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High T_g donor-embedded polyimides for second-order nonlinear optical applications

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Abstract

We present here a class of processible donor-embedded nonlinear optical (NLO) polyimides exhibiting the high glass-transition temperature and exceptional thermal and chemical stability. Due to the rigidity of the donor-embedded structure, the stability of the electric field induced dipole orientation of the NLO chromophores was enhanced. A sizable second-order nonlinear optical coefficient was obtained.

Keywords: Polyimide; Addition polymerization; Nonlinear optics

1. Introduction

The second-order nonlinear optical (NLO) polymers have been attracting a lot of attention because of their potential use for second-harmonic generation (SHG) and for very high speed optical switching and modulation [1–3]. One of the key issues in realizing this potential is whether the NLO polymers have good temporal stability. For second-order NLO polymers utilizing an external electric field to achieve the orientation of the chromophores, the poling-induced order is thermodynamically unstable, especially at elevated temperatures. To prevent the randomization of the aligned chromophores various approaches have been used. One of the most considerable progresses is to use high glass transition temperature (T_g) polymer systems such as polyimides.

Aromatic polyimides have been widely used in the electronic industry because of their exceptional thermal, mechanical, optical, and dielectric properties [4]. The first use of polyimides as NLO materials was in guest/host systems [5]. To overcome the common problems appearing in doped systems, such as low loading density of chromophores, sublimation of chromophores at elevated temperatures and rapid relaxation of poling-induced order, the functionalized polyimides [6–8] had been studied widely and their better NLO thermal stability and nonlinearities had been demonstrated. However, the poor solubility of many polyimides in common organic solvents makes it difficult to obtain good optical quality films. Most NLO polyimides reported in the literature were synthesized via the standard, two-step condensation polymerization. Poly(amic acid) prepolymers were first synthesized by the reaction of a diamino monomer with a dianhydride monomer, and were spin-coated to form the uniform films. Films were then imidized by thermal cyclization at high temperatures during poling. Unfortunately, high poling field could not be applied for this film due to the release of small molecules (such as H_2O) in the process of imidization [9]. These problems severely hindered the further development of polyimides for practical applications. To circumvent them, the high T_g chromophore-functionalized polyimides could be synthesized via addition polymerization between NLO active diamino monomers and bismaleimides. In this paper, we report the detailed studies of such a polymer.

2. Experimental

All of the chemicals were purchased and used as received unless otherwise stated. The solvents were purified by distillation under reduced pressure over anhydrous magnesium sulfate and dried further over molecular sieves before used. ^1H NMR spectra were recorded on a VARIAN-200 spectrometer and the chemical shifts were referenced relative to TMS. MS spectra were recorded on an AEI MS-50 mass spectrometer. The elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer for C, H, and N

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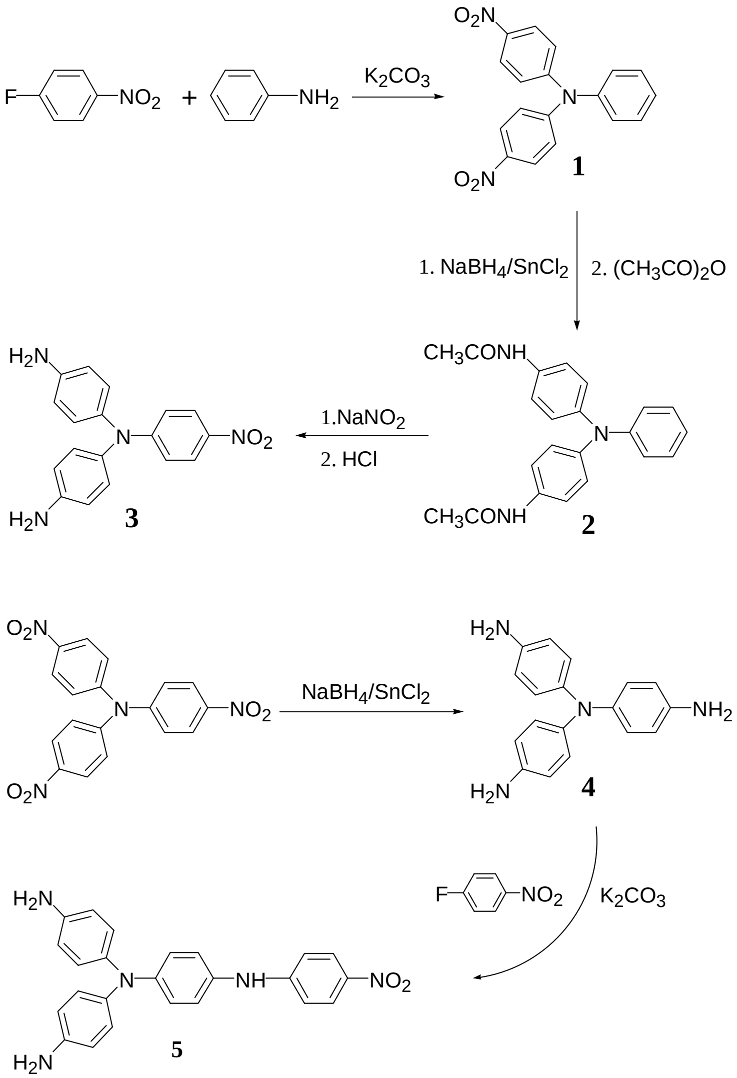
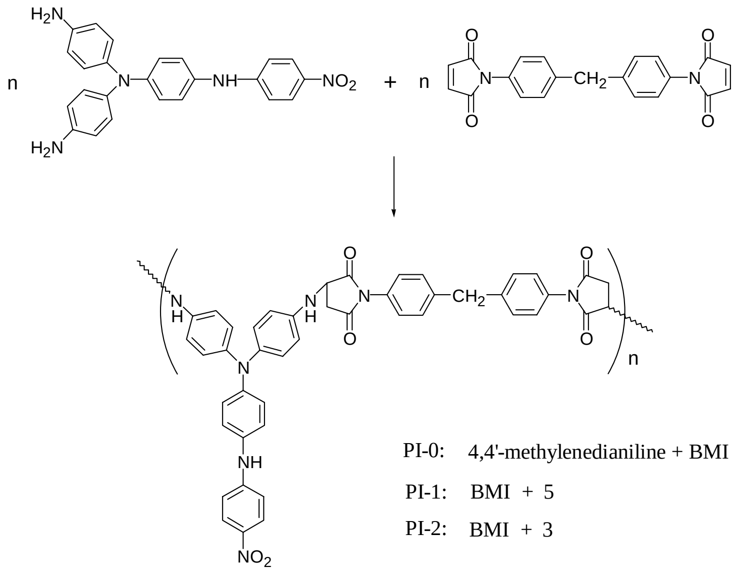


Scheme 1.



PI-0: 4,4'-methylenedianiline + BMI

PI-1: BMI + 5

PI-2: BMI + 3

Scheme 2.

determinations. FT-IR and UV–Vis spectra were recorded using an IBM IR/32 Fourier transform instrument and a Shimadzu-240 spectrophotometer, respectively. The thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC) studies were conducted on Perkin–Elmer DSC-7 series at a heating rate of 10°C/min. Gel permeation chromatography (GPC) analyses were carried out on a Perkin–Elmer Model 200 HPLC system using polystyrene as the standard and chloroform as the eluant.

The syntheses of monomers and polymers were shown in Schemes 1 and 2, respectively.

2.1. Syntheses of monomers

*2.1.1. 4,4′-Dinitrotriphenylamine (**1**)*

A mixture of 4.34 g (46.6 mmol) of freshly distilled aniline, 13.70 g (97.1 mmol) of *p*-fluoronitrobenzene and 8.50 g (61.5 mmol) of potassium carbonate was slurried in 60 ml of dimethylsulfone (DMSO) at 130°C for 7–8 h. After being cooled down to room temperature the reaction mixture was poured into 200 ml of cold water, the solid was collected by filtration and washed with water completely, and then with 25 ml of isopropyl alcohol three times. The crude product was recrystallized from glacial acetic acid to yield a yellow solid (10.21 g, 65%, mp 182–184°C). ^{1}H NMR (DMSO-d$_6$, ppm): δ 7.20 (d, $J = 8.5$ Hz, 2H), 7.28 (m, 3H), 7.51 (t, 2H), 8.17 (d, $J = 8.5$ Hz, 2H). MS: M$^+$, 355. Anal. Calcd. for $C_{18}H_{13}N_3O_4$: C, 64.48; H, 3.88; N, 8.36. Found: C, 64.21; H, 4.06; N, 8.47.

*2.1.2. 4,4′-Diacetaminotriphenylamine (**2**)*

Under nitrogen atmosphere, 30 ml of dimethylformamide (DMF) was added to a flask containing 6.70 g (20 mmol) of **1** and 45 g (200 mmol) of $SnCl_2 \cdot 2H_2O$. To this solution was added dropwise 1.50 g (40 mmol) of sodium borohydride in 10 ml of DMF. The reaction mixture was reacted at 60°C for 4 h. Then, it was cautiously poured into 200 ml of 1 M sodium hydroxide solution in an ice bath, and neutralized to pH 9 by dropwise addition of saturated sodium hydroxide solution. The collected solid was redissolved in 20 ml of chloroform to which 15 ml acetic anhydride was added dropwise. The mixture was stirred at ambient temperature for 1 h, and the solvent was removed by rotary evaporation. The residue was extracted with petroleum ether to yield a gray solid which was recrystallized from ethanol to give **2** (2.60 g, 36%, mp 217–218°C). ^{1}H NMR (DMSO-d$_6$, ppm): δ 2.03 (s, 6H); 6.86 (m, 6H); 7.21 (m, 1H); 7.43 (d, $J = 8.5$ Hz, 2H); 7.58 (d, $J = 8.5$ Hz, 4H); 9.82 (d, $J = 8.5$ Hz, 2H). MS: M$^+$, 359. Anal. Calcd. for $C_{22}H_{21}N_3O_2$: C, 73.54; H, 5.85; N, 11.70. Found: C, 73.75; H, 5.94; N, 11.72.

Compound **4** was prepared by the same method as the preparation of **2**. The product was obtained with a yield of 86% as white, shiny needle crystals (mp 242–244°C). ^{1}H NMR (DMSO-*d*$_6$, ppm): δ 6.52 (AB q, 6H); 6.60 (br, 6H); 6.89 (AB q, 6H). MS: M$^+$, 290. Anal. Calcd. for $C_{18}H_{18}N_4$: C, 74.48; H, 6.21; N, 19.31. Found: C, 74.24; H, 6.36; N, 19.17.

*2.1.3. 4,4′-Diamino-4″-nitrotriphenylamine (**3**)*

To a solution of 1.10 g (3 mmol) of **2** in 50 ml of glacial acetic acid was added 0.60 g (8.7 mmol) of sodium nitrite in 2 ml of water at 50°C. After 30 min, the resulting mixture was cooled and poured into 200 ml of cold water. The crude solid was extracted by ethyl acetate. After the evaporation of solvent, the residue was purified by column chromatography packed with silica gel in ethyl acetate/chloroform (volume ratio 5/1). The purified yellow powder was redissolved in 15 ml of glacial acetic acid and 5 ml of conc. HCl. The resulting solution was refluxed for 3 h and neutralized with saturated sodium bicarbonate aqueous solution. The precipitate was collected and purified by column chromatography with chloroform/methanol (volume ratio 5/1). 128 mg (13%, mp 273–274°C) of orange crystals **3** was obtained from the second major red band after the removal of solvent. ^{1}H NMR (DMSO-d$_6$, ppm): δ 4.67 (br, 4H); 6.43 (d, $J = 8.5$ Hz, 2H); 6.56 (d, $J = 8.5$ Hz, 2H); 6.97 (d, $J = 8.5$ Hz, 4H); 7.90 (d, $J = 8.5$ Hz, 2H). MS: M$^+$, 320. Anal. Calcd. for $C_{18}H_{16}N_4O_2$: C, 67.50; H, 5.00; N, 17.50. Found: C, 67.45; H, 5.11; N, 17.35.

*2.1.4. 4-(N,N-bis(p-aminophenyl)amino)-4′-nitrodiphenylamine (**5**)*

Under nitrogen atmosphere, a mixture of 0.82 g (2.8 mmol) of **4**, 0.4 g (2.8 mmol) of *p*-fluoronitrobenzene and 0.40 g of Na_2CO_3 powder was stirred in 25 ml of DMSO at 50–60°C for 1–2 days. The reaction was terminated when only trace of *p*-fluoronitrobenzene was detected by thin-layer chromatography. Then, the cooled mixture was poured into water and the precipitate was purified by column chromatography packed with silica gel in the eluant of ethyl ether/ethyl acetate (volume ratio 1:1). Finally, the recrystallization from ethyl acetate/hexane provided 0.18 g (15%, mp > 300°C) of **5**. ^{1}H NMR (DMSO-d$_6$, ppm): 4.67 (br, 4H); 6.43 (d, $J = 7.5$ Hz, 4H); 6.59 (d, $J = 7.5$ Hz, 2H); 6.72 (d, $J = 7.5$ Hz, 6H); 7.76 (d, $J = 7.5$ Hz, 2H); 8.23 (d, $J = 7.5$ Hz, 2H); 8.96 (s, 1H). MS: M$^+$, 411. Anal. Calcd. for $C_{24}H_{21}N_5O_2$: C, 70.07; H, 5.11; N, 17.03. Found: C, 70.32; H, 5.14; N, 16.81.

2.2. Thin-film preparation

The solution of bismaleimide (BMI) and **3** or **5** (molar ratio 1:1) in freshly distilled dimethylacetamide (DMAc) was heated at 70–80°C for ca. 6 h under nitrogen. The solution of prepolymer was filtered through a 0.2 μm syringe filter and spin-coated (around 3000 r/min) onto an indium–tin oxide (ITO) glass slide. The films were dried in a vacuum oven at 60°C for 2 days.

2.3. Poling properties and second-order nonlinearity measurements

The prepolymer films were poled/cured with a corona-discharge set-up, which was built into the sample chamber of a UV–Vis spectrophotometer [10], so that the poling efficiency could be monitored in situ. The poling conditions were as follows: poling voltage, 6–7 kV at the needlepoint; gap distance, 1 cm. The poling temperature and poling current were monitored and recorded by computer. The poling process was terminated when the poling current no longer increased with the increase of the poling temperature. The dynamic stability of the induced polar order was studied by annealing the sample at a rate of 5°C/min while monitoring the change of the film's order parameter.

The second-order NLO properties of poled films were characterized by SHG measurements. A mode-locked Nd:YAG laser (10 Hz repetition rate) was used as the fundamental light (1064 nm). The second-harmonic signal was detected and amplified by a photomultiplier tube. After amplification, it was averaged and transferred to digital signal, which was adopted and treated by computer. A z-cut quartz crystal was used as the reference sample.

3. Results and discussion

3.1. Synthesis of chromophores and their optical nonlinearities

Scheme 1 shows the pathways for the preparation of the diamino chromophores **3** and **5**. 4,4′-Diaminotriphenylamine and tris(*p*-aminophenyl)amine, the starting materials for **3** and **5**, respectively, were prepared through the reduction of the corresponding nitro compounds with sodium borohydride in the presence of $SnCl_2 \cdot 2H_2O$ in ethanolic medium. Initially, we tried to reduce the three nitro groups in tris(*p*-nitrophenyl)amine by hydrogen in a Parr pressure bottle with 10% Pd on charcoal. While the starting material was consumed completely, the reaction did not proceed further by bubbling hydrogen gas or by the addition of 10% Pd/C. Obviously, the present reaction conditions were not able to reduce all the nitro groups. We chose sodium borohydride–stanneous chloride in ethanolic medium [11] as a reductant for the multiple nitro groups. This reduction reaction proceeds, in a homogenous system, with favorable yields and easy work-up.

The reaction between amines and *p*-fluoronitrobenzene involves an SN_2 mechanism. As shown in the synthesis of **1**, when aniline is employed, the two H atoms can be substituted by *p*-nitrophenyl group smoothly, and the yield is quite high (65%). However, for the synthesis of **5** the reaction should proceed at lower temperature for longer time due to the presence of more active amino groups. The mono-substituted product was separated finally by column chromatography, so that the yield is 15% only.

It is critical that the decomposition temperature of diamino monomers should be high enough to undergo higher poling temperature. It has been demonstrated [12] that dialkylamino donor substitution is a serious source of chromophore instability at high temperatures; aryl substitution at amine donor sites provides greater increases in thermal stability, and in some case leaves the net nonlinearity unchanged or even increased. For example, the simple azo derivative 4-amino-4′-nitroazobenzene exhibits an impressively high decomposition temperature (T_d) of 345°C, but diphenyl substitution (4-*N*,*N*-diphenylamino-4′-nitroazobenzene) can enhance the stability up to 393°C, an increase by nearly 50°C. At the same time, the zero-frequency hyperpolarizability (β_0) increases by a factor of 2 (they are 52.3 and 105×10^{-30} esu, respectively) [13]. Similarly, the T_d of 4-*N*,*N*-dimethylamino-4′-nitrostilbene is 290°C, but the T_d of 4-*N*,*N*-diphenylamino-4′-nitrostilbene reaches 358°C (β_0 values of these two chromophores are 42.1 and 37.3×10^{-30} esu, respectively) [12]. Another key issue of chromophore design for the application of second-order nonlinear optics is absorption wavelength. That is, there should be lower absorption of the chromophores at the fundamental wavelength and frequency-doubling wavelength. To combine above considerations, we synthesized two triphenylamines (**3** and **5**). The experiments showed that the T_d of 4-(*N*,*N*-bis(*p*-aminophenyl)amino)-4′-nitrophenyldiamine (**5**) is 325°C and β_0 calculated from MOPAC AM1 program is 24.6×10^{-30} esu, which are much higher than those of the parent compound: 3,5-diamino-4′-nitrodiphenylamine (T_d, 226°C; β_0, 12.3×10^{-30} esu).[1] The maximum absorption of **5** in dioxane is 409 nm which is red-shifted by only 16 nm compared to the parent compound. Similarly, the chromophore **3** possesses a higher β_0 (20.1×10^{-30} esu), and its maximum absorption is 405 nm. These indicate that the increase of β_0 of **5** is from the extended conjugation but not from the resonance effect.

3.2. Polymer characterization

The preparation of the polymer required a rather extensive study. Considering the requirements for the prepolymer with proper molecular weight of main chain, the molar ratio of BMI to diamino chromophore was chosen as 1:1. The progress of the Michael-addition of diamine to the double bond of BMI was characterized by spectroscopic methods. The FT-IR spectrum of the prepolymer **PI-1** is shown in Fig. 1(a). According to the assignments of bands reported by DiCiulio [14], a strong absorption band at ~3100 cm^{-1} is associated with $\nu_{=C-H}$ of the maleimide ring and a very sharp band at 1150 cm^{-1} with ν_{C-N-C} of the maleimide

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[1] It was synthesized from 3,5-dinitroaniline in our lab. ^1H NMR (DMSO-d_6, ppm): 4.83 (br, 4H); 5.60 (s, 1H); 5.69 (s, 2H); 7.06 (d, $J = 9.0$ Hz, 2H); 8.22 (d, $J = 9.0$ Hz, 2H); 8.87 (s, 1H). MS: M + , 244. Anal. Calcd. for $C_{12}H_{12}N_4O_2$: C, 59.02; H, 4.92; N, 22.95. Found: C, 58.87; H, 4.69; N, 22.86.

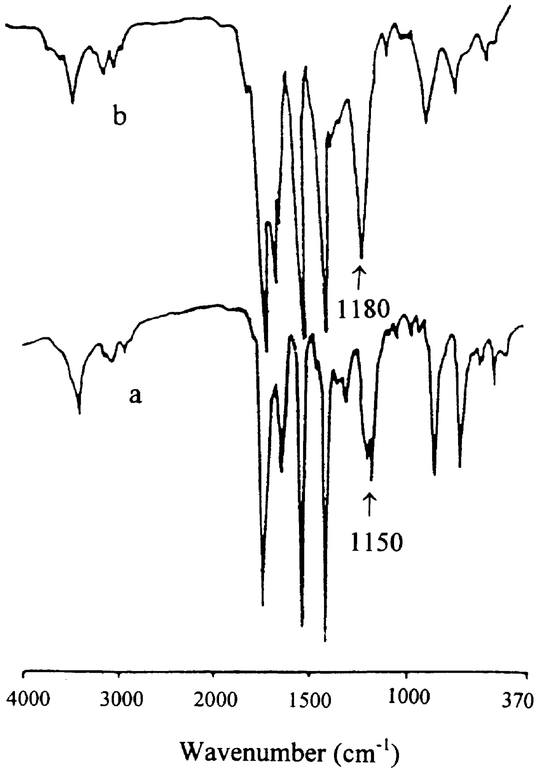

Fig. 1. FT-IR spectra of the prepolymer (a) and cured polymer (b) sample **PI-1**.

ring. Other identified bands of maleimide ring are ~830 and ~690 cm^{-1}. The band at 1150 cm^{-1} could be used for monitoring the polyaddition reaction process. On the other hand, the bands at 2900–2850 cm^{-1} ($\nu_{\text{-CH}_2\text{-}}$) and 1180 cm^{-1} ($\nu_{\text{C-N-C}}$) are due to the formation of succinimide ring in the polyaddition ring. After the prepolymer was thermally treated at elevated temperatures, the chain propagation further proceeded, which was expressed by the ratio of the band at 1180 cm^{-1} to the band at 1150 cm^{-1}, measuring the relative proportion of succinimide ring to maleimide ring. The FT-IR spectrum of polymer **PI-1**, obtained from thermal treatment of the prepolymer, is shown in Fig. 1(b). A very clear band at ~1180 cm^{-1} was observed. At the same time, the bands at ~1150, ~830, and ~690 cm^{-1}, due to maleimide ring, disappeared, which indicated the C=C bond of maleimide ring had reacted completely.

The ^1H NMR spectral assignments were also used to clearly establish conditions of polymerization and verified the type of chemistry portrayed in Scheme 2. A solution of BMI and **5** in DMSO-d_6 (1:1 stoichiometry) was heated at 150°C and monitored by ^1H NMR until no further changes were observed in the spectra for ca. 12 h. During the course of experiment, an absorption at ~7.21 and 4.67 ppm, exhibiting the presence of the olefinic protons of maleimide ring and the primary amino protons in **5**, respectively, disappeared gradually. Meanwhile, the broad D_2O-exchangeable signal at 6.0 ppm was observed and it was attributed to the secondary amino protons of the aspartimide moiety. Moreover, the new multiplet peaks at 2.72, 3.35 and 4.83 ppm is due to the protons of succinimide. Under the same conditions, we observed no spectral changes in solutions BMI or **5** heated alone.

The NLO polyimides cured at 220°C from their corresponding prepolymers are all soluble in polar solvents such as cyclohexanone, DMF, DMAc, and THF, etc. The molecular weights of the polymers can thus be estimated by GPC. Polymer **PI-1**, for example, has a weight-average molecular weight M_w of 15 600 with a polydispersity of 1.43 (relative to polystyrene standard).

3.3. Thermal properties of functionalized polyimides

The thermal and chemical stability of the polymer is exceptional as indicated by thermal analysis. As seen from Fig. 2(a), the T_g of **PI-1** is determined to be 324°C. The TGA experiment (Fig. 2(b)) shows that the value for T_5 (5% weight loss) is about 470°C. As for **PI-2**, its T_g and T_5 values are 276 and 462°C, respectively. Both values are significantly higher than those observed for **PI-0** (T_g, 267°C; T_5, 405°C). Generally, the T_g of a polymer with a given chromophore decreases with the increase of incorporation of the chromophore [15]. However, in our case, the chromophores are directly incorporated on the main chain. Significant increase of the thermal stability for the polymer **PI-1** or **PI-2** compared to that of **PI-0** is mainly a result of the

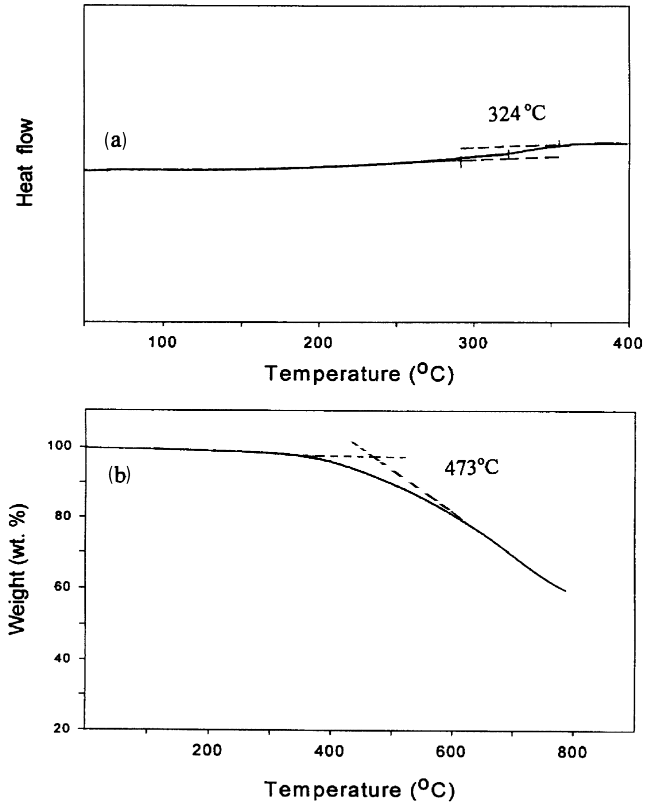

Fig. 2. DSC (a, top) and TGA (b, bottom) thermograms of **PI-1** (10°C/min, N_2).

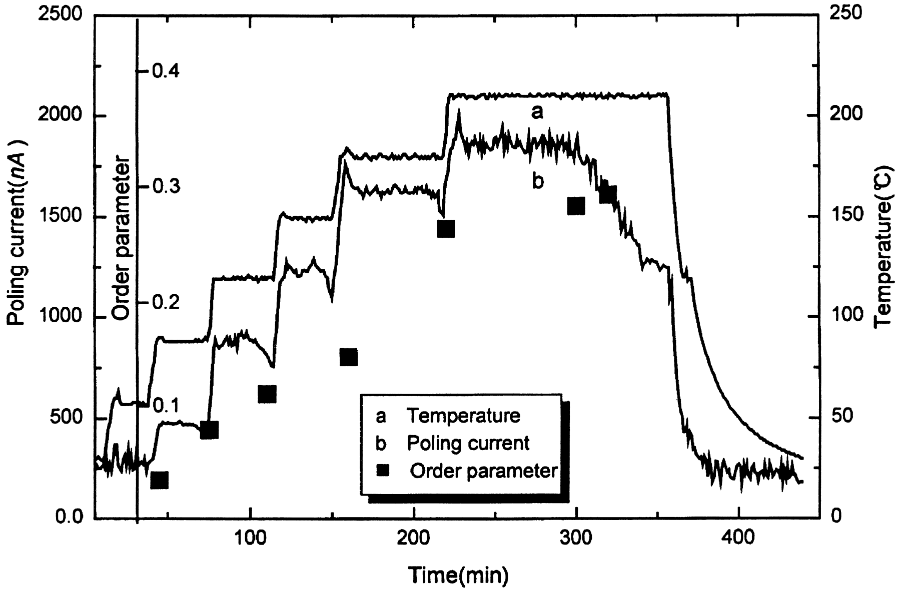

Fig. 3. The typical poling profile for **PI-1**.

donor-embedded structure. It is the increased rigidity of this structure that also leads to the fact that the T_d of **PI-1** (473°C) is far higher than that of chromophore **5** itself (T_d, 325°C). In other words, the thermal stability of the chromophores has been improved greatly by forming the donor-embedded structure.

3.4. Poling properties and nonlinearity measurements

As was well known, the degree of poling achieved for a particular polymeric system with a particular poling geometry is critical to an assessment of both the polymer and the poling method for producing second-order nonlinear optical polymers. The absorption spectrum of the polymers also changes with electric field poling. There are two electrochromic effects observed on poling [16]; that is, the peak absorbance decreases and the wavelength of maximum absorption shifts to the red. The absorption changes are directly related to the orientation of the chromophores and can be used as a means of evaluating the degree of orientation. If one assumes that the molecular electronic transition moment is parallel to the permanent ground state dipole moment, one can obtain the order parameter Φ by measuring the absorbance of an unpoled film A_0 and of a poled sample with light polarized perpendicular to the poling direction $A_\perp$:

$$\Phi = 1 - \frac{A_\perp}{A_0} \tag{1}$$

In our experiments the in situ simultaneous polymerization and poling technique was used. At the set poling temperature (T_p) the poling current (I_p) increased instantly and kept nearly constant, then it decreased slightly. While raising the T_p the I_p increased again. The procedure was repeated and the poling was terminated until the I_p no longer increased with the raising of the T_p. The saturation of Φ was reached and the value of 0.27 was obtained. Fig. 3 is a typical poling profile.

According to the one-dimensional rigid oriented gas model (1D ROGM) the macroscopic second-order nonlinear coefficient d_{33} can be written as [17,18]:

$$d_{33} = \frac{1}{2} N\beta f^{2\omega}(f^{\omega})^2 \frac{\mu E_p}{5kT} \tag{2}$$

where N is the number density of the chromophore in the polymer, f^{ω} and $f^{2\omega}$ are the Onsager type local field factors at the fundamental and doubling frequency, μ is the dipole moment of the chromophore, and E_p is the poling field. The quantity of last term can be related to Φ with well-known Langevin function. For our polyimides, chromophore number density is 9.6×10^{20} cm^{-3}, first hyperpolarizability β is 78.7×10^{-30} esu (the calculation value by AM1/FF after frequency correction) at 1064 nm, μ is 9.2 debye [19], E_p is evaluated from measured Φ following the procedures in Ref. [16] and is about 4.8 MV/cm. The refractive indices of the polyimide at fundamental and doubling frequency were unknown. According to the Sellmeier equation the values of n at 1064 and 532 nm can be estimated from the value of n at 632.8 nm (1.68 which was measured by ellipsometry). They are 1.742 and 1.625, respectively. Replacing the above parameters into Eq. (2) the d_{33} value of **PI-1** film is estimated to be 23.8 pm/V.

The SHG coefficients of **PI-1** are made relative to a z-cut quartz plate. The typical Maker fringe pattern could be observed for the case of both p-polarized and s-polarized fundamental beams. When **PI-1** film was poled at the optimum conditions as indicated in Fig. 3, a d_{33} value of 25.6 pm/V was obtained. The experimentally obtained d_{33}

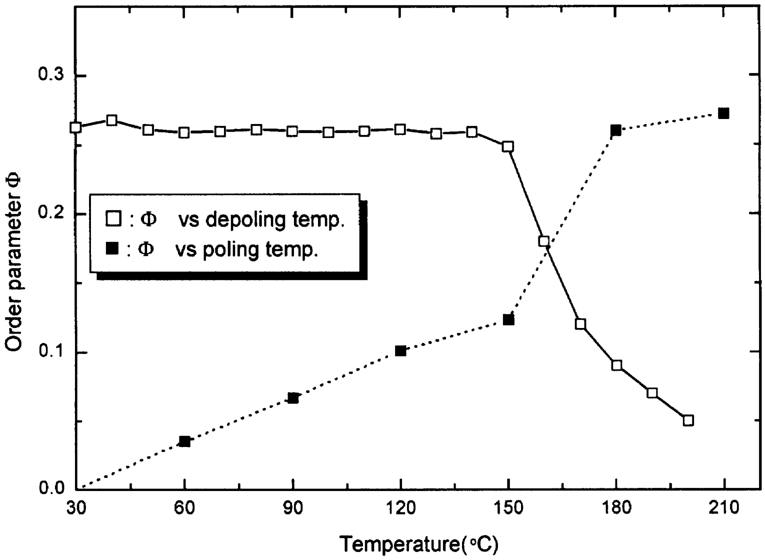

Fig. 4. Temperature profile of the poled order parameter for **PI-1**.

value is in good agreement with the theoretically calculated one. The value is reasonable and comparable in magnitude to d_{33} values of similar chromophore-functionalized NLO polymers.

The motivation to prepare this class of polymers was the expectation that they may exhibit a high stability at elevated temperatures. It is a very important requirement for their practical applications in electric–optic devices. To evaluate the high temperature stability of **PI-1**, we studied the NLO temporal stability by performing temperature-dependent Φ measurements. Fig. 4 shows the measurement profile. From the figure we can see that the order parameter Φ was quite stable until the temperature reached 150°C, and the large activity loss occurred at a temperature above 180°C. It is noted that the temperature range of faster change of Φ for the depoling curve is almost the same as that for the poling one. This coincidence implies that the thermal mobility for aligning NLO dipole moments on poling is the same as that for randomizing them on depoling; both processes of alignment and randomization of the NLO chromophore should be subjected to the same thermal activation [20]. Also noteworthy is that the poling conditions are clearly unoptimized at this point while the film integrity was maintained during poling. The stability of the induced polar order in such a polymer may be further improved by poling at a higher temperature. Unfortunately, it was limited by our poling apparatus.

4. Conclusion

We have prepared a class of processible NLO substituted polyimides, where the donor group is embedded in the polymer main chain, via addition polymerization. The extraordinary stability of the induced polar order and high T_g indicate that this class of polymers may meet the severe operating and processing temperature requirements for device applications. With the future efforts in introducing higher β chromophores, it should be possible to produce thermally stable polymer systems with large NLO responses.

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References

[1] Marks TJ, Ranter MA. Angew Chem Int Ed Engl 1995;34:155.
[2] Marder SR, Kippelen B, Jen AK-Y, Peyghambarian N. Nature 1997;388:845.
[3] Dalton LR. Chem Ind 1997;13:510.
[4] Cheng SZD, Arnold FE, Li F, Harris FW. Trends Polym Sci 1993;1:243.
[5] Wu JW, Valley JR, Ermer S, Binkley ES, Kenne JT, Lipscomb GF, Lytel R. Appl Phys Lett 1991;58:225.
[6] Lin JT, Hubbard MA, Marks TJ, Lin W, Wong GK. Chem Mater 1992;4:118.
[7] Becker MW, Sapochak LS, Ghosn R, Xu C, Dalton LR, Shi Y, Kalluri S, Steier WH, Jen AK-Y. Chem Mater 1994;6:104.
[8] Peng ZH, Yu LP. Macromolecules 1994;27:2638.
[9] Mortazavi MA, Knoesen A, Kowel ST, Higgins BG, Dienes A. J Opt Soc Am B 1990;6:733.
[10] Zhao K, Wang C, Feng Z, Ye C. High Tech Lett 1997;7:30.
[11] Sato T, Mitsuo N, Nishiki M, Inoue Y, Ooi Y. Chem Pharm Bull 1981;29:1443.
[12] Moylan CR, Twieg RJ, Lee VY, Swanson SA, Betterton KM, Miller RD. J Am Chem Soc 1993;115:12599.
[13] Moylan CR, Twieg RJ, Lee VY, Miller RD, Volksen W, Thackara JI, Walsh CA. Proc SPIE 1994;17:2285.

[14] DiCiulio C, Gautiier M, Jasse B. J Appl Polym Sci 1984;29:771.
[15] Zhao M, Bautista M, Ford WT. Macromolecules 1991;24:844.
[16] Page RH, Jurich MG, Reck A, Sen A, Twieg RJ, Swalen JD, Bjorklund GC, Willson CG. J Opt Soc Am B 1990;7:1239.
[17] Singer K, Sohn J, Lalama S. Appl Phys Lett 1986;49:248.
[18] Singer K, Kuzyk M, Sohn J. J Opt Soc Am B 1987;4:968.
[19] Wang C, Wang P, Zhu P, Ye C. Progr Nat Sci 1998;8:498.
[20] Tsutsumi N, Matsumoto O, Sakai W, Kiyotsukuri T. Macromolecules 1996;29:592.