



Synthesis and property of fluorinated polyimides with double bond end groups for UV-cured coating



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ARTICLE INFO

Article history:

Received 19 December 2015
Received in revised form 26 April 2016
Accepted 11 May 2016

Keywords:

Polyimides
Fluorinated
UV-cured
Coating

ABSTRACT

The fluorinated polyimides with double bond end groups (G-FPIs) based on 4,4'-(hexafluoroisopropylidene) diphthalic anhydride, 4,4'-(hexafluoroisopropylidene) dianiline, 4-aminobenzoic acid and glycidyl methacrylate were synthesized via a typical two-step imidization method. The structure and properties of G-FPIs were characterized by Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (¹HNMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). It was determined that all G-FPIs were the amorphous phase and easily soluble in many polar organic solvents, and the G-FPIs had high glass-transition temperature (T_g). Then, UV-curable coatings were prepared from G-FPIs, and the properties were evaluated by real-time fourier transform infrared (RTIR), thermogravimetric analysis (TGA), UV-vis spectroscopy, water contact angle and water absorption test. Results showed that these coatings possessed favorable double bond conversion, excellent thermal stability, higher optical transparency and lower moisture uptakes. Moreover, the coatings exhibited good hardness and excellent gloss. Due to the outstanding combination properties, these UV-cured coatings based on G-FPIs could be considered as potential candidates for photoelectric, microelectronic and aerospace materials.

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1. Introduction

Aromatic polyimides are a class of high performance polymeric materials containing imide rings, which are well-known for their excellent thermal stability, electrical and mechanical properties [1–4]. They are widely implemented in a breadth of high technology industries, such as aerospace, automobile, flexible displays and printed circuit boards [5–9]. However, their applications are often limited due to their high melting temperature, deep color and limited solubility in most common organic solvents [10,11]. In order to overcome these problems and meet the requirements of unique fields, a growing amount of researches have been focused on the preparation of functional polyimides, to elucidate properties such as good solubility, high transparency, low dielectric constant, high refractive index and so forth.

It is conventionally known that the incorporation of symmetric fluorinated substituents into polymers reduces dielectric constant because of the mutual repulsion of the outermost shell electrons of fluorine atoms, the relatively small dipole of C-F bonds,

and the large free volume of trifluoromethyl groups, resulting in low intermolecular cohesive energy and low chain packing efficiency [12]. Since 1964, when fluorinated polyimides (FPIs) were invented, a large number of FPIs have been reported due to their excellent heat resistance, reduced coloration, and lower moisture absorption [13–16]. For example, the Shundrina [17] synthesized highly fluorinated aromatic polyimides based on hexafluoro-2,4-toluenediamine and commercially available dianhydrides (6FDA and ODPDA) via a one-pot high temperature polycondensation in a benzoic acid melt. Tong et al. [18] reported FPIs with high fractional free volume from 6FDA and aromatic diamines with bulky triptycene and pendent phenyl moieties. These FPIs demonstrated excellent solubility, high thermal stability and outstanding mechanical properties.

Over the past decade, substantial effort has been focused on the introduction of a cross-linkable structure to the end of oligomer chains, internal groups, or pendant groups of macromolecules. Many cross-linkable FPIs have been widely synthesized and implemented in many fields [19]. For example, Inoue et al. [20] reported photo-sensitive cross-linkable FPIs with a low dielectric constant that can be applied in photoresist. Wang, et al. [21] synthesized a series of photo-sensitive cross-linkable FPIs with excellent transparency for optical waveguide device applications. Yao et al. [16]

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prepared cross-linkable FPIs with higher molecular weight as a potential matrix for constructing optoelectronic devices. However, the curing temperature of above FPIs is up to 250 °C, which maybe cause badly damage to the devices and limit the applications.

As a strategy to solve the problem, excellent solution processability and lower cured temperature by ultraviolet (UV)-curing technology may be an optimal choice due to the advantages of its environmental safety, quick curing, high efficiency, solvent-free formulation, low energy consumption and enhanced performance [22]. In recent years, many photo-sensitive cross-linkable polymers with double bond end groups have been extensively reported and used for UV-cured coatings [23,24]. Therefore, designing and preparing cross-linkable UV-cured coatings with higher thermal stability and transparency for temperature-resisting coating, packaging materials, buffer coat layers, integrated circuits and interlayer dielectric coating in microelectronic fields will be a significant work. To the best of our knowledge, few publications have been presented pertaining to UV-curable coatings based on photo-sensitive FPIs.

Herein, a series of FPIs with double bond end groups (G-FPIs) were synthesized using 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 4,4'-(hexafluoroisopropylidene) dianiline (6FpDA), 4-aminobenzoic acid (4ABA), and glycidyl methacrylate (GMA) as monomers. Subsequently, UV-cured coatings based on G-FPIs were prepared, the thermal, optical and other properties were evaluated. The results demonstrate that all coatings possess excellent thermal property, high optical transparency, adequate hardness and outstanding gloss.

2. Experiment

2.1. Materials

The materials and solvents to prepare oligomers and coatings are as follows: 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, 98%), 4-aminobenzoic acid (4ABA, 98%) and glycidyl methacrylate (GMA, 99%) were purchased from Aladdin (Shanghai, China). 4,4'-(hexafluoroisopropylidene) dianiline (6FpDA, 98%) was provided by Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). 1-methyl-2-pyrrolidinone (NMP, 99%) and 1,3-dichlorobenzene (DCB, 98%) was obtained from adamas reagent Co., Ltd. (Shanghai, China). Triphenylphosphine (TPP) and hydroquinone (HQ) were produced by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Trimethylolpropane triacrylate (TMPTA) and Irgacure 184 were kindly supplied by Jiangsu Kuangshun Photosensitivity New-Material Stock Co., Ltd. (Wuxi, China).

The solvents to evaluate the solubility of oligomers are as follows: *N,N'*-dimethylacetamide (DMAc), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), chloroform (CHCl₃), acetone, toluene, ethanol were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Propylene glycol monomethyl ether acetate (PGMEA) was kindly supplied by Suzhou Rui Hong Electronic Chemicals Co., Ltd. (Suzhou, China).

2.2. Synthesis of FPIs with double bond end groups

A solution-imidization technique was employed to synthesize G-FPIs, as show in Scheme 1. Firstly, 6FpDA (2.089 g, 6.25 mmol) was added into a three-necked round bottom flask and 7.5 g NMP was used to dissolve the diamine. 6FDA (5.553 g, 12.50 mmol) mixed with 16.5 g NMP were then slowly dropped into the above solution with vigorous mechanical stirring under nitrogen purging. The mixture solution was allowed to react for 8 h at room temperature. Secondly, 4ABA (1.800 g, 13.13 mmol), 12.5 g 1,3-dichlorobenzene and 8.5 g NMP were slowly added into the above

Table 1

The molar ratios of each component in the reaction mixtures (mmol).

Samples	6FpDA	6FDA	ABA	GMA
FPI	6.25	12.50	13.13	0
G-FPIs-1	6.25	12.50	13.13	4.59
G-FPIs-2	6.25	12.50	13.13	7.23
G-FPIs-3	6.25	12.50	13.13	9.85

solution, and the poly(amic acid) solution was obtained after constantly stirring the reactants for 16 h at room temperature. The FPIs solution was then formed by thermal imidization in a 200 °C oil bath for another 12 h. Lastly, GMA (1.400 g, 9.85 mmol) with TPP (0.042 g, 0.16 mmol), HQ (0.042 g, 0.38 mmol) dissolved in 1.5 g NMP was slowly added into the FPIs solution after the temperature decreased to 110 °C. The G-FPIs-3 solution was obtained after constantly stirring the reactants for 8 h. Then the G-FPIs-3 solution was precipitated with methanol and re-dissolved in NMP. A gray precipitate was recovered and dried in a vacuum oven at 80 °C for 24 h to obtain G-FPIs-3. The synthetic procedure of other polymers was similar to G-FPIs-3 and the molar ratios of each compositions in the reaction mixtures were listed in Table 1.

2.3. Preparation of UV-cured coatings

UV-cured coating was prepared by mixing polyimides (FPIs or G-FPIs, 55 wt%), reactive diluent (TMPTA, 11 wt%), and photoinitiator (Irgacure184, 4 wt%). The viscosity of the coating could be adjusted by changing the amount of solvent (DMAc, 30 wt%). The coating was uniformly casted on a glass slide (the size was 5 cm × 10 cm and cleaned with alcohol before using) and baked at 100 °C for 2 h, and then exposed to a 200 mJ/cm² dose of UV irradiation using the Fusion UV Systems (USA, F300S).

2.4. The characterizations of FPIs and G-FPIs

The Fourier transform infrared spectroscopy (FT-IR) spectra (ABB BOMEN, Canada) of FPIs and G-FPIs-3 were collected using an ABB BOMEN FTLA 2000-104 spectrometer with a KBr disk. The proton nuclear magnetic resonance (¹H NMR) spectra (Bruker, Switzerland) of FPIs and G-FPIs-3 were collected with a Bruker Avance Digital 400 MHz spectrometer using tetramethylsilane as an internal reference and dimethylsulfoxide (DMSO) as a solvent. The molecular weight of FPIs and G-FPIs was measured by gel permeation chromatography (GPC) using an AGILLENT 1100 (Waters, America), THF as the eluent at a constant flow rate of 1 mL/min, polystyrene was used as the standard to construct a calibration curve. The glass transition temperature (*T_g*) of FPIs and G-FPIs was measured by a Mettler-Toledo DSC822e (Switzerland). The temperature range was from 30 to 300 °C at a constant rate of 15 °C/min under nitrogen flow. The X-ray diffraction (XRD) measurement of FPIs and G-FPIs was performed on a Bruker D8 Advance with Cu Ka radiation (40 kV, 40 mA) at a scanning rate of 4°/min from 5 to 50°.

2.5. The characterizations of UV-cured coatings

Thermogravimetric analysis (TGA) of coatings was performed on cured samples (about 10 mg) using a Mettler Toledo STAR thermogravimetric analyzer (TGA1100SF, Mettler Toledo, Switzerland), with a heating rate of 15 °C/min from 25 to 800 °C, nitrogen was used as the purge gas at a 50 mL/min flow rate. König hardness (PH-5858, BYK, Germany) of coatings was the testing mode (ASTM D 4366), with the values reported in seconds (s). Pencil hardness (BY Shanghai Pushen Chemical Machinery Co., Ltd.) of coatings was measured using ASTM D 3363. Adhesion test (QFH, Tianjin Jingke material testing machine factory) of coatings was performed

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