Preparation and Properties of Thermally Stable Copolyimides Based on Novel Second-Order Nonlinear–Optical Chromophore Containing Diamines

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ABSTRACT: Thermally stable copolyimides were prepared from two novel second-order nonlinear optical chromophores containing diamines, 4-nitro-4′-[N-(4,6-di-β-aminoethylamino)-1,3,5-triazin-2-yl]aminoazobenzene (**M1**) and 4-nitro-4′-[N-(4,6-di-4-aminophenylamino)-1,3,5-triazin-2-yl]aminoazobenzene (**M2**); two codiamines, 4,4′-diamino-3,3′-dimethyl diphenylmethane (MMDA) and bis-(3-aminopropyl)-1,1′,3,3′-tetramethyldisiloxane (SiDA); and 3,3′,4,4′-diphenyl ether tetracarboxylic acid dianhydride (OPDA). All copolyimides possess high glass transition temperatures (T_g's) between 237 and 271°C. Copolyimides based on **M2** do not exhibit an obvious change in T_g as the **M2** content is increased, while those based on **M1** show a slight decrease in T_g as the **M1** content is increased. All copolyimides exhibit high thermal decomposition temperatures. The copolyimides are soluble in aprotic solvents such as NMP, DMAc, DMF, DMSO, and 1,4-butyrolactone. Some are even soluble in common low boiling point solvents such as THF and chloroform. The refractive index of a copolyimide is increased as the chromophore content is increased, while the birefringence of a copolyimide does not exhibit strong dependence on the chromophore content. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1619–1626, 2000

Key words: copolyimide; thermally stable; side chain; triazine; characterization

INTRODUCTION

Organic poled polymers offer great promise for the fabrication of integrated optical devices due to their large electro-optic coefficients, low dielectric constants, and flexibility in fabrication.[1–8] However, a number of issues have to be thoroughly addressed before they have any commercial value. Three of these crucial issues are the high temporal stability of the dipole orientation, large optical nonlinearity, and minimum optical loss.[3] Recent studies on side-chain polyimides for second-order nonlinear optics show some encouraging improvements in the stability of dipole orientation due to the high glass transition temperatures of polyimides. Miller et al.,[9] Yu et al.,[10] Jen et al.,[11] and some other groups[12–19] developed new nonlinear optical (NLO) polyimide systems. All these side-chain polyimides exhibit excellent properties, especially high-temperature orientation stability. Yu and coworkers[10,20,21] synthesized NLO copolyimides that exhibit a high glass transition temperature (T_g) and high thermal stability. They found that the copolymerization ap-

proach would offer the opportunity to study the effects of the chromophore loading level on the T_g, the thermal stability, and the optical nonlinearity of the side-chain polyimides. It has been already proven that the second-order optical nonlinearity of the poled polymers would be improved with an increase of the chromophore loading level. In guest–host systems, however, as the chromophore loading level increases, the T_g and the thermal stability decrease dramatically. This plasticization effect is not so obvious in the side-chain copolyimdes.[10,20,21] The research indicates that the copolyimides are the materials of choice for high thermal stability within a tolerable trade-off range in optical nonlinearity.

Apart from high orientation stability and optical nonlinearity, low optical loss is also extremely important. As pointed out by a number of researchers,[3,22] the effort to enhance optical nonlinearity often presents the risk of pushing the optical band edge too close to the operating wavelength of the electro-optic devices. The low-energy tails of the absorption bands of the chromophores can extend several hundreds of nanometers into the long wavelength region. Kowalczyk et al.[23] proved that these chromophore absorption tails were the main causes of the optical losses of the NLO polymers. As even a small absorption at the operating wavelength of electro-optic devices can be detrimental, it is important to make NLO chromophores as transparent as possible without compromising the molecule's nonlinearity. In this article, two second-order nonlinear optical chromophores (**M1** and **M2**) were synthesized using [2,4-di(2-aminoethylamino)-1,3,5-triazin-2-yl]-amino or [2,4,-di(*p*-aminophenylamino)-1,3,5-triazin-2-yl]amino as electron-donor groups. These new synthesized molecules have hyperpolarizability values similar to that of Disperse Red 1 (DR1), while the maximum absorption wavelengths were no larger than 400 nm.[24] Two series of new side-chain NLO copolyimides based on these chromophores were synthesized and characterized. 4,4′-Diamino-3,3′-dimethyl diphenylmethane was used as the co-diamine monomer to increase the organosolubility of the copolyimides.[25] A small amount of a silicon-containing diamine, bis-(3-aminopropyl)-1,1′,3,3′-tetramethyldisiloxane, was also used to promote adhesion between the copolyimides and the glass substrate. The effects of the chromophore loading level on the T_g and other physical properties of the copolyimides were also studied.

EXPERIMENTAL

Materials

4-Amino-4′-nitroazobenzene (DO3) and 4,4′-diamino-3,3′-dimethyl diphenylmethane (MMDA) were synthesized in our lab.[2] 2,4,6-Trichloro-1,3,5-triazine (lab reagent) was purchased from the Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and purified by recrystallization in benzene prior to reaction. Bis-(3-aminopropyl)-1,1′,3,3′-tetramethyldisiloxane (SiDA) (lab reagent) was purchased from the Tokyo Chemical Industry Co., Ltd., and used as received. Ethylenediamine (analytical reagent grade) and *p*-phenylenediamine (analytical reagent grade) were purchased from the Shanghai Reagent Co. (Shanghai, China) and used as received. 3,3′,4,4′-Diphenyl ether tetracarboxylic acid dianhydride (OPDA) (industrial product) was purchased from the Shanghai Research Institute of Synthetic Resins (Shanghai, China) and dried at 190°C for 2 h before use. *N*-Methyl-2-pyrrolidone (NMP; analytical reagent grade) was purchased from the Shanghai Reagent Company and dried over molecular sieves before use. Acetic anhydride (analytical reagent grade) and triethylamine (analytical reagent grade) were purchased from the Shanghai No. 1 Reagent Co. (Shanghai, China) and the Shanghai No. 3 Reagent Co. (Shanghai, China), respectively, and used as received. Common reagents used in organic synthesis such as sodium carbonate and hydrochloric acid were used as received. Common solvents for solubility measurement such as cyclohexane, toluene, acetone, tetrahydrofuran (THF), chloroform, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and 1,4-butyrolactone were used without purification.

Synthesis of 4-Nitro-4′-[*N*-(4,6-di-β-aminoethylamino)-1,3,5-triazin-2-yl]aminoazobenzene (M1) (Scheme 1)

DO3 (4.84 g, 0.02 mol) was dissolved in 30 mL ethanol. The solution was cooled in an ice-water bath to below 5°C. 2,4,6-Trichloro-1,3,5-triazine (3.69 g, 0.02 mol) was then added and then a 40 wt % sodium carbonate aqueous solution was used to neutralize the solution. The solution was stirred for another 6 h before being slowly added to a mixture of ethylenediamine (2.40 g, 0.04 mol), water (30 mL), and hydrochloric acid (36%, 3.7 mL, 0.043 mol) under the protection of nitrogen.
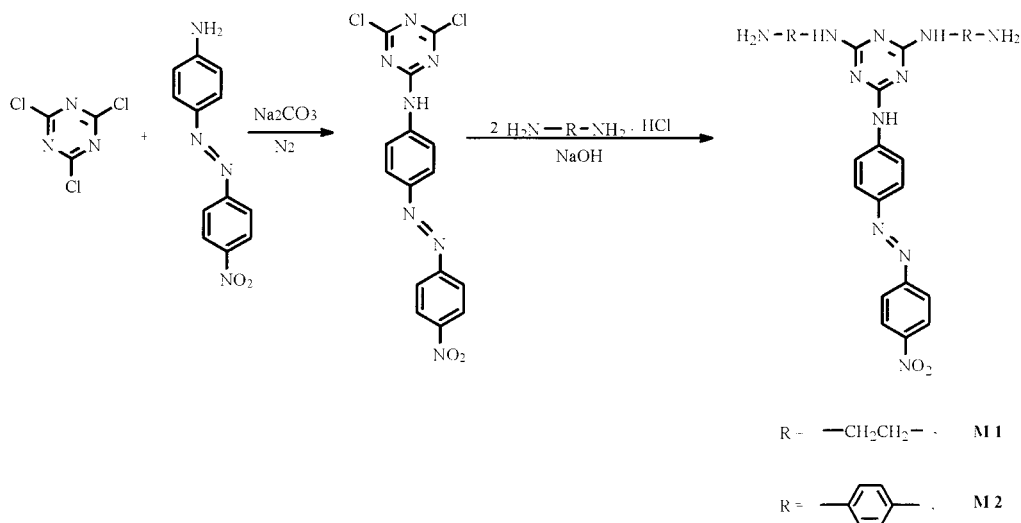
Scheme 1   Synthesis of diamine monomers bearing NLO chromophore.

The mixture was stirred at 40°C for 5 h and then heated to 80°C to remove ethanol by distillation while being neutralized with a 40 wt % sodium carbonate aqueous solution at the same time. Water (100 mL) was then added and the mixture was heated to 100°C and refluxed for another 4 h. After cooling, the mixture was basified to a pH value of 10. The resulting solid (6.05 g, 69.2%) was collected by filtration and washed with water. The product was purified by being dissolved in

100 mL water while keeping the pH value at 5. The mixture was stirred at 50°C for 30 min under the protection of nitrogen and then filtered. The filtrate was basified to a pH value of 10 and then extracted with diethyl ether three times. Upon the removal of diethyl ether by distillation, orange–red crystals were obtained; mp 173°C.

^{1}H-NMR (DMSO-d_6): δ = 7.96 (s; 2H), 7.92 (s; 2H), 6.61 (s; 2H), 6.58 (s; 2H), 3.22–3.45 (m; 11H) and 1.23 (t; 4H). IR (KBr): 3481, 3355 (NH$_2$),
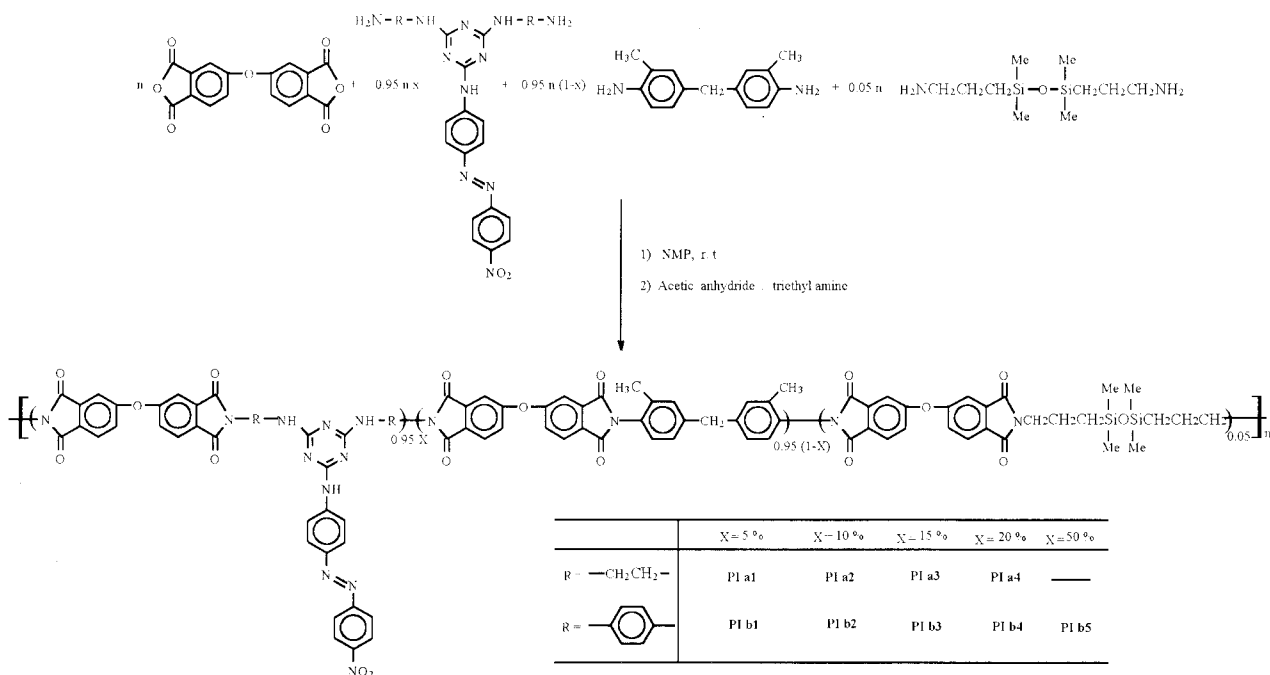
Scheme 2   Synthesis of copolyimides.

Table I Synthesis and Physical Properties of the Copolyimides

Sample	Pl a1	Pl a2	Pl a3	Pl a4	Pl b1	Pl b2	Pl b3	Pl b4	Pl b5
X	5%	10%	15%	20%	5%	10%	15%	20%	50%
Chromophore loading level (wt %)[a]	2.25	4.41	6.49	8.50	2.23	4.43	6.33	8.22	17.79
$[\eta]$[b]	0.57	0.76	0.38	0.32	0.32	0.37	0.45	0.50	0.37
T_g (°C)[c]	252	251	250	237	260	267	270	271	263
T_d (°C)[d]	530	590	593	575	569	568	580	577	552

[a] Chromophore loading level was calculated by using DO3 as the actual NLO chromophore.
[b] Measured at 30°C using NMP as the solvent; the standard concentration is 1 g/dL.
[c] Measured with DSC under the protection of N_2 with a scan rate of 20°C/min.
[d] Initial thermal decomposition (on-set) temperature measured with TGA under the protection of N_2 with a scan rate of 20°C/min.

1502, 1327 (N=O), and 1415, 808 (triazine) cm^{-1}. UV/Vis (ethanol): λ_{max}/nm = 401.

$C_{19}H_{23}N_{11}O_2$ (437.47): Calcd: C, 52.17%; H, 5.30%; N, 35.22%. Found: C, 52.72%; H, 4.75%; N, 31.83%.

Synthesis of 4-Nitro-4′-[*N*-(4,6-di-4-aminophenylamino)-1,3,5-triazin-2-yl]aminoazobenzene (M2) (Scheme 1)

M2 was synthesized with a procedure similar to that used in the synthesis of **M1** apart from replacing ethylenediamine with *p*-phenylenediamine. Yield: 69.4%. mp 160°C.

^{1}H-NMR (DMSO-d_6): δ = 7.95 (s; 2H), 7.92 (s; 2H), 6.56–6.68 (m; 12H), 3.42 (s; 3H), and 3.28 (s; 4H). IR (KBr): 3481, 3362 (NH$_2$), 1505, 1326

(N=O), and 1410, 805 (triazine) cm^{-1}. UV/vis (ethanol): λ_{max}/nm = 374.

$C_{27}H_{23}N_{11}O_2$ (533.56): Calcd: C, 60.78%; H, 4.35%; N, 28.88%. Found: C, 60.08%; H, 4.51%; N, 26.20%.

Preparation of the Copolyimides

The following polymerization procedure exemplifies the synthesis of copolyimdes **PI a1–a4** and **PI b1–b5** (see Scheme 2). Added to a mixture of the diamine monomer **M1** (0.2 g, 0.460 mmol), MMDA (0.938 g, 4.143 mmol), and SiDA (0.060 g, 0.242 mmol) in 18 mL of NMP was OPDA (1.503 g, 4.845 mmol). After stirring at room temperature for 4 h, the resultant poly(amic acid) (PAA) was imidized with a mixture of acetic anhydride
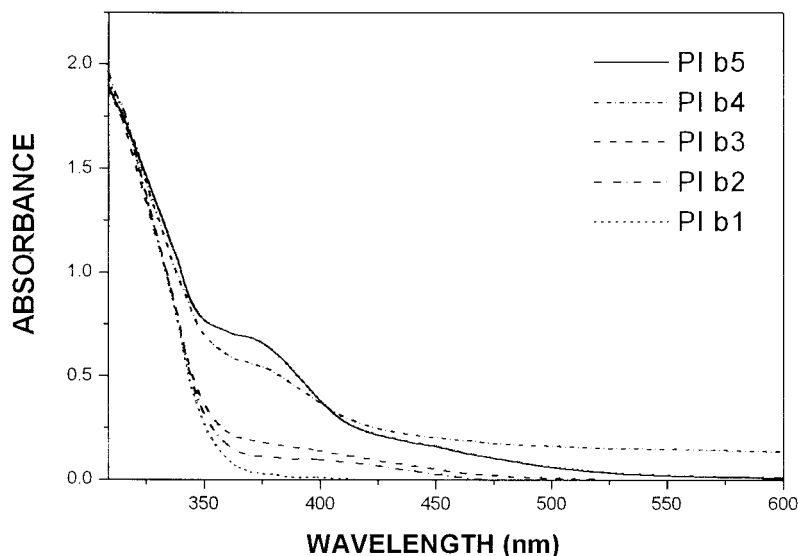
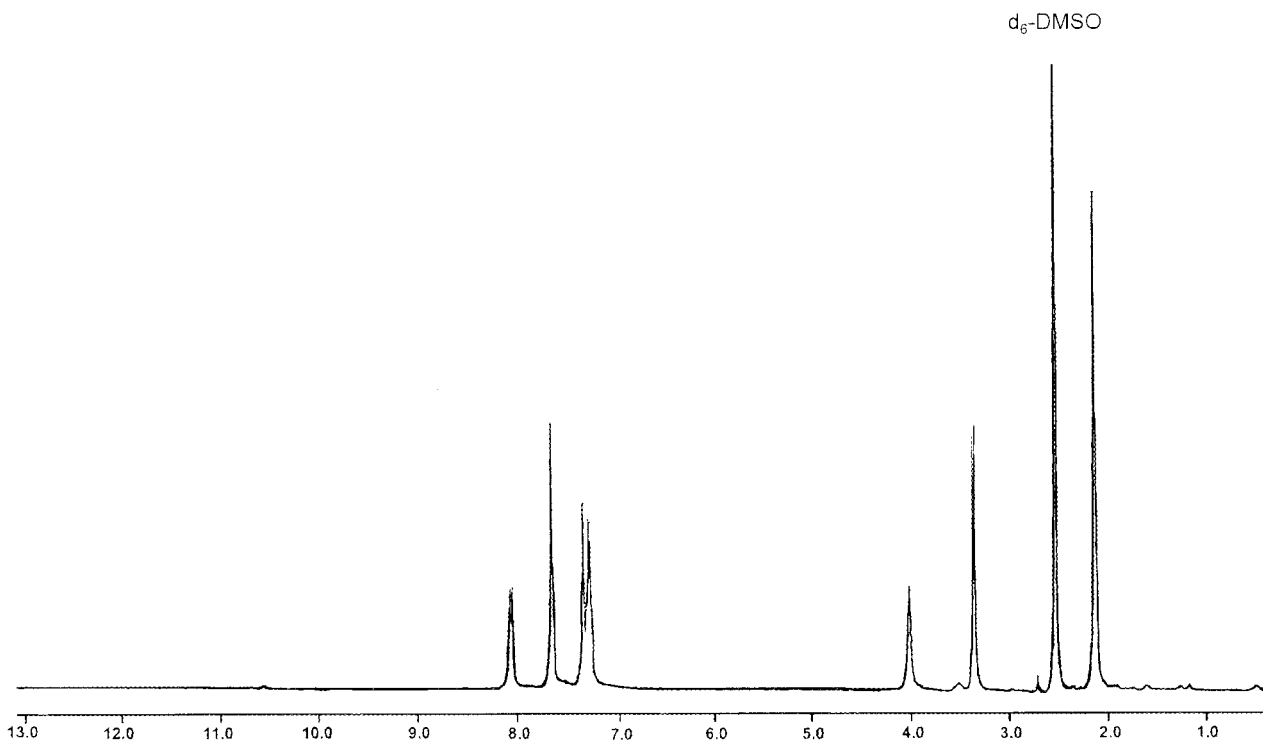**Figure 1** UV-vis spectra of **PI b1–b5**.

Figure 2 ^{1}H-NMR spectrum of **PI a2**.

and triethylamine (diamine/acetic anhydride/triethylamine = 4 : 36 : 9 in mol ratio) at 25°C for 48 h. The resultant polyimide (**PI a2**) was precipitated into a mixture of methanol and water (100 mL/100 mL). The copolyimide was then further purified by extraction with methanol for 48 h and then dried at 80°C under a vacuum for 2 days.

Characterization

The FTIR spectra of copolyimide thin films were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer. The thin films were cast from the dilute copolyimide solutions on KBr. A

Perkin–Elmer Lambda 20 UV-vis spectrophotometer was used to record the UV-vis spectra of the dilute copolyimide solutions (10^{-4} M) in NMP using NMP as the reference. The solubility of the copolyimides was determined by observing the solubility of the solid copolyimides in various solvents at room temperature. The intrinsic viscosity of the copolyimides was measured with an Ubbelodhe viscometer using NMP as the solvent at 30°C. The standard concentration was 1 g/dL. The T_g's of the copolyimides were determined by differential scanning calorimetry (DSC). The DSC curves were recorded on a Perkin–Elmer Pyris I

Table II   Solubility of Copolyimides in Various Organic Solvents (25°C)

Polyimide	Cyclohexane	Toluene	Acetone	THF	Chloroform	1,4-Butyrolactone	NMP	DMAc	DMF	DMSO
Pl a1	−	−	−	+	+	+	+	+	+	+
Pl a2	−	−	−	+	+	+	+	+	+	+
Pl a3	−	−	−	+	+	+	+	+	+	+
Pl a4	−	−	−	+	+	+	+	+	+	+
Pl b1	−	−	−	+−	+−	+	+	+	+	+
Pl b2	−	−	−	+−	+−	+	+	+	+	+
Pl b3	−	−	−	−	+−	+	+	+	+	+
Pl b4	−	−	−	−	+−	+	+	+	+	+
Pl b5	−	−	−	−	−	+	+	+	+	+

+: Soluble; +−: partially soluble; −: insoluble.

Table III Refractive Indices and Birefringence of the Copolyimides

Measurements	Samples					
	Pl a1	**Pl a2**	**Pl b1**	**Pl b2**	**Pl b3**	**Pl b4**
n_{TE}	1.654 ± 0.005	1.655 ± 0.005	1.657 ± 0.005	1.663 ± 0.005	1.670 ± 0.005	1.676 ± 0.005
n_{TM}	1.624 ± 0.005	1.626 ± 0.005	1.625 ± 0.005	1.631 ± 0.005	1.639 ± 0.005	1.640 ± 0.005
$n_{TM} - n_{TE}$	-0.030 ± 0.010	-0.029 ± 0.010	-0.032 ± 0.010	-0.032 ± 0.010	-0.031 ± 0.010	-0.036 ± 0.010

Refractive indices and birefringence were measured with the m-Line method with a wavelength of 632.8 nm.

DSC under the protection of N_2. The scan rate was 20°C/min. All samples experienced two heating processes from 25 to 300°C, and the second one was recorded. The thermal stability of the copolyimides was characterized by thermogravimetric analysis (TGA). The TGA curves were recorded on a Perkin–Elmer TGA7 under the protection of N_2. The scan rate was 20°C/min. Refractive indices of the copolyimide films were measured by the m-Line method using a prism coupling apparatus. The laser source was a polarized He—Ne laser (632.8 nm). The NMP solutions of the copolyimides ($\approx$15% m/m) were filtered through 0.5 μm syringe filter and then spin-coated onto glass slides. The films were kept in a vacuum oven at 140°C for 24 h to ensure the complete removal of the residual solvent.

RESULTS AND DISCUSSION

Synthesis and Characterization of Copolyimides

Every copolyimide was synthesized using a traditional two-step synthetic method that includes polycondensation between a diamine and a dianhydride to form a PAA and chemical imidization to form a polyimide. MMDA was used as a comonomer to increase the solubility of the copolyimides while still retaining a reasonably high rigidity and thus the glass transition temperature.[25] The addition of SiDA may help to increase the adhesion of the copolyimides with the glass substrate. The intrinsic viscosities of all the copolyimides are between 0.32 and 0.76 (see Table I).

For all of the two series of copolyimides, the clear appearance of $\approx$1776 and $\approx$1721 cm^{-1} bands characteristic of C=O stretching in imide rings and the $\approx$1373 cm^{-1} band characteristic of C—N stretching in imide rings indicate the existence of the imide groups. The characteristic absorption peaks of the triazine ring at $\approx$1411 cm^{-1} and the nitro groups at $\approx$1330 cm^{-1} also indicate the existence of the NLO chromophore.

The UV-vis spectra of **PI b1–b5** are shown in Figure 1. It is observed that **PI b1–b5** are almost completely transparent at wavelengths greater
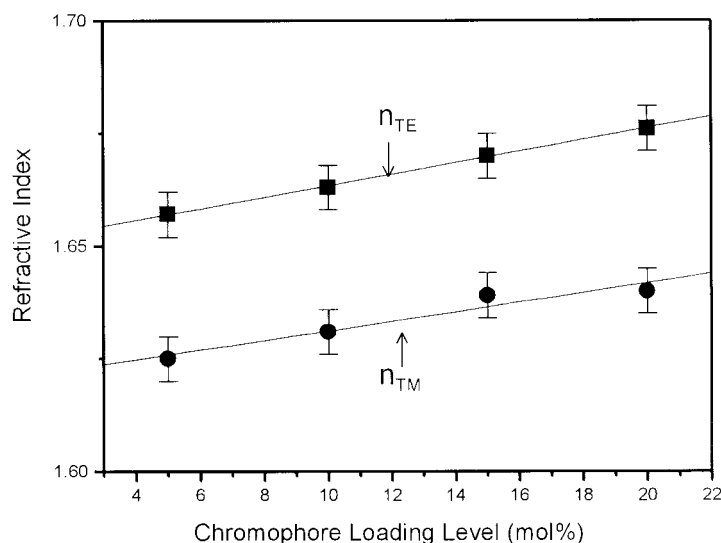
Figure 3 Relationship between the refractive indices and the chromophore loading level of **PI b**.

than 500 nm. As the NLO chromophore loading level is increased, the characteristic absorption of **M2** at ≈370 nm increased.

The ^{1}H-NMR spectrum of **PI a2** is shown in Figure 2. It is observed there is almost no unimidized amic acid remaining as almost no peaks appeared at δ (ppm) above 10.

Solubility of Copolyimides

The solubilities of the copolyimides in various solvents are listed in Table II. It is observed that all the copolyimides prepared are soluble in strongly polar organic solvents such as NMP, DMAc, DMF, DMSO, and 1,4-butyrolactone. **PI a1–a4** show better solubility than that of **PI b1–b5** and can even be dissolved in some common low boiling point solvents such as THF and chloroform. The better solubility of **PI a1–a4** may be caused by the existence of more flexible backbones in **PI a1–a4** than in **PI b1–b5**. As the NLO chromophore loading level increases, the solubility of the copolyimides decreases. Both **PI b1** and **PI b2** show reasonable solubility in THF and chroloform, while **PI b5**, which has the highest chromophore loading level, is not soluble in either of the solvents.

Thermal Properties of Copolyimides

The T_g's of all the copolyimides are listed in Table I. It is observed that all the copolyimides, even those with high NLO chromophore loading levels, show quite high T_g's. The T_g of each **PI a** copolyimide is lower than that of the **PI b** copolyimide with the identical NLO chromophore loading level. This is due to the higher flexibility of the —CH_2—CH_2— linkages in **PI a** than of the corresponding p-phenylene linkages in **PI b**. The effect of the high flexibility of the —CH_2—CH_2— linkage on the T_g also leads to the gradual decrease in the T_g as the NLO chromophore loading level is increased in **PI a** (see Table I). The T_g of the **PI b** series, however, does not show an obvious decrease as the NLO chromophore loading level is increased. The retention of a high T_g as the chromophore loading level is increased is one of the most important advantages of a side-chain system over a guest–host system.

Apart from a high T_g, the copolyimides also require a high thermal stability because the polymer films have to be poled around the glass transition temperatures to generate an optical nonlinearity. The initial decomposition temperatures

(T_d's) of all the copolyimides are listed in Table I. It was observed that all the copolyimides possess high thermal stability: This high thermal stability would ensure high-temperature poling of the copolyimides.

Refractive Indices of Copolyimides

The refractive index of the mode having its electric field in the plane of the film (transverse electric) is n_{TE}. The refractive index of the mode having its electric field perpendicular to the plane of the film (transverse magnetic) is n_{TM}. The refractive indices of both TE and TM modes (n_{TE}, n_{TM}) and birefringence ($n_{TM} - n_{TE}$) of some of the copolyimides are listed in Table III. These polymer films are birefringent as evidenced by the difference between the refractive indices of the TE and TM modes. The refractive indices of the TE mode (in-plane) are larger than those of the TM mode (out-of-plane), which implies that the polyimide backbone intends to lie in the plane of the film. The relationship between the refractive indices and the chromophore loading level of **PI b** is shown in Figure 3. It is observed that as the NLO chromophore loading level is increased the refractive indices of both TE and TM modes increase almost linearly due to the relatively higher refractive indices of the chromophores, while the birefringence does not show an obvious change.

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