Available online at www.sciencedirect.com
ScienceDirect
European Polymer Journal 43 (2007) 4382–4388
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Ordered porous films based on fluorinated polyimide derived from 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride and 3,3′-dimethyl-4,4′-diaminodiphenylmethane

Xutong Han [a], Ye Tian [b], Lihua Wang [b,*], Changfa Xiao [a], Biqian Liu [b]

[a] Tianjin Municipal Key Laboratory of Fiber Modification and Functional Fiber, Tianjin Polytechnic University, Tianjin 300160, PR China
[b] Center of Molecular Sciences, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, PR China

Received 29 April 2007; received in revised form 14 June 2007; accepted 27 June 2007
Available online 18 July 2007

Abstract

One of fluorinated polyimides was synthesized from 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 3,3′-dimethyl-4,4′-diaminodiphenylmethane (DMMDA) by two-steps method, which had good solubility and hydrophilicity. 6FDA-DMMDA polyimide was dissolved in chloroform ($CHCl_3$) and cast on a glass substrate in a humid atmosphere. It was found that 6FDA-DMMDA/$CHCl_3$ solution was easy to form ordered porous structure at high concentration, and the reason was discussed in detail. In addition, the influences of solution concentration, the atmosphere humidity, were also tested.

Keywords: Ordered porous films; Fluorinated polyimide; Highly humid atmosphere; Synthesize

1. Introduction

Regular arranged microporous polymer films have attracted much attention due to their potential applications in the field of optical apparatus, scaffold for catalysis, biotechnology, etc. [1–4]. Among those methods for preparing micropatterned surfaces, casting of polymer solutions under high humidity, as pioneered by Francois et al. [5], is famous in recent years. Many research groups have reported such a regular hexagonal microporous structure from the cast film of various polymers, which includes rod-coil block copolymers [6], star polymers [7,8], dendritic copolymers [9,10], amphiphilic copolymers [11,12], hydrophobic polymers [13,14], etc.

Semifluorinated polyimides have good solubility in organic solvents, lower dielectric constant without forfeiture of thermal stability, etc. [15–18]. They are, therefore, excellent candidates for microelectronics applications such as interlayer dielectrics and flexible circuitry carriers [19,20]. We have prepared a serials of fluorinated polyimides [16,19,21], and successfully obtained the regular porous film by using one of them prepared from 2,2′-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,

* Corresponding author. Tel.: +86 10 6265 0812; fax: +86 10 6255 9373.
E-mail address: wanglh@iccas.ac.cn (L. Wang).

0014-3057/$ - see front matter
doi:10.1016/j.eurpolymj.2007.06.043

2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF) in highly humid atmosphere [21]. Both 6FDA and BDAF contain CF_3 groups in their chemical formula, which is beneficial to improve its solubility. But this kind of structure of 6FDA-BDAF also leads to the poor hydrophilicity, which is disadvantaged for stabilizing the arranged water droplets. The previous research has showed that the 6FDA-BDAF/$CHCl_3$ solutions could form regular porous patterns only at low concentrations ($<1\ g\ L^{-1}$) and the higher concentrations only caused irregular patterns. Therefore, the effort to search for the suitable PI that can prepare regular patterns at high concentrations should be carried on.

In this paper, we prepared another soluble polyimide derived from 6FDA and 3,3′-dimethyl-4,4′-diaminodiphenylmethane (DMMDA). DMMDA contained no fluorine groups. The methyl in aromatic groups of DMMDA could enhance its flexibility, which assured the solubility of PI. This kind of PI might form regular porous patterns at a high solution concentration. Its structure and physical properties were characterized. The honeycomb-patterned microporous films of the fluoro-polyimide were prepared by simple casting its solution on a glass substrate under controllable humid conditions. Some affecting factors, such as the solution concentration, the hydrophilicity and the humidity, on the pattern regularity of the polyimide porous films were tested.

2. Experimental

2.1. Materials

2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) (99%) was purchased from Fluoro Chemical Corporation and was recrystallized from acetic anhydride before use. 3,3′-dimethyl-4,4′-diaminodiphenylmethane (DMMDA) was purchased from Shanghai EMST Corporation, and dried before use. Commercially available *N*,*N*-dimethylformamide (DMF, analysis grade, Beijing Chemical Reagents Company), were purified on distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 Å). Water was purified by a Millipore system (Milli-Q, Millipore). Chloroform ($CHCl_3$), acetic anhydride and triethylamine (TEA) were used as received (analysis grade, Beijing Chemical Reagents Company). 6FDA-BDAF polyimide was synthesized by our lab before.

2.2. Polymer synthesis

A two-step solution-imidization technique was employed to synthesize 6FDA-DMMDA polyimide. A three-necked flask equipped with an addition funnel and a N_2 inlet was charged with a solution of DMMDA in DMF, then 6FDA was added all at once. The mole ratio and solid content of DMMDA/6FDA mixture were 1:1 and 10–12 wt%, respectively. The reaction mixture was reacted for 8–12 h at room temperature in N_2 atmosphere to yield a viscous poly(amic acid) solution. The chemical imidization was carried out with acetic anhydride and triethylamine at room temperature for 14–18 h. The reaction mixture was then added to ethanol solution. The precipitate was collected, washed with water, and dried in vacuo at 160 °C to obtain the solid of polyimide.

2.3. Film preparation

The honeycomb films were prepared by following steps: 6FDA-DMMDA was dissolved in chloroform and formed the 6FDA-DMMDA/chloroform solution with a series of concentrations. And then, 100 μL of 6FDA-DMMDA/chloroform solution was cast on 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 due to 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 due to emulsification. After complete evaporation of the solvent and water, a thin opaque film with porous honeycomb-like structure was remained.

2.4. Measurements

Fourier transform infrared spectroscopic (FT–IR) analysis was performed on Nicolet IR560 spectrometer. ^1H NMR and ^{19}F NMR spectra were registered using a Varic ECA-600 spectrometer with DMSO-d_6 as a solvent. Gel permeation chromatography (GPC) analysis of the polymer was performed using THF as the eluant. Thermogravimetric analyses (TGA) was performed on a TGA-2050 thermal analyzer using a heating rate of 20 K/min in N_2. The glass transition temperature was determined by