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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(γ_{33}) at the wavelength of 832 nm for polymer thin films poled were in the range of 20-30pm/V.

KEYWORDS

Nonlinear optical;
Hybrid;
Polyimide;
Electro-optical property.

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 chromophore ,hydroxyl polymide 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 other reagents and solvents were obtained commercially and were used as received.

IR spectra of the prepared thin films were obtained on a KBr pellet using Nicolet AVATAR 360 spectrometer. To examine the optical characteristics of materials with addition of sample light transmission was measured in ultraviolet and visible range by means of spectrophotometer(shimadzu UV-240). The fracture surfaces of hybrid thin films were examined on the HITACHI X-650 Scanning Electron Microscope (SEM). HITACHI H-600 Transmission Electron Microscope(TEM) measured the particle sizes. Thermogravimetric analysis(TGA) and differential scanning calorimetry(DSC) were performed on NETZSCH STA449C. The programmed heating range was from room temperature to 800^{0}C, at a heating rate of 10^{0}C/min under nitrogen atmosphere. The measurement was taken using 6-10mg samples. TGA and DSC curves were recorded. X-ray diffraction (XRD) patterns of SiO_2 were obtained with a CuKα X-ray source and a step of 0.02(2θ) and run from $2\theta=680^0$ at room temperature. The elemental analysis was determined on the Foss Heraeus CHN-O-Rapid.

Synthesis of a NLO chromophore

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^{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^{0}C. The mixture was added dropmise into a solution of N-2-hydroxyethyl-N-methylaniline (15.1000g, 0.10mol) with abundance HAc-NaAc. The mixture was stirred at 40-50^{0}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, $-CH_2CH_2O-$, 2H), 3.73(s, $-CH_2CH_2O-$, 2H), 2.46(s, $-CH_3$, 3H). Anal. Calcd for $C_{21}H_{20}N_6O_2$: C, 62.38%; H, 4.95%; N, 20.79%. Found: C, 62.48%; H, 4.89%; N, 20.82%.

Hydroxyl polyimide synthesis

The polymerization was conducted in a dry nitrogen flushed three-neck flask with a magnetic stirrer, reverse Dean-stark trap, and reflux condenser filled dry xylene. A stoichimetric amount of PMDA (1.636g, 7.5mmol) was added to a solution of 6FHP(2.7470g, 7.5mmol) in 30mL DMAC at 0^{0}C. The solution was then warmed to room temperature and magnetically stirred overnight under nitrogen to form the poly(amic acid) solution. Dry xylene(30mL) was added to the flask, and the poly(amic acid) was thermally cyclized in an oil bath at 160^{0}C for 5h under nitrogen atmosphere. The resulting solution was added dropwise into a solution of methanol/water(1:1,V/V,50ml) and 2NHCl(10mL) in a high-speed blender to obtain the polyimide M. The product was filtered and washed with methanol/water (1:1,10ml) for three times, and dried at 60^{0}C under vacuum for 24h. M^{1}H NMR (300MHz, CD_3COCD_3, ppm): 10.62(s, OH, 2H), 8.32(s, ArH, 2H), 7.62(s, ArH, 2H), 7.31(d, ArH, 2H), 7.10(d, ArH, 2H). Anal. Calcd for $C_{25}H_{10}F_6N_2O_6$: 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

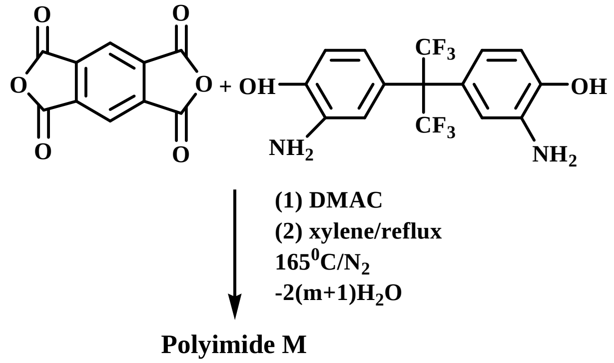

Figure 1 : Synthetic route for hydroxyl polyimide

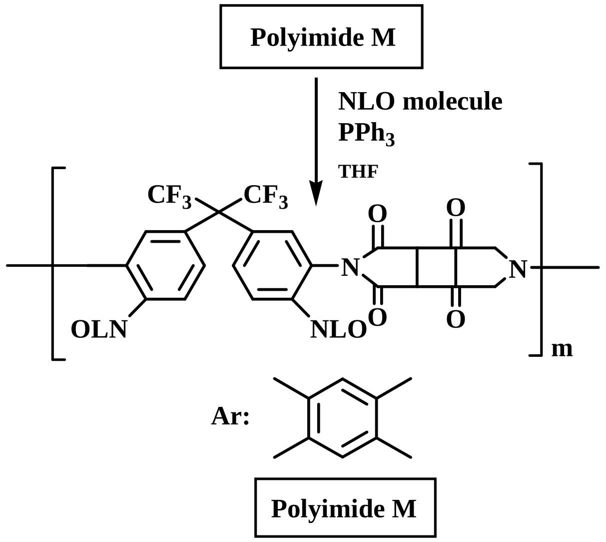

Figure 2 : Synthetic route for PMDA-6FHP-NLO polyimide

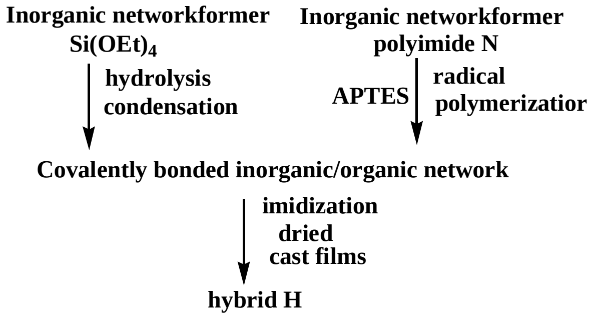

Figure 3 : Synthesis of polyimide/silica hybrid

and has a M_n of 16,600, an M_w of 37,400 with a polydispersity of 2.30(polystyrenes as standards). The synthetic route was shown in figure 1.

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 reprecipitated into the solution of methanol/water. The product was filtered out and washed with methanol/water for several times, and dried at 60^0C under vacuum for 24h. N ^{1}H NMR (300MHz, CD_3COCD_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), 7.07(s, ArH, 4H), 6.56(s, ArH, 4H), 6.20(s, ArH, 4H), 4.20(s, $-CH_2CH_2O-$, 4H), 3.66(s, $-CH_2CH_2O-$, 4H), 2.40(s, $-CH_3$, 6H). Anal. Calcd for $C_{67}H_{46}F_6N_{14}O_{10}$: 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 2.

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 evapora-

TABLE 1 :Reactant summary and properties of polyimide and hybrid systems

Materials	TEOS(wt%)	polyimide(g)	APTES(ml)	HCl(ml)	H_2O(ml)	THF(ml)	Appearance^a(ml)	T_g^b(^{0}C)	T_d^c(^{0}C)	γ_{33}(pm/V)
N	0							213	352	30
H-1	5	2.55	0.20	0.10	0.25	30	Transparent	336	448	28
H-2	10	2.55	0.20	0.25	0.53	30	Transparent	338	451	25
H-3	15	2.55	0.20	0.50	1.02	30	Transparent	341	453	23
H-4	22.5	2.55	0.20	0.65	2.10	30	Transparent	343	456	20

^{a}UV-Vis spectrum was observed; ^{b}Experimental results from DSC; ^{c}Experimental results from TGA

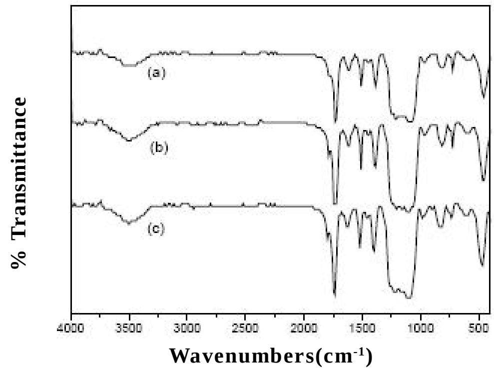

Figure 4 : FT-IR spectrums of H-1(a), H-3(b) and H-4(c)

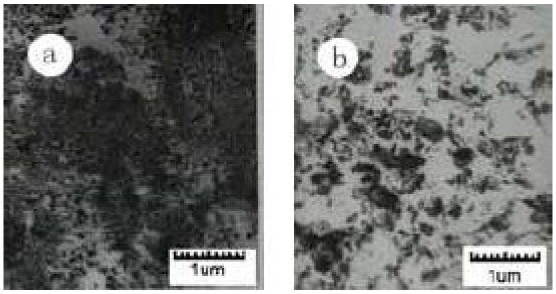

Figure 5 : SEM photographs of H-2(a) and H-4(b)

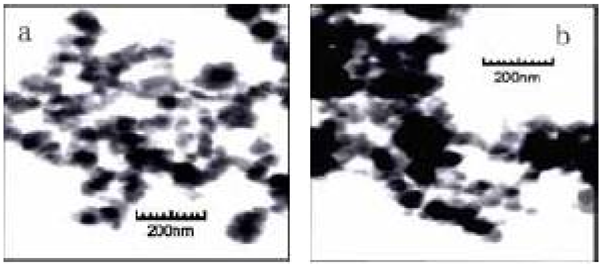

Figure 6 : TEM photographs of H-2(a) and H-4(b)

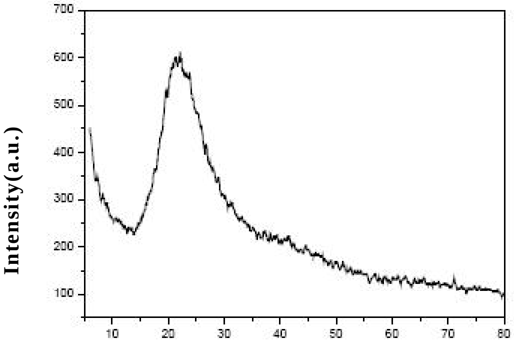

Figure 7 : XRD patterens of the H-3

tion conditions. The synthetic route was shown in figure 3. TABLE 1 summarized the various hybrid systems fabricated for this study.

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, 1774cm^{-1} for all samples as shown in Figure 4. The absorption band around 1000~1140cm^{-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 1520cm^{-1}(ν_{as}, -N=N-), 1364cm^{-1}(ν_{str}, -C-N-C-), 1345cm^{-1}(ν_{s}, -NO_2), 1378cm^{-1} (wagging CH_2), 695cm^{-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,) 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 centered at $2\theta=21.82^0C$ respectively; originating from amorphous phase of aromatic polyimide. This result also indicated that covalent bonding(Si-O-Si) between the organic and inorganic components enhanced miscibility.

To examine thermal activities of hybrid materials in higher temperature range and their thermal decomposition characteristics, DSC and TGA experiments were carried out on NETZSCH STA449C with the heating rate 10^0C/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 enhanced thermal stability of hybrid materials was due to the formation of network of polyimide and the inorganic 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 $336\sim362^0C$. Based on what was mentioned the above, the compatibility of the PI/SiO_2 hybrid could be enhanced 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 application.

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) coefficient 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 thickness 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 thickness 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 γ_{33} values were listed in TABLE 1. From the TABLE 1, the γ_{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 applications.

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 analysis and differential scanning calorimetry behaviors indicate excellent thermal stability. The resulting polyimide/silica hybrids exhibited a relatively high $T_{g-}336^0C$ and thermal stability up to 448^0C. Large EO coefficient values (20-30pm/V) at the wavelength of 832 nm were achieved and the values remained well.

ACKNOWLEDGMENT

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