Electronic Supplementary Information

Highly Transparent and Flexible Polyimide/ZrO$_2$ Nanocomposite Optical Films with Tunable Refractive Index and Abbe Number

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Experimental Section

Materials

9,9-Bis(4-(4-amino-3-benzyloxyphenoxy)phenyl fluorene (F-DA) was prepared according to previous literature.\textsuperscript{51} 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (Chriskev) was purified by vacuum sublimation. All other reagents were used as received from commercial sources. Poly(o-hydroxy-imide)s, FOH-6FPI and FOH-CHPI were prepared according to the previous reported.\textsuperscript{8c, S2}

Polymer Synthesis

Synthesis of FOH-6FPI was used as an example to illustrate the general synthesis route used to produce the polyimides (Scheme 1). The stoichiometric mixture of the diamine F-DA (1.12 g, 2.00 mmol), the dianhydride 6FDA (0.89 g, 2.00 mmol), and a few drops of isoquinoline in m-cresol (7 mL) was stirred at ambient temperature under nitrogen for 5 h, then the mixture was increased to 170-180 °C and maintained at the temperature for 16 h. After the solution was cool to ambient temperature, the viscous solution was then poured slowly into 300 mL of methanol with stirring. The precipitated polymer was collected by filtration, washed thoroughly with hot methanol, and dried in vacuum at 150°C for 15 h. The inherent viscosity of the obtained polyimide FOH-6FPI was 0.71 dL/g (measured at a concentration of 0.5 g/dL in DMAc at 30 °C). The IR spectrum of FOH-6FPI (film state) exhibited broad absorption bands in the region of 3000 to 3700 cm\textsuperscript{-1} (O-H stretch) and characteristic imide absorption bands at 1782 (asymmetrical C=O), 1717(symmetrical C=O), 1388 (C-N), 1357 (C-F), and 747 cm\textsuperscript{-1} (imide ring deformation); Yield: 98%. The \textsuperscript{1}H NMR result (DMSO-\textit{d}_6, \textit{δ}, ppm): FOH-6FPI 6.51 (d, 4H), 7.01 (d, 4H), 7.20 (m, 6H), 7.40 (m, 6H), 7.73 (s, 2H), 7.93 (d, 4H), 8.12 (d, 2H), and 10.03 (s, 2H, OH). Inherent viscosity and solubility behavior of the obtained polyimides are summarized in Table S1. FOH-6FPI shows excellent solubility in many organic solvents, and could be casting into highly flexible and transparent film.
Moreover, the inherent viscosity of the obtained polyimide **FOH-CHPI** was 0.65 dL/g (measured at a concentration of 0.5 g/dL in DMAc at 30 °C). The IR spectrum of **FOH-CHPI** (film) exhibited broad absorption bands in the region of 3000 to 3700 cm⁻¹ (O-H stretch) and characteristic imide absorption bands at 1779 (asymmetrical C=O), 1719 (symmetrical C=O), 1388 (C-N), and 748 cm⁻¹ (imide ring deformation); Yield: 99%. Anal. Calcd for (C₄₇H₃₂N₂O₈)ₙ (752.77): C, 74.99 %; H, 4.28 %; N, 3.72 %. Found: C, 72.95 %; H, 4.76 %; N, 3.68 %.

**Preparation of PI/ZrO₂ Hybrid Films**

The synthesis of PI/ZrO₂ hybrid **F-6FZr50** was used as an example to illustrate the general synthesis route for producing the hybrid **F-6FZrX** (Scheme 1). Firstly, 0.05 g (0.050 mmole) of **FOH-6FPI** was dissolved in 3ml of DMAc, and then 0.10 ml of acetic acid was added very slowly into the PI solution and further stirred at room temperature for 30 min. Secondly, 0.21 ml (0.62 mmole) of Zr(OBu)₄ dissolved in butanol was added drop-wise into the above solution by a syringe, and then stirred at room temperature for 30 min. Finally, the resulting precursor solution of **F-6FZr50** was filtered by 0.45 mm PTFE filter and poured into a 6 cm glass Petri dish. The hybrid optical film with thickness of 19±3 μm could be obtained by subsequent heating program at room temperature for 6 h, 60 °C for 6 h, 150 °C for 3 h, 250 °C for 1 h to remove the solvent, then the film was hard baked at 300 °C for 1h under vacuum condition. The flexible and transparent PI/ZrO₂ hybrid optical films with different zirconia contents could be successful prepared by the procedure mentioned above. In addition, the thin hybrid film (thickness: 500-600nm) were also prepared by spin-coating method on a glass plate or silicon wafer at 1000-3000 rpm for 30 s and subsequent heating program as mention above. Furthermore, the IR spectrum (Figure S1c, S1d) of hybrid film F-6FZr50 and F-CHZr50 revealed additional absorption bands at 600 to 650 cm⁻¹ (Zr-O-Zr), which is also similar to that in the previous report.⁵³

**Preparation of zirconia and titania films**
The pure zirconia film was prepared by the following procedure: 7.7 g (0.02 moles) of Zr(OBu)₄ and 15 ml of butanol were added to a 50 ml round bottom flask. Secondly, the acetic acid was added very slowly into the above Zr(OBu)₄ solution and stirred at room temperature for 1 h. To prepare the zirconia thin film, the precursor solution was filtered by a 0.2 mm PTFE filter previously and then spin-coated onto a glass plate or silicon wafer at 1000 rpm for 30 s. Finally, the coated film was soft baked by multi-step heating procedure at 60 °C for 30 min, 150 °C for 30 min, and 250 °C for 30 min to remove the solvent. Then the film was hard baked at 300 °C for 1 h to afford zirconia thin film. According to DSC thermograms (Figure S2), the endothermic peak of ZrO₂ was located at 40-250 °C which was the solvent elimination and water dehydration. In addition, no peak was found at 300 °C indicated this is suitable temperature in heating procedure, and the Zr-OH groups of the hydrolyzed precursors condensed progressively to form Zr–O–Zr structures which resulted in an enhanced refractive index. The exothermic peak at 450-500 °C was crystallization of ZrO₂. While, the preparation of the titania film was according to previous report, but only heated to 300 °C in this study.

Measurement
Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer with resolution 1 cm⁻¹ and number of scans 4. ¹H NMR spectra were measured on a JEOL JNM-AL 300 MHz spectrometer in DMSO-d₆, using tetramethylsilane as an internal reference, and peak multiplicity was reported as follows: d, doublet; m, multiplet. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. DSC analyses were performed on a TA Instruments Q-20 at a scan rate of 10 °C/min in flowing nitrogen (20 cm³/min). Thermogravimetric analysis (TGA) conducted with a TA Instruments Q50, and experiments were carried out on approximately 6-8 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm³/min) at a heating rate of 20 °C/min. Coefficient of thermal expansion (CTE) and glass transition temperatures (T_g) were measured by a dilatometer (TA instrument
The TMA experiments were conducted from 50 to 450 °C at a scan rate of 10 °C/min by a tensile probe under an applied constant load of 50 mN. $T_g$ was taken as the onset temperature of probe displacement on the TMA traces. The CTE data were determined in the range of 50–200 °C by tensile probe with Tension mode. Ultraviolet-visible (UV-vis) spectra of the obtained films were recorded on Hitachi U-4100 UV-vis-NIR spectrophotometer. An ellipsometer (SOPRA, GES-5E) was used to measure the refractive index ($n$) of the prepared films in the wavelength range of 300–800 nm, and the thickness ($h$) was also determined simultaneously. In-plane ($n_{TE}$), and out-of plane ($n_{TM}$) refractive indices of the films formed on the silica substrates were measured using a prism coupler (Metricon, PC-2000) at wavelengths of 632.8nm at room temperature. The in-plane/out-of-plane birefringence ($\Delta n$) was calculated as $\Delta n = n_{TE} - n_{TM}$. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (25 °C) on a PANalytical-X’Pert PRO MPD X-ray diffractometer (45 kV, 20 mA), using graphite-monochromatized Cu-Kα ($\lambda =1.5418$ Å) radiation. The microstructure of the prepared films was examined by using a JOEL JEM-1230 transmission electron microscope (TEM) at an operating voltage of 100 kV. For TEM imaging, the hybrid films were first embedded in epoxy resin and then microtomed to about 80 nm thick at room temperature with a diamond knife.
Table S1. Inherent Viscosities$^a$ and Solubility$^b$ of the Polyimides

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\eta_{inh}$ (dL/g)$^a$</th>
<th>NMP</th>
<th>DMAc</th>
<th>DMF</th>
<th>DMSO</th>
<th>m-Cresol</th>
<th>THF</th>
<th>CHCl$_3$</th>
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</thead>
<tbody>
<tr>
<td>FOH-6FPI</td>
<td>0.71</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>–</td>
</tr>
<tr>
<td>FOH-CHPI</td>
<td>0.65</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>–</td>
<td>–</td>
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</tbody>
</table>

$^a$ Measured at a polymer concentration of 0.5 g dL$^{-1}$ in DMAc at 30 °C. $^b$ The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent. (+++) soluble at room temperature, (+) soluble on heating, (+-) partial soluble on heating, and (--) insoluble even on heating.

Table S2. Thermal properties of the hybrid films with ZrO$_2$ and TiO$_2$

<table>
<thead>
<tr>
<th>Index</th>
<th>Thermal Properties T$_g$ (°C)$^a$</th>
<th>CTE (ppm/K)$^b$</th>
<th>$T_d$ (°C)$^c$</th>
<th>$T_{d10}$ (°C)$^c$</th>
<th>$R_{w800}$ (%)$^d$</th>
<th>Inorganic content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOH-6FPI</td>
<td>257</td>
<td>87</td>
<td>395</td>
<td>425</td>
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<tr>
<td>F-6FZr10</td>
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<td>505</td>
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<tr>
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<td>38</td>
<td>500</td>
<td>485</td>
<td>595</td>
<td>530</td>
</tr>
</tbody>
</table>

$^a$ Glass transition temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C min$^{-1}$ by tension mode. $^b$ The CTE data was determined over a 50–200 °C range by tension mode. $^c$ Temperature at which 5% and 10% weight loss occurred, respectively, recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 30 cm$^3$/min. $^d$ Residual weight percentages at 800 °C under nitrogen flow. $^e$ Experimental inorganic content estimated from TGA curves.
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