $CHCl_3$, (C) THF. Other conditions: polymer concentration, 50 mg/mL; spreading volume, 50 μL; substrate, silicon plate; relative humidity, 90%; temperature, 20˚C.



Scheme 1. The chemical structures of BTDA–DMMDA.

prepared by spreading BTDA–DMMDA/$CHCl_3$ solution (50 mg/mL) onto five kinds of substrates. As shown in Fig. 2, honeycomb structures are obtained on silicon and glass plates, although both of them displayed some imperfections, while attempts to prepare ordered porous films on the hydrophobic substrates are unsuccessful. The reason is that the water droplets are hard to be adsorbed onto the hydrophobic substrates, which makes its function as a steady template become weaker, so that the formation of highly ordered porous structure is unfeasible and that the more hydrophobic substrate, the more obvious phenomenon(Fig. 2A–C). In short, it is the hydrophilic substrates that are suitable to fabricate ordered microporous films.

3.4. Influence of solvents

It is a well-known fact that the solvent used in Breath Figures method must be of volatility. In this syudy, CH_2Cl_2, $CHCl_3$, and THF are selected to study the influence of the solvent on pattern formation. As can be seen in Fig. 3, all the solutions can fabricate orderly microporous films, but the porous structure formed with CH_2Cl_2 as solvent are more regular, $CHCl_3$ took second place and then THF. This is because CH_2Cl_2 volatilized fastest, and THF has the slowest evaporation rate. When the solvent volatilize faster, the water droplets will need less time to condense and maintain on the surface of the solution, which prevents the droplets from coalescing, and limits the imperfections. In addition, the surface tension is different for the solutions with different solvents, which decides whether the water droplets can stable and further influences the morphology of porous. In conclusion, the best-ordered pattern with typical hexagonal honeycomb structure (Fig. 3A) is obtained with CH_2Cl_2 as solvent for such a polymer (Scheme 1).

4. Conclusions

BTDA–DMMDA, a kind of soluble polyimide, was synthesized and characterized. This polymer had a relatively low molecular weight and exhibited excellent thermal stability and good solubility. Typical hexagonal honeycomb structure with 1 μm of pore diameter was obtained for such a polymer. Furthermore, several influencing factors on the formation of ordered microporous, such as the concentration of the solution, the substrates, and the solvents were investigated. The results showed that the best-ordered pattern with strong periodicity, regularity, and a large, defect-free area was fabricated by spreading 50 mg/mL of BTDA–DMMDA/CH_2Cl_2 solution onto silicon plate.

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