Synthesis and electro-optic properties
of fluorine-containing polyimide

Qiu Fengxian[1]   Zhou Yuming[2]   Yang Yanfang[3]   Liu Juzheng[2]   Cao Zhuangqi[3]

([1] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China)

([2] School of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China)

([3] Guided Wave Optoelectronics Device Laboratory, Department of Physics, Shanghai Jiaotong University, Shanghai 200240, China)

Abstract: The fluorine-containing organic polymer was synthesized from 3, 3', 4, 4'-Bisphenyltetracarboxylic (BPDA), and 2, 2-Bis (3-amino-4-hydroxyyphenyl) hexafluoropropane (6FHP). It is a first-step preparation of a preimided hydroxy-containing polyimide, followed by the covalent bonding of an active chromophore, dispersed red 19 (DR19), onto the backbone of the polyimide via the Mitsunobu reaction. The nonlinear optical (NLO) containing polyimide was synthesized. The differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA) exhibited T_g and the temperature T_d at which 5% mass losses occurring of polymer were 248 and 309 ℃, respectively. A reflective electro-optic (EO) modulator using this polymer was fabricated. The optical nonlinearities were determined to be $d_{33} = 5.209 \times 10^{-9}$ esu (poling voltage of 3.6 kV, 205 ℃) and $d_{33} = 7.418 \times 10^{-9}$ esu (poling voltage of 3.8 kV, 210 ℃) by the second harmonic generation method in in-situ condition at a fundamental wavelength of 1 064 nm. The EO coefficients γ_{33} of the polymer layer in the EO modulator were determined to be 2.182 pm/V (poling voltage of 3.6 kV, 205 ℃) and 3.107 pm/V (poling voltage of 3.8 kV, 210 ℃) at 1 064 nm by an attenuated-total-reflection (ATR) method.

Key words: nonlinear optical; electro-optic property; polyimide

Polyimide polymer functionalized with nonlinear optical (NLO) chromophores have received considerable attention in the development of photonics and optoelectronics-based technologies, due to its large electro-optic (EO) coefficients, low dielectric contents desirable for high-speed devices, and flexibility in fabrication[1–5]. Polyimides are commonly synthesized by the reaction of dianhydrides with diamines to provide poly (amic acid) precursor polymers, followed by a high-temperature imidization process to produce the desired polyimides. However, this two-step approach makes it difficult to obtain the quantitative transformation from amic form to amide ring, and it limits the choice of nonlinear optical chromophores because of the high temperature reaction required. We present a one-step preparation of a preimided hydroxy-containing polyimide, followed by the covalent bonding of a chromophore onto the backbone of the polyimide via the Mitsunobu reaction. By the introduction of the chromophore at the last stage through very mild Mitsunobu condensation, the chromophore-containing diamine synthesis and harsh imidization process of the poly (amic acid) are avoided.

In this study, we synthesized the polyimide and reported the detailed studies on the characterization of the polymer. A reflective EO polymer light modulator based on attenuated-total-reflection (ATR) was fabricated using the polyimide as EO material. And the investigation on the performance of this EO modulator indicates that it successfully encoded electrical signals onto reflected light without perceptible distortion or retardation, which demonstrates the suitability of the NLO polyimide for the application in actual EO devices.

1   Experimental

1.1   Reagents

N-dimethylacetamide (DMAC) were stirred over powered calcium hydride overnight and then distilled under reduced pressure and stored over 0.4 nm molecular sieves. 3, 3', 4, 4'-Bisphenyltetracarboxylic (BPDA) and 2, 2-Bis (3-amino-4-hydroxyyphenyl) hexafluoropropane (6FHP) used in the polyimide synthesis were obtained from TCI and used without further purification. Dispersed red 19 was obtained from the

Acros Organics. Tetrahydrofuran (THF) was purified by distillation and other reagents were obtained commercially.

1.2　Polymer synthesis

The polymerization was conducted in a dry nitrogen flushed three-neck flask with a magnetic stirrer, a reverse dean-stark trap, and reflux condenser filled with dry xylene. A stoichimetric amount of 3, 3', 4, 4'-Bisphenyltetracarboxylic (BPDA) (1.471 1 g, 5 mmol) was added to a solution of 2, 2-Bis (3-amino-4-hydroxyyphenyl) hexafluoropropane (6FHP) (1.731 3 g, 5 mmol) in 30 mL DMAC at 0 ℃. The solution was then warmed to room temperature and magnetically stirred overnight under nitrogen to form the poly (amic acid) solution. Distilled xylene (30 mL) was added to the flask, and the poly (amic acid) was thermally cyclized in an oil bath at 160 ℃ for 5 h under nitrogen atmosphere. The PPh$_3$(1.311 5 g, 5 mmol) and dispersed red 19 (3.303 3 g, 10 mmol) was dissolved in DMAC (15 mL). Diethyl azodicarboxylate (DEAD) (0.850 2 g, 5 mmol) was added dropwise into the solution under nitrogen atmosphere. The reaction mixture was stirred for 2 d at room temperature, and then the resulting reaction solution was added dropwise into an agitated solution of methanol/water (1 : 1, 30 mL) and 2 mol/L HCl (5 mL) in a high-speed blender. The collected solid further precipitated in THF (10 mL) was reprecipitated into the solution of methanol/water. The product was filtered out and washed with methanol/water for several times, and dried at 60 ℃ under vacuum for 24 h. Yield: 4.55 g (70%). Anal. Calcd for $C_{47}H_{29}F_6N_6O_8$: C, 61.37%; H, 3.16%; N, 9.14%. Found: C, 61.43%; H, 3.12%; N, 9.32%. The molecular weight can be measured by GPC and has an M_n of 23 400, an M_w of 58 200 with a polydispersity of 2.49 (polystyrenes as standards). The synthetic process is shown in Fig. 1.
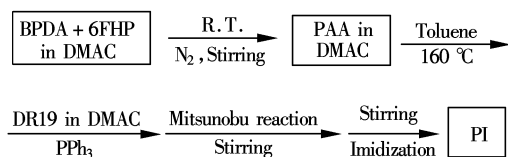

Fig. 1　Synthesis of the polyimide

1.3　Instrumentation

FT-IR spectra of the prepared hybrids were obtained between 4 000 and 400 cm^{-1} on a KBr pellet using a Nicolet AVATAR 360 FT-IR spectrometer. A minimum of 32 scans was signal-averaged with a resolution of 2 cm^{-1} in the 4 000 to 400 cm^{-1} range. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on NETZSCH STA449C. The programmed heating range was from room temperature to 800 ℃, at a heating rate of 10 ℃/min under nitrogen atmosphere. The measurement was taken using 6 to 10 mg samples. UV-vis spectrum was recorded on a Shimadzu UV-240 spectrometer.

2　Results and Discussion

2.1　Characterization and physical properties of PI

Fig. 2 illustrates the FT-IR spectra of the prepared polyimide. The characteristic peaks of symmetric C=O stretching and asymmetric C=O stretching of the imides group were clearly visible at 1 719 and 1 772 cm^{-1}, respectively. The assignment of the stretching of the imides ring was at 1 374 cm^{-1}. Besides, the FT-IR spectrum consisted of some peaks located at 1 513 cm^{-1} (ν_{as}, —N=N—), 1 374 cm^{-1} (ν_{str}, —C—N—C—)[6-7]. ^{1}HNMR (300 MHz, CD$_3$COCD$_3$, ppm): 8.38(d, ArH, 4H), 8.05(s, ArH, 4H), 7.34(d, ArH, 2H), 7.12(d, ArH, 2H), 7.06(s, ArH, 2H), 6.54(s, ArH, 2H), 6.20(s, ArH, 4H), 4.18(s, —CH$_2$CH$_2$O—, 4H), 3.65(s, —CH$_2$CH$_2$O—, 4H), 10.62(s, OH, 1H). The PI was soluble in many organic solvents such as NMP, THF, DMF, chloroform, acetone, bromobenzene and so on. The differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA) exhibited high T_g and the temperature T_d values at which 5% mass losses occurring of polymer were 248 and 309 ℃, respectively. This TGA showed that the initial decomposition temperature of PI was much higher than T_g, indicating that high temperature electric poling was feasible without damaging the chromophore. The UV-vis spectra of the prepared polyimide, UV-vis (DMF) was λ_{max} = 498 nm.
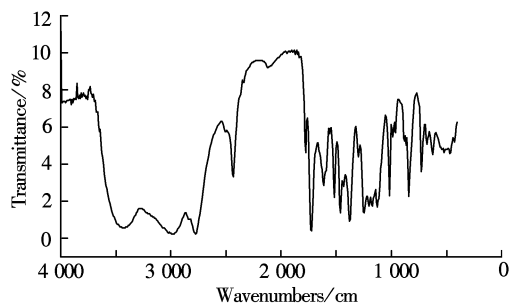

Fig. 2　FT-IR spectrum of polyimide

2.2　Polymer film preparation and poling characterization

To obtain optical-quality films, N-Methyl-2-pyrrolidone (NMP) was selected as the optimal spin casting solvent, as it is capable of leading to appropriate vis-

cosity. The polymer solution was filtered through a 0.45 μm Teflon membrane filter to remove insoluble particles and was then spin-coated at 1 000 r/min. The film was then dried under vacuum at 110 ℃ for 12 h to remove the residual solvent. For the further alignment of the dipole moment of the chromophore, the PI film was electrically poled with a corona discharge poling method at a temperature of 205 ℃ with a poling voltage of 3.6 kV and 210 ℃ with a poling voltage of 3.8 kV, respectively. The distance between the sample surface and the needle electrod was 1 cm. Then the PI film was cooled to room temperature in the presence of the electric field.

2.3 Device fabrication and electro-optic characterization

A reflective EO polymer light modulator was fabricated using PI as the EO material. The test sample consisted of a high-index prism, a thin silver film, a poled material layer, a buffer layer, and a base gold film. The silver film was thermally evaporated onto the hypotenuse face of a high-index prism as the first electrode. A polymer was spin-coated onto the silver substrate to a thickness of 1 to 2 μm, 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 5.68 μm. Finally, a gold film was deposited onto the buffer layer as the base electrode. The electro-optic characterization of the PI layer in the EO modulator was conducted by an improved ATR technique as shown in Fig. 3[8]. The electro-optic coefficient γ_{33} of the EO polymer layer in the EO modulator can be determined according to the following equation:

$$\gamma_{33} = -\frac{2n_1\cos\theta}{kn_3^3 E}\Delta I \qquad (1)$$

where γ_{33} is the EO coefficient of the polymer; n_1 and n_3 are the refractive indices of the prism and the polymer film, respectively; E is the applied electric field; ΔI is the modulated light intensity; θ is the light incident angle, which is defined as the modulator's working interior angle; and k is the slope value of the fall-off the ATR resonance dip[8].
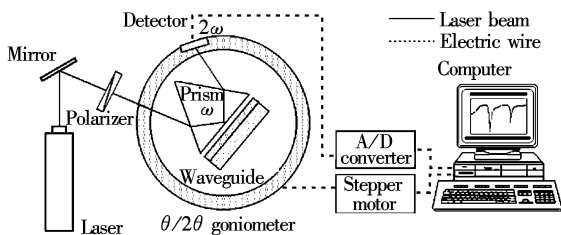

Fig. 3 Schematic diagram of an improved ATR apparatus

2.4 Electro-optic properties of PI

The EO characterization of the polyimide layer in this modulator was conducted by an ATR technique. The resulting reflected light intensity was recorded as a function of the incident angle along with the rotation of a $\theta/2\theta$ computer-controlled goniometer. Fig. 4 shows a reflectivity scan obtained for TM-polarized light of $\lambda = 1$ 064 nm with this multilayer prototype device. Each of the sharp dips corresponds to a TM waveguide mode, and five waveguide modes can be identified within the angular range of 52 to 56°. As the TM_1 guide mode is of the narrowest resonance width, which means the largest k value in Eq.(1), and was most the refractive index change in the EO polymer layer induced by the applied electric field, the angle near the TM_1 resonance dip was chosen as the modulator's working interior angle θ[9]. The values of EO coefficients of the PI at different temperatures and poling voltages determined according to Eq.(1) are listed in Tab.1. The polymer can be regarded as a promising material for EO device fabrication in virtue of its easy synthetic accessibility, excellent film-forming properties, good and fast EO response and high long-term stability of NLO properties at elevated temperature. Moreover, the EO coefficient can be further enhanced by modification of the NLO chromophore, increase of the NLO chromophore concentration and/or optimization of the poling process to achieve larger orientation degree of the chromophore dipole moments.
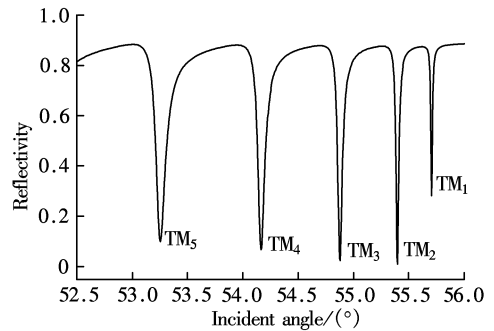

Fig. 4 ATR spectra of the polyimide

Tab.1 Optical properties of polymer layer in the EO modulator

Thickness/ μm *	Temperature/℃	Poling voltage/kV	d_{33}/ (10^{-9}esu) **	γ_{33}/ (pm·V^{-1}) ***
5.68	205	3.6	5.209	2.182
5.68	210	3.8	7.418	3.107

Notes: * Thickness of polyimide polymer layer in the EO modulator determined by the improved m-line method.

** Optical nonlinearities of polyimide layer in the EO modulator determined by the ATR technique at 1 064 nm.

*** Electro-optic coefficients of polyimide layer in the EO modulator determined by the ATR technique at 1 064 nm.

3   Conclusion

We synthesized a fluorine-containing organic polyimide polymer via the Mitsunobu reaction. The differential scanning calorimetry and thermogravimetric analysis behavior indicated excellent thermal stability. The optical nonlinearities d_{33} of this polymer were determined to be 5.209×10^{-9} esu (3.6 kV, 205 ℃), 7.418×10^{-9} esu (3.8 kV, 210 ℃) and the EO coefficients γ_{33} were determined to be 2.182 pm/V (3.6 kV, 205 ℃), 3.107 pm/V (3.8 kV, 210 ℃) at 1 064 nm by an ATR method.

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含氟聚酰亚胺的合成及电光性能

邱凤仙[1]   周钰明[2]   杨艳芳[3]   刘举正[2]   曹庄琪[3]

([1] 江苏大学化学化工学院,镇江 212013)
([2] 东南大学化学化工学院,南京 210096)
([3] 上海交通大学物理系导波光电子器件实验室,上海 200240)

摘要:以含氟的二胺 5,5'-(六氟异丙基)-二-(2-氨基苯酚)及二酐 3,3',4,4'-苯四甲酸二酐(BP-DA)为单体,首先合成了经酰胺化的主链上带有活性羟基的含氟聚酰亚胺,再通过 Mitsunobu 反应将活性生色分子分散红-19 共价链接到聚酰亚胺的侧链骨架上,合成了非线性光学(NLO)含氟聚酰亚胺. 示差扫描量热分析(DSC)测得其玻璃化转变温度为 248 ℃,热重分析(TGA)测得其 5% 失重的热分解温度为 309 ℃,将制得的含氟聚酰亚胺制成反射电光调制器,由二次谐波条件于 1 064 nm 处测得不同温度下的非线性系数 d_{33} 为 5.209×10^{-9} esu (极化电压 3.6 kV,205 ℃)和 7.418×10^{-9} esu (极化电压 3.8 kV,210 ℃),用衰减全反射法测得其电光系数 γ_{33} 为 2.182 pm/V (3.6 kV, 205 ℃)和 3.107 pm/V (3.8 kV,210 ℃).

关键词:非线性光学;电光性能;聚酰亚胺
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