Preparation and electro-optical properties of PMDA-6FHP-NLO polyimide/ SiO$_2$

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ABSTRACT

Transparent Nonlinear Optical(NLO) inorganic/organic(polyimide/silica) hybrid composites with covalent links between the inorganic and the organic networks were prepared by the sol-gel method. The silica content in the hybrid films was varied from 0 to 22.5/wt%. The prepared PI hybrids were characterized by IR, UV-Vis, thermogravimetric analysis(TGA), X-ray diffraction(XRD), scanning electron microscopy(SEM) and Transmission Electron Microscope(TEM). They exhibit fair good optical transparency. The SiO$_2$ phase is well dispersed in the polymer matrix. DSC and TGA results show that these hybrid materials have excellent thermal stability. The polymer solutions could be spin coated on the indium-tin-oxide(ITO) glass to form optical quality thin films. The electro-optic coefficients($\gamma_{33}$) at the wavelength of 832 nm for polymer thin films poled were in the range of 20-30pm/V.

INTRODUCTION

There has been great interest in the development of second-order nonlinear optical (NLO) polymeric materials for photonics applications. A number of NLO polymers have been developed to exhibit large second harmonic coefficients, comparable to those of the inorganic NLO materials which are currently in use in devices. NLO materials have potential applications in optical signal processing, switching and frequency generation(making use of processes such as harmonic generation, frequency mixing, and optical parametric oscillation), and may also contribute to optical data storage, optical communication, and image processing$^{[1-4]}$.

For practical applications, these NLO polymeric materials must retain the high optical quality thin films, high optical damage thresholds, sufficiently large and stable NLO susceptibilities, low optical propagation loss and feasibility of device fabrication$^{[5-10]}$. Inorganic glasses, however, are excellent photonic media because of their high optical quality and extremely low optical losses. Therefore, combining inorganic glass and organic photofunctional molecules is probably one of the best ways of getting optical materials with large optical non-linearity and low losses. In addition to this, the use of highly cross-linked silica matrix can remarkably reduced the thermal relaxation of the molecular dipoles$^{[11-12]}$.

In this study, we synthesized an electrooptical chro-
mophore, hydroxyl polyimide based on the fluorine-containing monomers, PMDA-6FHP (Figure 1.) and side-chain NLO polyimide PMDA-6FHP-NLO (Figure 2.). We reported the sol-gel synthesis of organic-inorganic silica waveguide materials (Figure 3.), and investigated the optical properties, thermal properties and micrographs study.

**EXPERIMENTAL**

**Materials and characterization**

N,N-dimethylacetamide (DMAC) were stirred over powered calcium hydride overnight and then distilled under reduced pressure and stored over 4Å molecular sieves. The 2,2-Bis(3-amino-4-hydroxyphenyl) hexafluoropropane (6FHP) was obtained from TCI and used without further purification. The Pyromellitic dianhydride (PMDA) was obtained from Beijing chemistry agent plant. The 3-aminopropyltriethoxysilane, APTES was purchased from Nanjing shuguang chemical plant. Tetrahydrofuran (THF) was purified by distillation and further recrystallized from toluene/methanol (4:1) to give a bright red crystal. ^1^H NMR (300MHz, acetone-d$_6$, ppm): 10.61 (s, OH, 1H), 8.05 (s, ArH, 2H), 8.00 (s, ArH, 2H), 7.83 (s, ArH, 2H), 7.11 (s, ArH, 2H), 6.56 (s, ArH, 2H), 6.20 (s, ArH, 2H), 4.20 (s, -CH$_2$CH$_2$O-, 2H), 3.73 (s, -CH$_2$CH$_2$O-, 2H), 2.46 (s, -CH$_3$, 3H). Anal. Calcd for C$_{21}$H$_{20}$N$_6$O$_2$: C, 62.38%; H, 4.95%; N, 20.79%. Found: C, 62.48%; H, 4.89%; N, 20.82%.

**Hydroxyl polyimide synthesis**

To a stirred solution of p-nitroaniline (13.8g, 0.10 mol) in methanol/HCl (50%, V/V, 50mL) was added sodium nitrite (6.9000g, 0.10mol) in ice-water (15%, m/m) at 0°C[13-14]. The mixture was stirred at this temperature for 1h. Meanwhile stirred solution of purified by distillation aminobenzene (9.3g, 0.10mol) in HCl (50mL, 1mol·L$^{-1}$). Then these two solutions were mixed and added sodium nitrite (6.9000g, 0.10mol) in ice-water (15%, m/m) at 0°C. The mixture was added dropwise into a solution of N-2-hydroxyethyl-N-methylaniline (15.1000g, 0.10mol) with abundance HAc-NaAc. The mixture was stirred at 40-50°C for 20min. The mixture solution was cooled down and placed for 2h, and the solid was collected by filtration and further recrystallized from toluene/methanol (4:1) to give a bright red crystal. ^1^H NMR (300MHz, acetone-d$_6$, ppm): 10.61 (s, OH, 1H), 8.05 (s, ArH, 2H), 8.00 (s, ArH, 2H), 7.83 (s, ArH, 2H), 7.11 (s, ArH, 2H), 6.56 (s, ArH, 2H), 6.20 (s, ArH, 2H), 4.20 (s, -CH$_2$CH$_2$O-, 2H), 3.73 (s, -CH$_2$CH$_2$O-, 2H), 2.46 (s, -CH$_3$, 3H). Anal. Calcd for C$_{25}$H$_{10}$F$_6$N$_2$O$_6$: C, 54.74%; H, 1.82%; N, 5.11%. Found: C, 54.79%; H, 1.79%; N, 5.15%. The molecular weight can be measured by GPC.
**Synthesis of PMDA-6FHP-NLO polyimide**

The polyimide M (PMDA-6FHP, 1.097g, 0.5 mmol), PPh$_3$ (0.393g, 1.5mmol) and 4-(N-2-hydroxyethyl-N-methylanino)-4’-(p-nitrobenzene-diazenyl)azobenzene (NLO chromophere) (0.404g, 1.00mmol) were dissolved in THF (15ml). Diethyl azodicarboxylate (DEAD) (0.2600g, 1.50mmol) was added dropwise into the solution under nitrogen atmosphere. The reaction mixture was stirred for 2 days at room temperature, and then the resulting reaction solution was added dropwise into an agitated solution of methanol/water (1:1,30ml) and 2N HCl (5ml) in a high-speed blender. The collected solid further precipitated in THF (10ml) are precipitated into the solution of methanol/water. The product was filtered out and washed with methanol/water for several times, and dried at 60°C under vacuum for 24h. N$^1$H NMR (300MHz, CD$_3$COCD$_3$, ppm): 8.36 (s, ArH, 2H), 8.05 (s, ArH, 4H), 8.00 (s, ArH, 4H), 7.85 (s, ArH, 4H), 7.62 (s, ArH, 2H), 7.32 (d, ArH, 2H), 7.11 (d, ArH, 2H), 7.11 (s, ArH, 2H), 6.56 (s, ArH, 4H), 6.20 (s, ArH, 4H), 4.20 (s, -CH$_2$CH$_2$O-, 4H), 3.66 (s, -CH$_2$CH$_2$O-, 4H), 2.40 (s, -CH$_3$, 6H). Anal. Calcd for C$_{67}$H$_{46}$F$_6$N$_{14}$O$_{10}$: C, 60.91%; H, 3.48%; N, 14.85%. Found: C, 60.95%; H, 3.44%; N, 14.90%. The molecular weight can be measured by GPC and has a M$_n$ of 26,800, an M$_w$ of 42,700 with a polydispersity of 1.60 (polystyrenes as standards). The synthetic route was shown in figure 1.

**Synthesis of inorganic-organic hybrid materials**

Hybrid materials were successfully synthesized via sol-gel process. Its technique is based on creating two individual homogeneous inorganic and organic solutions, which are then mixed together and allowed to react at room temperature with carefully controlled evaporation.

<table>
<thead>
<tr>
<th>Materials</th>
<th>TEOS (wt%)</th>
<th>polyimide (g)</th>
<th>APTES (ml)</th>
<th>HCl (ml)</th>
<th>H$_2$O (ml)</th>
<th>THF (ml)</th>
<th>Appearance$^a$</th>
<th>$T_g^{b,c}$ (C)</th>
<th>$T_d^{b,c}$ (C)</th>
<th>$\gamma_{33}$ (pm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>5</td>
<td>2.55</td>
<td>0.20</td>
<td>0.10</td>
<td>0.25</td>
<td>30</td>
<td>Transparent</td>
<td>213</td>
<td>352</td>
<td>30</td>
</tr>
<tr>
<td>H-2</td>
<td>10</td>
<td>2.55</td>
<td>0.20</td>
<td>0.25</td>
<td>0.53</td>
<td>30</td>
<td>Transparent</td>
<td>336</td>
<td>448</td>
<td>28</td>
</tr>
<tr>
<td>H-3</td>
<td>15</td>
<td>2.55</td>
<td>0.20</td>
<td>0.50</td>
<td>1.02</td>
<td>30</td>
<td>Transparent</td>
<td>338</td>
<td>451</td>
<td>25</td>
</tr>
<tr>
<td>H-4</td>
<td>22.5</td>
<td>2.55</td>
<td>0.20</td>
<td>0.65</td>
<td>2.10</td>
<td>30</td>
<td>Transparent</td>
<td>341</td>
<td>453</td>
<td>23</td>
</tr>
</tbody>
</table>

$^a$UV-Vis spectrum was observed; $^b$Experimental results from DSC; $^c$Experimental results from TGA
RESULTS AND DISCUSSION

Figure 4 illustrated the FT-IR spectra of the prepared polyimide-silica hybrid H-1, H-3 and H-4. The characteristic absorption bands of the imide group were observed at 730, 1377, 1715, 1774 cm\(^{-1}\) for all samples as shown in Figure 4. The absorption band around 1000–1140 cm\(^{-1}\) gradually increased intensity with increasing silica content, consisted with the formation of the three-dimensional Si-O-Si network in the hybrid film\[^{15,16}\]. The broad absorption around 3100–3500 cm\(^{-1}\) were assigned to the Si-OH reside, formed in the hydrolysis of alkoxy groups of TEOS. This band was barely detectable in the spectrum of H-1 with a lower silica content but increased its intensity in that of C-4 with a high silica content\[^{17}\]. Besides, the FT-IR spectrum consists of some peaks located at 1520 cm\(^{-1}\) (\(\nu_{as}, -N=N-\)), 1364 cm\(^{-1}\) (\(\nu_{s}, -C-N-C-\)), 1345 cm\(^{-1}\) (\(\nu_{as}, -NO_2\)), 1378 cm\(^{-1}\) (wagging CH\(^2\)), 695 cm\(^{-1}\) (wagging N-H), indicating that the silica xerogel networks were composed of Si-O-Si backbones and some organic groups.

Figure 5 and figure 6 showed the SEM and TEM micrographs of the prepared polyimide-silica hybrid thin films H-2 and H-4. In most cases, surface morphology of materials is of great importance for many technical applications requiring well-defined surfaces or interfaces. From figure 5, no phase separation could be observed. That was, covalent bonding (Si-O-Si) between the organic and inorganic components enhanced miscibility. They were homogeneously and uniformly dispersed at a molecular level. When the silica content was below 15wt%, the silica particle size was 50nm, which showed in Figure 6. However, when the silica content was increased to 22.5wt%, the particle size was increased to 80nm. The increase in the silica particle size clearly resulted from the increase in the aggregation tendency as the silica content and the silica particle number were increased. These micrographs showed the fine interconnected or co-continuous phases morphology, which improved the efficiency of stress transfer mechanisms between the two components.

XRD measurements were conducted to estimate the crystallinity of the hybrid materials (H-2, H-3) is shown in figure 7. A diffractogram typical of amorphous samples could be seen. The XRD patterns of the hybrid film (H-3) displayed only a very broad hump cen-
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tered at 20–21.82°C respectively; originating from amor-
phous phase of aromatic polyimide. This result also indi-
cated that covalent bonding(Si-O-Si) between the or-
ganic and inorganic components enhanced miscibility.

To examine thermal activities of hybrid materials in
higher temperature range and their thermal decomposi-
tion characteristics, DSC and TGA experiments were

carried out on NETZSCH STA449C with the heating
rate 10°C/min under nitrogen. Their data listed in

TABLE 1. Compared with the pure polyimide N, the
initial degradation temperature(Td) of hybrid materials
increased with the increase of TEOS moiety. The en-

hanced thermal stability of hybrid materials was due to
the formation of network of polyimide and the inor-
ganic moieties, which resulted from the restriction of
polymer chain mobility and becomes more intertwined
with the rigid silica network. Therefore, the existence of
covalent bonds between polyimide and silica impose
even more restrainted to chain movement in hybrids.

DSC analysis showed glass transition temperature (Tg)
for the polyimide-silica network in the hybrids at
336–362°C. Based on what was mentioned the above,
the compatibility of the PI/SiO$_2$ hybrid could be en-
hanced via incorporating polymer matrix with inorganic
silica covalently. The chemical bonding not only restricted
the migration of inorganic silicates but also hindered the
aggregation of silanol$^{[18]}$. It was estimated that these
materials would be pretty good for the practical appli-
cation.

High-quality films could be easily prepared from
the polyimides and hybrids solutions in NMP by spin
coating on ITO glass. The electro-optic (EO) coeffi-
cient measurement of our nanohybrid was performed
at a wavelength of 832 nm. The test sample consisted
of a high-index prism, a thin silver film, a poled material
layer, a buffer layer, and a base silver film. The silver
film was thermally evaporated onto the hypotenuse face
of a high-index prism as the first electrode. The thick-
ness of the film was about 55nm. A polymer was spin
coated onto the silver substrate to a thickness of 1-
2μm, which can support four or five surface-plasmon
modes with TE or TM polarization. A polymer buffer
layer was then coated onto the polyimide film to a thick-
ess of 3-5μm or so. Corona discharge poling was
performed by alignment of the chromophore dipoles in
a high static electric field while the polyimide was heated
to high mobility close to its glass transition temperature.
The poling voltage was 1500 V. Finally, another silver
film was deposited onto the buffer layer as the second
electrode. The $\gamma_{33}$ values were listed in TABLE 1. From

the TABLE 1, the $\gamma_{33}$ coefficients of hybrids were
smaller than corresponding polyimide. This was due to
the content of chromophore is smaller than the pure
polyimide. Therefore, these results showed that these
polymers might be useful in photonic device applica-
tions.

CONCLUSION

Transparent Nonlinear Optical(NLO) inorganic/
organic waveguide films systems had been prepared in
situ sol-gel process. They have network structure and
silica particles were uniformly dispersed in the nanoscale.
Covalent bonding(Si-O-Si) between the organic and
inorganic components enhanced miscibility between the
silica and the copolymer. The thermogravimetric analy-
sis and differential scanning calorimetry behaviors indica-
ted excellent thermal stability. The resulting polyimide/
silica hybrids exhibited a relatively high $T_g$ 336°C and
thermal stability up to 448°C. Large EO coefficient val-
ues (20-30pm/V) at the wavelength of 832 nm were
achieved and the values remained well.

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