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Second-order Optical Nonlinearity of Thiazolylazo Chromophores Containing Hydroxyl Groups

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ABSTRACT

*Bathochromic thiazolylazo second-order nonlinear optical chromophores (NLOphores) having 2-hydroxyethyl group(s) in a molecule have been prepared. The tris(2-hydroxyethyl) derivatives showed the best relaxation behaviour among the non-, mono-, bis- and tris(2-hydroxyethyl) ones doped in poly(methyl methacrylate-*co*-methacrylic acid). © 1998 Elsevier Science Ltd. All rights reserved*

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1 INTRODUCTION

Second-order optical nonlinear polymers for electro–optic (E–O) materials are required to have large nonlinear optical (NLO) responses and to show improved relaxation behaviour. These polymers normally contain NLOphores with large molecular hyperpolazabilities (β). The molecular design of the NLOphores having a strong intramolecular push-pull system, a bathochromic shift and an intense ε value are important [1]. Bathochromic heteroaromatic NLOphores have been reported to show high second-order optical nonlinearity [2–7]. In order to obtain materials with improved

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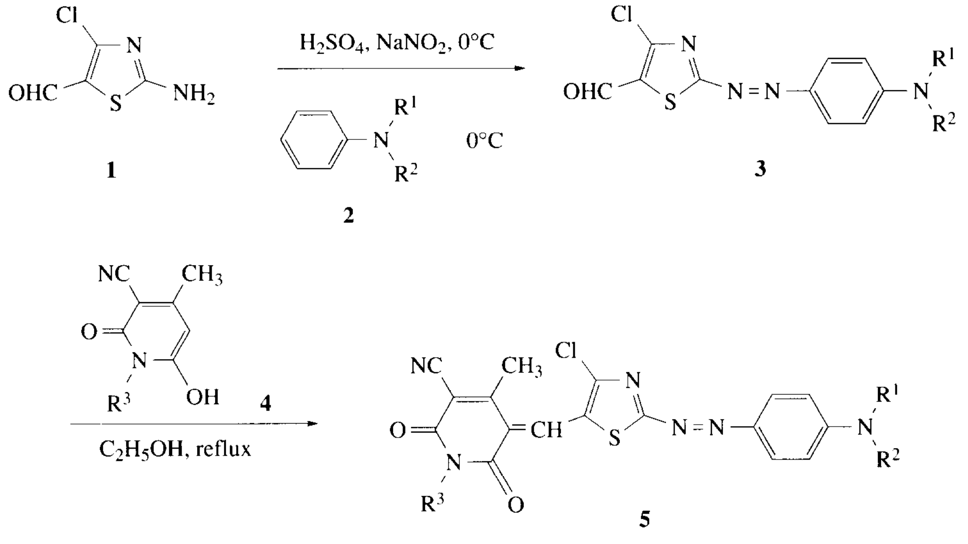
relaxation behaviour, the NLOphores are doped in high *Tg* polymers and bonded or cross-linked with polymers [8–10]. If the NLOphores are bathochromic, have large ε values and contain functional groups which can interact with the matrix polymer, the polymer may show large second-order nonlinearity and improved relaxation behaviour. We describe here the second-order optical nonlinearity of bathochromic thiazolylazo NLOphores having non-, mono-, bis- and tris(2-hydroxyethyl) groups doped in poly(methyl methacrylate-*co*-methacrylic acid).

2 RESULTS AND DISCUSSION

2.1 Synthesis of thiazolylazo NLOphores 5

Thiazolylazo NLOphores **5** were obtained by the diazotization-coupling reaction of aminothiazole **1** with anilines **2** to form azo intermediates **3**, followed by the condensation reaction with pyridones **4** in moderate yields, as shown in Scheme 1.



Scheme 1

2.2 Physical properties of the NLOphores

The physical and second-order NLO properties of **5** are indicated in Table 1. The absorption maxima of **5** in chloroform were observed at around

TABLE 1
Physical and NLO Properties of Thiazolylazo NLOphores **5**

Compound	R^1	R^2	R^3	λ_{max} *(log ε)*[a] *nm*	*Td*[b] *°C*	*Solubility*[c] *mmol* dm^{-3}	*Film thickness* *μm*	d_{33}[d] *pm* V^{-1}
5a	C_2H_5	C_2H_5	C_2H_5	681 (4.95)	236	2.2	0.14	1.0
5b	C_2H_4OH	C_2H_5	C_2H_5	664 (4.89)	235	0.36	0.10	2.6
5c	C_2H_4OH	C_2H_4OH	C_2H_5	648 (4.58)	210	0.27	0.17	2.1
5d	C_2H_5	C_2H_5	C_2H_4OH	691 (4.73)	238	0.78	0.15	1.9
5e	C_2H_4OH	C_2H_5	C_2H_4OH	679 (4.81)	233	0.18	0.17	3.4
5f	C_2H_4OH	C_2H_4OH	C_2H_4OH	656 (4.13)	189	0.14	0.14	1.1

[a] Measured in $CHCl_3$.
[b] Measured by TG–DTA analysis with heating rate of 10°C min^{-1} under an air atmosphere.
[c] Measured in $CHCl_3$ at 25°C.
[d] 2.0 mol% in poly(methyl methacrylate-*co*-methacrylic acid).

648–691 nm. The decomposition temperatures (Td's) of these NLOphores measured by TG–DTA analysis were around 200°C, being sufficiently stable under the poling conditions (110°C, 2 min). The solubility of compound **5** in chloroform at 25°C was very much less than that of DR 1 (72 mmol dm^{-3}), owing to the polar structures of the thiazolyl and pyridone moieties in the NLOphores.

2.3 Film preparation and second harmonic generation (SHG) measurement

The NLOphores **5** (0.043 mmol) were dissolved in a THF solution (2.0 ml) of poly(methyl methacrylate-*co*-methacrylic acid) (20 mg) at room temperature. The NLOphores **5** were not soluble enough in organic solvents such as dichloromethane and chlorobenzene. The NLOphores were most soluble in THF. The olefinic moiety in the NLOphores **5** was hydrolyzed in ethanol to afford the starting materials. The THF solution was filtered (0.50 μm), put on an ITO glass, spin-coated (800 rpm, 20 s), and dried overnight under vacuum. The refractive indices of the films were 1.50 and 1.55 at the fundamental (1064 nm) and second harmonic wavelength (532 nm), respectively. The film was poled (7.0 kV cm^{-1}, 2 min) with heating (110°C). After cooling the film to room temperature, the applied high voltage was removed. The SHG of the film was measured by the Maker fringe method using a Nd:YAG laser as an exciting light source. A d_{33} value was determined by the mean square methods using the relationship of SH light intensity and an incident angle of the poled film as described in our previous paper [11]. A 1 mm-thick y-cut quartz ($d_{11} = 0.33\ pmV^{-1}$) was used as a reference.

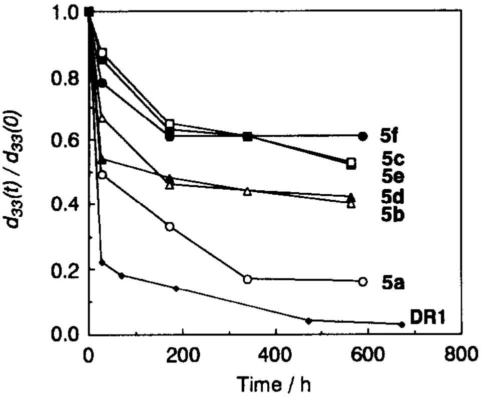


Fig. 1. Relaxation behaviour of the SH signal of the poled films at 50°C under an air atmosphere.

2.4 Second order nonlinearity of poly(methyl methacrylate-*co*-methacrylic acid) films doped with the NLOphores 5

The results are also summarized in Table 1. The d_{33} values were observed in the range of 1.0 to 3.4 pm V^{-1}.

The relaxation behaviour of the poled film is shown in Fig. 1. The NLOphores **5** showed improved relaxation behaviour compared to DR 1, probably due to their longer and more polar skeleton with respect to DR 1. The decay ratio of a 4.5 mol% poly(methyl methacrylate-*co*-DR 1) has been reported to be 55% after 300 h at room temperature [12]. Though the thiazolylazo NLOphores were doped in the low *Tg* matrix (105°C), the decay ratio of **5f** having tris(2-hydroxyethyl)groups was 40% at 50°C after 600 h. The improved relaxation behaviour of this compound can be attributed to the formation of an ester linkage between the NLOphore and the matrix during the heating and poling process.

3 EXPERIMENTAL

3.1 Instruments

Melting points were measured with a Yanagimoto MP-S2 micro melting point apparatus. NMR spectra were measured with a Jeol α-400 spectrometer. Mass spectra were taken on a Shimadzu QP-1000 spectrometer. UV spectra were measured with Shimadzu UV-160A and Hitachi U-4000 spectrometers. Thermal analysis was performed with a Rigaku TA-200 instrument. Refractive index was determined by a Mizojiri Kogaku

DVA-36VWLD ellipsometer. Film thickness was measured with Dektak 3030 surface profile measuring system.

3.2 Materials

Poly(methyl methacrylate-*co*-methacrylic acid) (*Tg*: 105°C, Mw: 3400, molar ratio in the copolymer: methyl methacrylate/methacrylic acid = 6/4) was purchased from Tokyo Kasei Co., Ltd. 2-Amino-4-chloro-5-formylthiazole (**1**) [13] and 3-cyano-6-hydroxy-2-pyridones **4** [14, 15] were prepared as described in the literature.

3.3 Synthesis of 4-(4-Chloro-5-formyl-2-thiazolylazo)anilines 3

Sodium nitrite (550 mg, 8 mmol) was added to concentrated sulfuric acid (4.8 ml), heated to 70°C and then cooled to 0°C. To an aqueous solution (20 ml) of **1** was added concentrated sulfuric acid (5 ml) and the liquor was then cooled to 0°C. Nitrosylsulfuric acid was then added to **1** and the mixture was stirred at 0°C for 2 h. It was then added to an ethanol solution of the appropriate aniline (8 mmol) at 0°C. The pH of the mixture was adjusted to 5.0 and the liquor was stirred at room temperature overnight. After the reaction was completed, the product was extracted with ethyl acetate. The extract was dried and concentrated. The product was purified by column chromatography (SiO_2-AcOEt). Physical and spectral data are shown below.

3a: *4-(4-Chloro-5-formyl-2-thiazolylazo)-*N,N*-diethylaniline*
Yield 51%; M.p. 204–205°C, ^1H NMR ($CDCl_3$) δ 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); MS (EI, 70 eV) m/z (%) 324 (24) [$M^+ + 2$], 322 (58) [M^+], 307 (39), 148 (100), 105 (31), 104 (20); UV(EtOH) 564 nm (48700).

3b: *4-(4-Chloro-5-formyl-2-thiazolylazo)-*N*-ethyl-*N*-(2-hydroxyethyl)aniline*
Yield 38%; M.p. 186–187°C; ^1H NMR ($CDCl_3$) δ 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); MS (EI, 70 eV) m/z (%) 340 (8) [$M^+ + 2$], 338 (21) [M^+], 309 (39), 307 (100), 133 (61), 105 (21), 104 (22), 103 (20), 77 (16); UV (EtOH) 560 nm (38500).

3c: *4-(4-Chloro-5-formyl-2-thiazolylazo)-*N,N*-bis(2-hydroxyethyl)aniline*
Yield 42%; M.p. 202–205°C; ^1H 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); MS (EI, 70 eV) m/z (%) 356 (8) [$M^+ + 2$], 354

(18) [M$^+$], 325 (40), 323 (100), 149 (31), 105 (32), 104 (36), 103 (25), 77(16); UV (EtOH) 562 nm (39800).

3.4 Synthesis of Thiazolylazo NLOphores 5

To an ethanol solution (75 ml) of 3-cyano-6-hydroxy-2-pyridones **4** (2 mmol) was added 4-(4-chloro-5-formyl-2-thiazolylazo)anilines **3** (2 mmol) and the mixture refluxed for 30 min. After the reaction was completed, the mixture was cooled to 0°C. The resulting precipitate was filtered, dried and purified by column chromatography (SiO_2–AcOEt). Physical and spectral data are given below. EIMS spectra of these compounds could not be measured due to their low volatility.

5a: *3-[4-Chloro-2-[4-(diethylamino)phenylazo]-5-thiazolymethylidene]-5-cyano-1-ethyl-4-methylpyridine-2,6-dione*
Yield 79%; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J=7.2 Hz, 3H), 1.32 (t, J=7.2 Hz, 6H), 2.67 (s, 3H), 3.58 (q, J=7.2 Hz, 4H), 4.07 (q, J=7.2 Hz, 2H), 6.79 (d, J=9.4 Hz, 2H), 8.01 (d, J=9.2 Hz, 2H), 8.15 (s, 1H). $C_{23}H_{23}ClN_6O_2S$ (483.0): calculated C 57.20, H 4.80, N 17.40; found C 57.33, H 4.97, N 16.98.

5b: *3-[4-Chloro-2-[4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenylazo]-5-thiazolylmethylidene]-5-cyano-1-ethyl-4-methylpyridine-2,6-dione*
Yield 66%; ^{1}H NMR (DMSO-d_6) δ 1.12 (t, J=7.3 Hz, 3H), 1.22 (t, J=7.3 Hz, 3H), 2.62 (s, 3H), 3.65–3.74 (m, 6H), 3.88 (q, J=7.3 Hz, 2H), 7.08 (d, J=9.2 Hz, 2H), 7.89 (d, J=9.2 Hz, 2H), 8.04 (s, 1H). $C_{23}H_{23}ClN_6O_3S$ (499.0): calculated C 55.36, H 4.65, N 16.84; found C 54.89, H 4.75, N 16.50.

5c: *3-[4-Chloro-2-[4-[bis(2-hydroxyethyl)amino]phenylazo]-5-thiazolylmethylidene]-5-cyano-1-ethyl-4-methylpyridine-2,6-dione*
Yield 73%; ^{1}H NMR (DMSO-d_6) δ 1.12 (t, J=6.9 Hz, 3H), 1.23 (br s, 2H), 2.61 (s, 3H), 3.69 (t, J=5.5 Hz, 4H), 3.76 (t, J=5.5 Hz, 4H), 3.88 (q, J=6.9 Hz, 2H), 7.12 (d, J=9.5 Hz, 2H), 7.88 (d, J=9.5 Hz, 2H), 8.03 (s, 1H). $C_{23}H_{23}ClN_6O_4S$ (515.0): calculated C 53.64, H 4.50, N 16.32; found C 53.26, H 4.45, N 16.05.

5d: *3-[4-Chloro-2-[4-(diethylamino)phenylazo]-5-thiazolylmethylidene]-5-cyano-1-(2-hydroxyethyl)-4-methylpyridine-2,6-dione*
Yield 71% ^{1}H NMR (DMSO-d_6) δ 1.20–1.26 (m, 7H), 2.62 (s, 3H), 3.52 (t, J=6.0 Hz, 2H), 3.66 (q, J=7.0 Hz, 4H), 3.94 (t, J=6.0 Hz, 2H), 7.04 (d, J=9.0 Hz, 2H), 7.90 (d, J=9.0 Hz, 2H), 8.03 (s, 1H). $C_{23}H_{23}ClN_6O_3S$ (499.0): calculated C 55.36, H 4.65, N 16.84; found C 54.95, H 4.80, N 16.53.

5e: *3-[4-Chloro-2-[4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenylazo]-5-thiazolylmethylidene]-5-cyano-1-(2-hydroxyethyl)-4-methylpyridine-2,6-dione*
Yield 80%; ^{1}H NMR (DMSO-d_6) δ 1.19–1.25 (m, 5H), 2.62 (s, 3H), 3.52 (t, $J=6.1$ Hz, 2H), 3.66–3.73 (m, 6H), 3.94 (t, $J=6.6$ Hz, 2H), 7.08 (d, $J=9.2$ Hz, 2H), 7.88 (d, $J=9.2$ Hz, 2H), 8.02 (s, 1H). $C_{23}H_{23}ClN_6O_4S$ (515.0): calculated C 53.64, H 4.50, N 16.32; found C 53.21, H 4.67, N 16.02.

5f: *3-[4-Chloro-2-[4-[bis(2-hydroxyethyl)amino]phenylazo]-5-thiazolylmethylidene]-5-cyano-1-(2-hydroxyethyl)-4-methylpyridine-2,6-dione*
Yield 71% ^{1}H NMR (DMSO-d_6) δ 2.63 (s, 3H), 3.52 (t, $J=6.3$ Hz, 2H), 3.68 (t, $J=5.1$ Hz, 4H), 3.76 (t, $J=5.1$ Hz, 4H), 3.94 (t, $J=6.3$ Hz, 2H), 7.12 (d, $J=9.9$ Hz, 2H), 7.89 (d, $J=9.9$ Hz, 2H), 8.04 (s, 1H). $C_{23}H_{23}ClN_6O_5S$ (531.0): calculated C 52.03, H 4.37, N 15.83; found C 51.89, H 4.47, N 15.42.

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