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Second-Order Optical Nonlinearity of In Situ Prepared Polyurethanes Having Thiazolylazo Chromophores

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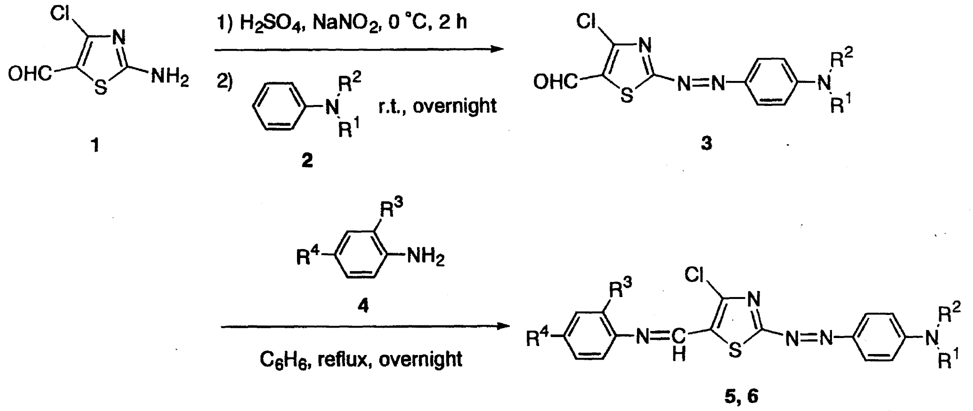
The in situ prepared polyurethane films of the thiazolylazo NLOphores showed d_{33} values of 38—49 pm V^{-1}. The temporal stability of the poled NLOphore was in the following order of the polymers: network > side chain > main chain.

Second-order nonlinear optical (NLO) materials are required to have both a large nonlinearity and improved temporal stability after poling. Bathochromic intramolecular charge-transfer NLO chromophores (NLOphores) with intense molar absorption coefficients, such as heteroaromatic π-conjugated compounds, have been reported to show large second-order nonlinearity.[1—14] To improve the temporal stability of the poled NLOphores, cross-linked polymers attached with the NLOphores look quite promising.[15] Therefore, the second-order nonlinearity of the in situ prepared side chain, main chain, and network polyurethanes having the benzothiazolylazo NLOphores has been examined.

Results and Discussion

Scheme 1 shows the synthesis of thiazolylazo NLOphores **5** and **6**. 2-Amino-4-chloro-5-formylthiazole (**1**) was diazotized and coupled with substituted anilines **2** to form thiazolylazo intermediates **3**, followed by condensation reaction with 4-aminophenols **4** to give **5** and **6** in moderate yields.

Table 1 gives the physical properties of thiazolylazo NLOphores **5** and **6**. The absorption maxima of **5** and **6** in chloroform were observed at around 539—560 nm, be-



Compd	R^1	R^2	R^3	R^4
5b	C_2H_4OH	C_2H_4OH	H	H
5c	C_2H_4OH	C_2H_5	H	OH
5d	C_2H_4OH	C_2H_4OH	H	OH
6a	C_2H_5	C_2H_5	CH_3	H
6b	C_2H_4OH	C_2H_4OH	CH_3	H
6c	C_2H_4OH	C_2H_5	CH_3	OH
6d	C_2H_4OH	C_2H_4OH	CH_3	OH

Scheme 1. Synthesis of thiazolylazo NLOphores **5** and **6**.

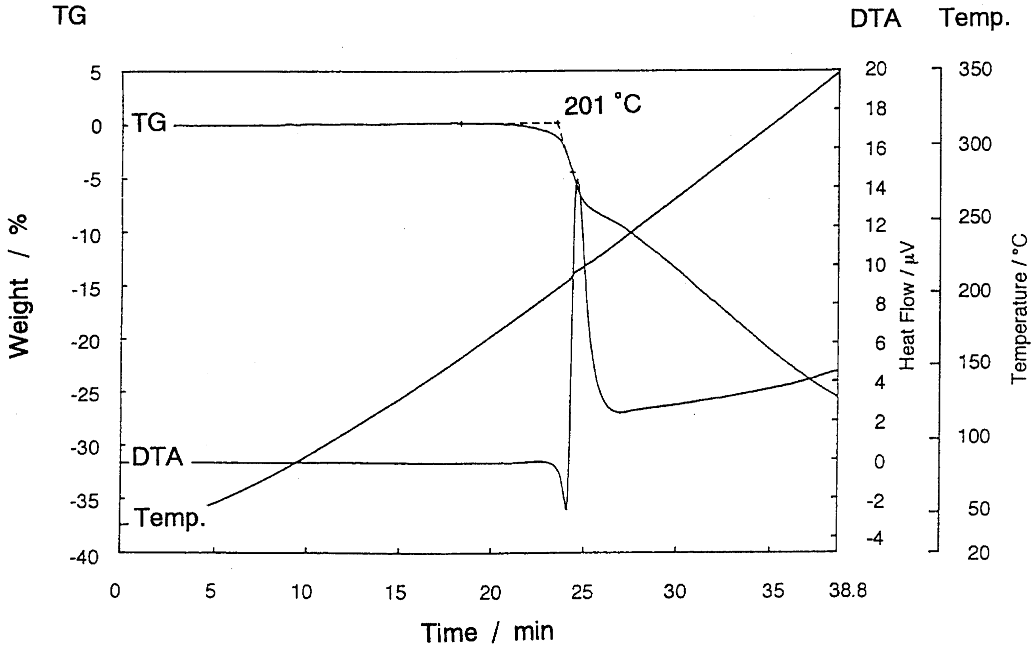


Fig. 1. TG-DTA analysis of **6b**.a) Heated at 10 °C min^{-1} under an air atmosphere.

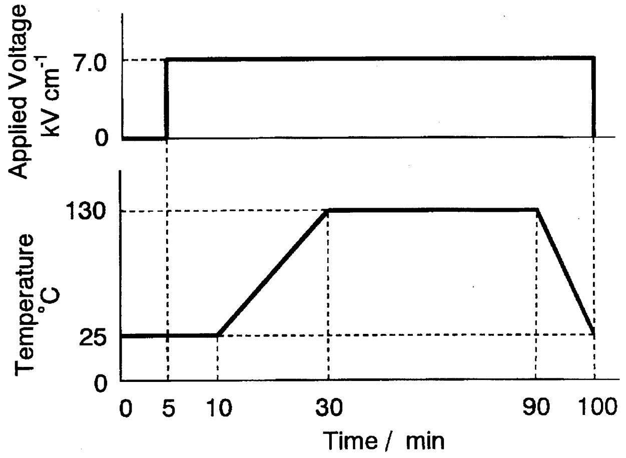


Fig. 2. Heating and poling diagram.

Table 1. Properties of Thiazolylazo NLOphores **5** and **6**

Compd	λ_{max} (log ε)$^{a)}$	$T_d$$^{b)}$	Solubility$^{c)}$
	nm	°C	mmol dm^{-3}
5b	539 (4.47)	209	1.3
5c	560 (4.42)	208	0.23
5d	543 (3.87)	204	0.54
6a	546 (4.60)	206	68
6b	539 (4.51)	201	2.5
6c	552 (4.59)	214	0.52
6d	539 (3.99)	229	1.4

a) Measured in $CHCl_3$. b) Measured by TG-DTA analysis (10 °C min^{-1} under an air atmosphere. c) Measured in $CHCl_3$ at 25 °C.

ing more bathochromic than that of Disperse Red 1 (DR 1, λ_{max}: 482 nm). Azo dyes are intramolecular charge-transfer chromophores. The thiazolyl and *N*,*N*-disubstituted anilino moieties act as electron acceptors and donative moieties, respectively. The NLOphores **6** were more hypsochromic than **5**, due to the steric hindrance of the methyl group (R^3) to prevent π-conjugation of the molecule. The absorption maximum of **6** was bathochromic in the order of the derivatives; **6c** > **6a** > **6b**, **6d**, partly due to the electronegativity of the oxygen atom at the 2-hydroxyethyl moiety(ies), which makes the electron donative ability of the anilino moiety weak. Log ε of NLOphores **5** and **6** were 3.87—4.59.

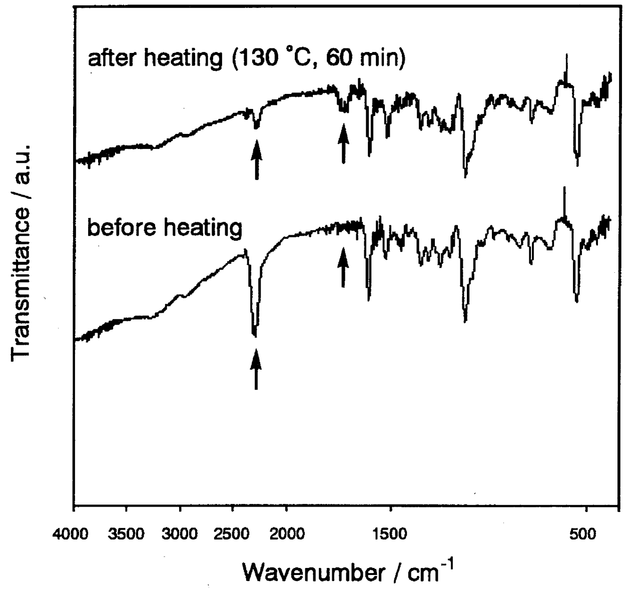
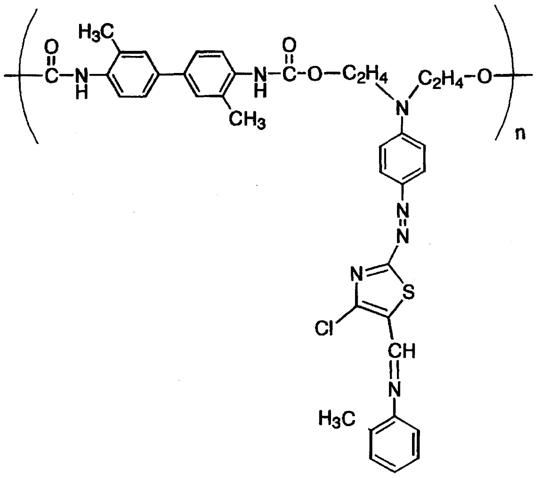
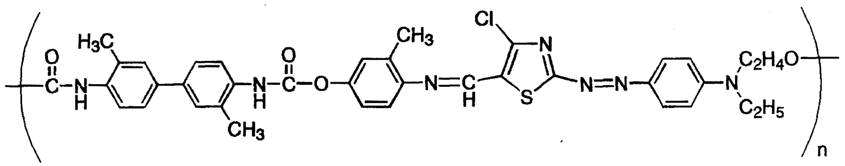


Fig. 3. FTIR spectra of **polymer 6d**.

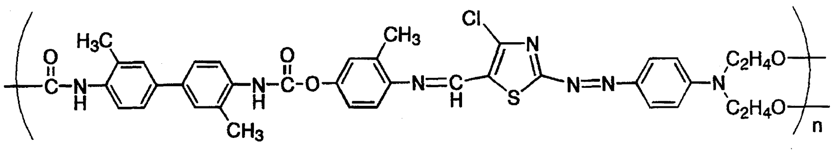
Since chloroform and tetrahydrofuran (THF) were good solvents for the film preparation, the solubility of the NLOphores was examined. NLOphores **5** and **6** were less soluble than DR 1 (72 mmol dm^{-1}) in chloroform at 25 °C. The solubilities of the methyl derivatives **6** were higher than those of the unsubstituted ones **5**, due to the steric effect of



Polymer 6b (side chain polyurethane)



Polymer 6c (main chain polyurethane)



Polymer 6d (network polyurethane)

Scheme 2. Plausible structures of the in situ prepared polymers.

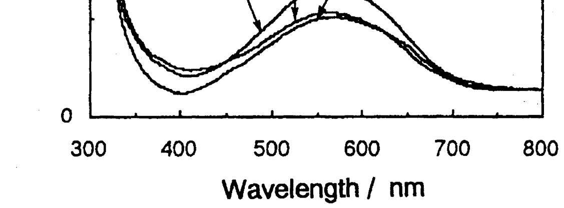


Fig. 4. Change in UV spectra of **polymer 6d**.

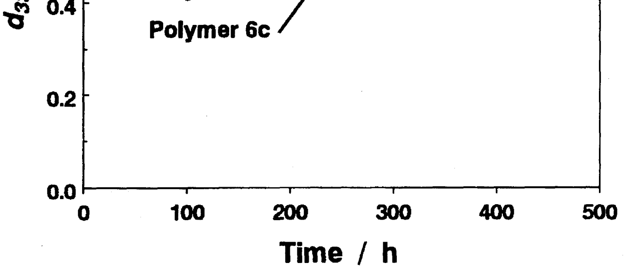


Fig. 5. Temporal stability of the second harmonic signal of polymer films at 50 °C. a) d_{33} (t) represents the d_{33} value at t h after poling.

the methyl group at R^3 to increase the dihedral angle between the R^3-substituted aryl group and the thiazolylazo moiety. In NLOphores **5** and **6**, the solubility was in the order of the hydroxy derivatives: non > di > tri. The polar hydroxy group in the molecules could decrease the solubility. However, NLOphores **6** were sufficiently soluble in THF to prepare films.

A typical example of the TG-DTA analysis of **6b** is shown

Table 2. Properties of Polymer Films

Polymers	λ_{max} a)	Film thickness	Dye concentration b)	Refractive index		Φ	d_{33} c)
	nm	μm	wt %	532 nm	1064 nm		pm V^{-1}
Polymer **6b**	558	0.09	62	1.85	1.78	0.32	49
Polymer **6c**	573	0.07	62	1.85	1.78	0.25	44
Polymer **6d**	570	0.09	54	1.85	1.78	0.29	38

a) Film. b) Calculated on the basis of the polymer structure. c) Measured with fundamental wavelength of 1064 nm.

in Fig. 1. A sharp endothermic peak was observed at around 200 °C, followed by an immediate exothermic peak with decreasing weight. After this measurement, a black residue was formed. These results indicated that the NLOphores **6b** decomposed upon melting. The decomposition temperature (T_d), as defined in Fig. 1, is 201 °C. The T_d's of the NLOphores **6** are given in Table 1. No remarkable differences in the T_d's between NLOphores **5** and **6** and among the non-, bis-, and tris(hydroxyethyl) derivatives were observed.

Since polyurethanes derived from the NLOphores **6** with 4,4′-diisocyanato-3,3′-dimethylbiphenyl were insoluble in such organic solvents as acetone, chloroform, and THF, polyurethane film was directly prepared on a glass surface under poling. NLOphores **6b**, **6c**, and **6d** were dissolved in a THF solution of 4,4′-diisocyanato-3,3′-dimethylbiphenyl at room temperature. The solution was sonicated, filtered, spin coated, and dried at room temperature. After these procedures, the film was heated under poling, as indicated in Fig. 2.

The polymerization reaction was monitored by measuring the FTIR spectra. Figure 3 shows typical spectra of the film before and after the process. The characteristic peak of the isocyanato group at 2277 cm^{-1} almost disappeared, and that of the carbonyl group appeared at 1718 cm^{-1}, indicating the formation of polyurethanes. Since the polymer films were thin, the glass transition temperature (T_g) and molecular weight of the polymers could not be measured. The plausible structures of the polyurethanes are shown in Scheme 2. NLOphores **6b**, **6c**, and **6d** could form the side-chain **polymer 6b**, the main-chain **polymer 6c**, and the network **polymer 6d**, respectively.

The change in the UV spectra of an in situ prepared polyurethane film of **6d** is shown in Fig. 4. The absorbance at 570 nm decreased after poling, and then slightly increased after 500 h. The order parameter (Φ) is defined in the following equation: $\Phi = [A(\text{before poling}) - A(\text{after poling})]/A(\text{before poling})$, where A(before poling) and A(after poling) represent the absorbance at the maximum absorption before and after poling, respectively. The Φ value of the film was calculated to be 0.29.

The properties of the films are given in Table 2. The films were very thin. The Φ values were calculated in the range of 0.25—0.32. The second-order nonlinear optical coefficients (d_{33}) were measured to be 38—49 pm V^{-1}.

Figure 5 shows the temporal stability of the polymer films. The poled NLOphores were more stable in the following order of the films: **polymer 6d** > **polymer 6b** > **polymer 6c**. The network polymer was most stable among the network, side chain, and main chain polymers, due to the lowest mobility of the NLOphores. The decay ratio of the network **polymer 6d** was only 25% at 50 °C after 500 h.

In conclusion, we prepared polyurethane films having bathochromic and soluble thiazolylazo second-order NLOphores. The temporal stability was in the following order of the polymers: network > side chain > main chain.

Experimental

Instruments. The melting points were measured with a Yanagimoto MP-S2 micro-melting-point apparatus. NMR spectra were measured with a JEOL α-400 spectrometer using tetramethylsilane as an internal standard. Mass spectra were taken on Shimadzu QP-1000 and 9020-DF spectrometers. UV spectra were measured with Shimadzu UV-160A and Hitachi U-4000 spectrometers. A thermal analysis was performed with a Rigaku TA-200 instrument. The refractive index was determined by a Mizojiri Kogaku DVA-36VWLD ellipsometer. The film thickness was measured with a Dektak 3030 surface-profile measuring system.

Materials. *N*,*N*-Disubstituted anilines **2** and aminophenols **4** were purchased from Tokyo Kasei Co., Ltd. 2-Amino-4-chloro-5-formylthiazole (**1**) was prepared as described in the literature.[16)]

Synthesis of 4-Chloro-2-[4-(*N*,*N*-disubstituted amino)phenylazo]thiazole-5-carbaldehyde 3. To concd sulfuric acid (4.8 mL) was added sodium nitrite (550 mg, 8 mmol); the solution was heated at 70 °C. To an aqueous solution (20 mL) of **1** was added concd sulfuric acid (5 mL), the resulting mixture was cooled to 0 °C. To a mixture of **1** was added nitrosyl hydrogensulfate; the resulting mixture was stirred at 0 °C for 2 h. After the reaction was completed, the mixture was added to an ethanol solution of an aniline (8 mmol) at 0 °C. After the pH value of the mixture was adjusted to 5.0, the mixture was stirred at room temperature overnight. After the reaction was completed, product was extracted with ethyl acetate, dried over anhydrous sodium sulfate, and purified by column chromatography (SiO_2–AcOEt). The physical and spectral data are given below.

4-Chloro-2-[4-(diethylamino)phenylazo]thiazole-5-carbaldehyde (3a): Yield 51%; mp 204—205 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.30$ (t, $J = 7.2$ Hz, 6H), 3.55 (q, $J = 7.2$ Hz, 4H), 6.76 (d, $J = 9.5$ Hz, 2H), 7.93 (d, $J = 9.5$ Hz, 2H), 10.04 (s, 1H); EIMS (70 eV) *m*/*z* (rel intensity) 324 ($M^+ + 2$; 24), 322 (M^+; 58), 307 (39), 148 (100), 105 (31), 104 (20); UV (EtOH) 564 nm (48700).

4-Chloro-2-{4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenylazo}thiazole-5-carbaldehyde (3b): Yield 38%; mp 186—187 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.30$ (t, $J = 7.1$ Hz, 3H), 1.81 (br s, 1H), 3.63 (q, $J = 7.1$ Hz, 2H), 3.69 (t, $J = 5.9$ Hz, 2H), 3.94 (t, $J = 5.9$ Hz, 2H), 6.82 (d, $J = 9.4$ Hz, 2H), 7.93 (d, $J = 9.4$ Hz, 2H), 10.05 (s, 1H); EIMS (70 eV) *m*/*z* (rel intensity) 340 ($M^+ + 2$; 8), 338 (M^+; 21), 309 (39), 307 (100), 133 (61), 105 (21), 104 (22), 103 (20), 77 (16); UV (EtOH) 560 nm (38500).

2-{4-[Bis(2-hydroxyethyl)amino]phenylazo}-4-chlorothia-

zole-5-carbaldehyde (3c): Yield 42%; mp 202—205 °C; ^{1}H NMR ($CDCl_3$) δ = 1.26 (br s, 2H), 3.82 (t, J = 5.0 Hz, 4H), 4.00 (t, J = 5.0 Hz, 4H), 6.83 (d, J = 9.5 Hz, 2H), 7.96 (d, J = 9.5 Hz, 2H), 10.06 (s, 1H); EIMS (70 eV) m/z (rel intensity) 356 (M^++2; 8), 354 (M^+; 18), 325 (40), 323 (100), 149 (31), 105 (32), 104 (36), 103 (25), 77 (16); UV (EtOH) 562 nm (39800).

Synthesis of 4-Chloro-2-[4-(dialkylamino)phenylazo]-5-(substituted phenyliminomethyl)thiazoles 5 and 6. To a benzene solution (30 mL) of an aniline **4** (2.0 mmol) was added 4-chloro-2-[4-(*N*,*N*-disubstituted amino)phenylazo]thiazole-5-carbaldehyde **3** (1.0 mmol); the resulting mixture was refluxed using a Dean-Stark trap overnight. After the reaction was completed, the solvent was removed. The resulting precipitate was dried and purified by column chromatography (SiO_2–AcOEt). The physical and spectral data of **5** and **6** are given below.

2-{4-[Bis(2-hydroxyethyl)amino]phenylazo}-4-chloro-5-phenyliminomethylthiazole (5b): Yield 41%; mp 209 °C (decomp); ^{1}H NMR (DMSO-d_6) δ = 3.62—3.68 (m, 8H), 4.92 (br s, 2H), 7.01 (d, J = 9.2 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 2H), 7.42 (d, J = 7.6 Hz, 2H), 7.81 (d, J = 9.2 Hz, 2H), 8.64 (s, 1H); EIMS (70 eV) m/z (rel intensity) 431 (M^++2; 5), 429 (M^+; 10), 398 (26), 150 (44), 104 (54), 93 (100), 77 (65). Found: C, 55.33; H, 4.77; N, 16.54%. Calcd for $C_{20}H_{20}ClN_5O_2S$: C, 55.88; H, 4.69; N, 16.29%.

4-Chloro-2-{4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenylazo}-5-(4-hydroxyphenyliminomethyl)thiazole (5c): Yield 49%; mp 208 °C (decomp); ^{1}H NMR (DMSO-d_6) δ = 1.18 (t, J = 6.5 Hz, 3H), 3.55—3.65 (m, 6H), 4.91 (br s, 1H), 6.80 (d, J = 8.9 Hz, 2H), 6.98 (d, J = 9.5 Hz, 2H), 7.28 (d, J = 8.9 Hz, 2H), 7.81 (d, J = 9.5 Hz, 2H), 8.61 (s, 1H), 9.70 (s, 1H); EIMS (70 eV) m/z (rel intensity) 431 (M^++2; 1), 429 (M^+; 3), 398 (8), 150 (33), 110 (100). Found: C, 55.77; H, 4.87; N, 16.64%. Calcd for $C_{20}H_{20}ClN_5O_2S$: C, 55.88; H, 4.69; N, 16.29%.

2-{4-[Bis(2-hydroxyethyl)amino]phenylazo}-4-chloro-5-(4-hydroxylphenyliminomethyl)thiazole (5d): Yield 48%; mp 204 °C (decomp); ^{1}H NMR (DMSO-d_6) δ = 3.61—3.75 (m, 8H), 4.92 (br s, 2H), 6.81 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 9.2 Hz, 2H), 7.26 (d, J = 9.2 Hz, 2H), 7.81 (d, J = 9.0 Hz, 2H), 8.61 (s, 1H), 9.64 (br s, 1H); EIMS (70 eV) m/z (rel intensity) 445 (M^+; 1), 167 (29), 109 (100), 93 (17). Found: C, 53.96; H, 4.70; N, 15.31%. Calcd for $C_{20}H_{20}ClN_5O_3S$: C, 53.87; H, 4.52; N, 15.71%.

4-Chloro-2-[4-(diethylamino)phenylazo]-5-(2-tolyliminomethyl)thiazole (6a): Yield 53%; mp 206 °C (decomp); ^{1}H NMR ($CDCl_3$) δ = 1.28 (t, J = 7.2 Hz, 6H), 2.37 (s, 3H), 3.52 (q, J = 7.2 Hz, 4H), 6.75 (d, J = 9.3 Hz, 2H), 7.02 (d, J = 7.2 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.94 (d, J = 9.3 Hz, 2H), 8.53 (s, 1H); EIMS (70 eV) m/z (rel intensity) 413 (M^++2; 39), 411 (M^+; 91), 396 (15), 368 (29), 148 (100), 133 (42), 91 (53). Found: C, 60.99; H, 5.36; N, 16.50%. Calcd for $C_{21}H_{22}ClN_5S$: C, 61.23; H, 5.38; N, 17.00%.

2-{4-[Bis(2-hydroxyethyl)amino]phenylazo}-4-chloro-5-(2-tolyliminomethyl)thiazole (6b): Yield 54%; mp 201 °C (decomp); ^{1}H NMR (DMSO-d_6) δ = 2.31 (s, 3H), 3.63—3.74 (m, 8H), 4.93 (br s, 2H), 7.02 (d, J = 9.2 Hz, 2H), 7.17—7.27 (m, 4H), 7.83 (d, J = 9.2 Hz, 2H), 8.53 (s, 1H); EIMS (70 eV) m/z (rel intensity) 445 (M^++2; 15), 443 (M^+; 35), 412 (79), 150 (69), 104 (100), 77 (40). Found: C, 56.97; H, 4.95; N, 15.21%. Calcd for $C_{20}H_{20}ClN_5O_2S$: C, 56.82; H, 4.99; N, 15.78%.

4-Chloro-2-{4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenylazo}-5-(4-hydoroxy-2-methylphenyliminomethyl)thiazole (6c): Yield 52%; mp 214 °C (decomp); ^{1}H NMR (DMSO-d_6) δ = 1.16 (t, J = 7.1 Hz, 3H), 2.27 (s, 3H), 3.54—3.66 (m, 6H), 4.91 (br s, 1H), 6.62 (dd, J = 8.5 and 2.6 Hz, 1H), 6.67 (d, J = 2.6 Hz, 1H), 6.97 (d, J = 9.4 Hz, 2H), 7.10 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 9.4 Hz, 2H), 8.52 (s, 1H), 9.54 (s, 1H); EIMS (70 eV) m/z (rel intensity) 445 (M^++2; 7), 443 (M^+; 16), 412 (34), 150 (51), 124 (100), 77 (42). Found: C, 56.53; H, 5.44; N, 16.10%. Calcd for $C_{21}H_{22}ClN_5O_2S$: C, 56.82; H, 4.99; N, 15.78%.

2-{4-[Bis(2-hydroxyethyl)amino]phenylazo}-4-chloro-5-(4-hydoroxy-2-methylphenyliminomethyl)thiazole (6d): Yield 52%; mp 229 °C (decomp); ^{1}H NMR (DMSO-d_6) δ = 2.27 (s, 3H), 3.60—3.68 (m, 8H), 4.92 (br s, 2H), 6.62 (dd, J = 8.5 and 2.7 Hz, 1H), 6.67 (d, J = 2.7 Hz, 1H), 7.00 (d, J = 9.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 9.5 Hz, 2H), 8.52 (s, 1H), 9.54 (s, 1H); EIMS (70 eV) m/z (rel intensity) 461 (M^++2; 2), 459 (M^+; 5), 428 (8), 150 (15), 124 (100), 77 (37). Found: C, 54.81; H, 4.79; N, 14.52%. Calcd for $C_{21}H_{22}ClN_5O_3S$: C, 54.84; H, 4.82; N, 15.23%.

Formation of in situ Prepared Polymers. NLOphore (0.01 mmol) was dissolved in a THF solution (1.0 mL) of 4,4′-diisocyanato-3,3′-dimethylbiphenyl (0.01 mmol for **6b** and **6c**, and 0.015 mmol for **6d**) at room temperature. The solution was sonicated (42 kHz, 100 W, 2 min), filtered (0.5 μm), spin coated (800 rpm, 20 s), and dried (5 min) at room temperature. The film was heated under poling (7 kV cm^{-1}) in an oven. The heating and poling diagram is shown in Fig. 2. After cooling the film to room temperature, the second-order NLO coefficient (d_{33}) was measured immediately (after poling 0 h). The film was then kept at 50 °C.

Second Harmonic Generation (SHG) Measurement. The SHG of the film was measured by the Maker fringe method using a Q-switched Nd : YAG laser (λ = 1064 nm). A 1 mm-thick y-cut quartz (d_{11} = 0.33 pm V^{-1}) was used as a reference. The d_{33} value was determined by mean-square methods using the relationship of the second-harmonic light intensity and the incident angle of the poled film, as described in our previous paper.[17—19]

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