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Formation of deformed honeycomb-patterned films from fluorinated polyimide

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Abstract

Fabrication of honeycomb-patterned films from one of the soluble fluoro-polyimides in a humid atmosphere was reported in this paper. This polyimide was synthesized from 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 4,4′-methylene dianiline (MDA) by two-step method. The obtained polyimide kept excellent rigidity and thermal stability, and especially, exhibited good solubility both in strong bipolar solvents and in common organic solvents. By blowing airflow across the surface of the deposited solution horizontally, the pores locating at the windward side of the film could change their morphologies from circle to ellipse, while the pores at the leeward side were almost kept their shapes. A detailed research about the pore deformation on various regions in a same film was carried out. At last, the differences in pattern formation between dynamic and static environment were tested, and the results showed that pores fabricated under flowing atmosphere were smaller and more regular than those formed under static condition.

Keywords: Honeycomb pattern; Soluble fluoro-polyimide; Deformed pore morphology

1. Introduction

Microporous films with honeycomb structures have attracted great interest due to their potential applications in chemical sensors [1], optical apparatus [2], biology [3], tissue engineering [4], and micrographics [5], etc. Recently, François et al. reported a new method of using water microspheres as templates to fabricate ordered porous structures [6–9]. They cast the solution of polystyrene–polyparaphenylene block copolymer in carbon disulfide onto a substrate in a high humid atmosphere. After the solvent and water droplets evaporated completely, a film with regular honeycomb pores was formed. For the convenience of manipulation, this method aroused much attention. Many polymer materials have been used to prepare honeycomb-like films, which includes rod–coil block copolymers [10,11], star polymers [12], dendritic copolymers [13,14], amphiphilic copolymers [15–17], hydrophobic polymers [18,19], etc.

Aromatic polyimide (PI) materials have been widely researched for the past decade due to their excellent dielectric, thermal, adhesive and dimension stability, etc. [20–23]. However, most commercial polyimides are usually insoluble in common organic solvents which limits their extensive application. For this reason, it is difficult for them to fabricate honeycomb patterns using water droplets as templates. Yabu et al. [24] solved this problem by using poly(amic acid)s/polyion complex to prepare honeycomb films in highly humid atmosphere and then by imidization of poly(amic acid)s to obtain polyimide films. However, imidization is a chemical treatment, which destroys the previous structures of the films. If one kind of soluble polyimides is used to directly fabricate regular porous films in humid atmosphere, the imidization process can be avoided. Semifluorinated polyimides are the suitable PIs due to their good solubility in organic solvents without forfeiture of thermal stability, etc. [25–30]. The industrialization of 6FDA greatly promotes the development of

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semifluorinated polyimide. Utilizing 6FDA as the monomer to polymerize polyimides is popular in recent years.

In the present study, we synthesized one of the soluble semifluorinated polyimides from 6FDA and MDA. The structure of the fluorinated polyimide was characterized by FT-IR, ^{1}H NMR and ^{19}F NMR. Then, 6FDA–MDA/$CHCl_3$ solutions were cast on glass substrates to form honeycomb films. By blowing airflow across the surface of the deposited solution horizontally, the pore structures can be deformed from circle to ellipse. Moreover, the differences in pattern formation between dynamic and static environment were also tested.

2. Experimental

2.1. Materials

2,2′-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (99%, Fluoro Chemical Co.) was recrystallized from acetic anhydride before use. 4,4′-Methylene dianiline (MDA) (98%, Beijing Chemical Reagent Co.) was recrystallized from ethanol. Commercially available solvents, *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*′-dimethylacetamide (DMAc), dimethyl sulphoxide (DMSO), tetrahydrofuran (THF), chloroform ($CHCl_3$), acetone and methanol (MeOH) were purchased from Beijing Chemical Reagent Corporation, and were of analytical grade. DMF was purified on distillation under reduced pressure over CaH_2 and stored over molecular sieves (4 Å). Water was purified by a Millipore system (Milli-Q, Millipore). Acetic anhydride and triethylamine (TEA) were used as received (analytical grade, Beijing Chemical Reagent Co.).

2.2. The synthesis of 6FDA–MDA

6FDA–MDA was synthesized from the two-step route. To a completely dried three-necked flask, equipped with a stirrer and a N_2 inlet, was added a solution of MDA in DMF and then 6FDA was added all at once. The mole ratio and solid content of 6FDA/MDA mixture were 1:1 and 10 wt%, respectively. The mixture reacted for 8 h at room temperature in N_2 atmosphere, yielding a viscous poly(amic acid) solution. The chemical imidization was carried out with acetic anhydride (the dehydration reagent) and TEA (the catalyzer) at room temperature for 10 h. The reaction mixture was then added to ethanol solution. The precipitate was collected by filtration, washed with water, and dried in vacuum at 160 °C to obtain the solid of the fluorinated polyimide.

2.3. Film preparation

6FDA–MDA was dissolved in $CHCl_3$ at first, and then, the polymer solution was put into two different types of humid environment: the static and the dynamic environments. In static environment, the polymer solution was directly cast on glass substrates at room temperature in a chamber whose relative humidity could be controlled. In dynamic environment, moist airflow through a tube with a diameter of 4.0 mm blew across (the velocity of the moist airflow was ~20 to 60 m/min) the surface of the polymer solution under ambient conditions (70–95% relative humidity). After the solvent evaporated completely, the films were obtained.

2.4. Measurements

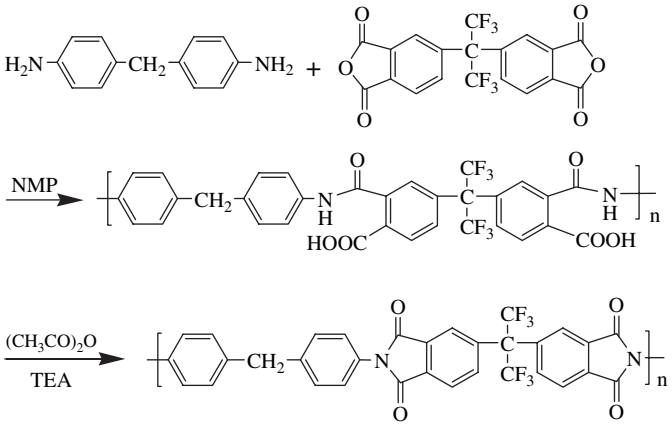
GPC analysis of the polymer was performed using THF as the eluant. Fourier transform infrared spectroscopic (FT-IR) analysis was performed on Nicolet IR560 spectrometer. ^{1}H NMR and ^{19}F NMR spectra were performed using a Varic ECA-600 spectrometer using DMSO-d_6 as the solvent. Thermogravimetric analyses (TGA) were performed on a TGA-2050 thermal analyzer using a heating rate of 20 mL/min in N_2. The glass transition temperature was determined by differential scanning calorimetry (Seiko DSC200) from 100 to 400 °C at the heating rate of 10 K/min. Mechanical properties of the film were measured on a TS-2000 at room temperature with film specimens at the rate of 5 mm/min. The solubility was determined by dissolving 1 g of 6FDA–MDA in 9 g of solvent (10 wt%) at room temperature, with mechanically stirring in nitrogen for 24 h.

The surface morphologies of the microstructured films were characterized by scanning electron microscopy (SEM, JEOL SEM4500, Tokyo, Japan) carried out at a 30-kV accelerating voltage.

3. Results and discussion

3.1. Polymer characterization

6FDA–MDA was successfully polymerized by the conventional two-step polymerization method, involving ring-opening polyaddition forming poly(amic acid) and subsequently chemical cyclodehydration using acetic anhydride as dehydration reagent and TEA as the catalyzer. The chemical structure and schematic synthetic route of this polymer are shown in Scheme 1.



Scheme 1. Synthetic route for 6FDA–MDA.