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Synthesis and characterization of novel polyimide-based NLO materials from poly(hydroxy-imide)s containing alicyclic units (II)

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Abstract

A series of polyimide-based second-order nonlinear optical (NLO) materials were synthesized from poly(hydroxy-imide)s containing alicyclic units, followed by the Mitsunobu reaction with NLO chromophores. The resulting polymers were highly soluble in aprotic polar solvents such as DMF, DMAc, NMP, etc. The NLO polyimides exhibited the inherent viscosity range of 0.22–0.50 dL/g. Molecular structural characterization for the resulting polymers was achieved by ^{1}H-NMR, FT-IR, and UV-visible spectroscopies. The glass transition temperature for the resulting NLO polyimides was in the range of 161°C–233°C and most of them showed high thermal stability. The polymer solutions could be spin coated on the indium–tin-oxide (ITO) glass or quartz disc substrates to form the optical quality thin films. The electro-optic coefficients (r_{33}) at the wavelength of 1.3 μm for polymer thin films poled around the glass transition temperature were in the range of 2–6 pm/V. And, long-term thermal stability of the dipole alignment was observed up to ca. 140°C. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimide-based second-order nonlinear optical materials; Poly(hydroxy-imide)s; Electro-optic coefficients

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1. Introduction

In recent years, polymeric materials with second-order nonlinear optical (NLO) properties have been extensively studied for use in photonic applications such as high speed photonic switching devices and electro-optic modulators [1–3]. 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. Although it is extremely difficult to synthesize materials which possess the material requirement for practical applications, numerous approaches have been developed to utilize these NLO polymeric materials for use in real applications [1,2]. But, the thermal stability of the NLO orientation alignment, optical nonlinearity, and optical loss are needed to improve for device applications.

Recently, high glass transition temperature polymers such as aromatic polyimides [4–6] were developed as polymeric backbones for the purpose of restraining the relaxation of the noncentrosymmetric chromophore-alignment induced by an electric field. Among them, NLO functionalized aromatic polyimides have shown promising potential in device applications because of the higher temperature alignment stability, better mechanical properties, and processability than other polymeric systems such as a side chain system and a guest–host NLO chromophore–polyimide system. However, most of the functionalized NLO polyimide were prepared from the corresponding polyamic acids via thermal treatments. It was reported that polyimides derived from polyamic acids exhibited the poor reproducibility of the optical quality including the optical propagation loss and side NLO chromophores also decomposed during the imidization process at a high curing temperature [4,5]. The optical propagation loss of these NLO polyimides may still need to be improved for device applications.

Very recently, we have synthesized polyamideimides containing NLO chromophores in the direct polycondensation, in order to enhance the stability of dipole alignment and their solubility by the incorporation of amide groups into NLO polyimides [4,5]. The direct polycondensation of NLO polyimides without a curing step could ameliorate the optical property of NLO polymers by reducing the

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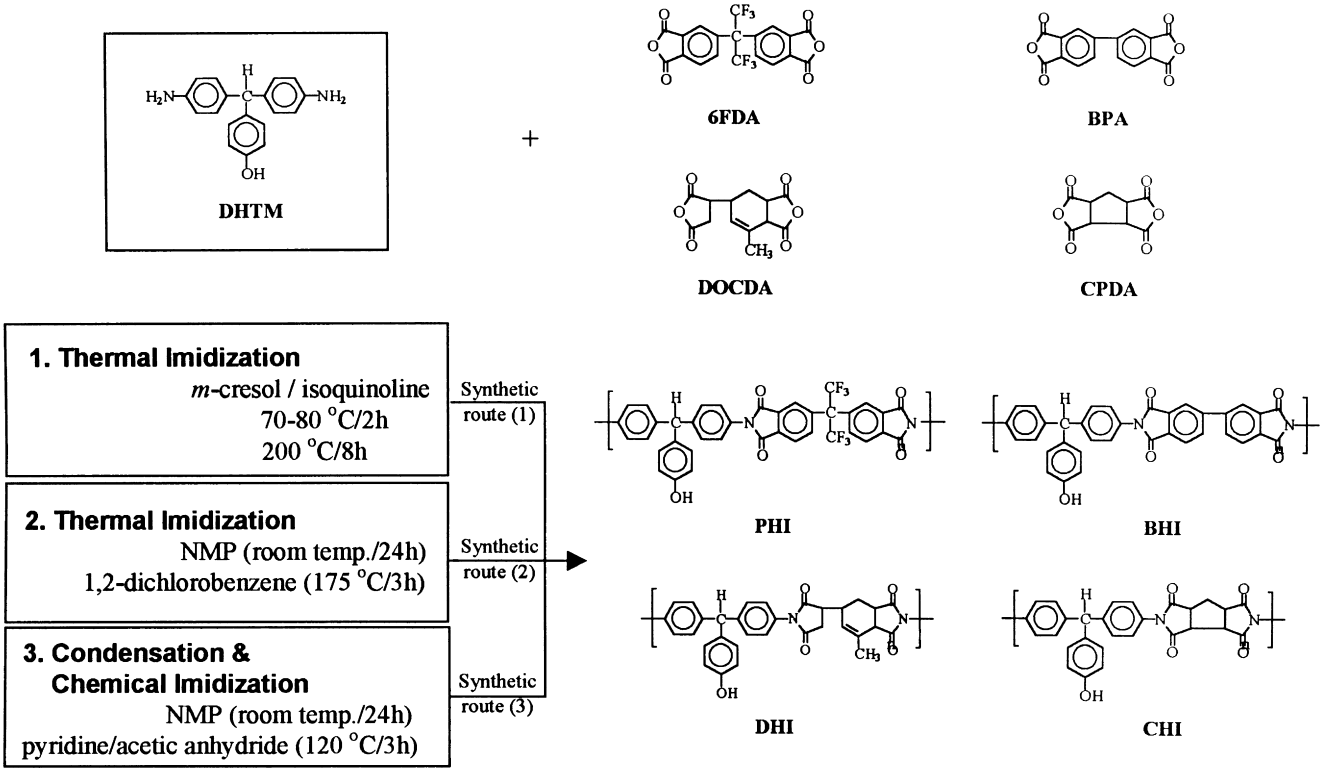


Scheme 1. Preparation of poly(hydroxy-imide)s by different synthetic routes.

optical propagation loss, while the reproducibility of optical quality including the optical propagation loss for NLO polyimides derived from poly(amic acid) was poor [4,6]. The resulting NLO polymamideimides were highly soluble in aprotic polar solvents. The polymer solutions could be spin coated on the ITO glass or quartz disc substrates to form the optical quality thin films. In addition, NLO polyamideimides, associate with a high glass transition temperature led to the improvement of the thermal stability of NLO polymers and the thermal stability of dipole alignment.

In the present article, we have synthesized a series of polyimide-based second-order NLO materials from poly (hydroxy-imide)s containing both fluorinated and alicyclic units in the main chain, followed by the Mitsunobu reaction with NLO chromophores [7]. The introduction of alicyclic and propellar-like structure into the polyimide backbones enhances the solubility of NLO polyimides, rendering their processability, while NLO polyimides are mostly insoluble to limit their characterization and processing (see Scheme 1). We chose the polyimide backbone in the main chain for the purpose of restraining the relaxation of the noncentrosymmetric chromophore-alignment induced by an electric field. We should also stress that the direct synthesis of NLO polyimides in mild conditions could improve the optical property of NLO polymers by reducing the optical propagation loss without the decomposition of NLO chromophores during the imidization process at a high curing temperature.

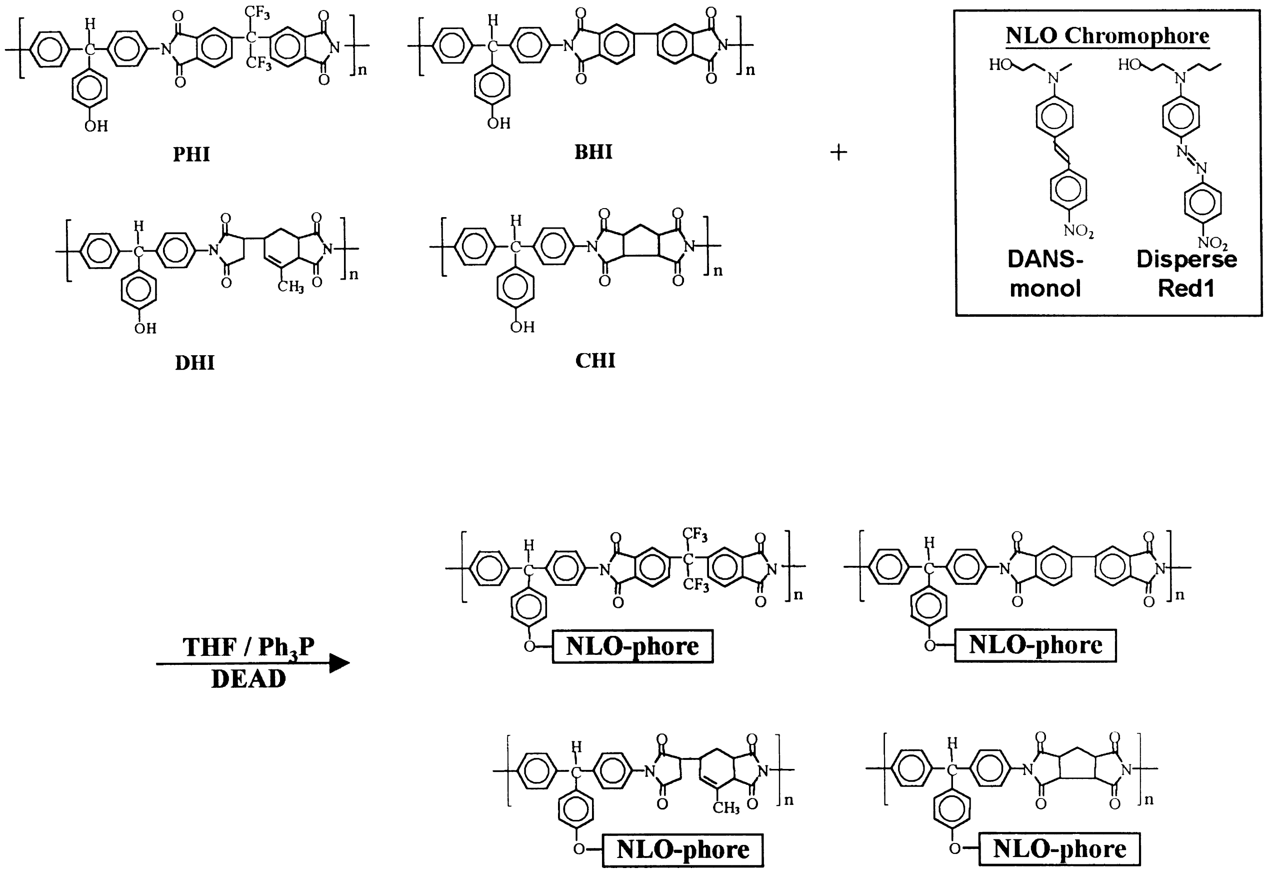
2. Experimental

2.1. Instrumentation

^{1}H-NMR spectra were recorded with the use of a Bruker AM-300 spectrometer, and chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. FT-IR spectra were measured as KBr pellets on a Perkin Elmer spectrometer Paragon 1000 PC, and frequencies were given in reciprocal centimeters. A Perkin Elmer UV-visible spectrometer Lambda 14 was used for UV-visible spectral data. Melting point determinations were made using a Fisher-Johns melting point apparatus. Thermal analyses were carried out on a Dupont TGA 9900 thermogravimetric analyzer under a nitrogen atmosphere at the heating rate of 10°C/min. Perkin Elmer 7 thermal analysis equipment was used for DSC thermogram. Thin films were prepared by spin-coating the solution on a ITO coated glass or other substrates. The film thickness was measured by a surface profilometer (Tencor instruments, α-step 300). The electro-optic coefficient (r_{33}) at the function of the electric field was measured by simple reflection method [8].

2.2. Materials

The 4-[N–(2–hydroxyethyl)–N–methylamino]-4′-nitrostilbene (DANS–monol), 4,4′-diamino-4″-hydroxytriphenylmethane (DHTM) were synthesized according to the literature procedures [9,10]. The 4-4′-(hexafluoro



Scheme 2. Synthesis of side-chain NLO polyimides by Mitsunobu reaction.

isopropylidene)diphthalic anhydride (6FDA), 4-4′-biphthalic anhydride (BPA), dispersed red 1 (DR1) and diethyl azodicarboxylate (DEAD) were obtained from Aldrich Chemical Co. and 1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA), 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexane-1, 2-dicarboxylic anhydride (DOCDA) were obtained from TCI Chemical Co. Other chemicals used were purchased from Aldrich Chemical Co. and used without further purification. All solvents were used after purification according to conventional methods.

2.3. Synthesis of polyimide-based NLO materials

A series of polyimide-based second-order NLO materials from poly(hydroxy-imide)s containing both fluorinated and alicyclic units in the main chain followed by the Mitsunobu reaction with NLO chromophores, were synthesized by the following procedures, as shown in Schemes 1 and 2.

2.3.1. Synthesis of poly(hydroxy-imide)s [11]

2.3.1.1. Poly(hydroxy-imide) (PHI-1) from DHTM and 6FDA by synthetic route (1) A stoichiometric amount of 6FDA (1.38 g, 3.1 mmol) was added to a solution of DHTM (0.9 g, 3.1 mmol) in freshly distilled *m*-cresol (20 ml) at room temperature. The resulting mixture was stirred for 1 h. Isoquinoline (5 wt.%) in *m*-cresol (6 ml) was added to the reaction mixture. The resulting mixture was heated slowly to 80°C with stirring for 3 h. The viscous solution was heated slowly to 200°C and then refluxed for 6 h under 200°C. After cooling to room temperature, the solution was poured into 30 ml of methanol, yielding a precipitated light yellow polymer (PHI). The product was collected by filtration, washed thoroughly with water and hot methanol, and dried under vacuum at 90°C for 24 h. Yield = 91.1%.

2.3.1.2. PHI from DHTM and 6FDA by synthetic route (2) To a solution of DHTM (0.9 g, 3.1 mmol) in 20 ml of NMP at room temperature, a stoichiometric amount of 6FDA (1.38 g, 3.1 mmol) was added with a solid content of 15 wt.% in NMP. The solution was continuously stirred at room temperature for 24 h. To the reaction mixture, 3.0 ml of 1,2-dichlorobenzene was added and then the reaction temperature was raised to 175°C. After the reaction mixture was kept at 175°C for 3 h, the resulting viscous solution was poured into a large excess of methanol and filtered. The precipitated polymer was washed several times with water and methanol, and then the polymer obtained was dried at 100°C for 12 h in vacuum.

2.3.1.3. PHI from DHTM and 6FDA by synthetic route (3) To a solution of DHTM (0.9 g, 3.1 mmol) in 20 ml of NMP at room temperature, a stoichiometric amount of 6FDA (1.38 g, 3.1 mmol) was added with a solid content of 15 wt.% in NMP. The solution was continuously stirred at room temperature for 24 h. To the reaction mixture, 1.5 ml of acetic anhydride and 1.8 ml of pyridine were added and then the reaction temperature was raised to 120°C. After the reaction mixture was kept at 120°C for 3 h, the resulting viscous solution was poured into a large excess of methanol and filtered. The precipitated polymer was washed several times with water and methanol, and then the polymer obtained was dried at 100°C for 12 h in vacuum.

2.3.1.4. Poly(hydroxy-imide) (BHI) from DHTM and BPA In a similar procedure for preparation of PHI-1, BHI was obtained. Yield = 94.5%.

2.3.1.5. Poly(hydroxy-imide) (DHI) from DHTM and DOCDA In a similar procedure for preparation of PHI-1, the poly(hydroxy-imide) (DHI) was obtained. Yield = 90.6%.

2.3.1.6. Poly(hydroxy-imide) (CHI) from DHTM and CPDA In a similar procedure for preparation of PHI-1, the poly (hydroxy-imide) (CHI) was obtained. Yield = 98.4%.

2.5. Synthesis of polyimide-based NLO materials

Synthesis of side-chain polyimide-based NLO materials was carried out by the Mitsunobu reaction of poly(hydroxy-imide)s with NLO chromophores, as shown in Scheme 2.

2.5.1. Synthesis of PHI-DANS and PHI-DRI

PHI (0.5 g, 0.716 mmol), triphenyl phosphine (Ph_3,P) (0.282 g, 1.074 mmol), and DANS-monol (0.32 g, 1.074 mmol) were dissolved in fresh THF (20 ml) successively, respectively. The flask was flushed with dry nitrogen. Diethyl azodicarboxylate (0.208 g, 1.074 mmol) in THF was added slowly dropwise to the mixture. The reaction mixture was further stirred at room temperature for 48 h and was then added dropwise into an agitated solution of methanol (300 ml). The collected precipitate was redissolved in THF and reprecipitated into the large excess of methanol. The precipitate was filtered and washed with methanol. The polymer was further purified by Soxhlet extraction with methanol for 24 h and dried at 60°C under vacuum for 24 h to afford the side-chain NLO polyimide. Yield = 92.9%. Also, a polyimide-based NLO material containing DR1 was prepared in a similar procedure described before, with the yield of 86.6% (PHI-DR1).

2.5.2. Synthesis of BHI-DANS, BHI-DR1, DHI-DANS, DHI-DR1, CHI-DANS, and CHI-DR1

In a similar procedure for the preparation of PHI-DANS, the corresponding NLO polyimides were obtained as a dark red solid. Yields = 77.7%, 80.7%, 82.7%, 85.7%, 68.7% and 71.9%, respectively.

2.6. Thin film preparation and optical measurements

The polymer dissolved in cyclohexanone or *r*-butyrolactone at a concentration of range of 10–15 wt.%, depending on the desired film thickness. The polymer solution was filtered through a 0.2 μm membrane filter using a syringe and spin-coated at the range of 800–1200 rpm for 60 s on the ITO glass or quartz disc substrates for several measurements on electro-optic coefficient, UV-visible spectra, and refractive indices. After coating, the films were dried at 90°C under vacuum for 24 h to remove residual solvent.

2.6.1. Measurement of the refractive index and the thickness

The refractive index, n, at a wavelength 1.3 μm and thickness, d, of the polymer films were measured by determining the propagation constants of at least the two lowest order transverse electric optical guided modes for samples coated on a glass substrate. The modes were excited by a diode laser beam that was prism coupled into the film. Using the propagation constants, the mode equation of a three-layer waveguide was solved for n and d. The thickness was confirmed with α-step surface or depth profiler.

2.6.2. Poling process

Polymer films were prepared by spin-coating on glass coated ITO, and then aluminium or gold electrode were evaporated on top of the polymer film, or the polymer films were sandwiched between two glasses coated ITO. To align the chromophores, a film was slowly heated to near T_g temperature and then a positive voltage was applied to the top electrode and ITO was grounded. After 10 min, the heater was turned off and the film was allowed to cool below 30°C, at which point the voltage was turned off.

2.6.3. Electro-optic measurements

The electro-optic coefficient, r_{33}, of the poled films was measured at a wavelength of 1.3 μm using a simple reflection method [8]. A Soleil-Babinet compensator was used to bias the DC intensity at the half maximum intensity. The phase retardation between the p and s waves was modulated at about 170 Hz. The amplitude of modulated intensity was determined using a lock-in amplifier, which can be used to calculate the r_{33} values.

3. Results and discussion

3.1. Synthesis of polyimide-based NLO materials

The synthesis of polyimide-based NLO materials was carried out in a two-step reaction. The first step was for the synthesis of poly(hydroxy-imide)s and the second for the incorporation of the NLO chromophores to the polymer

Table 1
Inherent viscosities of poly(hydroxy-imide)s by different synthetic routes with various mole ratios

Polymers	Mole ratio (dianhydride : diamine)	Inherent viscosity		
		Thermal imidization		Condensation and chemical imidization
		m-cresol (acid solvent)	NMP (base solvent)	
PHI	1 : 1	0.43	0.30	—
	1 : 1.1	0.51	—	—
	1 : 1.2	0.31	0.23	0.17
DHI	1 : 1	0.17	0.22	—
	1 : 1.1	0.13	0.10	0.08
	1 : 1.2	0.22	0.15	—

backbone by the Mitsunobu reaction. The synthesis of poly(hydroxy-imide)s was quite straightforward via the direct polymerization between a hydroxy-containing diamine (DHTM) as a propellar-like structure and dianhydride monomers. The polymerization was carried out by three different synthetic routes: thermal imidization in both *m*-cresol and isoquinoline, by both NMP and 1,2-dichlorobenzene, and condensation followed by the chemical imidization with both acetic anhydride and pyridine at various mole ratios of monomers (see Scheme 1). The results for the synthesis of poly(hydroxy-imide)s are summarized in Table 1. Table 1 shows that polycondensation between dianhydride and diamine gives a higher molecular weight polyimide in *m*-cresol than in NMP as follows: The water produced during imidization is miscible to the reaction medium in NMP and the produced water could destroy the amide linkage of polyamic acid by hydrolysis. It yields a relatively low molecular weight polymer. However, in the case of the direct thermal imidization with *m*-cresol and isoquinoline, the produced water is immiscible to the reaction medium in m-cresol. Hence, the water could be immediately removed and no remarkable decrease in the molecular weight of polymers was obtained without the hydrolysis of the amide linkage. With this reason, poly(hydroxy-imide)s with relatively high molecular weight were obtained in the direct thermal imidization with *m*-cresol and isoquinoline [11].

The polyimide-based NLO materials were synthesized by the Mitsunobu reaction of poly(hydroxy-imide)s with hydroxy-containing NLO chromophores, as shown in Scheme 2. It should be noted that this synthetic method for the polyimide-based NLO materials has some advantages: (i) we can prepare the polyimide-based NLO materials in a mild condition without decomposition of NLO chromophores during the imidization process at a high curing temperature and (ii) we can easily incorporate many kinds of NLO chromophores containing hydroxy group into the polyimide backbone. The synthetic results and thermal properties are shown in Table 2. The yield of NLO polyimides were in the range of 71%–93%. Previously, the similar values were obtained [12]. The resultant polymers have moderately inherent viscosity values in the range of 0.21–0.50 dl/g, which was determined with an Ubbelohde viscometer at a concentration of 0.5 g/dl in NMP at 30°C. It indicates that the molecular weight of the polymers obtained was not very high. Also, Table 3 summarizes

Table 2
Polymerization results and thermal properties of the NLO polyimides

Polymers	Yield[a] (%)	η_{inh}[b] (dl/g)		T_g (°C)	T_m[c] (°C)	T_{ID}[d] (°C)
		Poly(hydroxy-imide)/NLO polyimide				
PHI-DR1	86.62	0.43	0.45	209.6	—	289.9
PHI-DANS	92.86	0.43	0.50	214.8	—	290.8
BHI-DR1	77.69	0.21	0.27	161.3	—	190.2
BHI-DANS	80.72	0.21	0.25	162.2	—	194.9
DHI-DR1	82.69	0.18	0.21	177.8	—	229.1
DHI-DANS	85.71	0.18	0.22	179.6	—	230.1
CHI-DR1	68.69[e]	0.24	0.35	220.5	—	275.6
CHI-DANS	71.88[e]	0.24	0.28	232.7	—	281.5

[a] The yield was determined from the ratio of the obtained amount of polymers precipitated in MeOH to the theoretical amount of NLO PI with 100% coupling.

[b] Temperature at which initial loss of mass was observed.

[c] T_m was not observed (amorphous polymer).

[d] Inherent viscosity in NMP.

[e] NLO-CHIs was slightly soluble in MeOH.

Table 3
Solubility of the NLO polyimides. S: Soluble P: Partially soluble I: Insoluble

Solvents	Polymers			
	PHI-DR1, PHI-DANS	BHI-DR1, BHI-DANS	DHI-DR1, DHI-DANS	CHI-DR1, CHI-DANS
DMF	S	P	S	P
DMSO	S	P	I	P
NMP	S	P	S	P
γ-Butyrolactone	S	P	S	P
Cyclohexanone	S	P	S	P
THF	S	P	S	P
$CHCl_3$	S	P	S	P
M.C.	S	P	S	P
Acetone	S	P	P	P
Hexane	I	I	I	I

the solubility of the polyimide-based NLO materials obtained. Two of them, such as PHI and DHI derivatives, were soluble in polar solvents such as cyclohexanone, DMSO, DMF, DMAc, and THF, etc. It indicates that the incorporation of fluorinated group and the less rigid alicyclic groups into NLO polyimides enhances their solubility.

3.2. Structural characterization of NLO-polyimides

After the post-Mitsunobu reaction of poly(hydroxy-imide)s with hydroxy-containing NLO chromophores, the polyimide-based NLO materials were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR, and UV-visible spectroscopies. Fig. 1 shows the FT-IR spectra of a propellar-like, hydroxy-containing diamine (DHTM), PHI, and a NLO-polyimide (PHI-DANS): The spectrum of the PHI showed characteristic peaks at about 1786 cm^{-1} and 1725 cm^{-1}for the symmetric and asymmetric vibration bands of the C=O linkage in the cyclic imide group, respectively. After the PHI coupled with DANS-monol in the Mitsunobu reaction, a broad hydroxy peak of PHI at 3400–3250 cm^{-1} almost completely disappeared, indicating that the Mitsunobu

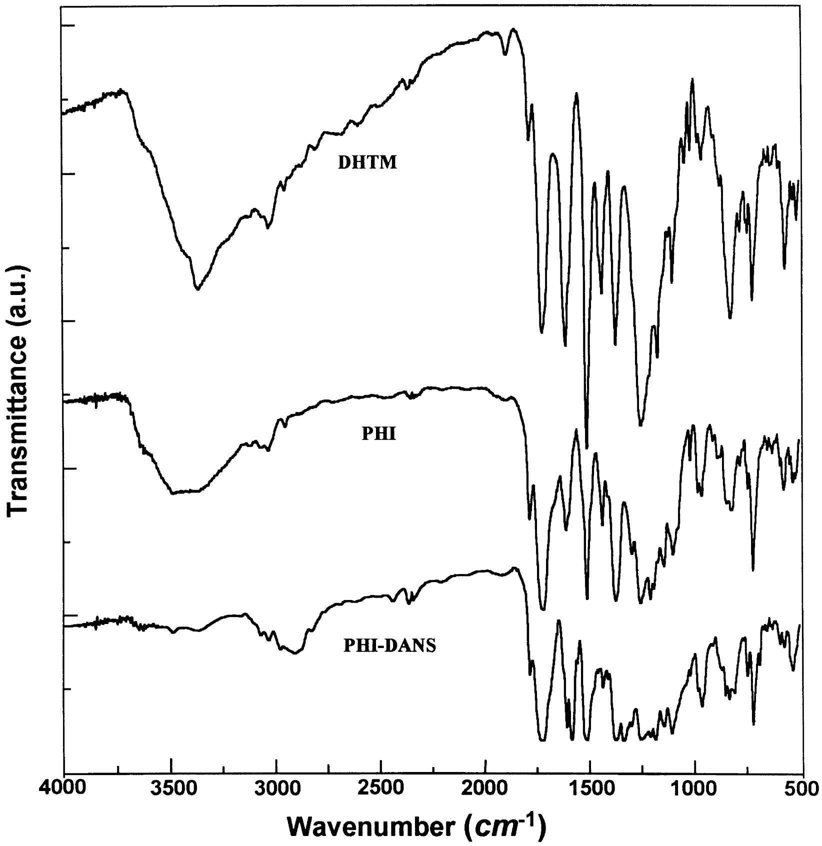


Fig. 1. FT-IR spectra of the DHTM, PHI and PHI-DANS.

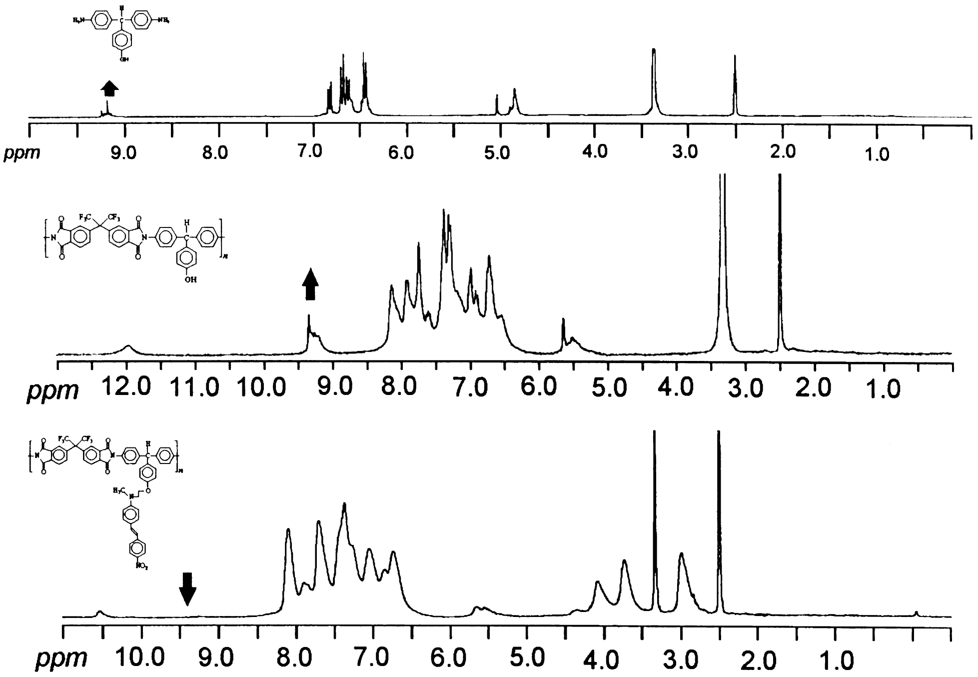


Fig. 2. ^{1}H-NMR spectra of the DHTM (in acetone-d_6), PHI (in DMSO-d_6), and PHI-DANS (in DMSO-d_6).

reaction occurred quantitatively. Fig. 2 represents the ^{1}H-NMR spectra of a DHTM, PHI, and PHI-DANS. In the spectrum of PHI, the aromatic hydroxy proton peak showed at 9.3 ppm. The post-Mitsunobu coupling reaction between hydroxyl polyimides and hydroxyl chromophores was monitored by ^{1}H-NMR. The hydroxyl proton peaks at 9.3 ppm completely disappeared in a PHI-DANS. The peaks of the aromatic ring protons also appeared in the region 6.5–8.2 ppm together with aromatic stilbene proton peaks.

Fig. 3 shows the UV-visible spectra of the NLO polyimides. NLO polyimide has an absorption maximum peak

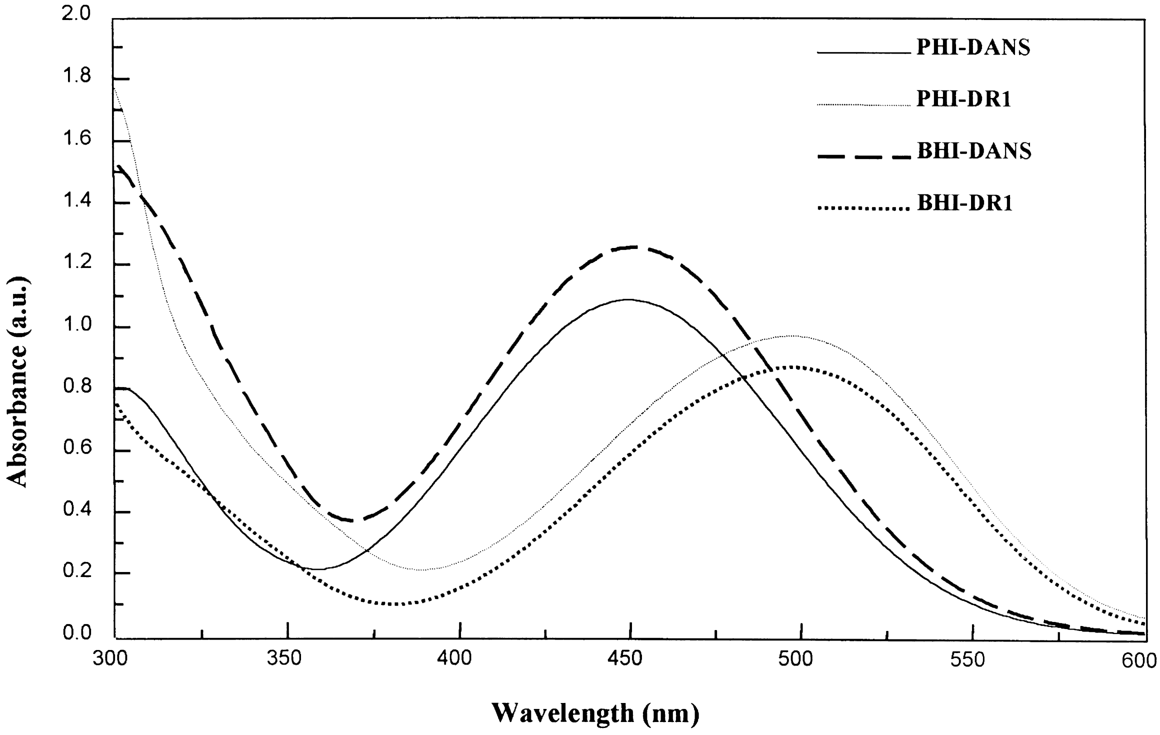


Fig. 3. UV-visible spectra of the NLO polyimides in THF.

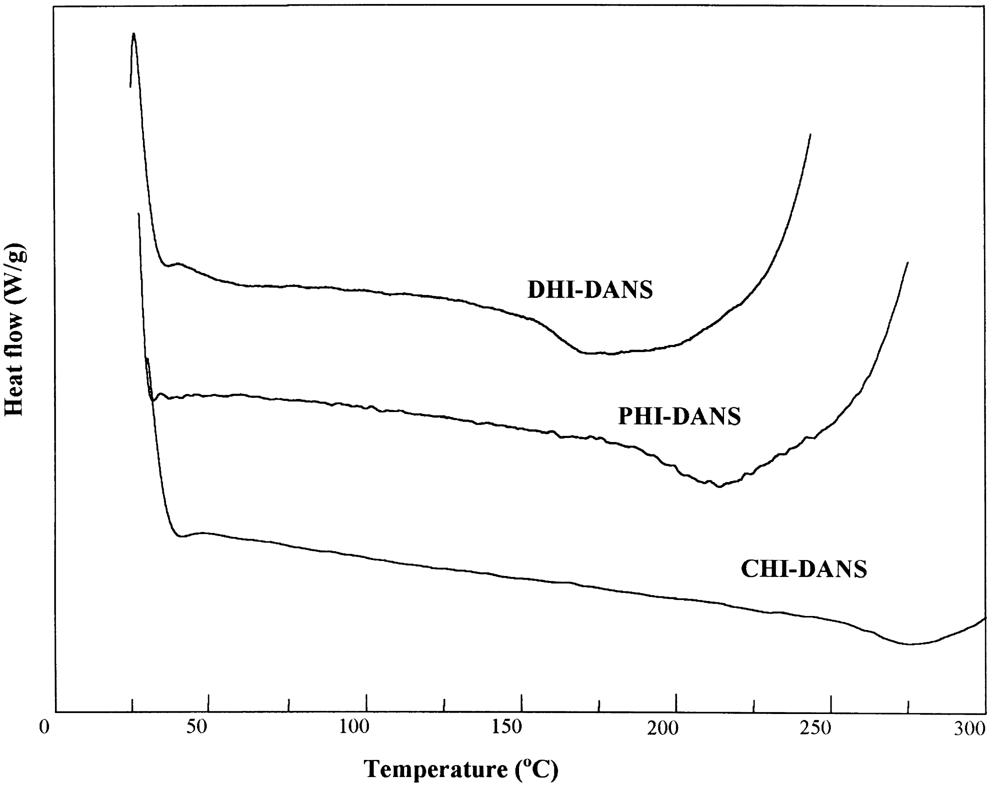


Fig. 4. DSC diagrams of DHI-DANS, PHI-DANS and CHI-DANS at the heating rate of 10°C/min under a nitrogen atmosphere.

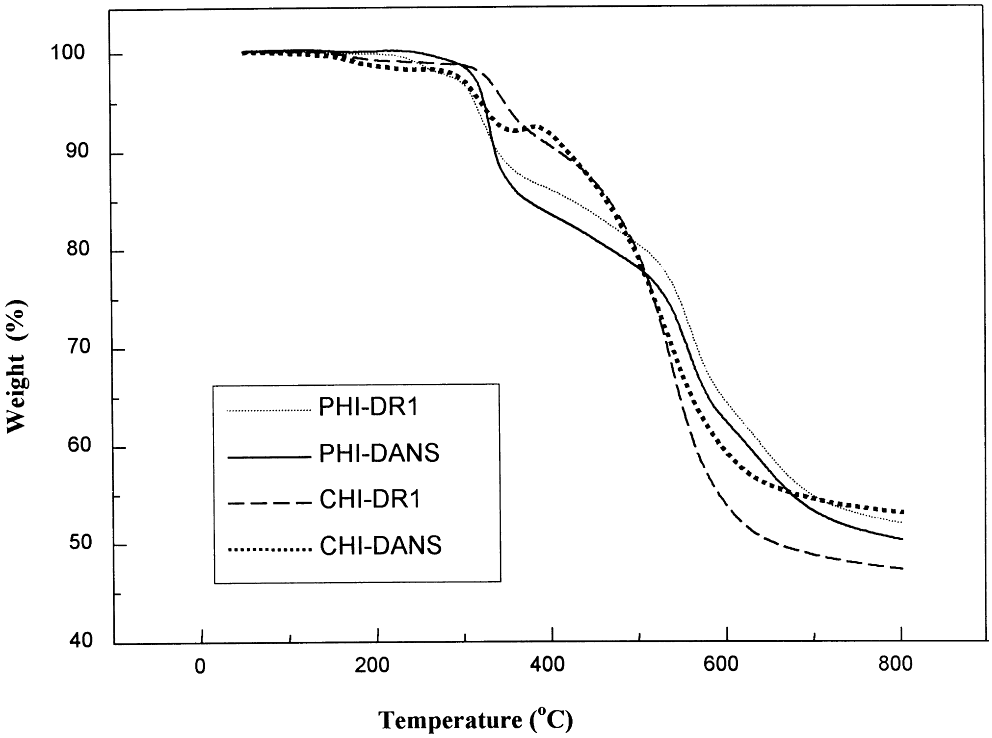


Fig. 5. TGA traces of the NLO polyimides at the heating rate of 10°C/min under a nitrogen atmosphere.

Table 4
Linear and nonlinear optical data of NLO polyimides

Polymers	λ_{max} (nm) (NLO-PI)	Spin coating condition	n^a (1.3 μm)	r_{33} (nm)^b (1.3 μm)
PHI-DR1	497	13 wt.% in cyclohexanone	1.6185	5.8
PHI-DANS	449	13 wt.% in cyclohexanone	1.6101	5.9
BHI-DRI	498	Poor[c]	ND[d]	ND[d]
BHI-DANS	452	Poor[c]	ND[d]	ND[d]
DHI-DR1	499	17 wt.% in γ-butyrolactone	1.62	3.7
DHI-DANS	453	17 wt.% in γ-butyrolactone	1.62	2.1
CHI-DR1	499	Poor	ND[d]	ND[d]
CHI-DANS	452	Poor	ND[d]	ND[d]

[a] Indices of refraction was determined from waveguiding experiments.
[b] Electro-optic coefficient.
[c] Poor thin film.
[d] ND-Not determined because of poor thin film.

of ca. 449–498 nm, mainly resulting from $\pi-\pi^*$ electronic transitions of the NLO chromophore. A similar UV behaviour suggests that the absorption maximum wavelength (λ_{max}) of NLO polyimides was affected a little by the stiffness of the backbone. Therefore, these analytical results clearly show the formation of polyimide-based NLO polymers by the incorporation of NLO chromophore into the polymer backbone with quantitative conversions after the post-Mitsunobu reaction.

3.3. Thermal stability of NLO-polyimides

Thermal properties of the NLO polyimides were examined by thermogravimetric analysis (TGA) and a differential scanning calorimetry (DSC). The thermal properties of the NLO polyimides are summarized in Table 2. The DSC diagrams of the PHI-DANS, the DHI-DANS, and the CHI-DANS showed the T_g's of 215°C, 178°C and 233°C, respectively (see Fig. 4). All NLO polymers with the moderate glass transition temperature range of 161°C–233°C, requested by a polymeric photonic device development group [12], could be very suitable to prevent the relaxation of the dipole alignment at the operation temperatures below 125°C. It is also feasible for the device fabrication of the typical multi-layered channel waveguides such as an electrode/clad/core/clad/electrode stacking structure. This is because NLO polymers with a higher glass transition temperature of higher than 250°C offers some difficulty in fabricating the multi-layered channel waveguides, at the same time the surface of NLO polymer thin films can be damaged during spin-coating process for the top cladding layer [2]. The thermal stability of the resulting NLO polyimides was evaluated by TGA analysis under a nitrogen atmosphere at a heating rate of 10°C/min. All the NLO polyimides, except BHI-based NLO materials, showed a good thermal stability up to 230°C (see Table 2). The weight loss of NLO polyimides over 230°C is caused by the decomposition of NLO chromophores, compared with the t.g.a. diagram of NLO chromophores, as the polyimide backbones decompose above 300°C from TGA traces of poly(hydroxyimide)s. Typical TGA curves showed that the initial decomposition temperatures for the PHI-DANS, PHI-DR, CHI-DANS, and CHI-DR were observed before 275°C (see Fig. 5). The TGA studies showed that PHI-DANS is the most stable polymer among them: It started its weight loss at about 291°C under nitrogen. The first one might be related to the loss of a NLO chromophore because these polymers have a relative thermal stability. The second weight loss process might be related to the polymer backbone.

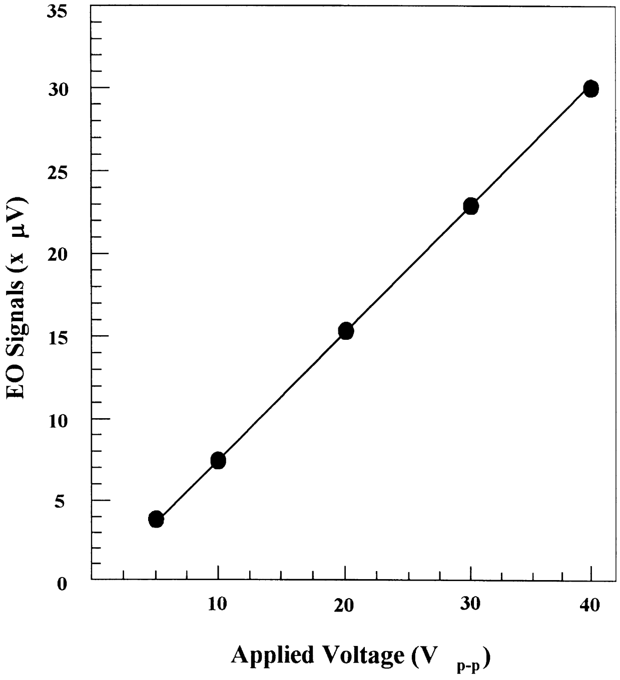


Fig. 6. Linear electro-optic coefficient of DHI-DANS as a function of applied voltage.

3.4. Optical property of NLO-polyimides

Optical-quality thin films (2–3 μm) of the side-chain polyimides were prepared by spin-coating the polymer solutions in cyclohexanone onto ITO glass substrate, and then

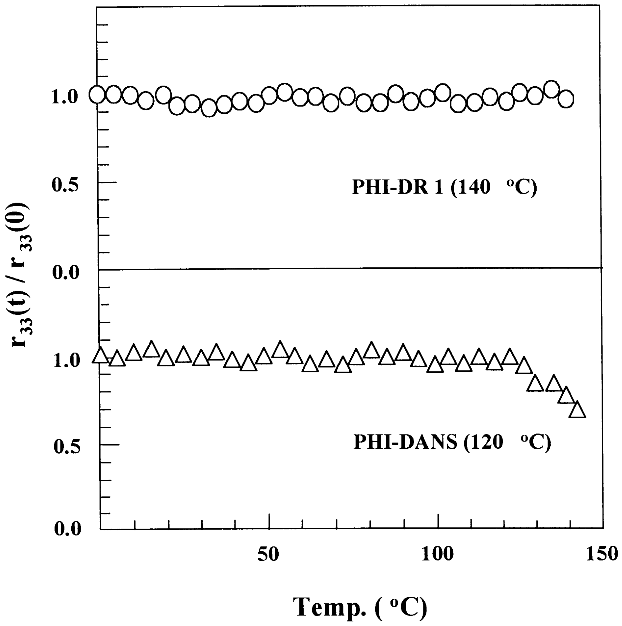


Fig. 7. Thermal stability of electro-optic properties of NLO polyimides.

aluminium or gold electrode were evaporated on top of the polymer film, or the polymer films were sandwiched between two glasses coated with ITO. Dipole alignment of the NLO polymers can be achieved by DC contact poling. A film was slowly heated to near T_g temperature and then a positive voltage was applied to the top electrode and ITO was grounded. After 10 min, the heater was turned off and the film was allowed to cool below 30°C, at which point the voltage was turned off. Table 4 shows the measured electro-optic (EO) coefficients of polymer films at 1.3 μm at different poling conditions. The results showed that the synthesized NLO side-chain polyimides exhibited a large EO coefficient (r_{33}) and a good thermal stability of dipole alignment. Linear EO coefficients of DHI-DANS as a function of applied voltage (V_{p-p}) are shown in Fig. 6. As the applied voltage increased, the EO signal of DHI-DANS increased. The optimized r_{33} value for NLO-PHI and NLO-DHI at the poling field of 100 V/μm were 5–6 pm/V and 2–4 pm/V measured at 1.3 μm, respectively. The temporal and long-term stability of the nonlinear properties for the poled polymers was studied by monitoring the EO signal. The EO signal for PHI-DR1 and PHI-DANS remained stable up to 140°C and 120°C, respectively (Fig. 7). These results overcome the relaxation problem in poled NLO polymeric systems, owing to the higher glass transition temperature by imide groups. Long-term stability of the dipole alignment of EO property for PHI-DR1 was observed up to 110°C and 115°C, as about >80% retention of the effective NLO coefficients, r_{eff}, was observed when the poled NLO-PHI sample was heated for over 350 min (Fig. 8).

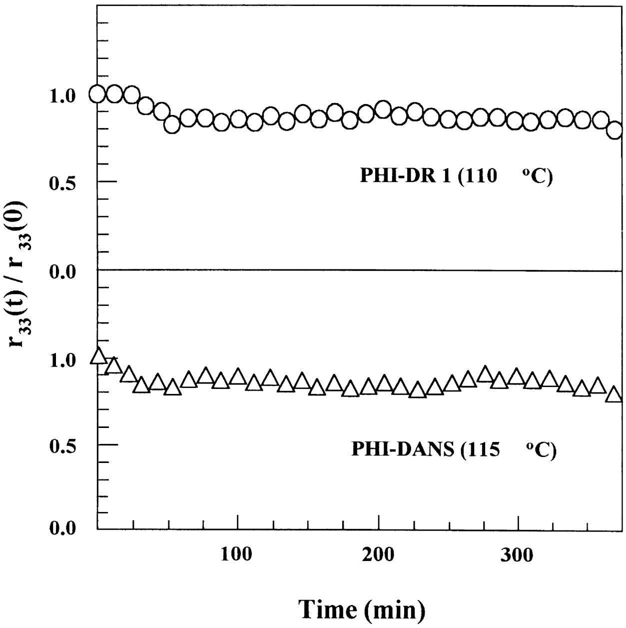
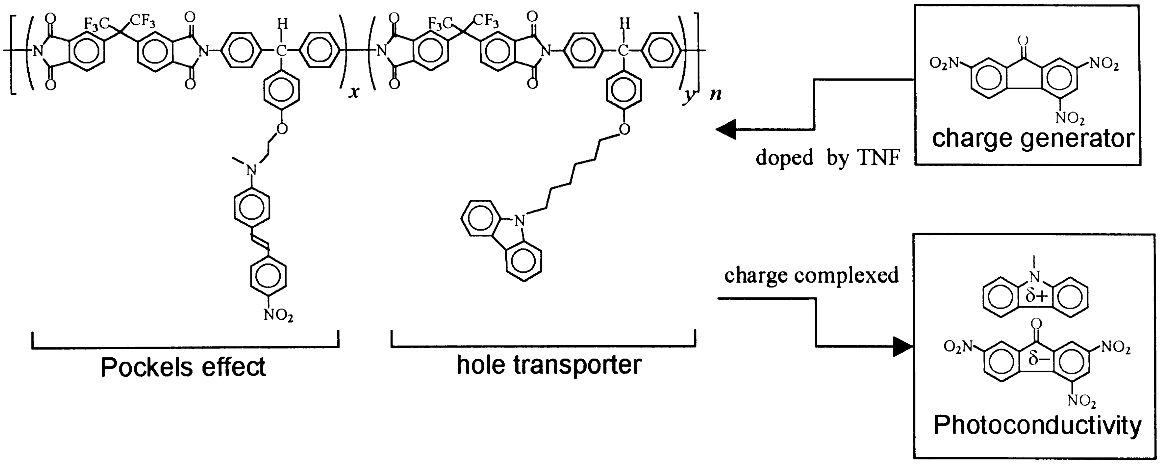


Fig. 8. Temporal stability of electro-optic properties of NLO polyimides.

In addition, very recently, we synthesized novel photorefractive polymer [13] containing a NLO chromophore with carbazole moiety as hole transporter by Mitsunobu reaction of poly(hydroxy-imide)s with both NLO chromophore and a carbazole moiety (see Scheme 3). The present photorefractive polymer doped with 2,4,7-trinitro-9-fluorenone as a strong acceptor shows the formation of a charge-transfer complex with the carbazole moieties to provide photosensitivity. At present, the photorefractive properties of the polymer are being studied by the four-wave mixing and two-beam coupling techniques. Therefore, this synthetic method for the polyimide-based NLO materials has some advantages: (i) we can prepare the polyimide-based NLO materials in a mild condition without decomposition of NLO chromophores during the imidization process at a high curing temperature and (ii) we can easily incorporate many kinds of NLO chromophores as well as other functionalized groups containing hydroxy group into the polyimide backbone, yielding multi-functional polymers.

4. Conclusion

A series of polyimide-based second-order NLO materials were synthesized from poly(hydroxy-imide)s containing alicyclic units, followed by the Mitsunobu reaction with NLO chromophores. This synthetic method for the polyimide-based NLO materials has some advantages: (i) we can prepare the polyimide-based NLO materials in a mild condition without decomposition of NLO chromophores during the imidization process at a high curing temperature and (ii) we can easily incorporate many kinds of NLO chromophores containing hydroxy group into the polyimide backbone. The resulting polymers were highly soluble in aprotic polar solvents such as DMF, DMAc, NMP, etc.



Scheme 3. Chemical structure of side-chain photorefractive polyimides by Mitsunobu reaction.

The NLO polyimides exhibited the inherent viscosity range of 0.22–0.50 dL/g. Molecular structural characterization for the resulting polymers was achieved by ^{1}H-NMR, FT-IR, and UV-visible spectroscopies. The glass transition temperature for the resulting NLO polyimides was in the range of 161°C–233°C and most of them showed high thermal stability. The polymer solutions could be spin coated on the ITO glass or quartz disc substrates to form the optical quality thin films. The electro-optic coefficients (r_{33}) at the wavelength of 1.3 μm for polymer thin films poled around the glass transition temperature were in the range of 2–6 pm/V. And, long-term thermal stability of the dipole alignment was observed up to ca. 140°C.

Acknowledgements

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