Formation of Honeycomb Films Based on a Soluble Polyimide Synthesized from 2,2′-Bis [4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane Dianhydride and 3,3′-Dimethyl-4,4′-diaminodiphenylmethane

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ABSTRACT: A soluble polyimide was synthesized from 2,2′-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA) and 3,3′-dimethyl-4,4′-diaminodiphenylmethane (DMMDA) by a two-step method, and it had good solubility both in strong bipolar solvents and in common low-boiling-point solvents. The BPADA–DMMDA polyimide was dissolved in chloroform ($CHCl_3$) and cast onto a glass substrate in a humid atmosphere. The BPADA–DMMDA/$CHCl_3$ solution easily formed honeycomb films. Some affecting factors, such as the polymer solution concentration, atmospheric humidity, and solvent volatility, were tested. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 618–623, 2008

Key words: films; polyimides; self-assembly; surfaces

INTRODUCTION

Porous polymer films with a perfect arrangement provide interesting properties for various potential applications. They can be used, for example, as filters in separation,[1] as building materials in tissue engineering,[2] and as scaffolds in catalysis.[3] Among those methods used for preparing micropatterned surfaces, the casting of polymer solutions under high humidity, as pioneered by François et al.,[4] has been famous in recent years. They cast a solution of poly(*para*-phenylene) in carbon disulfide (CS_2) onto a substrate in a highly humid atmosphere. After the solvent and water droplets had evaporated completely, a film with regular honeycomb pores was formed. Subsequently, many research groups have reported such a regular hexagonal microporous structure from the cast films of various polymers, including rod–coil block copolymers,[5] star polymers,[6,7] dendritic copolymers,[8,9] amphiphilic copolymers,[10,11] and hydrophobic polymers.[12,13]

Aromatic polyimide materials have been widely researched for the past decade because of their excellent dielectric, thermal, adhesive, and dimensional stability and are mainly used in the aerospace and electronic industries in the forms of films and moldings.[14–16] However, most commercial polyimides are usually insoluble in common organic solvents, and this limits their extensive applications. For this reason, it is difficult for them to fabricate honeycomb patterns with water droplets as templates. One of the successful approaches to increasing the solubility of polyimides is the introduction of flexible linkages into the polymer backbone, such as the ether (—O—),[17] isopropylidene [—C(CH_3)_2—],[18] or fluorated isopropylidene [—C(CF_3)_2—] groups.[19] They exhibit reasonable thermal stability and good mechanical properties.

Recently, we have reported a series of fluorinated polyimides and successfully fabricated regular porous films from these polyimides.[20,21] In generally, the price of fluorated polyimides is high and limits their further application. Therefore, it is necessary to replace fluorated groups with some cheaper flexible groups. In this study, we prepared another soluble polyimide derived from a bis(ether anhydride) containing flexible ether linkages and isopropylidene units, 2,2′-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA), and 3,3′-dimethyl-4,4′-diaminodiphenylmethane (DMMDA). BPADA contained ether and methyl groups, and DMMDA had methyl in aromatic groups, both of which could enhance the flexibility of the polyimide and ensure its solubility. Its structure and physical properties were

characterized. The honeycomb-patterned microporous films of this polyimide were prepared by the simple casting of its solution onto a glass substrate under controllable humid conditions. Some affecting factors, such as the solution concentration, atmospheric humidity, and solvent volatility, on the pattern regularity of the polyimide porous films were tested.

EXPERIMENTAL

Materials

BPADA and DMMDA were purchased from Shanghai EMST Corp. (Shanghai, China) and dried before use. Commercially available N,N-dimethylformamide (DMF; analysis-grade; Beijing Chemical Reagents Co., Beijing, China) was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 Å). Water was purified with a Milli-Q system (Millipore). Chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), 1,2-dichloroethane (1,2-$C_2H_4Cl_2$), acetic anhydride, and triethylamine (TEA) were used as received (analysis-grade; Beijing Chemical Reagents).

Polymer synthesis

A two-step solution-imidization technique was employed to synthesize the BPADA–DMMDA polyimide. A three-necked flask equipped with an addition funnel and an N_2 inlet was charged with a solution of DMMDA in DMF, and then BPADA was added all at once. The molar ratio and solid content of the BPADA/DMMDA mixture were 1 : 1 and 10–12 wt %, respectively. The reaction mixture was reacted for 8–12 h at room temperature in an N_2 atmosphere to yield a viscous poly(amic acid) solution. The chemical imidization was carried out with acetic anhydride and TEA at room temperature for 14–18 h. The reaction mixture was then added to an ethanol solution. The precipitate was collected, washed with water, and dried *in vacuo* at 160°C to obtain the solid polyimide.

^{1}H-NMR [400 MHz, 25°C, dimethyl sulfoxide-d_6 (DMSO-d_6), δ, ppm]: 1.65–1.69 [s, 6H, $Ar_2C(CH_3)_2$], 2.22–2.25 (s, 6H, Ar—CH_3), 4.03–4.05 (s, 2H, Ar—CH_2—Ar), 7.11–8.08 (20H, ArH). IR (υ, cm^{-1}): 2947–2931 (asymmetric acyclic C—H stretch), 2873–2855 (symmetric acyclic C—H stretch), 1780 (asymmetric C=O stretch) 1725 (symmetric C=O stretch), 1601–1490 (aromatic C=C stretch), 1380 (C—N stretch), 1244 (asymmetric C—O stretch), 726 (imide ring deformation).

Film preparation

The honeycomb films were prepared with the following steps. BPADA–DMMDA was dissolved in one kind of volatilized solvent and formed a BPADA–DMMDA solution with a series of concentrations. Then, 100 μL of the BPADA–DMMDA solution was cast onto a glass substrate at room temperature in a chamber whose relative humidity could be controlled (80–95% relative humidity). The solvent started to evaporate, and condensed water droplets were deposited on the solution surface because of evaporative cooling. The water droplets were packed regularly by lateral capillary forces among themselves. The transparent polymer solution became turbid along with the solvent evaporation because of emulsification. After complete evaporation of the solvent and water, a thin, opaque film with a porous, honeycomb-like structure remained.

Measurements

^{1}H-NMR spectra were registered with a Varic ECA-600 spectrometer (JEOL Ltd., Japan) with DMSO-d_6 as a solvent. Fourier transform infrared (FTIR) spectroscopy analysis was performed on Nicolet IR560 spectrometer (Nicolet, Madison, WI). Gel permeation chromatography (GPC) analysis of the polymer was performed with tetrahydrofuran (THF) as the eluant. The glass-transition temperature was determined by differential scanning calorimetry (DSC; DSC200, Seiko, Japan) from 100 to 400°C at a heating rate of 10 K/min. Thermogravimetric analysis (TGA) was 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 BPADA–DMMDA in 9 g of solvent (10 wt %) at room temperature, which was then mechanically stirred in nitrogen for 24 h.

The surface morphology of the microstructured films was characterized with scanning electron microscopy (SEM) carried out on a JEOL SEM4500 at a 30-kV accelerating voltage and 10 μA.

RESULTS AND DISCUSSION

Polymer characterization

Scheme 1 shows the synthetic route for the BPADA–DMMDA polyimide by the conventional two-step polymerization method, which involved ring-opening polyaddition forming poly(amic acid) and subsequent chemical cyclodehydration. The complete imidization of the polyimides was confirmed by FTIR spectra. The absorptions at 1780 and 1725 cm^{-1} were assigned to asymmetric and symmetric C=O stretching vibrations in amide groups, and that at 726 cm^{-1} was attributed to imide ring deformation, with the C—N stretching peak at 1380 cm^{-1}, but there were no amide groups near 3360 (N—H
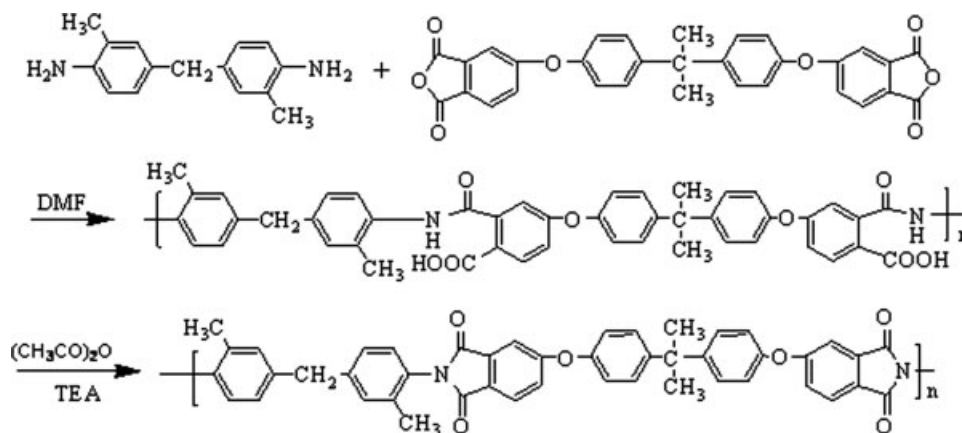
Scheme 1 Synthesis route for BPADA–DMMDA.

stretching) or 1650 cm^{-1} (amide C=O strength); this indicated that BPADA–DMMDA had been fully imidized. Moreover, all hydrogen peaks in ^{1}H-NMR were in good agreement with the proposed polymer structure. The aromatic protons were detected around 7.1–8.1 ppm, depending on the position in the aromatic ring. The sharp single peak observed at about 1.6 ppm meant the methyl in isopropyl. Another single peak at about 2.2 ppm meant the methyl in the aromatic ring. The peak at about 4.0 ppm was assigned to the hydrogen in methylene.

The GPC analysis based on linear polystyrene standards gave a weight-average molecular weight of 145,900 and a relatively narrow polydispersity of 1.84 for BPADA–DMMDA (Table I). Its thermal properties were characterized with DSC for testing the glass-transition temperature and with TGA for the decomposition temperature (Table I). Thermal behavior data for BPADA–DMMDA are also summarized in Table I. A glass transition was observed at 253°C (glass-transition temperature), demonstrating the admirable rigidity of BPADA–DMMDA. TGA showed a 10 wt % loss of BPADA–DMMDA at 507°C (decomposition temperature), showing its good thermal stability.

The solubility was determined with 1 g of BPADA–DMMDA dissolved in 9 g of solvent (10 wt %) at room temperature. Table II summarizes its solubility. BPADA–DMMDA exhibited good solubility in polar organic solvents such as N-methylpyrrolidone (NMP), dimethylacetamide (DMAC), DMF,

and DMSO and in common low-boiling-point solvents such as THF and CHCl$_3$. Because of the incorporation of flexible groups into the polymer, the polyimides exhibited excellent solubility toward test solvents.

Influence of the concentration

The process of forming the honeycomb films can be described as follows. First, water droplets condensed on the surface of the solution because of cooling by solvent evaporation. Second, because of the incompatibility of the organic solvent and water as well as the hydrophilic/hydrophobic balance of the polymer solution, water droplets were closely packed at the surface of the solution. Third, after the water and solvent evaporated completely, honeycomb films were prepared.

Figure 1 shows the SEM images fabricated from various BPADA–DMMDA/CHCl$_3$ solution concentrations (1, 5, 15, and 30 g/L). As shown in Figure 1(B–D) (the concentrations were 5, 15, and 30 g/L, respectively), honeycomb structures were clearly formed, and the arrangement of the pores was regular, whereas Figure 1(A) (1 g/L) exhibits a broad pore size distribution and a disordered arrangement. The average diameter of the pores decreased from
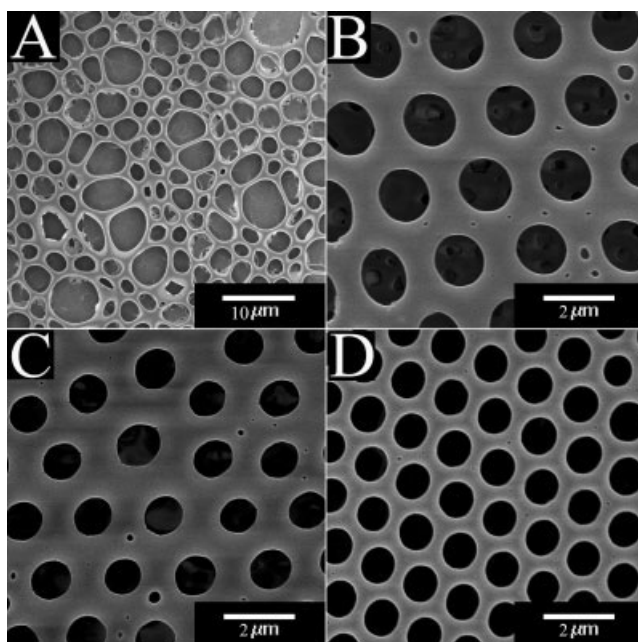
TABLE I
Physical Properties of BPADA–DMMDA

Polymer	M_w	M_w/M_n	T_g (°C)	T_d (°C)
BPADA–DMMDA	145,900	1.84	253	507

M_w = weight-average molecular weight; M_n = number-average molecular weight; T_g = glass-transition temperature; T_d = decomposition temperature.

TABLE II
Solubility of BPADA–DMMDA

Solvent	BPADA–DMMDA
NMP	+
DMAC	+
DMF	+
DMSO	+
THF	+
CHCl$_3$	+
CH$_2$Cl$_2$	+
1,2-C$_2$H$_4$Cl$_2$	+
MeOH	−

+ = soluble; − = insoluble.

Figure 1 SEM images of the porous structure in BPADA–DMMDA films prepared with different solution concentrations: (A) 1, (B) 5, (C) 15, and (D) 30 g/L. The temperature was 20°C, the relative humidity was 95%, and the spreading volume was 100 mL.

4 to 0.9 μm with the concentration increasing from 1 to 30 g/L.

It was proved[22,23] that water was indeed responsible for the regular structure in which monodispersed water droplets were closely packed in a hexagonal arrangement and acted as a template around which the polymer assembled. The capacity of the polymer to precipitate at the solution/water interface was a key parameter in the establishment of the honeycomb morphology. We previously reported[20,24] that some polymer molecules could gather on the surface of the solution and form a thin surface film. This thin surface film could stabilize water droplets, and

this was important for pattern formation. Only the thin surface film had appropriate strength that could stabilize the water droplets and fabricate regular structures. The solution concentration could influence the strength of the thin surface film easily. When the concentration of the polymer solution was too low, the strength of the surface thin film was weak because few molecules were contained in the solution. Neighboring water droplets could easily coalesce and resulted in an irregular pattern [Fig. 1(A)]. The strength of the thin surface film was strong enough to stabilize water droplets with the concentration increasing, leading to more regular patterns [Fig. 1(B)]. When the solution concentration was continuously enlarged, most of the polymer solutions could not form regularly patterned films because of too many polymer molecules gathered on the surface of the solutions.[4–11] These molecules not only fabricated a compact surface skin but also increased the solution viscosity; both prevented water droplets from immersing into the solution and therefore led to an irregular arrangement of pores or fewer pores on the film. However, BPADA–DMMDA still could fabricate a honeycomb pattern at high concentrations (15 and 30 g/L). This should be attributed to the hydrophobic property of BPADA–DMMDA. We previously reported[12] that poly(phenylene oxide) (PPO) could form a regular microporous film in a large range of solution concentrations (from 2 to 70 g/L) and that the pore size was almost equal when the concentration varied from 5 to 30 g/L. We believed that this phenomenon was caused by the hydrophobic property of PPO. Just like PPO, BPADA–DMMDA also was a linear polymer and contained many hydrophobic groups in its molecule. This character determined that even though there were a lot of BPADA–DMMDA molecules in the solution, the amounts of the molecules that could gather on the surface of the solution were limited. Therefore, the strength of the surface film
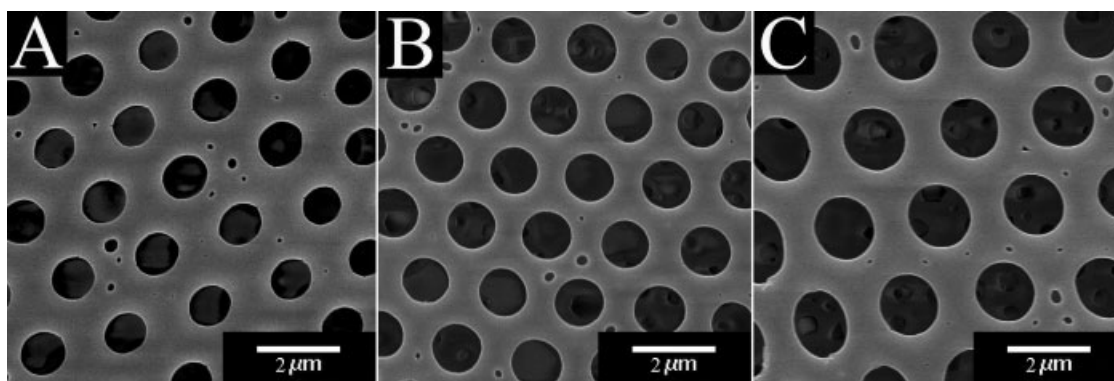
Figure 2 SEM images of the porous structure in BPADA–DMMDA films prepared with various humidities: (A) 80, (B) 85, and (C) 95%. The temperature was 20°C, the concentration was 5 g/L, and the spreading volume was 100 mL.
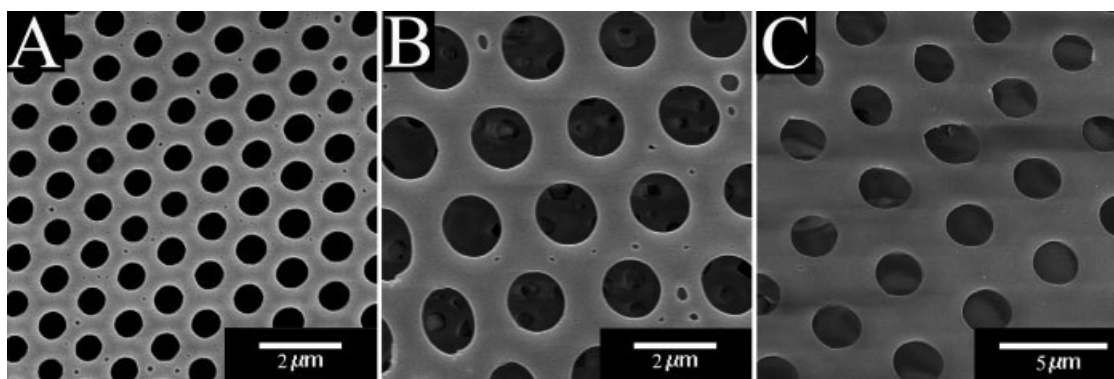
Figure 3 SEM images of the porous structure in BPADA–DMMDA films prepared with different solvents: (A) CH_2Cl_2, (B) $CHCl_3$, and (C) $1,2-C_2H_4Cl_2$. The temperature was 25°C, the concentration was 5 g/L, the relative humidity was 95%, and the spreading volume was 100 µL.

did not change much at the concentration of 30 g/L, which was suitable for the fabrication of regular pore structures.

Influence of the humidity

To investigate the influence of the relative humidity on pattern formation, a BPADA–DMMDA/$CHCl_3$ solution (5 g/L) was used to fabricate porous polymer films, other conditions being kept constant. The humidity was set to 80, 85, and 95%, respectively. As shown in Figure 2, the pore size enlarged from 1.0 to 1.4 µm with an increase in the humidity. Moreover, the pores were more regular as the humidity increased. The two-dimensional array of water microspheres was a template for the porous structure of the honeycomb film, and the size of a water microsphere was one of the determining parameters of the pore size. The humidity of the atmosphere influenced the water condensation at the air–polymer solution interface and, consequently, affected the pore size and regularity of the micropore arrangement. It is safe to say that high humidity was needed to form orderly porous films for this polymer. The regularity of the water droplet arrangement at high humidity was best in comparison with those at others. Evaporation at low humidity (<80%) gave nearly no pores on the polymer film.

Influence of the solvent volatility

CH_2Cl_2, $CHCl_3$, and $1,2-C_2H_4Cl_2$ were selected to further study the influence of the solvent volatility on pattern formation. CH_2Cl_2 evaporated fastest, and $1,2-C_2H_4Cl_2$ had the slowest evaporation rate. As can be seen in Figure 3, all the solutions could form honeycomb films, but the pore sizes were different. The size increased from about 0.7 to 3.5 µm along with decreasing solvent volatility. This was because the

solvent with a low evaporation rate evaporated slowly. The droplets therefore had more time to coalesce and grow on the surface of the solution, and this caused the pores to enlarge.

CONCLUSIONS

A soluble polyimide based on a dianhydride monomer (BPADA) and a diamine monomer (DMMDA) was synthesized and characterized. The obtained polyimide had excellent rigidity and thermal stability and especially exhibited good solubility. The BPADA–DMMDA/$CHCl_3$ solutions could form regular porous patterns in a large range of concentrations. Moreover, more ordered structures were obtained at high concentrations. Through changes in the relative humidity and the types of solvents, the pore size could be modified. A high humidity and a low volatilized solvent led to large pores.

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