PII: S0032-3861(97)00459-X

Polymer Vol. 39 Nos. 8–9, pp. 1719–1726, 1998

0032-3861/97/$17.00+0.00

Second-order NLO polyamideimides based on functionalized stilbene derivatives: direct polycondensation and characterization

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(Received 17 March 1997; revised 27 May 1997)

Polyamideimides having nonlinear optical (NLO)-active chromophores were synthesized by direct polycondensation of 4-[*N,N′*-bis(2-aminoethyl)amino]-4′-nitrostilbene (DANS-diamine) with oxy-bis[*N*-(4-phenylene)-trimellitic imide] (BCI), *N*-(3-carboxyphenyl)-trimellitimide (BTI) and trimellitic anhydride chloride (TMAC). The direct polycondensation of NLO polyamideimides without a curing step may ameliorate the optical property of NLO polymers by reducing the optical propagation loss. The resulting polymers were highly soluble in aprotic polar solvents such as DMF, DMAc, NMP, etc. The NLO polyamideimides exhibited the inherent viscosity range of 0.14–0.33 dl g^{-1}. Molecular structural characterization for the resulting polymers was achieved by ^{1}H n.m.r., *FT*i.r. and u.v.–visible spectroscopies. The glass transition temperature for the resulting NLO polyamideimides was in the range 142–224°C and they showed thermal stability up to 260°C. The polymer solutions could be spin coated onto indium–tin-oxide (ITO) glass or quartz disc substrates to form optical quality thin films. The electro-optic coefficients (r_{33}) at the wavelength of 1.3 μm, measured by a simple reflection method, for polymer thin films poled around the glass transition temperature were in the range 1.9–7.4 pm V^{-1}. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: nonlinear optical polyamideimides; stilbene derivatives; direct polycondensation)

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[1–9]. For practical applications, these NLO polymeric materials must retain 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 requirements for practical applications, numerous approaches have been developed to utilize these NLO polymeric materials for use in real applications and the performance of the polymers has been enhanced[3,10]. However, 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[11–16] and aromatic polyesters [17,18] 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 due to 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 polyimides were prepared from the corresponding polyamic acids via thermal treatment. It was reported that polyimides derived from polyamic acids exhibited poor reproducibility of optical quality, including optical propagation loss, and side NLO chromophores also decomposed during the imidization process at a high curing temperatures[7,8,19]. 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 by the direct polycondensation of 4-[*N,N′*-bis(2-aminoethyl)amino]-4′-nitrostilbene (DANS-diamine) with oxy-bis [*N*-(4-phenylene)-trimellitic imide] (BCI), *N*-(3-carboxyphenyl)-trimellitimide (BTI) and trimellitic anhydride chloride (TMAC), in order to enhance the stability of dipole alignment and their solubility by the incorporation of amide groups into NLO polyimides. We should stress that the direct polycondensation of NLO polyimides without a curing step could ameliorate the optical property of NLO polymers by reducing the optical propagation loss, while the reproducibility of optical quality including the optical propagation loss for NLO polyimides derived from polyamic acids was poor[7,8,19]. The resulting NLO polyamideimides were highly soluble in aprotic polar solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), etc. The polymer solutions could be spin coated onto indium–tin-oxide (ITO) glass or quartz disc substrates to form optical quality thin films. Furthermore, NLO polyamideimides associated with a high glass transition

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temperature led to the improvement of the thermal stability of NLO polymers and the thermal stability of dipole alignment. Note that these side-chain NLO polyamideimides have several advantages, including higher temperature alignment stability, better mechanical properties and lower optical propagation loss than other polyimides derived from polyamic acids.

In this paper, we discuss the direct polycondensation and characterization of aromatic polyamideimides containing a pendant NLO chromophore by the Yamazaki reaction of DANS-diamine with BCI, BTI and TMAC.

EXPERIMENTAL

Instrumentation

^{1}H n.m.r. spectra were recorded with the use of a Bruker AM-200 spectrometer, and chemical shifts were reported in ppm with tetramethylsilane or an internal standard. *FT*i.r. spectra were measured as KBr pellets on a Perkin Elmer spectrometer Paragon 1000 PC, and frequencies were given in cm^{-1}. A Perkin Elmer u.v.–visible spectrometer Lambda 14 was used for u.v.–visible spectral data. Thermal analyses were carried out on a Dupont TGA 9900 thermogravimetric analyser under a nitrogen atmosphere at a heating rate of 10°C min^{-1}. Perkin Elmer 7 thermal analysis equipment was used for d.s.c. thermograms. Thin films were prepared by spin-coating the solution on an 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}) as a function of the electric field was measured by a simple reflection method.

Materials

4-[*N,N'*-Bis(2-hydroxyethyl)amino]-4'-nitrostilbene (DANS-diol) and 4-[*N,N'*-bis(2-aminoethyl)amino]-4'-nitrostilbene (DANS-diamine) were synthesized according to literature procedures[1,2,7,8,11–16]. Chemical reagents were obtained from Aldrich Chemical Co. and used without further purification. All solvents were used after purification according to conventional methods.

Synthesis of monomers

Scheme 1 shows the synthetic routes to the monomers of DANS-diamine, BTI, and BCI.

Synthesis of DANS-diol. DANS-diol as a second-order NLO chromophore was prepared as described in the literature[2,8]

DANS-diphthalimide. DANS-diol (1.5 g, 4.57 mmol), triphenylphosphine (3.598 g, 13.7 mmol), and phthalimide (2.018 g, 13.7 mmol) were dissolved in THF (20 ml) in a 200 ml two-neck flask. Diethyl azodicarboxylate (2.389 g, 13.7 mmol) in THF (6 ml) was added dropwise to the reaction mixture. The resulting mixture was stirred for 12 h, and the desired product precipitated out. The red solid was collected by filtration and recrystallized from chloroform/hexane (vol. ratio 1:5). Yield 57%, m.p. 230°C. ^{1}H n.m.r. ($CDCl_3$, ppm): δ 3.68 (t, $-NCH_2-$), 3.89 (t, $-CH_2O-$), 6.79 (d, vinyl proton), 6.89 (d, aromatic protons), 7.05 (d, vinyl protons), 7.30 (d, aromatic protons), 7.49 (d, aromatic protons), 7.67 (m, phthalimide protons), 7.78 (m, phthalimide protons), 8.13 (d, aromatic protons). *FT*i.r. (KBr, cm^{-1}): 1775, 1712 (imide C=O).

Synthesis of DANS-diamine

To a three-neck flask containing DANS-diphthalimide (0.8 g, 1.36 mmol) and THF (20 ml) was added the hydrazine hydrate (0.389 g, 6.80 mmol). The mixture was refluxed for 6 h under a nitrogen atmosphere and then cooled to room temperature. The precipitate was filtered out, and the filtrate was dried under a vacuum, yielding a red solid. Ethanol (20 ml) was then added to the solid and the resulting mixture was stirred for 15 min at *ca.* 50°C. The insoluble part was removed by filtration. Water was then added dropwise to the filtrate, and the dark red product crystallized out. The crude product was recrystallized from MeOH/water. Yield 46.2%, m.p. 159°C (d.s.c. result). ^{1}H n.m.r. (DMSO-d_6, ppm): δ 1.50 (d, amine protons), 2.67 (t, $-CH_2NH_2-$), 3.31 (t, $-CH_2N-$), 6.71 (d, aromatic protons), 7.03 (d, vinyl protons), 7.36 (d, vinyl protons), 7.41 (d, aromatic protons), 7.70 (d, aromatic protons). *FT*i.r. (KBr, cm^{-1}): 3460–3280 (NH stretch).

Synthesis of BCI

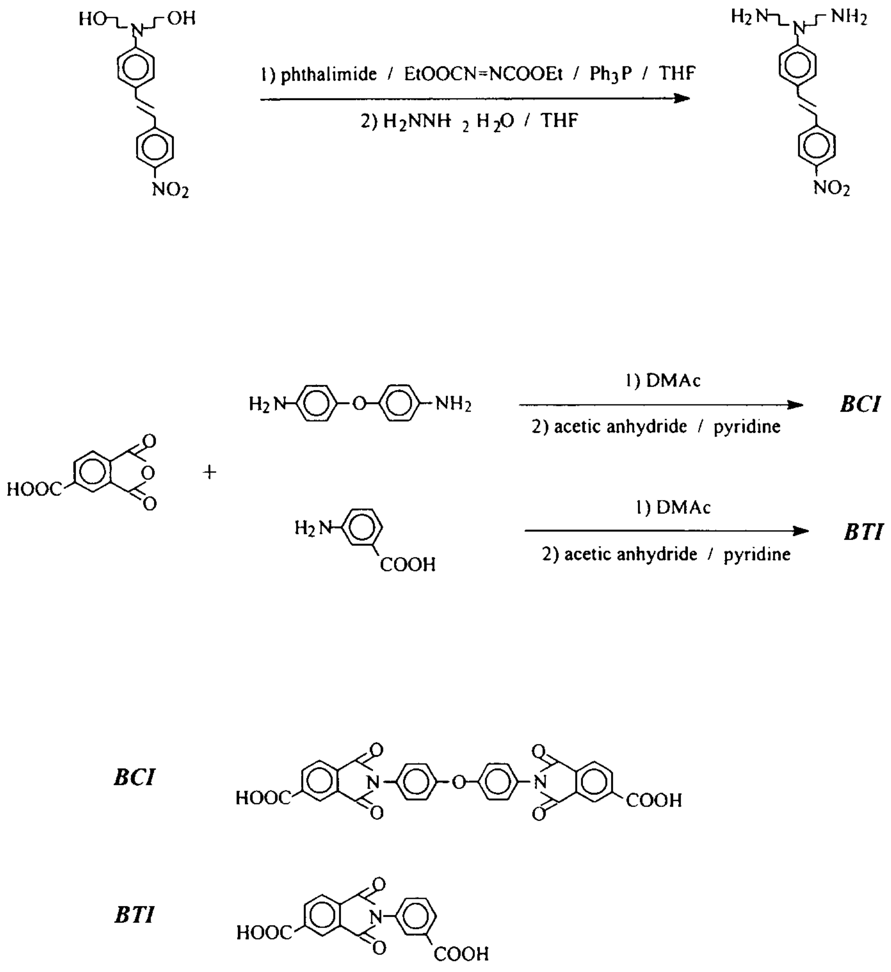
A 100 ml four-neck round-bottomed flask containing of 4,4'-diaminophenyl ether (ODA, 10 g, 0.5 mol) was dissolved in DMAc (40 ml) at 0°C. Trimellitic anhydride (TMA, 19.2 g, 1.0 mol) in DMAc (106 ml) was added dropwise to the reaction solution. The resultant solution was then warmed to room temperature and magnetically stirred for 6 h under a nitrogen atmosphere. To the reaction mixture was added a mixture of acetic anhydride (12 ml) and pyridine (3 ml). The reaction temperature was then raised to 150°C and the solution was reacted for 5 h. After cooling to room temperature, the precipitated yellow monomer was collected by filtration, and washed thoroughly with acetone. The crude product was recrystallized from DMAc. Yield 74%, m.p. 374°C. ^{1}H n.m.r. (DMSO-d_6, ppm): δ 8.4 (d, aromatic protons), 8.3 (s, aromatic protons), 8.1 (d, aromatic protons), 7.6 (d, aromatic protons), 7.3 (d, aromatic protons). *FT*i.r. (KBr, cm^{-1}): 1798, 1740 (imide C=O stretch), 1695 (amide C=O stretch).

Synthesis of BTI

BTI was synthesized by chemical imidization of 3-aminobenzoic acid (ABA) with TMA, in a similar way to the synthesis of BCI. Yield 67%, m.p. 414°C. ^{1}H n.m.r. (DMSO-d_6, ppm): δ 8.45 (d, aromatic protons) 8.2 (s, aromatic protons), 8.05 (d, aromatic protons), 8.09 (s, aromatic protons), 8.02 (d, aromatic protons), 7.8–7.6 (m, aromatic protons). *FT*i.r. (KBr, cm^{-1}): 1780, 1720 (imide C=O stretch), 1695 (amide C=O stretch).

Polymerization for NLO-BCI and NLO-BTI[20–22]

Polymerization was carried out by the following procedures, as shown in *Scheme 2*. Triphenylphosphite (0.56 g, 1.838 mmol) dissolved in 1 ml of pyridine was added to a stirred solution of DANS-diamine (0.3 g, 0.92 mmol) and lithium chloride (0.08 g) in 5 ml of NMP over 30 min under a nitrogen atmosphere. BCI (0.504 g, 0.92 mmol) or BTI (0.477 g, 0.92 mmol) in NMP (5 ml) was added dropwise into the reaction solution. The reaction temperature was then raised to 100°C and the solution was reacted for 6 h at 100°C. After cooling to room temperature, the solution was poured into 400 ml of methanol, yielding a precipitated stringy dark red polymer. The product was collected by filtration, washed thoroughly with water and hot methanol and dried under vacuum at 100°C for 24 h.



Scheme 1 Synthetic routes to the monomers of DANS-diamine, BTI, and BCI

One-pot polymerization for NLO-TMAC[23]

The polymerization was conducted in a dry nitrogen-fluxed flask at room temperature with a concentration of 15% solids by weight in DMAc. A stoichiometric amount of trimellitic anhydride chloride (0.3226 g, 1.53 mmol) was added to a solution of DANS-diamine (0.53 g, 1.53 mmol) and pyridine (1.5 ml) in DMAc (10 ml) at 0°C. The reaction solution was then warmed to room temperature and magnetically stirred overnight under nitrogen to form the poly(amic acid) solution. The viscosity of the solution increased during this period greatly. Dry xylene (5 ml) was added to the flask, and the poly(amic acid) was thermally cyclized at 160°C for 4 h. Water that was eliminated by the ring-closure reaction was separated as a xylene azeotrope at the same time. The resulting solution was added dropwise into an agitated solution of methanol (400 ml) and 2 N HCl (8 ml) to obtain the dark red polyamideimide. The polymer was redissolved in DMAc (40 ml) and further purified by reprecipitating into a solution of methanol (400 ml) and 2 N HCl (8 ml) from its DMAc solution. The polymer was then filtered and dried at 100°C under vacuum for 24 h (see *Scheme 2*).

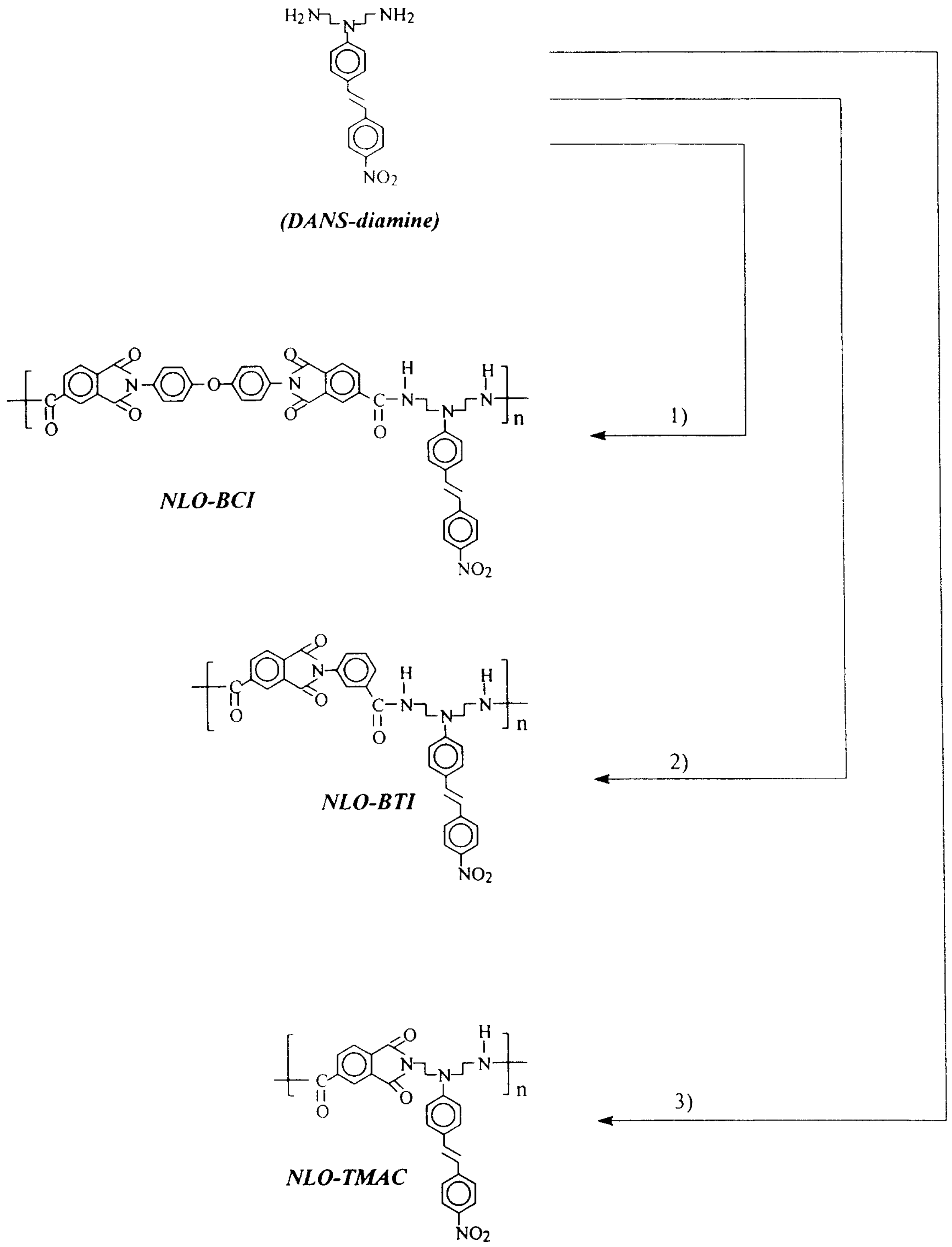
Film preparation and optical measurements

The polymer was dissolved in γ-butyrolactone/DMAc (vol. ratio 1:1) at various concentrations, depending on the desired film thickness. The polymer solution was filtered through a 0.2 μm membrane filter using a syringe and spin-coated on the ITO glass or quartz disc substrates for several measurements of the electro-optic coefficient, u.v.–visible spectra, and refractive indices. The thin films were dried to remove the residual solvent under vacuum for 12 h at 65°C.

The refractive index (n) and thickness (d) of the polymer films at a wavelength of 1.3 μm were measured by waveguide experiments. The thickness was confirmed with an α-step surface profiler (Tencor instruments, α-step 300). The electro-optic coefficient (r_{33}) of the poled films was measured at a wavelength of 1.3 μm using a simple reflection method[24].

RESULTS AND DISCUSSION

A DANS chromophore containing dihydroxy groups (DANS-diol) as a second-order NLO chromophore was prepared as described in the literature[1,2,12–16]. The conversion of the DANS chromophore containing dihydroxy groups into a DANS chromophore containing diamino groups (DANS-diamine) was achieved by the Mitsunobu reaction followed by hydrazinolysis[11–16]. BCI and BTI were prepared by the chemical imidization of 4,4′-diaminophenyl ether or 3-aminobenzoic acid (ABA) with trimellitic anhydride (TMA), respectively (see *Scheme 1*). The chemical structures of all monomers were identified by *FT*i.r. and ^{1}H n.m.r. spectroscopies. The NLO polyamideimides were prepared by the direct polycondensation of DANS-diamine with BTI or BCI in the presence of metal salts and phosphorous compounds, according to the Yamazaki and Higashi phosphorylation reaction, as shown



Scheme 2 Direct polycondensation for the NLO polyamideimides of NLO-BCI and NLO-BTI, and one-pot polymerization for the NLO polyamideimides of NLO-TMAC

in *Scheme 2*[20–22]. *N*-Methyl-2-pyrrolidone (NMP) was used as the solvent for the polymerization: other aprotic solvents, such as *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) are also suitable for the polymerization medium. We also synthesized an NLO polyamideimide of NLO-TMAC by one-pot polymerization of DANS-diamine with TMAC[23]. The condensation polymerization of DANS-diamine with TMAC prepared the preimidized, hydroxy NLO polymers as a polyamic acid, followed by the ring-closure reaction, yielding an NLO polyamideimide. The ring-closure imidization process of the polyamic acid was achieved by heating thermally up to 160°C for 4 h in the presence of xylene added sequentially, generating water which was azeotropically removed by a Dean–Starke apparatus. The viscosity of the reaction medium was increased gradually with the polycondensation reaction time.

The resulting polymers were highly soluble in aprotic polar solvents such as DMF, DMAc, NMP, etc. (see *Table 1*). This indicates that the incorporation of amide groups into NLO polyimides enhances their solubility of polyimide-based NLO polymers. The polymerization results and physical properties are shown in *Table 2*. The viscosity of the NLO polyamideimide solution was

Table 1 Solubility of the NLO polyamideimides

Polymer	Solvent								
	NMP	DMAc	DMF	DMSO	γ-Butyrolactone	THF	$CHCl_3$	EtOH	MeOH
NLO-BCI	+ +	+ +	+ +	+ +	+ +	+ −	− −	− −	− −
NLO-BTI	+ +	+ +	+ +	+ +	+ +	+ −	− −	− −	− −
NLO-TMAC	+ +	+ +	+ +	+ +	+ +	+ −	− −	− −	− −

+ +, soluble; + −, partially soluble; − −, insoluble

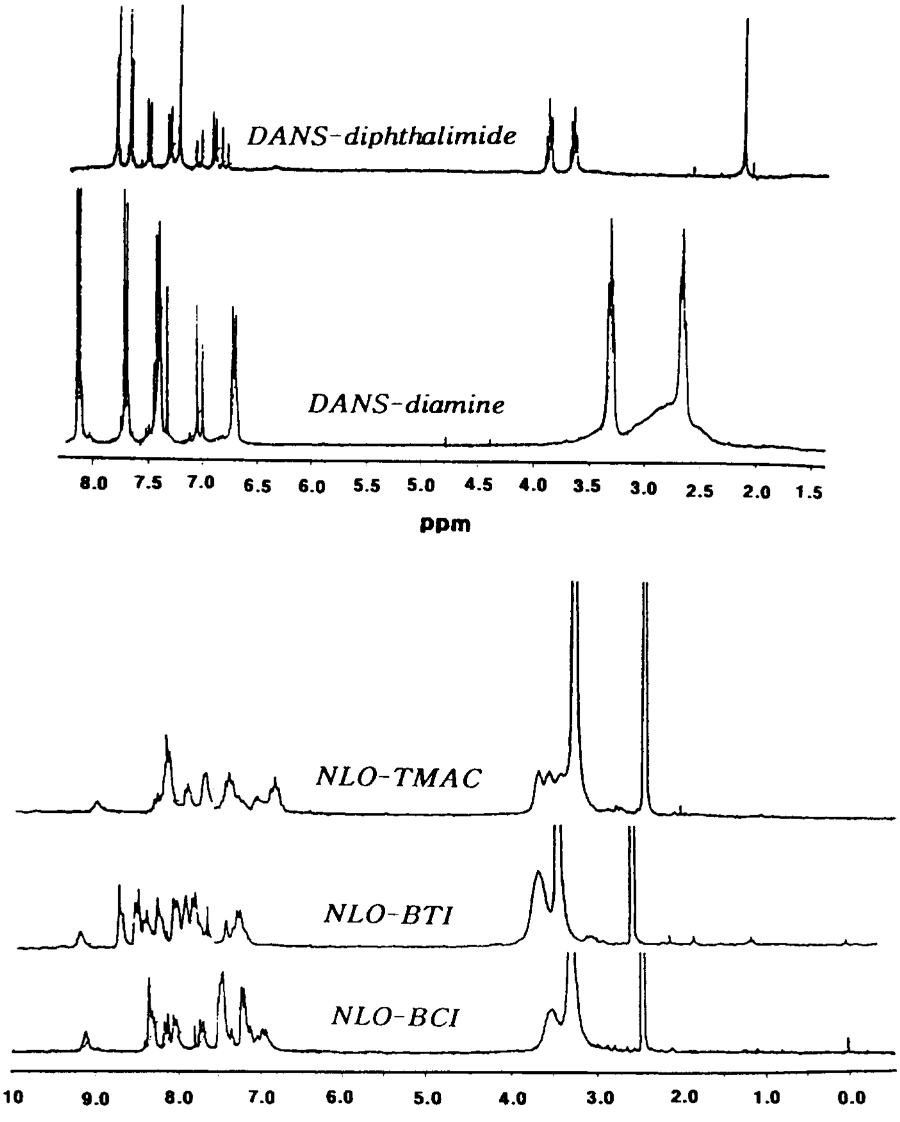


Figure 1 ^{1}H n.m.r. spectra of the DANS chromophores and NLO polyamideimides

Table 2 Polymerization results and physical properties of the NLO polyamideimides

Polymer	Yield (%)	η_{inh} (dl g^{-1})^a	T_{ID}^b (°C)	T_g (°C)
NLO-BCI	96	0.33	260	224
NLO-BTI	95	0.19	220	178
NLO-TMAC	72	0.14	220	142

[a] Inherent viscosity in NMP at 30°C
[b] Initial decomposition temperature

determined with an Ubbelohde viscometer at a concentration of 0.5 g dl^{-1} in NMP at 30°C. *Table 2* shows that all the NLO polyamideimides have low inherent viscosity values in range of 0.14–0.33 dl g^{-1}, indicating that the molecular weight of the polymers obtained was not very high. However, soluble polyamideimides containing NLO chromophores by direct polycondensation without an imidization process would be promising materials for device applications, due to the improvement of the optical property of NLO polymers by reducing the optical propagation loss, while the thin films of NLO polyimides

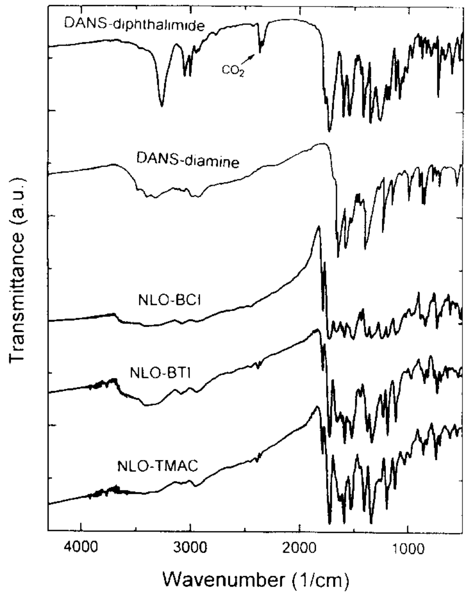


Figure 2 *FT*i.r. spectra of the DANS chromophores and NLO polyamideimides

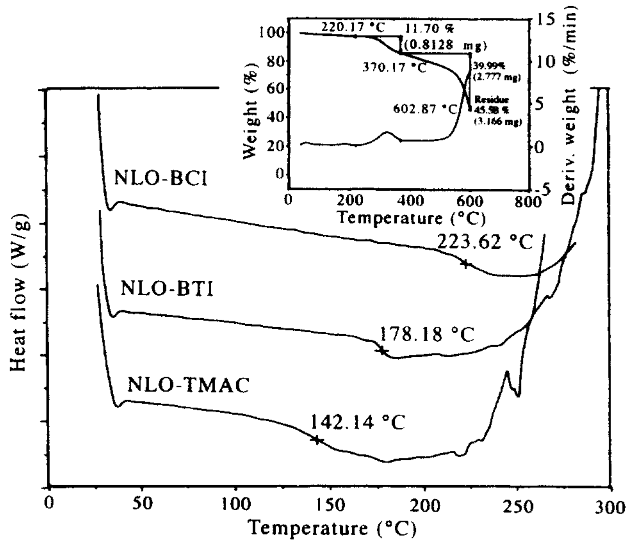


Figure 4 D.s.c. diagrams of NLO-BCI, NLO-BTI and NLO-TMAC as well as a t.g.a. trace of NLO-BTI in a box with the heating rate of 10°C min^{-1} under a nitrogen atmosphere

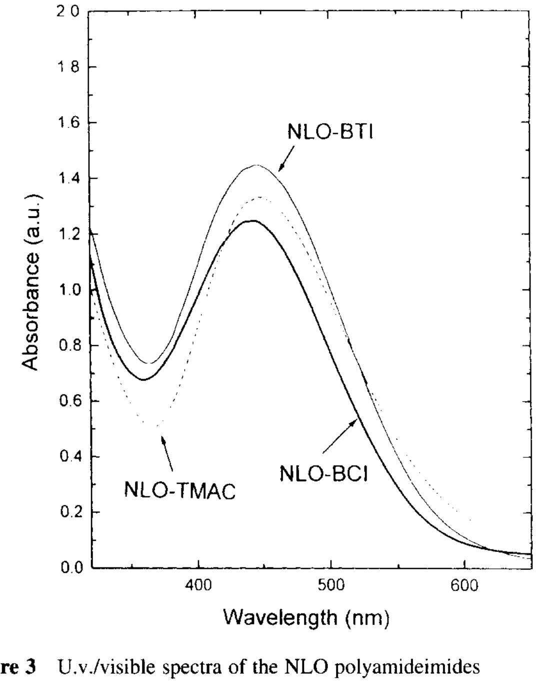


Figure 3 U.v./visible spectra of the NLO polyamideimides

derived from polyamic acids with thermal treatment exhibited poor reproducibility of the optical quality including the optical propagation loss in a waveguide structure [8,19].

The structures of the NLO polyamideimides were characterized by typical spectroscopic techniques. *Figure 1* represents the ^{1}H n.m.r. spectra of a DANS-diamine chromophore and NLO polyamideimides, including a DANS-diphthalimide. In the spectra of both DANS chromophores and NLO polyamideimides, the aliphatic proton peaks adjacent to the nitrogen atoms appeared at the region of 2.3–3.8 ppm. The peaks of the aromatic ring protons also appeared in the region 6.5–8.5 ppm together with aromatic stilbene proton peaks.

Figure 2 shows the *FT*i.r. spectra of NLO polyamideimides for NLO-BCI and NLO-BTI: The spectra of the NLO polyamideimide showed characteristic peaks at about 1660 cm^{-1} for the C=O stretching vibration band of amide and about 1782 and 1725 cm^{-1} for the symmetric and asymmetric vibration bands of the C=O linkage in the cyclic imide group, respectively. An *FT*i.r. spectrum of NLO-TMAC shows the characteristic carbonyl bands of an imide group and an amide group at 1794 and 1736 cm^{-1}, and 1665 cm^{-1}, respectively.

The u.v.–visible spectra show a typical absorption maximum (λ_{max}) at 451, 447 and 449 nm for the NLO-TMAC, NLO-BCI and NLO-BTI due to the $\pi-\pi^*$ electronic transition of a DANS chromophore, respectively (see *Figure 3*). These analytical results clearly show the formation of polyamideimide-based NLO polymers by the incorporation of a chromophore into the polymer backbone. Similar u.v. behaviour suggests that the absorption maximum (λ_{max}) of NLO polyamideimides was affected a little by the stiffness of the backbone.

Thermal properties of the NLO polyamideimides were examined by thermogravimetric analysis (t.g.a.) and differential scanning calorimetry (d.s.c.). The thermal properties of the NLO polyamideimides are summarized in *Table 2*. The d.s.c. diagrams of the NLO-TMAC, NLO-BTI and NLO-BCI showed T_gs of 142, 178 and 224°C, respectively (see *Figure 4*). NLO polymers with a moderate glass transition temperature in the range 140–200°C, requested by a polymeric photonic device development group[25,26], could be very suitable for preventing relaxation of the dipole alignment at operation temperatures of below 125°C. It is also feasible for the device fabrication of multi-layered channel waveguides such as an electrode/clad/core/clad/electrode stacking structure. This is because NLO polymers with a glass transition temperature higher than 200°C offer some difficulty in fabricating multi-layered channel waveguides; at the same time the surface of NLO polymer thin films can be damaged during the spin-coating process for the top cladding layer[25,26]. The thermal stability of the resulting NLO polyamideimides was evaluated by t.g.a. under a nitrogen atmosphere at a heating rate of 10°C min^{-1}. Typical t.g.a. curves showed that the initial decomposition temperatures for NLO-TMAC and NLO-BTI were observed around 220°C. A t.g.a. curve shows that

Table 3 Linear and nonlinear optical data for NLO polyamideimides

Polymers	λ_{max} (nm)	n[a] (1.3 μm)	V_p[b] (V μm)	r_{33} (pm V)[c] (1.3 μm)
NLO-BCI	447	1.643	154	1.9
NLO-BTI	449	1.656	141	6.8
NLO-TMAC	451	1.660	155	7.4

[a] Indices of refraction were determined from waveguiding experiments
[b] Poling electric field at the poling temperature of $T_g + 5$°C
[c] Electro-optic coefficient

NLO-BTI was initially decomposed at temperatures of around 220°C (see *Figure 4*). All of the NLO polyamideimides showed good thermal stability up to 220°C. The weight loss of polyamideimides above 220°C is due to the decomposition of DANS chromophores, compared with the TGA diagram of NLO chromophores, since the polyamideimide backbones decompose above 300°C from t.g.a. traces of polyamideimides.

The refractive indices (n) at the wavelength of 1.3 μm for the unpoled polymer films were measured by determining the propagation constants of at least the two lowest-order transverse electric optical guided modes for samples cast 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 for a three-layer waveguide was solved for n and d. The thickness of a thin film was confirmed with the α-step surface profiler (Tencor instruments, α-step 300). Linear and nonlinear optical data for NLO polyamideimides are summarized in *Table 3*. The refractive indices of NLO-TMAC, NLO-BTI and NLO-BCI were found to be 1.660, 1.656 and 1.643, respectively. We measured the electro-optic coefficients (r_{33}), for the poled films of NLO-TMAC, NLO-BTI and NLO-BCI.

Table 3 shows the measured electro-optic coefficients of polymer films at 1.3 μm at different poling conditions. It has been known that the electro-optic coefficient of side-chain NLO polyamideimides depends on the loading content of the chromophore side chain, the hyperpolarizability (β) of the chromophore itself and the poling field strength[27]. As shown in *Table 3*, the r_{33} values of the polyamideimide bearing the DANS chromophore poled at 141, 154 and 155 V μm^{-1} were observed at the highest value of 1.9, 6.8 and 7.4 pm V^{-1} for NLO-BCI, NLO-BTI and NLO-TMAC, respectively. All of the electro-optic coefficients (r_{33}) values remained unchanged at room temperature within 20 days and the 80% of the initial electro-optic coefficient (r_{33}) value for the NLO materials of NLO-BTI remained after heating at 100°C for 10 h.

To conclude, we synthesized soluble polyamideimides containing NLO chromophores by direct polycondensation, in order to enhance their solubility by the incorporation of amide groups into the NLO polyimide backbones. We should stress that the direct polycondensation of NLO polyimides without a curing process, associated with a high glass transition temperature, led to the improvement of the thermal stability of the NLO polymers, the thermal relaxation of the dipole alignment as well as the optical property of the NLO polymers, while the NLO polyimides derived from polyamic acids exhibited poor reproducibility of the optical quality including the optical propagation loss and the thermal decomposition of the NLO chromophores during the imidization process at a high curing temperature. A multi-layered channel waveguide device of an electrode/clad/core/clad/electrode stacking structure is currently being fabricated and evaluated.

CONCLUSION

Soluble polyamideimides having NLO-active chromophores were successfully synthesized by Yamazaki polymerization of DANS-diamine with oxy-bis[N-(4-phenylene)-trimellitic imide] (BCI), N-(3-carboxyphenyl)-trimellitimide (BTI), N-(3-carboxyphenyl)-trimellitimide (BTI) and trimellitic anhydride chloride (TMAC) without an imidization process. The resulting polymers were highly soluble in aprotic polar solvents such as DMF, DMAc, NMP, etc. The NLO polyamideimide retained the inherent viscosity range of 0.14–0.33 dl g^{-1}. They exhibited a higher T_g and thermal stability up to 220°C. These resulting polymers can be easily processed into thin films with good optical quality. The electro-optic coefficient, r_{33}, of the poled polymer films was in the range 1.9–7.4 pm V^{-1} for the NLO materials of NLO-BTI and NLO-BCI. All of the electro-optic coefficients (r_{33}) values remained unchanged at room temperature within 20 days and 80% of the initial electro-optic coefficient (r_{33}) value for the NLO materials of NLO-BTI remained after heating at 100°C for 10 h.

ACKNOWLEDGEMENTS

This research was financially supported by the Electronics and Telecommunications Research Institute (ETRI).

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