Polymer 76 (2015) 280–286

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis and characterization of highly-fluorinated colorless polyimides derived from 4,4′-((perfluoro-[1,1′-biphenyl]-4,4′-diyl)bis(oxy))bis(2,6-dimethylaniline) and aromatic dianhydrides

Hyeonuk Yeo, Munju Goh, Bon-Cheol Ku, Nam-Ho You*

Carbon Composite Materials Research Center, Institute of Advanced Composites Materials, Korea Institute of Science and Technology, Eunha-ri san 101, Bondong-eup, Wanju-gun, Jeollabuk-do, 565-905, Republic of Korea

ARTICLE INFO

Article history:
Received 3 July 2015
Received in revised form
2 September 2015
Accepted 8 September 2015
Available online 9 September 2015

Keywords:
Polyimide
Refractive index
High fluorine content
Dielectric constant
Polymer optics

ABSTRACT

The authors report the synthesis and characterization of a polyimide (PI) series derived from 4,4′-((perfluoro-[1,1′-biphenyl]-4,4′-diyl)bis(oxy))bis(2,6-dimethylaniline) (8FBPODMA). The 8FBPODMA monomer containing a perfluorobiphenyl group with two 2,6-dimethylaniline units connected by an ether bond was synthesized and polycondensed with several aromatic dianhydrides, including 4,4′-biphthalic anhydride (BPDA), 4,4′-oxydiphthalic anhydride (ODPA), pyromellitic dianhydride (PMDA), and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), by the traditional two-step imidization procedure. All PIs shows high optical transparency, higher than 80% at 500 nm for a thickness of *ca.* 10 μm and good thermal properties. The thermal decomposition temperatures ($T_{10\%}$) of the PIs are in the range of 507–527 °C and the glass transition temperatures (T_g) are in the range of 280–345 °C. In addition, the PIs have low refractive indices because of their high fluorine contents. In particular, 8FBPODMA–6FDA shows a very low refractive index (1.5389) and a low birefringence (0.0054) at 637 nm.

1. Introduction

Aromatic polyimides (PIs) have been developed for a wide range of applications, including automobile, aviation, aerospace, and electronic industries, owing to their excellent chemical resistance, thermal stability, and electrical properties [1–10]. However, polyimides which have strong absorption in the visible region, a deep reddish color, and a high dielectric constant, are the main obstacles that limit any optoelectronic and microelectronic applications [11,12]. This is because PIs have not only conjugated aromatic structures but also form charge transfer complexes between electron donor and electron acceptor moieties in the polymer chains [13–15]. To overcome these problems of PIs, many effort has been focused on synthesis of Low-k and colorless PIs, without deterioration of the resulting PIs [16–20]. There are several approaches to prepare colorless PIs, including the introduction of flexible and unsymmetrical linkages or noncoplanar monomers and bulky or fluoro-containing substituents [21,22]. Fluorination is one of the most widely used methods to reduce the dielectric constant while lowering moisture absorption and improving solubility and optical properties [23–26]. However, the aforementioned procedure results in a decrease of packing density of the polymers that may reduce thermal properties. Thus, a breakthrough in the tradeoff between solubility/transparency and positive properties such as high thermal properties has remained challenging [27]. The introduction of aromatic diamine containing methyl groups at the ortho position is common and is considered an effective method to improve optical transparency and thermal properties, not only because the introduction of methyl groups at the ortho position of aromatic diamine can induce a twisted structure between C–N imide bonds which prevents formation of an intermolecular charge-transfer complex (CTC), but also because methyl groups at the ortho position of aromatic diamine which can prevent free rotation of the C–N imide bond, which is effective in increasing the glass transition temperature [28]. Moreover, incorporation of fluorine atoms which have low electric polarity and high electronegativity can result in low refractive index, dielectric constant, optical loss, and moisture absorption characteristics for many applications, such as electronic coating and in electronic devices [29–31]. In particular, to reduce dielectric properties and optical

---

* Corresponding author.
E-mail address: polymer@kist.re.kr (N.-H. You).

http://dx.doi.org/10.1016/j.polymer.2015.09.019
0032-3861/

opaqueness is necessary for application to transparent optoelectronics.

In this study, we design a new diamine which contains eight fluorine atoms and methyl groups at the ortho position. It was expected that the methyl groups at the ortho position of the diamines would enhance glass-transition temperature (T_g) while improving optical transparency because the methyl groups can prevent intermolecular packing and free rotation between C–N imide bonds in the polymer chains. Moreover, the highly fluorinated diamine can endow a low refractive index and low-dielectric constant for the resulting PIs. The structure–property relationships, dielectric constant, and thermal properties of the polyimides are investigated in detail.

2. Experimental section

2.1. Measurements

^{1}H (600 MHz), ^{13}C (150 MHz) NMR spectra were recorded on an Agilent 600 MHz Premium COMPACT NMR spectrometer. ^{1}H and ^{13}C NMR spectra were obtained by using tetramethylsilane (TMS) as an internal standard and $CDCl_3$ as a solvent. Elemental analysis and mass spectrum analysis were performed at the Center for University-wide Research Facilities at Jeonbuk National University. The surface functional groups of the PI films were analyzed by using a Fourier transform-infrared spectroscopy (FT-IR Spectrophotometer, Nicolet IS10, USA). Thermogravimetric analysis (TGA) was carried out with a TA 50 (TA Instruments, USA) under nitrogen gas flow at a heating rate of 10 °C/min. Glass transition temperatures of the PI films were measured by DSC analysis with a Q 50 (TA Instruments, USA) under nitrogen gas flow at a heating rate of 10 °C/min. Dynamic mechanical thermal analyses (DMA) were evaluated from PI films (30 mm length, 10 mm wide, and *ca.* 50 μm thickness) on a DMA (TA Instruments, DMA Q800, USA) at a heating rate of 3 °C/min with a load frequency of 1 Hz in air. The UV–visible spectra were recorded on a JASCO V-670 spectrometer. Inherent viscosities of the PAA precursors in NMP solution (0.5 g/dL) at 30 °C were measured using a Malvern Y510 viscometer. The densities of the films were measured by digital readout density gradient column (Ray-Ran, UK). The out-of-plane ($n_{TM} = n_{xy}$) and in-plane ($n_{TE} = n_z$) refractive indices of PI films were measured with a Metricon PC-2000 prism coupler with a He–Ne laser light source (wavelength: 637, 1306.5, and 1549.5 nm). The birefringence (Δn) was calculated to measure the difference between n_{TE} and n_{TM}. The average refractive index was calculated according to the equation: $n_{AV} = [(2n_{TE}{}^2 + n_{TM}{}^2)/3]^{1/2}$. The dielectric constant (ε) was calculated by the estimated n_{AV} according to Maxwell's equation: $\varepsilon = n^2$.

2.2. Materials

Decafluorobiphenyl, 4-amino-3,5-xylenol, and 4-aminophenol were obtained from TCI, and used without further purification. Aromatic dianhydrides, 4,4′-biphthalic anhydride (BPDA), 4,4′-oxydiphthalic anhydride (ODPA), pyromellitic dianhydride (PMDA), and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were purchased from TCI, and used after sublimation. Other commercially available chemicals were used as received. Dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) were purified by a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). All reactions were performed under an argon atmosphere.

2.3. Monomer synthesis

2.3.1. 4,4′-((Perfluoro-[1,1′-biphenyl]-4,4′-diyl)bis(oxy))bis(2,6-dimethylaniline) (8FBPODMA)

Decafluorobiphenyl (7.83 g, 23.4 mmol), 4-amino-3,5-xylenol (6.76 g, 49.3 mmol), K_2CO_3 (5.38 g, 38.9 mmol), and DMF (50 ml) were mixed, and the solution was stirred at 120 °C overnight. Following concentration of the solution by evaporation, the crude products were then diluted with methyl tert-butyl ether and washed with $NaHCO_3$ (aq) and brine. After drying over $MgSO_4$, the products were concentrated. After purification by flash chromatography on silica gel (12:1 = $CHCl_3$:EtOAc, $R_f = 0.35$) and recrystallization in ethanol, the compound **8FBPODMA** (11.5 g, 20.3 mmol, 86.7%) was obtained as a white powder. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 6.70$ (s, 4H, Ar–*H*), 3.48 (s, 4H, –N*H*$_2$), 2.18 (s, 12H, Ar–C*H*$_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 149.21$, 145.59, 143.87, 142.63, 140.90, 139.31, 136.58, 123.00, 116.10, 101.85, 17.88 ppm. MS (p-ESI): *m*/*z*: calcd for $C_{28}H_{20}F_8N_2O_2 + H^+$: 569.15; found: 569.10. Elemental analysis: calcd for $C_{28}H_{20}F_8N_2O_2$: C 59.16, H 3.55, N 4.93; found: C 59.10, H 3.62, N 4.85.

2.3.2. 4,4′-((Perfluoro-[1,1′-biphenyl]-4,4′-diyl)bis(oxy))dianiline (8FBPOA)

Similarly to the synthetic procedure of **8FBPODMA**, the **8FBPOA** was synthesized from decafluorobiphenyl (2.00 g, 5.99 mmol), 4-aminophenol (1.37 g, 12.6 mmol), K_2CO_3 (1.08 g, 7.81 mmol), and DMF (10 ml) as a yellow solid (2.25 g, 4.40 mmol, 73.5%). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 6.90$ (d, *J* = 8.7 Hz, 4H), 6.66 (d, *J* = 8.7 Hz, 4H), 3.61 (s, 4H) ppm. MS (API+): *m*/*z*: calcd for $C_{24}H_{12}F_8N_2O_2 + H^+$: 513.08; found: 512.99. Elemental analysis: calcd for $C_{24}H_{12}F_8N_2O_2$: C 56.26, H 2.36, N 5.47; found: C 56.26, H 2.47, N 5.34.

2.4. Polymer synthesis

The PI films were fabricated by a conventional two-step method. First, a NMP solution of the diamine monomer and a dianhydride was stirred for 1 day under inert atmosphere to obtain viscous poly(amic acid) (PAA) precursor. Second, the prepared PAA solution was cast on the several substrates and thermally annealed at 150 °C for 30 min, 200 °C for 30 min, 250 °C for 1 h. Subsequently, the films were used, as is, in optical measurements and thermal analysis after removal from substrates. The monomer, **8FBPODMA**, was polymerized with 4 kinds of dianhydrides, PMDA, BPDA, ODPA, and 6FDA, and **8FBPOA** was reacted only with PDMA. The polyimides, 8FBPODMA–PMDA, –BPDA, –ODPA, –6FDA, and 8FBPOA–PDMA were named **PMDA**, **BPDA**, **ODPA**, **6FDA**, **PMDA′**, respectively. For preparation of the PAA solution, the following polymerization method was used. **8FBPODMA** (0.50 g, 0.88 mmol) and NMP (2.00 ml) were put into a 10 ml flask under an argon atmosphere. After the monomer was dissolved by stirring, dianhydride, 6FDA (0.39 g, 0.88 mmol), was added in the flask. Additionally, NMP (1.47 ml) was added in order to adjust the monomers content to 20 wt%. The mixture was stirred at room temperature for 1 day to obtain a viscous PAA solution. Other PAA solutions were prepared by similar procedure to **6FDA** and their inherent viscosities were in the range of 0.26–1.26 (measurement condition: NMP (0.5 g/dL) solution, 30 °C).

3. Results and discussion

3.1. Synthesis and characterization of monomer

The novel diamine monomer, 4,4′-((perfluoro-[1,1′-biphenyl]-4,4′-diyl)bis(oxy))bis(2,6-dimethylaniline) (**8FBPODMA**), containing