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Temporal Stability of Azo Second-order Nonlinear Optical Chromophores Linked with Perfluorocyclopentenyl Moiety

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Abstract

The temporal stability of azo second-order nonlinear optical chromophores linked with a perfluorocyclopentenyl moiety doped in polymers was examined. The retention of second-order nonlinear optical coefficient (d_{33}) of 1,2-bis[4-[4-[*N*-ethyl - *N*-(2-hydroxyethyl)amino]phenylazo]phenylthio]perfluorocyclopentene doped in poly(methyl methacrylate) after 530 h at 50°C was 5 %. That of 1,2-bis[4-(2,4-diaminophenylazo)phenylthio]perfluorocyclopentene doped in poly(methyl methacrylate-co-methacrylic acid) was improved to 45 % by the amido formation between azo dye and polymer matrix.

Key-words: Azo dye, Temporal stability, Second-order nonlinear optical coefficient (d_{33}), Functional dye, Perfluorocycloalkenyl

1. Introduction

Second-order nonlinear optical chromophores (NLOphores) are required to have high nonlinearity and excellent temporal stability^{1,2)}. In our previous paper, 1,2-bis[4-[4-[*N*-ethyl - *N*-(2-hydroxyethyl)amino]phenylazo]phenylthio]perfluorocyclopentene (**3b**), being more hypsochromic ($\lambda_{\max}$ = 448 nm (ϵ = 57500) in THF) than 4-nitrophenylazo-*N*-ethyl-*N*-(2-hydroxyethyl)aniline (DR 1, $\lambda_{\max}$ = 488 nm (ϵ = 31000)), has been reported to show higher second-order nonlinearity, due to its more intense molar absorption coefficient³⁾.

However, the temporal stability of **3b** doped in poly(methyl methacrylate) (PMMA) after 530 h at 50°C was much lower (5 % retention) than that of DR 1 (20 %). Therefore, we have tried to improve the temporal stability of azo NLOphore linked with perfluorocyclopentenyl moiety. Generally, the orientation of doped NLOphores can be stabilized in polymers having high transition temperature (T_g)⁴⁾. In our work, the temporal stability of **3b** after 530 h at 50°C was in the order of doped polymers: poly(methyl methacrylate-co-methacrylic acid) (poly(MMA-co-MAA), T_g = 105°C, 10 % retention) > polycarbonate (PC, 150°C, 7 %) > PMMA (105°C, 5 %). This result suggested that not only high T_g polymers but also polymers which form the covalent bonds with NLOphores could depress the relaxation behavior of oriented NLOphores. Therefore, the improvement of temporal stability of 1,2-

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bis[(arylazo)phenylthio]perfluorocyclopentenes doped in poly(MMA-co-MAA) has been examined in this report.

2. Experimental

2.1 Instruments

Melting points were measured by a Yanagimoto MP-S2 micro-melting-point apparatus. NMR spectra were taken on a JEOL α -400 spectrometer. Mass spectra were measured with Shimadzu QP-1000 and 9020-DF spectrometers. UV spectra were taken on Shimadzu UV-160A and Hitachi U-4000 spectrometers. Thermal analysis was performed with a Perkin-Elmer DSC-7 instrument. The refractive index was determined by a Mizojiri Kogaku DVA-36VWLD ellipsometer. The film thickness was measured by Dektak 3030 surface profile measuring system.

2.2 Materials

1,2-Bis(4-aminophenylthio)perfluorocyclopentene (**1**) and 1,2-bis[4-[4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenylazo]phenylthio]perfluorocyclopentene (**3b**) were prepared as described in our previous paper³. DR 1, 1-naphthylamine, *m*-phenylenediamine, and poly(MMA-co-MAA) (60:40, T_g = 105°C, M_w = 34000) were purchased from Tokyo Kasei Co., Ltd.

2.3 Synthesis of 1,2-Bis[4-(arylazo)phenylthio]perfluorocyclopentene (**3**)

To an acetic acid-propionic acid (5:1) mixed solution (10 ml) of 1,2-bis(4-aminophenylthio)perfluorocyclopentene **1** (5.0 mmol) was added conc. hydrochloric acid (4.0 ml, 45 mmol). The mixture was stirred for 30 min at room temperature. After the reaction was completed, the mixture was cooled to 0°C. To the mixture was added an aqueous solution (10 ml) of sodium nitrite (3.3 g, 20 mmol) and the mixture was stirred for 1 h at 0°C. To the mixture was added an acetic acid-propionic acid (5:1) mixed solution (10 ml) of arylamines **2** (20 mmol) and the mixture was

stirred for 1 h. The pH value of the solution was adjusted at 7.0 with an aqueous sodium hydroxide solution. The resulting precipitate was filtered and purified by column chromatography (SiO_2 , $\text{CH}_3\text{COOC}_2\text{H}_5$: C_6H_{12} = 1:1). Physical and spectral data of **3** are shown below.

1,2-Bis[4-[4-(diethylamino)phenylazo]phenylthio]perfluorocyclopentene (**3a**).

Yield 28 %; mp 164–165°C; ^1H NMR (CDCl_3) δ = 1.22 (t, J = 7.2 Hz, 12H), 3.45 (q, J = 7.2 Hz, 8H), 6.71 (d, J = 9.2 Hz, 4H), 7.55 (d, J = 8.7 Hz, 4H), 7.80 (d, J = 8.7 Hz, 4H), 7.82 (d, J = 9.2 Hz, 4H); ^{19}F NMR (CDCl_3 , ext. CF_3COOH) δ = -52.59 (2F), -29.62 (4F); EIMS (70 eV) m/z (rel. intensity) 742 (M^+ ; 26), 148 (100). Found: C, 59.50; H, 4.58; N, 10.87 %. Calcd for $\text{C}_{37}\text{H}_{36}\text{F}_6\text{N}_6\text{S}_2$: C, 59.83; H, 4.88; N, 11.31 %.

1,2-Bis[4-[4-[bis(2-hydroxyethyl)amino]phenylazo]phenylthio]perfluorocyclopentene (**3c**).

Yield 28 %; mp 121–124°C; ^1H NMR (CDCl_3) δ = 2.96 (br s, 4H), 3.73–3.77 (m, 8H), 3.95–3.96 (m, 8H), 6.97 (d, J = 7.2 Hz, 4H), 7.56 (d, J = 8.7 Hz, 4H), 7.82 (d, J = 8.7 Hz, 4H), 7.86 (d, J = 7.2 Hz, 4H); ^{19}F NMR (CDCl_3 , ext. CF_3COOH) δ = -51.93 (2F), -28.91 (4F); EIMS (70 eV) m/z (rel. intensity) 806 (M^+ ; 2), 582 (100). Found: C, 55.18; H, 4.51; N, 9.93 %. Calcd for $\text{C}_{37}\text{H}_{36}\text{F}_6\text{N}_6\text{O}_4\text{S}_2$: C, 55.08; H, 4.50; N, 10.42 %.

1,2-Bis[4-(4-aminonaphthylazo)phenylthio]perfluorocyclopentene (**3d**).

Yield 31 %; mp 222–223°C; ^1H NMR (CDCl_3) δ = 6.81 (d, J = 8.8 Hz, 2H), 7.03 (br s, 4H), 7.49 (t, J = 8.3 Hz, 2H), 7.62 (t, J = 8.3 Hz, 2H), 7.69 (d, J = 8.5 Hz, 4H), 7.94 (d, J = 8.5 Hz, 4H), 7.98 (d, J = 8.8 Hz, 2H), 8.21 (d, J = 8.3 Hz, 2H), 8.93 (d, J = 8.3 Hz, 2H); ^{19}F NMR (CDCl_3 , ext. CF_3COOH) δ = -52.18 (2F), -29.14 (4F); EIMS (70 eV) m/z (rel. intensity)

730 (M^+ ; 2), 142 (100). Found: C, 60.79; H, 3.47; N, 11.29 %. Calcd for $C_{37}H_{24}F_6N_6S_2$: C, 60.82; H, 3.31; N, 11.50 %.

1,2-Bis[4-(2,4-diaminophenylazo)phenylthio]-perfluorocyclopentene (3e).

Yield 36 %; mp 205–206°C; 1H NMR ($CDCl_3$) δ = 5.84 (d, J = 2.2 Hz, 2H), 6.02 (dd, J = 8.2 and 2.2 Hz, 2H), 6.07 (br s, 4H), 7.22 (br s, 4H), 7.35 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.4 Hz, 4H), 7.71 (d, J = 8.4 Hz, 4H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ = -52.58 (2F), -29.61 (4F); EIMS (70 eV) m/z (rel. intensity) 660 (M^+ ; 7), 107 (100). Found: C, 53.22; H, 3.55; N, 17.09 %. Calcd for $C_{29}H_{22}F_6N_8S_2$: C, 52.72; H, 3.36; N, 16.96 %.

2.4 Film Preparation

NLOphores **3a-e** (2.0 mol%) were dissolved in a chloroform solution of the polymer matrix. The mixture was filtered (0.5 μm), put on an ITO glass plate, and spin-coated (1000 rpm, 20 sec). The film was dried *in vacuo* for 3 h.

2.5 Corona-Poling

The film was heated to T_g (105°C) of poly(MMA-co-MAA) and corona-poled (7 kV cm^{-1} , 2 min or 30 min). After cooling the film, the applied high voltage was removed.

2.6 Second Harmonic Generation (SHG)

Measurement

The SHG of 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 plate (d_{11} = 0.33 pm V^{-1}) was used as the reference. The d_{33} value was determined by the mean square methods using the relationship between the second harmonic light intensity and the incident angle of the corona-poled film as described in our previous paper³⁾.

3. Results and Discussion

Scheme 1 shows the synthesis of NLOphores **3a-e**. Bis(arylamino) intermediate **1** was obtained by the reaction of 1,2-dichloroperfluoro-1-cyclopentene with 4-aminothiophenol in the presence of sodium hydride. Then, the intermediate **1** was diazotized and coupled with arylamines **2a-e** to afford the NLOphores **3a-e** in moderate yields.

The properties of NLOphores are given in **Table 1**. The absorption maxima of NLO-

Scheme 1

Table 1 Properties of NLOphores **3a-e** and films.

NLOphore	λ_{max} (ϵ) ^a nm	Td ^b °C	film thickness μm	refractive index		d_{33} ^c pm V^{-1}
				532nm	1064nm	
3a	444(59400)	290	0.55	1.54	1.50	7.3
3b	448(57500)	290	2.68	1.54	1.50	7.8
3c	445(60700)	277	1.78	1.54	1.50	10
3d	475(64700)	284	0.73	1.54	1.50	15
3e	460(56700)	269	0.60	1.54	1.50	12 ^d

^aMeasured in THF. ^bTG-DTA analysis (10°C min^{-1} , under air).

^cNLOphore: 2.0 mol%, corona poling: 7 kV cm^{-1} , 105°C, 2 min.

^dUnder the condition of 7 kV cm^{-1} , 105°C, and 30 min for corona-poling: d_{33} = 8.0 pm V^{-1} . Under the condition of 7 kV cm^{-1} , 105°C, 30 min, in the presence of DCC (1 eq for **3e**) for corona-poling: d_{33} = 7.9 pm V^{-1} .

phores **3a-e** were observed at around 444 – 475 nm in THF. The molar absorption coefficients were 56700 – 64700, being much larger than that of DR 1 ($\lambda_{\max} = 488$ nm, $\epsilon = 31000$ in THF). The decomposition temperatures (T_d 's) of NLOphores **3a-e** measured by TG-DTA analysis were observed at around 269–290°C, indicating that the NLOphores were sufficiently stable under the heating and corona poling conditions. The d_{33} values of the films were measured to be around 10 pm V⁻¹.

The temporal stability of NLOphores **3a-e** doped in poly(MMA-co-MAA) is shown in **Figure 1**. The stability was in the order of NLOphores: **3e** > **3b**, **3c**, **3d** >> **3a**. The temporal stability of hydroxy- and amino-free-**3a** was very low.

Next, the temporal stability of amino derivative **3e** corona-poled under different conditions is indicated in **Figure 2**. It is clear that NLOphore **3e** corona-poled for 30 min in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC), a catalyst for amido formation, was most stable.

These results indicated that the formation of amido linkage between the amino groups in **3e**

Fig. 1 Temporal stability of NLOphores **3a-e** doped in poly(MMA-co-MAA)

NLOphores **3a-e** (2.0 mol%) were corona-poled at 7 kV cm⁻¹ for 2 min at 105°C. The films were kept at 50°C. The change in relative d_{33} value with relaxation time is indicated.

and carboxy group in poly(MMA-co-MAA) could depress relaxation of the oriented NLOphore.

In conclusion, the temporal stability of azo NLOphores linked with a perfluorocyclopentenyl moiety was improved. The retention of d_{33} value was improved from 5 % for 1,2-bis[4-[4-[*N*-ethyl-*N*-(2-hydroxyethyl)-amino]phenylazo]phenylthio]perfluorocyclopentene doped in PMMA to 45 % for 1,2-bis[4-(2,4-diaminophenylazo)phenylthio]-perfluorocyclopentene doped in poly(MMA-co-MAA) by the amido formation between the azo NLOphore and polymer matrix.

Fig. 2 Temporal stability of NLOphores **3e** doped in poly(MMA-co-MAA)

NLOphore **3e** was corona-poled at 7 kV cm⁻¹ (a) for 2 min, (b) 30 min (in the absence of DCC), and (c) 30 min (in the presence of DCC), respectively. The films were kept at 50°C. The change in relative d_{33} value with relaxation time is indicated.

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ペルフルオロシクロペンテニル部位で結合した
アゾ系の二次非線形光学クロモファーの配向緩和松居正樹*・船曳一正夫*・村松広重*・柴田勝喜*・
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要 旨

ポリマーにドーブしたアゾ系の二次の線形光学クロモファーの配向緩和を検討した。PMMA 中にドーブされた 1,2-ビス[4-[4-[*N*-エチル-*N*-(2-ヒドロキシエチル)アミノ]フェニルアゾ]フェニルチオ]ペルフルオロシクロペンテンの 530 時間後, 50°C での二次の非線形光学定数 (d_{33}) は, 5% 保持されていた。メチルメタクリレートとメタクリル酸の共重合体中にドーブされた 1,2-ビス[4-(2,4-ジアミノフェニルアゾ)フェニルチオ]ペルフルオロシクロペンテンの配向緩和は, アゾ色素とポリマーマトリックス間のアミド結合の形成のために, d_{33} 値は 45% 保持まで改善された。