Novel Flexible and Transparent PI-TiO_2 Optical Films with High Refractive Index and Excellent Thermally Stability

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Introduction

In this study, the aromatic polyimide-nanocrystalline titania hybrid materials with tunable titania content and refractive index for both of thin film (100-500 nm in thickness) on glass and thick film (10-15 µm in thickness) (3STP50, RI=1.87) by solution casting were prepared, and the convenient synthetic route has been developed in our laboratory. Instead of using poly(amic acid) and polyimide with carboxylic acid end groups, the high weight-average molecular weight and organo-soluble polyimide with hydroxyl groups on each repeating units (3S-PHIb and F-PHIa) derived from new diamines, 4,4'-bis(4-amino-3-hydroxyphenylthio)diphenylsulfide (3S-2) and 9,9-bis(4-(4-amino-3-hydroxyphenoxy)phenyl)fluorene (F-2), with 4,4'-oxydiphthalic dianhydride (ODPA) or 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) could be used to prepare their titania hybrid materials. The hydroxyl groups could react with titanium butoxide (Ti(OBu)4) and provide organic-inorganic bonding on each repeating units. Two series of highly homogeneous hybrid films with different titania content were obtained using coating and thermal curing

Results and Discussion

The polyimides were highly soluble in polar solvents such as NMP, DMAc, DMF, and DMSO, and the enhanced solubility could be attributed to the introduction of flexible sulfide-links and bulky –CF3 groups, or kinked bulky fluorine moieties, and hydroxyl-groups into the polymer main chain. For 3S-PBI, the introduction of benzyl group made the highly solubility. Thus, the excellent solubility makes the polymer potential candidates for practical applications by dip-coating processes and further sol–gel process of PHIs. The thermal properties of the polyimides and hybrid materials were listed in Table 1. The TEM image of the **3STP50** shown in the Figure 1 exhibited the titania nanocrystallites with the average size of 3-5 nm were well dispersed in the hybrid material. The refractive index value of **3S-PHIb** hybrid materials about 1.64 to 1.87 at a typical wavelength of 633 nm, and **F-PHIa** about 1.68 to 1.81, and almost all the hybrid films had shorter than 400 nm and showed a high optical transparency (> 80 % at 450 nm).

Conclusions

Two series of novel soluble polyimides **3S-PHI** and **F-PHI** with hydroxyl groups were synthesized by one-step method from **F-2** and **3S-2** with ODPA and 6FDA, respectively. High refractive index polyimide titania hybrid optical films were successfully synthesized from the soluble polyimide with hydroxyl groups with titanium butoxide by controlling the organic/inorganic mole ratio. The introduction of fluorene and $–CF_3$ group enhance the transparency and solubility, and the sulfur-containing make the higher value of refractive index. For the thin films (100-500 nm), the refractive index could be tunable with titania content (1.64-1.87 of **3STP50** and 1.68-1.81 of **FTP50**). The hybrid thick films also possessed of flexible, good storage modulus, excellent thermal properties (T_g= 323 °C of **3STP50**, T_g= 365 °C of **FTP30**), low coefficient of thermal expansion (CTE= 42 ppm/ °C of **3STP50**, CTE= 49 ppm/ °C of **FTP50**), and optical transparency in the visible region.

Reference

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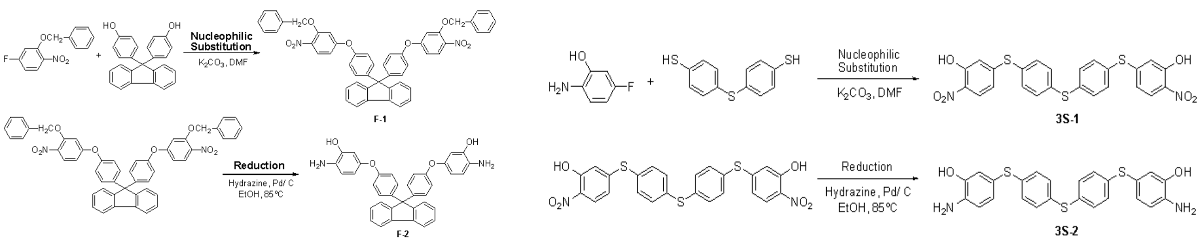
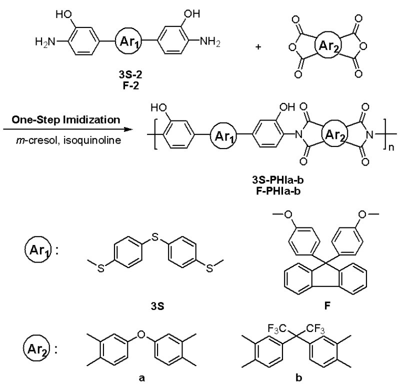
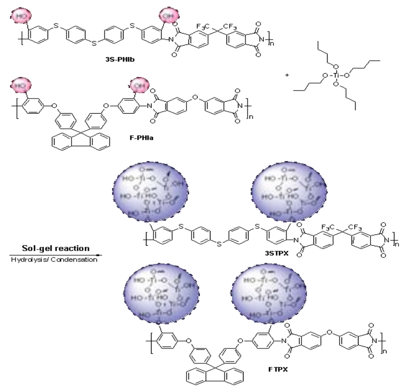


Scheme 1. Monomer synthesis



Scheme 2. Polymer Synthesis



Scheme 3. Hybrid Synthesis

Table 1. Thermal Properties of **3S-PHIb** (**F-PHIa**) and Hybrid Materials

Polymer	T_g (°C)[a]	T_g (°C)[b]	T_s (°C)[c]	CTE (ppm/K)[d]	T_d at 5% weight loss (°C)[e]		T_d at 10% wight loss (°C)[e]		Char yield (wt%)[f]
					N_2	Air	N_2	Air	
3S-PHIb	169	180	168	68	350	365	475	490	59
3STP10	-	283	271	60	500	495	565	550	70
3STP30	-	307	279	54	520	505	580	575	72
3STP50	-	323	303	42	535	525	600	570	82
F-PHIa	202	188	182	90	375	380	470	480	66
FTP10	-	325	260	67	525	505	570	555	74
FTP30	-	365	299	55	520	505	575	595	81
FTP50	-	-	317	49	510	535	580	610	86

[a] Midpoint temperature of the baseline shift on the second DSC heating trace (rate= 20°C/ min) of the sample after quenching from 400 °C to 50 °C (rate= 200 °C/ min) in nitrogen.
[b] Dynamic mechanical thermal analysis (DMA) was performed on PI film specimens (10 mm long, 5 mm wide, and 20-40μm thick) at a heating rate of 3 °C/ min with a load frequency of 1 Hz in air.
[c] Softening temperature measured by TMA with a constant applied load of 5 mN at a heating rate of 10 °C/ min by penetration mode.
[d] The CTE data was determined over a 50-200 °C range by film-fiber probe with expansion mode.
[e] Decomposition temperature, recorded via TGA at a heating of 20 °C/ min.
[f] Residual weight percentage at 800 °C in nitrogen.

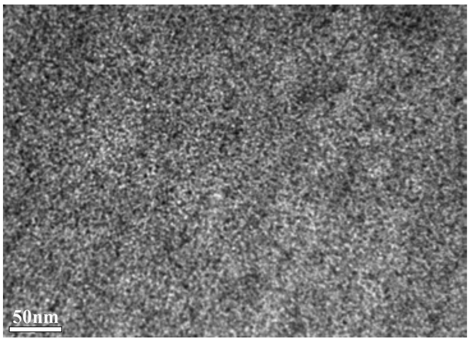


Figure 1. The TEM image of **3STP50**

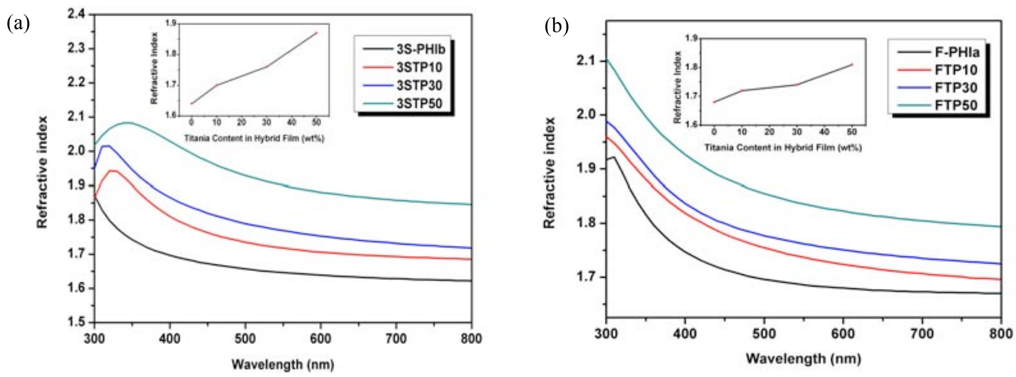


Figure 2. Variation of the refractive index of the (a) **3S-PHIb**、(b) **F-PHIa** and hybrid materials at wavelengths of 300-800 nm. The insert figure shows the variation of refractive index with titania content.

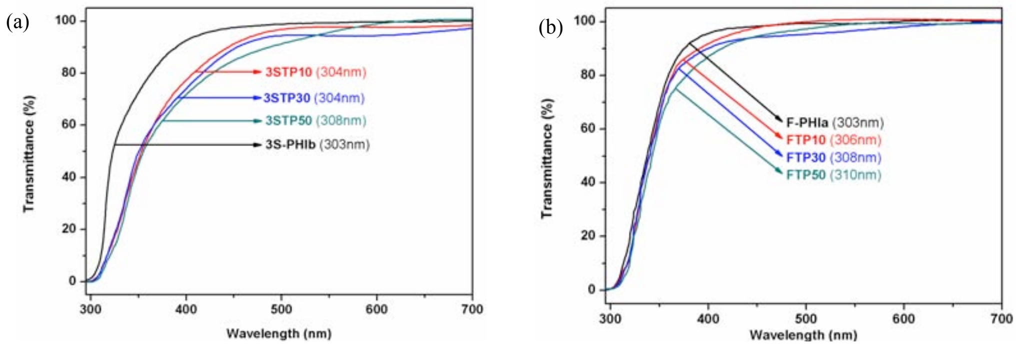


Figure 3. Transmittance UV-visible spectra of (a) **3S-PHIb**、(b) **F-PHIa** hybrid films (thickness: 100-500nm).