Temporal stability of second-order optical non-linearities depending on non-linear optically active groups of polyesters

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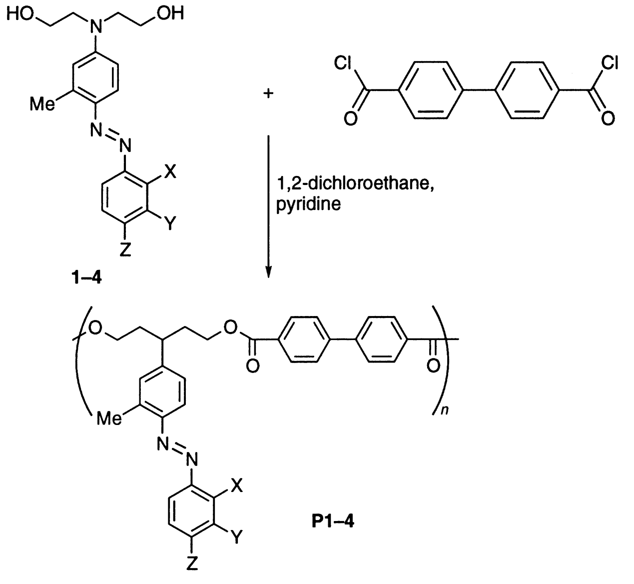
Four types of non-linear optical (NLO) polyesters with the same main chain and with different NLO-active groups have been synthesized. Second-order NLO properties of the corona-poled polyesters are studied by the second-harmonic generation (SHG) method. The structure of the NLO-active group affects not only the magnitude of the SHG coefficient (d_{33}) but also the temporal stability of d_{33}. Though all the polyesters show nearly the same glass transition temperature, the polyesters having NLO-active groups with larger dipole moments show better temporal stability, suggesting that the dipole moment has a significant effect on temporal stability.

Non-linear optical (NLO) polymers have been studied to develop electro-optic devices.[1,2] The NLO polymers usually include NLO-active groups having dipole moments, and show second-order optical non-linearity only when the NLO-active groups are aligned. Although the alignment of NLO-active groups can be achieved by an electric poling method, relaxation of the alignment can occur, especially at elevated temperature.

Many attempts have been made to restrain the relaxation, and the temporal stability of the dipolar orientation has been improved, for example with side-chain NLO polymers,[3–5] NLO polymers whose main chains include dialkylamino groups in the NLO-active groups,[6–8] introducing hydrogen-bonding groups in the main chain,[9] crosslinking,[7,10–12] and imidization.[13–15] Most of the above attempts have improved the relaxation by modifying the structures of the polymer matrix or the links between the main chain and the NLO-active group. There have been few reports investigating the dependence of the relaxation on the NLO-active groups, except that Kitipichai *et al.* have reported the influence of sizes of NLO-active groups.[7] A study of this dependence is useful in order to obtain NLO polymers with improved temporal stability.

Here we report the dependence for NLO polyesters whose main chains include dialkylamino groups in the NLO-active groups. Four types of polyesters with the same main chain and with different NLO-active groups were synthesized by polycondensation between 4,4′-biphenyldicarbonyl chloride and an NLO-active diol. NLO properties of the polyesters were studied by the second-harmonic generation (SHG) method, and were compared with one another. The magnitude and temporal stability of the SHG coefficient (d_{33}) are discussed in terms of the hyperpolarisability and the dipole moment of the NLO-active group.



1, P1 X, Y = H, Z = CN
2, P2 X = H, Y = CF_3, Z = CN
3, P3 X = NO_2, Y = H, Z = CF_3
4, P4 X = CF_3, Y = H, Z = NO_2

Scheme 1

Experimental

4-*N*,*N*-Bis(2-hydroxyethyl)amino-4′-cyano-2-methylazobenzene (1)

4-Cyanoaniline (5.91 g) was dissolved in a mixture of 36% hydrochloric acid (45 ml) and water (100 ml), and diazotized with sodium nitrite (3.80 g in 20 ml of water) at 4 °C. To this solution, *m*-tolyldiethanolamine (9.06 g) dissolved in a mixture of water (125 ml) and 36% hydrochloric acid (7.5 ml) was added dropwise at 4 °C within 45 min. After the addition was completed, the mixture was stirred for another 90 min at room temp. Potassium hydroxide solution was then added to neutralize the mixture. The precipitate was separated by filtration, washed with water, and dried *in vacuo*. The crude product (14.3 g) was recrystallized twice from ethanol and dried *in vacuo* to give 11.0 g (74%) of compound **1**: mp 159 °C; $\delta_H[(CD_3)_2SO]$ 2.6 (s, 3H, CH_3), 3.6 (s, 8H, CH_2), 4.9 (s, 2H, OH), 6.6–6.8 (br, 2H, aromatic), 7.6–8.1 (m, 5H, aromatic); ν/cm^{-1} (KBr) 1510, 1600 (aromatic C), 2230 (CN), 2930 (CH_2), 3430 (OH).

4-*N*,*N*-Bis(2-hydroxyethyl)amino-4′-cyano-2-methyl-3′-trifluoromethylazobenzene (2)

A mixture of 5-amino-2-cyanobenzotrifluoride (5.05 g) and 36% hydrochloric acid (25 ml) and water (55 ml) was stirred at room temp. for 20 min, and was cooled to 4 °C. Sodium nitrite (2.06 g in 10 ml of water) was gradually added to the mixture. After stirring for 2 h, ethanol (80 ml) was added and stirred another 20 min at 4 °C. To this solution, *m*-tolyldiethanolamine (5.30 g) dissolved in a mixture of water (70 ml), ethanol (20 ml) and 36% hydrochloric acid (4.0 ml) was added dropwise at 4 °C within 30 min. After the addition was completed, the mixture was stirred for 20 min at 4 °C and was stirred for another 60 min at room temp. Potassium hydroxide solution was then added to neutralize the mixture. The precipitate was separated by filtration, washed with water, and dried *in vacuo*. The crude product (10.0 g) was recrystallized from ethanol–hexane, and dried *in vacuo* to give 7.6 g (71%) of compound **2**: mp 167 °C; $\delta_H[(CD_3)_2SO]$ 2.6 (s, 3H, CH_3), 3.6 (s, 8H, CH_2), 4.9 (s, 2H, OH), 6.6–6.8 (br, 2H, aromatic), 7.6–8.3 (m, 4H, aromatic); ν/cm^{-1} (KBr) 1135, 1170, 1330 (CF_3), 1510, 1600 (aromatic C), 2230 (CN), 2950 (CH_2), 3300 (OH).

4-*N*,*N*-Bis(2-hydroxyethyl)amino-2-methyl-2′-nitro-4′-trifluoromethylazobenzene (3)

4-Amino-3-nitrobenzotrifluoride (10.31 g) was dissolved in a mixture of 36% hydrochloric acid (45 ml) and water (100 ml), and diazotized with sodium nitrite (3.80 g in 18 ml of water) at 4 °C. To this solution, *m*-tolyldiethanolamine (9.06 g) dissolved in a mixture of water (125 ml) and 36% hydrochloric acid (7.5 ml) was added dropwise at 4 °C within 20 min. After the addition was completed, the mixture was stirred for 30 min at 4 °C and was stirred for another 60 min at room temp. Potassium hydroxide solution was then added to neutralize the mixture. The precipitate was separated by filtration, washed with water, and dried *in vacuo*. The crude product (13.9 g) was recrystallized from ethanol–hexane, and dried *in vacuo* to give 5.1 g (25%) of compound **3**: mp 124 °C; $\delta_H[(CD_3)_2SO]$ 2.6 (s, 3H, CH_3), 3.6 (s, 8H, CH_2), 4.9 (s, 2H, OH), 6.6–6.8 (br, 2H, aromatic), 7.5–8.4 (m, 4H, aromatic); ν/cm^{-1} (KBr) 1140, 1170, 1330 (CF_3), 1350, 1540 (NO_2), 1510, 1600 (aromatic C), 2850–3000 (CH_2, CH_3), 3100–3400 (OH).

4-*N*,*N*-Bis(2-hydroxyethyl)amino-2-methyl-4′-nitro-2′-trifluoromethylazobenzene (4)

2-Amino-5-nitrobenzotrifluoride (10.31 g) was dissolved in a mixture of 36% hydrochloric acid (45 ml), ethanol (300 ml) and water (100 ml), and diazotized with sodium nitrite (3.80 g in 18 ml of water) at 4 °C. To this solution, *m*-tolyldiethanolamine (9.76 g) dissolved in a mixture of water (100 ml) and 36% hydrochloric acid (7.5 ml) was added dropwise at 4 °C within 15 min. After the addition was completed, the mixture was stirred for 10 min at 4 °C and was stirred for another 60 min at room temp. Potassium hydroxide solution was then added to neutralize the mixture. The precipitate was separated by filtration, washed with water, and dried *in vacuo*. The crude product (8.1 g) was recrystallized from butan-1-ol–hexane, and dried *in vacuo* to give 3.6 g (18%) of compound **4**: decomposed around 180 °C; $\delta_H[(CD_3)_2SO]$ 2.6 (s, 3H, CH_3), 3.6 (s, 8H, CH_2), 4.9 (s, 2H, OH), 6.7–6.9 (m, 2H, aromatic), 7.7 (d, *J* 9.1, 1H, aromatic), 7.9 (d, *J* 9.1, 1H, aromatic), 8.5–8.6 (m, 2H, aromatic); ν/cm^{-1} (KBr) 1150, 1170 (CF_3), 1320–1360 (CF_3, NO_2), 1500–1540 (aromatic C, NO_2), 1600 (aromatic C), 2850–3000 (CH_2, CH_3), 3200–3500 (OH).

Polymerization

All polyesters were prepared by the same procedure. One example for **P1** is detailed here. The compound **1** (0.581 g) and 4,4′-biphenyldicarbonyl chloride (0.500 g) were dissolved in a mixture of 1,2-dichloroethane (15 ml) and pyridine (3 ml). This solution was heated to reflux for 2.5 h under a nitrogen atmosphere, and was poured into ethanol (500 ml). The polymer precipitate was collected by filtration, and dried *in vacuo* to give 0.78 g (72%) of polymer **P1**: ν/cm^{-1} (KBr) 1510, 1600 (aromatic C), 1720 (C=O), 2230 (CN), 2900–3000 (CH_2, CH_3).

P2 (yield 78%): ν/cm^{-1} (KBr) 1140, 1170, 1320 (CF_3), 1505, 1600 (aromatic C), 1720 (C=O), 2230 (CN), 2900–3000 (CH_2, CH_3).

P3 (yield 69%): ν/cm^{-1} (KBr) 1130, 1180, 1320 (CF_3), 1360, 1540 (NO_2), 1510, 1600 (aromatic C), 1720 (C=O), 2900–3000 (CH_2, CH_3).

P4 (yield 66%): ν/cm^{-1} (KBr) 1140, 1180 (CF_3), 1320–1360 (CF_3, NO_2), 1530 (NO_2), 1510, 1600 (aromatic C), 1720 (C=O), 2900–3000 (CH_2, CH_3).

Characterization

^1H NMR spectra were obtained using a JEOL JMNFX-90-Q spectrometer (*J* values in Hz). FTIR spectra were recorded on a JASCO FT/IR-5M spectrometer. Melting points and glass transition temperatures (T_g) were determined by thermal analyses using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating rate of 10 °C min^{-1}. UV–VIS spectra of polymer films were taken with a Shimazu UV-2100 spectrometer. Intrinsic viscosities ($[\eta]$) were measured in *N*-methyl-2-pyrrolidone (NMP) at 30 °C using a Ubbelohde viscometer. Refractive indices in the visible range were determined using a Rudolph S2000 ellipsometer. Refractive indices in infrared range were extrapolated using the Cauchy's equation.

Molecular orbital calculations

Dipole moments (μ) and hyperpolarisabilities along μ (β) are important properties for NLO-active groups, because the values of d_{33} for electric-poled polymers depend on $\mu\beta$.[2] Moreover, μ is considered to affect the temporal stability of d_{33} through electrostatic interactions. When μ of an NLO-active group is large, electrostatic interactions acting on the NLO-active group are considered to be strong.

The μ and static β of NLO-active groups were calculated by the semi-empirical AM1 molecular-orbital (MO) method,[16] using the MOPAC program.[17,18] Geometry was fully optimized in the calculations. The β was calculated by a coupled Hartree–Fock method implemented in the program.[19]

Non-linear optical measurements

Thin films of the polyesters were prepared on glass substrates by spin-coating. 1,2-Dichloroethane and chloroform were used as solvent. The film thickness was monitored using a Dektak II profiler. The films were corona-poled in air using a needle electrode under following conditions: interelectrode distance, 15–30 mm; voltage, 10–20 kV; poling time, 2–5 min; and cooling time, 20 min. Negative voltage was applied to the needle electrode in the poling. SHG coefficients (d_{33}) were determined by the Maker-fringe technique.[20] A Continuum NY-81 Nd:YAG laser (pulse width = 8 ns, 10 Hz repetition) was used as an *s*-polarized fundamental source, and *p*-polarized second harmonic wave was detected. The value of d_{33} was assumed to be three times as large as d_{31}.[2] Absorbing effects of second-harmonic waves on d_{33} were allowed for through absorption coefficients at the second-harmonic wavelength.[21] A Y-cut quartz sample was used as a reference, $d_{11} = 0.5$ pm V^{-1}.

Results and Discussion

Synthesis

Four types of NLO-active diols **1–4** were synthesized *via* a diazo coupling reaction between substituted aniline and *m*-tolyldiethanolamine. The structures of diols **1–4** are shown in Scheme 1. The diols are different in the structures of acceptor groups, and their volumes are nearly the same. NLO polyesters were synthesized through polycondensation between the diol and 4,4′-biphenyldicarbonyl chloride (Scheme 1). All the NLO polyesters are the same in the structure of the main chain, while they differ in the structures of the NLO-active groups.

In the FTIR spectra of the polyesters, carbonyl absorption peaks appeared at 1720 cm^{-1}, indicating formation of ester groups. The absorption peaks due to acceptor groups in NLO-active groups, namely cyano group of polyester **P1**, cyano and trifluoromethyl groups of polyester **P2**, and nitro and trifluoromethyl groups of polyesters **P3** and **P4**, were observed in the spectra. The values of $[\eta]$ of the polyesters were around 0.1 dl g^{-1}, and the values of T_g of all the polyesters were nearly the same (Table 1).

Molecular orbital calculations

To estimate NLO properties of the NLO-active groups, MO calculations were performed. Since the NLO properties of the monomer diols were considered to be a reasonable representation of those of the NLO-active groups, the properties of the diols were calculated. The results are listed in Table 2. The calculated values of $\mu\beta$ of diols **2** and **4** were nearly the same, and were larger than those of diols **1** and **3**. These calculations predict that the values of d_{33} of polyesters **P2** and **P4** are larger than those of polyesters **P1** and **P3**. The calculated result for μ of the diols suggests that electrostatic interactions acting on NLO-active groups in polyesters **P2**, **P4**, **P3** and **P1** decrease that order.

Linear optical properties of polyesters

The UV–VIS absorption peaks (λ_{max}) of the polyester films ranged from 455 to 508 nm owing to their NLO-active groups. The observed λ_{max} and absorption coefficients (α) at 532 nm are given in Table 3. The values of α at 532 nm were above 5 μm^{-1}. These large values suggest that an absorption correction is necessary to determine d_{33} at a 1064 nm fundamental wavelength for the polyesters.

The observed refractive indices of the polyesters at 532 and 1064 nm are listed in Table 4. For each polyester, the refractive index at 532 nm was larger than that at 1064 nm, owing to the absorption of the NLO-active groups.

Non-linear optical properties of polyesters

Films of synthesized polyesters were corona-poled under various poling conditions, and their d_{33} values were measured using a 1064 nm fundamental wave. Each polyester was found to have an optimum poling temperature, which led to a maximum value of d_{33} under standard poling conditions: interelectrode distance, 30 mm; voltage, 12 kV; poling time, 5 min; and cooling time, 20 min. The optimum poling temperatures are considered to depend on two properties. One is the mobility of the NLO-active groups, and the other is the conductivity of the material.[22,23] At temperatures lower than the optimum poling temperatures, the mobility is too low to align NLO-active groups sufficiently, while at temperatures higher than the optimum, the conductivity reduces the effective poling electric field in the polyester film. The optimum poling temperatures of polyesters **P1**, **P2** and **P3** were the higher than their T_g by *ca.* 15 °C, whereas that of polyester **P4** was higher than its T_g by *ca.* 40 °C (Table 5). If the T_g corresponds to the motion of NLO-active groups, the difference in the optimum poling temperature can be interpreted in terms of a difference in the temperature dependence of conductivity.

Table 1 Intrinsic viscosity $[\eta]$ and glass transition temperatures T_g of polyesters

Polyesters	$[\eta]$/dl g^{-1}	T_g/°C
P1	0.10	115
P2	0.09	118
P3	0.09	113
P4	0.10	119

Table 2 Calculated dipole moments μ and hyperpolarisabilities along the dipole moments β of diols

Diols	$\mu/10^{-18}$ esu	$\beta/10^{-30}$ esu	$\mu\beta/10^{-48}$ esu
1	5.5	13.0	72
2	8.3	15.8	131
3	6.3	8.9	56
4	7.4	17.2	127

Table 3 UV–VIS absorption peaks (λ_{max}) and absorption coefficients α at 532 nm of polyesters

Polyesters	λ_{max}/nm	$\alpha/\mu m^{-1}$
P1	455	5.3
P2	469	8.2
P3	465	5.3
P4	508	10.0

Table 4 Refractive indices of polyesters

	Refractive index	
Polyesters	532 nm	1064 nm
P1	1.92	1.65
P2	1.99	1.68
P3	2.01	1.67
P4	1.85	1.70

The maximum values of d_{33} measured shortly after poling are listed in Table 5. The values of d_{33} of polyesters **P2** and **P4** were larger than those of polyesters **P1** and **P3**. This agrees with the MO calculations qualitatively, though values of calculated β are static values. Fig. 1 shows the temporal behaviour of d_{33} at room temperature. The value of d_{33} of polyester **P1** decayed rapidly to less than 10% of its initial value, and that of polyester **P3** decayed more slowly. Polyesters **P2** and **P4** showed fairly stable d_{33} at room temperature. The temporal behaviour was fitted well with the stretched exponential function [eqn. (1)][24,25]

$$\frac{d_{33}(t)}{d_{33}(0)}=\exp\left[-\left(\frac{t}{\tau}\right)^{v}\right](0<v\leqslant 1) \qquad (1)$$

where τ is the characteristic relaxation time at which d_{33} decayed to $1/e$ of its initial value, and v describes the breadth

Table 5 Optimum poling temperatures T_p and d_{33} of polyesters. d_{33} values were measured shortly after poling at a 1064 nm fundamental wavelength

Polyesters	T_p/°C	d_{33}/pm V^{-1}
P1	130	57
P2	130	230
P3	130	76
P4	160	170

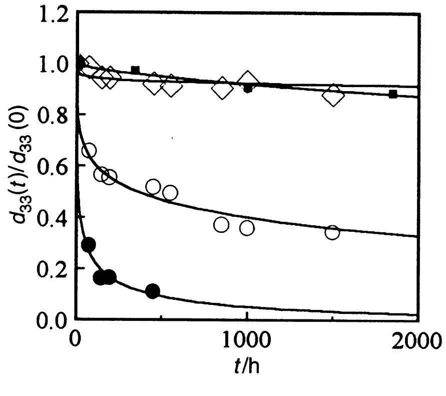


Fig. 1 Temporal behaviour of d_{33} at room temperature for (●) **P1**, (■) **P2**, (○) **P3** and (◇) **P4**. Solid lines represent the fit with the stretched exponential expression.

of the distribution in relaxation times. The fitted temporal parameters are listed in Table 6.

The temporal behaviour of d_{33} at 100 °C was also observed for polyesters **P2** and **P4** to distinguish their stability (Fig. 2). The temporal behaviour at 100 °C also fitted well with the stretched exponential function. The fitted temporal parameters are listed in Table 7. The stability of polyester **P2** was better than that of polyester **P4**. These observations about the temporal behaviour at both room temperature and 100 °C indicate that the temporal stability of d_{33} for the polyesters decreases in the order **P2**, **P4**, **P3** and **P1**. This order of temporal stability of the polyesters agreed with the order of the calculated dipole moment; the polyester having NLO-active groups with larger dipole moments showed better temporal stability.

The temporal stability of d_{33} has been considered to depend on various factors:[2] for example T_g,[26] free volume,[27–30] local molecular dynamics,[31] hydrogen bonding,[28,32–34] packing of polymer chains,[35] liquid crystalline phase,[36] dipole–dipole interaction between an chromophore and a matrix,[37] sizes of NLO-active groups[7] and trapped charge.[38] For the polyesters studied in the present paper, the observed difference in the temporal stability is considered to be independent of T_g, hydrogen bonding, packing of polymer chains, and sizes of NLO-active groups. The correlation between the calculated dipole moment of the NLO-active group and the temporal stability of the polyesters seems to suggest that the dipole moment has a significant effect on the temporal stability. One possible role of the dipole moment is as follows. Each NLO-active group experiences forces from other NLO-active groups through dipole–dipole interactions. Since movement of one NLO-active group changes the forces acting on other NLO-active groups, the motion of each NLO-active group depends on the motion of the other NLO-active groups. The dependence increases with increasing dipole moment of the NLO-active group. Such dipole–dipole interactions are assumed to prevent the NLO-active group from changing its orientation in the material.

Table 6 Temporal stability parameters of d_{33} with the stretched exponential expression [eqn. (1)] at room temp. for polyesters

Polyesters	v	τ/h
P1	0.31	30
P2	0.66	>10000
P3	0.27	1400
P4	0.14	>10000

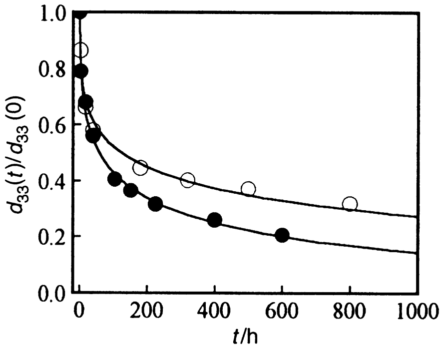


Fig. 2 Temporal behaviour of d_{33} at 100 °C for (○) **P2** and (●) **P4**. Solid lines represent the fit with the stretched exponential expression.

Table 7 Temporal stability parameters of d_{33} with the stretched exponential expression [eqn. (1)] at 100 °C for polyesters

Polyesters	v	τ/h
P2	0.30	400
P4	0.36	160

Conclusion

The temporal stability of d_{33} was studied for the NLO polyesters with different NLO-active groups. Though all the polyesters showed nearly the same T_g, the polyester having NLO-active groups with larger dipole moments showed better temporal stability, suggesting that the dipole moment has a significant effect on the temporal stability. Such a dependence of the temporal stability on the dipole moment is expected to apply to other NLO polymers. It is important to study the dependence for other NLO polymers, as well as advanced investigation for the NLO polyesters.

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