Bull. Chem. Soc. Jpn., 70, 3153—3158 (1997)

Perfluoroalkylsulfonyl-Substituted Azobenzenes as Second-Order Nonlinear Optical Chromophores

Masaki Matsui,* Ritsu Kawase, Kazumasa Funabiki, Hiroshige Muramatsu, Katsuyoshi Shibata, Yoshinao Ishigure,† Kazuo Hirota,†† Masahiro Hosoda,†† and Kazuo Tai††

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11

†Gifu Prefectural Industrial Technology Research Center, Kitaoyobi 47, Kasamatsu, Hashima, Gifu 501-61

††Research and Development Center, Unitika Ltd., Kozakura 23, Uji, Kyoto 611

(Received May 12, 1997)

4-Perfluoroalkylsulfonyl (R_fSO_2)-substituted azo nonlinear optical chromophores (NLOphores) showed enhanced second-order nonlinear coefficients (d_{33}) and improved relaxation behavior compared with the corresponding nitro compound (Disperse Red 1 (DR 1)) in both doped poly(methylmethacrylate) (PMMA) and pendanted methylmethacrylate (MMA) copolymer.

Much attention has been paid to the preparation of nonlinear optical (NLO) materials having large second-order nonlinearity and improved relaxation behavior. For electrooptic (E-O) materials, organic compounds such as azo compounds,[1] polyenes,[2] merocyanines,[3] naphthoquinomethanes,[4] arylethylene porphyrins,[5] and pyridinium betains[6] have been proposed as NLOphores. To show large second-order nonlinearity, the NLOphores are required to have a strong intramolecular push-pull system, a bathochromic shift and an intense ε value.[7] Nitro, alkylsulfonyl,[8] di and tricyanovinyl,[9] and heteroaromatic groups[10] are normally introduced into the molecule as a pull moiety of the NLOphores. Though the R_fSO_2 group shows the strongest electron-withdrawing nature (σ_p (CF_3SO_2) = 0.93) among R_fSO_2, alkylsulfonyl (σ_p (CH_3SO_2) = 0.68), and nitro ($\sigma_p(NO_2)$ = 0.78) groups, little is known about its functionality. Only anilino[11] and triarylazole NLOphores[12] bearing a R_fSO_2 group have been reported. The electron-withdrawing R_fSO_2 group can enhance the second-order nonlinearity of the derivatives. A long and rigid R_f moiety may also improve the relaxation behavior of the poled NLOphores. The second-order nonlinearity of R_fSO_2-substituted azo NLOphores is discussed in this report.

Results and Discussion

A series of NLOphores **2** bearing a R_fSO_2 group were obtained by the diazotization-coupling reaction of (perfluoroalkylsulfonyl)anilines **1** with 2-(*N*-ethylanilino)ethanol in moderate-to-good yields, as shown in Scheme 1. Other derivatives (**3d**, **4d**, and **5d**) were also obtained by the same procedure.

To examine the resonance enhancement of the nonlinearity, the wavelength-dependent second-order nonlinear optical coefficient of **2c** doped in PMMA was measured. Both the absorption band and d_{33} values are indicated in Fig. 1. The d_{33} values showed a maximum at 485 nm, and the peak value was about 5-times larger than that in the nonresonant region. Thus, the wavelength dispersion relation strongly reflected the absorption band of the NLOphore.

Table 1 indicates the physical and second-order NLO properties of **2** doped in PMMA. The decomposition temperatures (T_d's) of **2** were around 270—285 °C. This indicated that these NLOphores were sufficiently stable under the poling conditions (120 °C, 2 min). The 3-$C_4F_9SO_2$ derivative **2b** was the most hypsochromic among the NLOphores **2**.

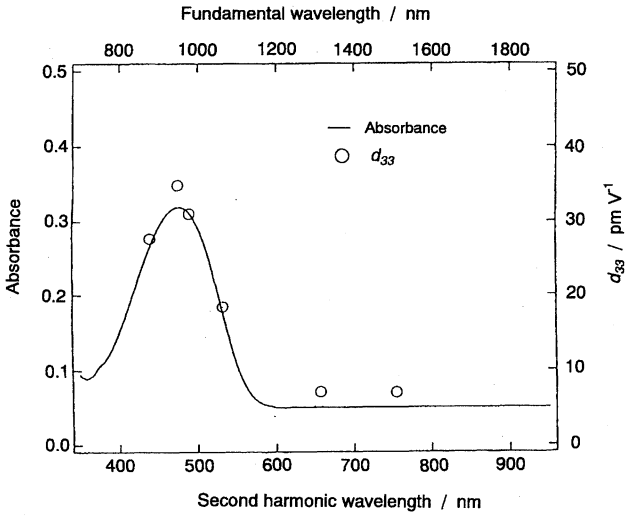
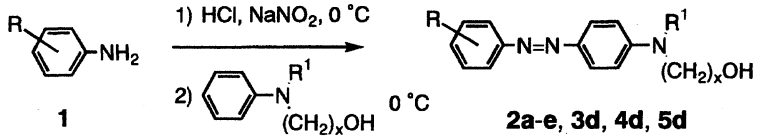


Fig. 1. Dispersion curve of **2c**. The d_{33} values were calculated using a rotational SHG Maker fringe method with fundamental wavelength of 900—1550 nm obtained by optical parametric oscillator (Spectra-Physica, MOPO-730). The d_{33} values were compared with the d_{11} value (0.33 pm V^{-1}) of y-cut quartz.



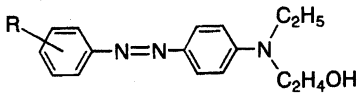
R = 4-NO_2, 3-$C_4F_9SO_2$, 4-$C_4F_9SO_2$, 4-$C_6F_{13}SO_2$, 4-$C_8F_{17}SO_2$

R^1 = C_2H_5, C_8H_{17}

x = 2, 8

Scheme 1.

Table 1. Physical and Second-Order NLO Properties of Azo NLOphores



Compd	R	λ_{max}[a]	Half wavelength[a]	T_d[b]	Film thickness	Reflective index		Φ	d_{33}[c]
		nm	nm	°C	Å	λ = 532 nm	λ = 1064 nm		pm V^{-1}
2a	4-NO_2	482	120	275	7400	1.52	1.49	0.20	17
2b	3-$C_4F_9SO_2$	463	130	270	5100	1.52	1.49	0.23	6.5
2c	4-$C_4F_9SO_2$	485	120	271	9400	1.52	1.49	0.27	27
2d	4-$C_6F_{13}SO_2$	487	124	285	9800	1.52	1.49	0.21	23
2e	4-$C_8F_{17}SO_2$	487	116	272	8300	1.52	1.49	0.20	19

a) in PMMA. b) Measured by TG-DTA analysis. c) Measured with fundamental wavelength of 1064 nm after poling (0 h). dye: 1.5 mol %.

No remarkable difference in the absorption maximum, half wavelength, and the shape of the absorption bands among the 4-nitro **2a** and 4-R_fSO_2 azo compounds **2c**—**2e** was observed, suggesting that the second-order nonlinear coefficients (d_{33}) of these NLOphores were comparable. The d_{33} values of the 4-R_fSO_2 NLOphores **2c**—**2e** were higher than that of the 4-NO_2 compound **2a**.

Figure 2 shows the change in the absorption spectra of the copolymer **10d** before and after poling. The absorption maximum around 491 nm decreased after poling with a slight bathochromic shift. The order parameter (Φ) of the NLOphore was calculated to be 0.21.[13] No remarkable change in the absorption maxima before and after poling (700 h) was observed, indicating that the NLOphore was not decomposed during the poling and relaxation process. The Φ values of the other NLOphores are also shown in Table 1. The Φ values were calculated to be between 0.20—0.27, indicating a similar orientation ratio of the NLOphores **2** under the same poling conditions.

The relaxation behavior of **2** doped in PMMA at 50 °C is depicted in Fig. 3. The stability was in the order of the substituents: $C_8F_{17}SO_2$ (**2e**) > $C_6F_{13}SO_2$ (**2d**) > $C_4F_9SO_2$ (**2c**) > NO_2 (**2a**). The rigidity of the R_f moiety could be attributed to the large van der Waals radius of the

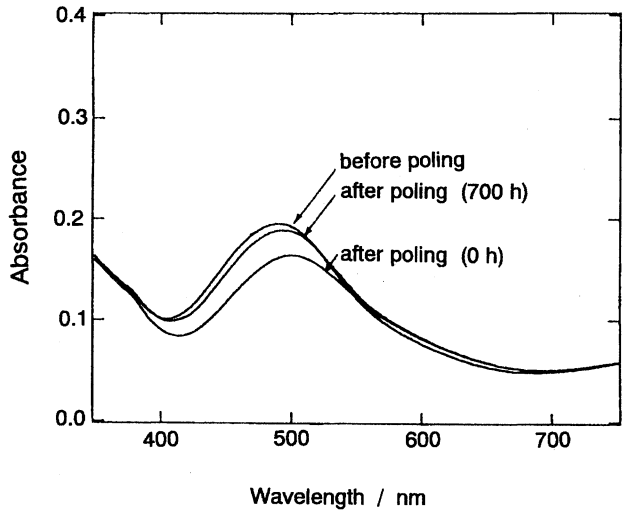


Fig. 2. Change in UV spectra before and after poling.

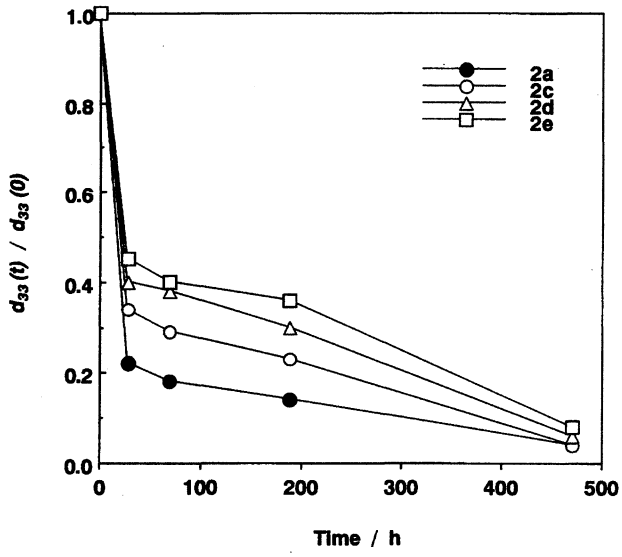


Fig. 3. Relaxation behavior of azo NLOphores doped in PMMA at 50 °C.

fluorine atom (F: 1.3 Å, H: 1.1—1.2 Å), which could depress the free rotation of the C–C bonds of the R_f moiety to improve the relaxation behavior in doped PMMA.

To further improve the relaxation behavior of the NLOphore, MMA copolymers **10**—**13** pendanted with the NLOphore were prepared, as shown in Scheme 2. Methacrylate monomers **6**—**9** were prepared by the reaction of NLOphores **2**—**5** with methacryloyl chloride in good yields. Copolymers **10**—**13** were prepared by radical copolymerization of the monomers with methyl methacrylate using 2,2′-azobisisobutyronitrile (AIBN) as an initiator in moderate-to-good yields.

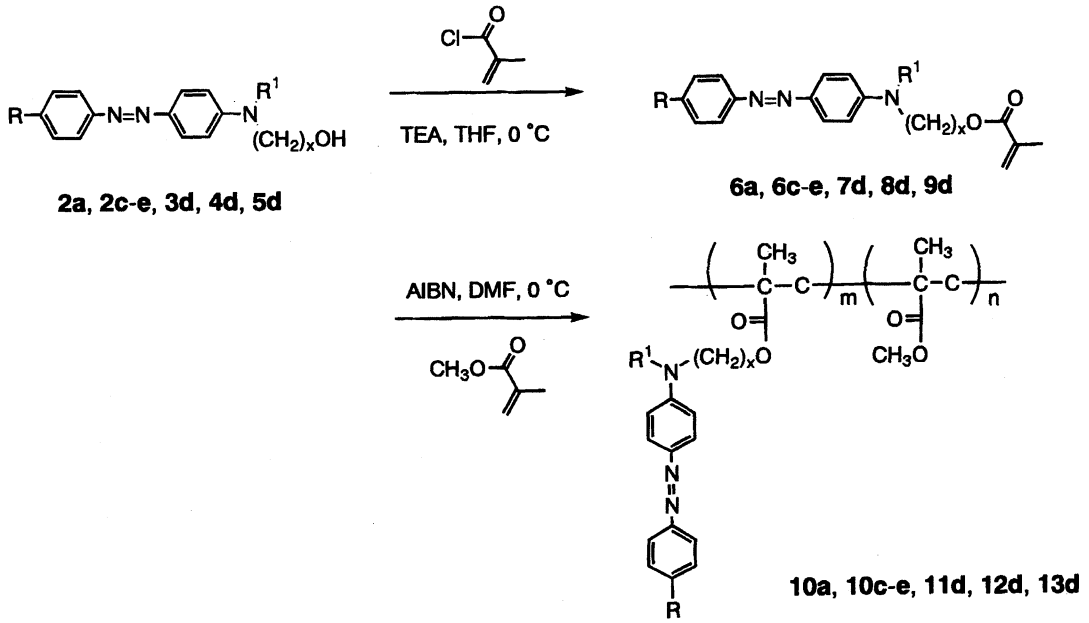
Table 2 summarizes the physical and second-order NLO properties of the copolymers **10**—**13**. No marked difference in the absorption maxima of the copolymers among nitro **10a** and R_fSO_2 compounds **10c**—**10e** was observed. The glass transition temperatures (T_g's) of copolymers **10c**—**10e**, containing different kinds of R_fSO_2 groups were similar, indicating that the R_f moiety scarcely affected T_g. The longer was the alkyl chain of the *N*,*N*-dialkyl moieties in the MMA copolymers **10d**—**13d**, the lower was the T_g, probably due to the free rotation of the C–C bonds in the alkyl group. The d_{33} values of copolymers **10c**—**10e**, **11d**, **12d**, and **13d**, pendanted with the R_fSO_2 azo NLOphore, were higher than that of the NO_2 compound **10a**.

Figure 4 shows the relaxation behavior of the copolymers **10** at 50 °C. As expected, MMA copolymers **10c**—**10e** were more stable than **10a**. The longer was the R_f moiety, the better was the stability. This result was the same as in the case of doped PMMA.

The relaxation behavior of copolymers **10d**—**13d** is indicated in Fig. 5.

The stabilities of MMA copolymers **10d**, **11d**, and **12d** were better than that of **13d**, due to the higher T_g of **10d**, **11d**, and **12d** than **13d**.

In conclusion, the R_fSO_2 substituent was more effective



Scheme 2.

Table 2. Physical and Second-Order NLO Properties of MMA Copolymers

Polymer	R	R^1	x	m[a]	n[a]	M_w[b]	T_g[c] / °C	λ_{max} / nm	Film thickness / Å	Reflective index λ = 532 nm	Reflective index λ = 1064 nm	d_{33}[d] / pm V^{-1}
10a	NO_2	C_2H_5	2	2.4	97.6	43000	124	492	800	1.52	1.49	25
10c	$C_4F_9SO_2$	C_2H_5	2	2.2	97.8	79000	122	490	700	1.52	1.49	53
10d	$C_6F_{13}SO_2$	C_2H_5	2	2.5	97.5	43000	123	491	700	1.52	1.49	44
10e	$C_8F_{17}SO_2$	C_2H_5	2	1.8	98.2	84000	123	490	900	1.52	1.49	28
11d	$C_6F_{13}SO_2$	C_8H_{17}	2	1.2	98.8	87000	119	490	1000	1.52	1.49	29
12d	$C_6F_{13}SO_2$	C_2H_5	8	1.9	98.1	75000	119	494	1100	1.52	1.49	40
13d	$C_6F_{13}SO_2$	C_8H_{17}	8	2.0	98.0	89000	112	492	1100	1.52	1.49	57

a) Calculated on the basis of ^{1}H NMR spectrum. b) Determined with a Waters 410 HPLC using PL gel MIXED-B and D (Polymer Laboratories) and chloroform as an eluent. c) Measured by DSC analysis. d) Measured with fundamental wavelength of 1064 nm after poling (0 h).

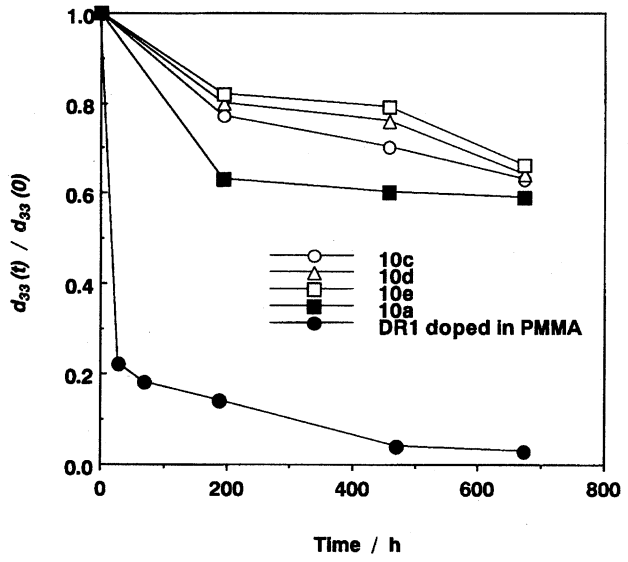


Fig. 4. Relaxation behavior of MMA copolymers **10**.

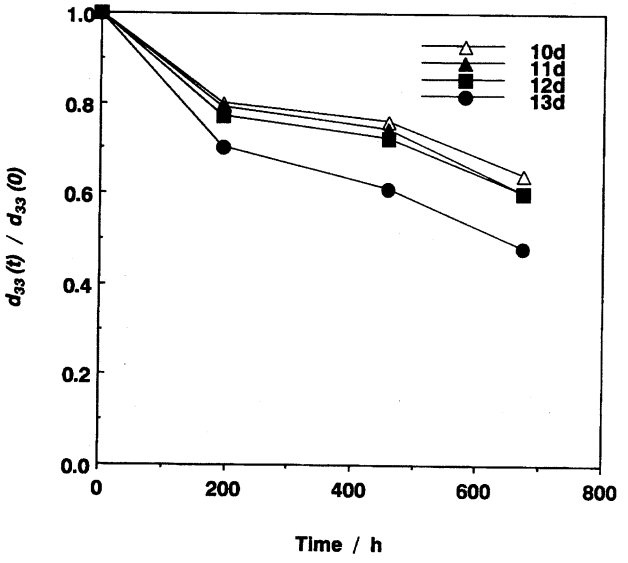


Fig. 5. Relaxation behavior of MMA copolymers **10d—13d**.

in both enhancing second-order optical nonlinearity and improving the relaxation behavior than the nitro group in doped and pendanted polymers. These results could be attributed to the strong electron-withdrawing, long and rigid nature of the R_fSO_2 substituent.

Experimental

Instruments: The melting points were measured with a Yanagimoto MP-S2 micro melting-point apparatus. The NMR spectra were taken on a JEOL α-400 spectrometer. The mass spectra were recorded on Shimadzu QP-1000 and 9020-DF spectrometers. The UV spectra were obtained by Shimadzu UV-160A and Hitachi U-4000 spectrometers. A thermal analysis was performed with Perkin–Elmer DSC-7 and Rigaku TAS-200 instruments. The refractive index was determined by a Mizojiri Kagaku DVA-36VWLD ellipsometer. The film thickness was measured with a Dektak 3030 surface-profile measuring system.

Synthesis of NLOphores 2—5. To an acetone–water mixed solution (10 ml) of an aniline (10 mmol) was added concd hydrochloric acid (2.5 ml, 30 mmol). To the mixture was added an aqueous solution (10 ml) of sodium nitrite (690 mg, 10 mmol) and stirred for 1 h at 0 °C. To the mixture was added an acetone solution (25 ml) of a coupling component (10 mmol) and stirred for 2 h at 0 °C. After neutralizing the mixture, the resulting precipitate was filtered and dried. The product was purified by column chromatography (SiO_2, CH_2Cl_2) and recrystallized from chloroform–hexane. The physical and spectral data are given below.

4-(4-Nitrophenylazo)-*N*-ethyl-*N*-(2-hydroxyethyl)aniline (2a): Yield 80%; mp 169—170 °C; ^{1}H NMR ($CDCl_3$) δ = 1.26 (t, J = 7.2 Hz, 3H), 1.62 (t, J = 5.6 Hz, 1H), 3.57 (q, J = 7.2 Hz, 2H), 3.63 (t, J = 5.6 Hz, 2H), 3.90 (q, J = 5.6 Hz, 2H), 6.81 (d, J = 9.3 Hz, 2H), 7.89 (d, J = 9.3 Hz, 2H), 7.92 (d, J = 9.3 Hz, 2H), 8.32 (d, J = 9.3 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 314 (M^+; 19), 283 (100), 133 (28); UV (EtOH) 482 nm (ε 27000).

4-[3-(Perfluorobutylsulfonyl)phenylazo]-*N*-ethyl-*N*-(2-hydroxyethyl)aniline (2b): Yield 70%; mp 83—84 °C; ^{1}H NMR ($CDCl_3$) δ = 1.26 (t, J = 6.7 Hz, 3H), 1.59 (br s, 1H), 3.59 (q, J = 6.7 Hz, 2H), 3.62 (t, J = 5.9 Hz, 2H), 3.90 (t, J = 5.9 Hz, 2H), 6.82 (d, J = 9.2 Hz, 2H), 7.76 (t, J = 7.8 Hz, 1H), 7.90 (d, J = 9.2 Hz, 2H), 7.99 (d, J = 7.8 Hz, 1H), 8.27 (d, J = 7.8 Hz, 1H), 8.47 (s, 1H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ = −2.93 (3F), −33.56 (2F), −43.10 (2F), −48.14 (2F); EIMS (70 eV) *m/z* (rel intensity) 551 (M^+; 23), 520 (100), 237 (92), 133 (48); UV (EtOH) 451 nm (ε 31000).

4-[4-(Perfluorobutylsulfonyl)phenylazo]-*N*-ethyl-*N*-(2-hydroxyethyl)aniline (2c): Yield 72%; mp 135—137 °C; ^{1}H NMR ($CDCl_3$) δ = 1.26 (t, J = 7.3 Hz, 3H), 1.71 (br s, 1H), 3.54 (q, J = 7.3 Hz, 2H), 3.58 (t, J = 5.9 Hz, 2H), 3.90 (t, J = 5.9 Hz, 2H), 6.81 (d, J = 9.1 Hz, 2H), 7.90 (d, J = 9.1 Hz, 2H), 8.01 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ = −2.95 (3F), −33.87 (2F), −43.02 (2F), −48.15 (2F); EIMS (70 eV) *m/z* (rel intensity) 551 (M^+; 12), 520 (73), 237 (100), 133 (44), 104 (21), 77 (20); UV (EtOH) 482 nm (ε 36000). Found: C, 43.61; H, 3.20; N, 7.83%. Calcd for $C_{20}H_{18}F_9N_3O_3S$: C, 43.56; H, 3.29; N, 7.62%.

4-[4-(Perfluorohexylsulfonyl)phenylazo]-*N*-ethyl-*N*-(2-hydroxyethyl)aniline (2d): Yield 59%; mp 130—132 °C; ^{1}H NMR ($CDCl_3$) δ = 1.27 (t, J = 7.0 Hz, 3H), 1.65 (br s, 1H), 3.58 (q, J = 7.0 Hz, 2H), 3.64 (t, J = 5.8 Hz, 2H), 3.90 (t, J = 5.8 Hz, 2H), 6.82 (d, J = 9.2 Hz, 2H), 7.91 (d, J = 9.2 Hz, 2H), 8.02 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ = −2.95 (3F), −33.59 (2F), −41.97 (2F), −43.90 (2F), −44.86 (2F), −48.28 (2F); EIMS (70 eV) *m/z* (rel intensity) 651 (M^+; 8), 620 (47), 238 (96), 237 (100), 226 (10), 134 (20); UV (EtOH) 482 nm (ε 34000). Found: C, 40.64; H, 2.67; N, 6.44%. Calcd for $C_{22}H_{18}F_{13}N_3O_3S$: C, 40.56; H, 2.79; N, 6.45%.

4-[4-(Perfluorooctylsulfonyl)phenylazo]-*N*-ethyl-*N*-(2-hydroxyethyl)aniline (2e): Yield 40%; mp 108—110 °C; ^{1}H NMR ($CDCl_3$) δ = 1.30 (t, J = 7.0 Hz, 3H), 1.65 (br s, 1H), 3.58 (q, J = 7.0 Hz, 2H), 3.64 (t, J = 6.1 Hz, 2H), 3.90 (t, J = 6.1 Hz, 2H), 6.82 (d, J = 9.3 Hz, 2H), 7.91 (d, J = 9.3 Hz, 2H), 8.02 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ = −2.95 (3F), −33.58 (2F), −41.91 (2F), −43.68 (2F), −43.89 (2F), −44.06 (2F), −44.88 (2F), −48.28 (2F); EIMS (70 eV) *m/z* (rel intensity) 751 (M^+; 6), 720 (8), 719 (18), 620 (22), 239 (18), 237 (100), 134 (27); UV (EtOH) 481 nm (ε 38000). Found: C, 38.69; H, 2.47; N, 5.82%. Calcd for $C_{24}H_{18}F_{17}N_3O_3S$: C, 38.36; H, 2.41; N, 5.59%.

4-[4-(Perfluorohexylsulfonyl)phenylazo]-*N*-ethyl-*N*-(8-hydroxyoctyl)aniline (3d): Yield 68%; mp 91—92 °C; ^{1}H NMR ($CDCl_3$) δ = 1.25 (t, J = 5.8 Hz, 3H), 1.30—1.40 (m, 12H), 1.67 (br

s, 1H), 3.39 (t, J = 7.8 Hz, 2H), 3.49 (q, J = 7.8 Hz, 2H), 3.66 (q, J = 5.8 Hz, 2H), 6.72 (d, J = 9.2 Hz, 2H), 7.90 (d, J = 9.2 Hz, 2H), 8.00 (d, J = 8.6 Hz, 2H), 8.10 (d, J = 8.6 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 735 (M^+; 1), 237 (100), 133 (25), 69 (18), 55 (19); UV (EtOH) 487 nm (ε 35000).

4-[4-(Perfluorohexylsulfonyl)phenylazo]-*N*-(2-hydroxyethyl)-*N*-octylaniline (4d): Yield 34%; mp 102—103 °C; ^{1}H NMR ($CDCl_3$) δ = 0.90 (t, J = 7.6 Hz, 3H), 1.29—1.35 (m, 12H), 1.68 (br s, 1H), 3.48 (t, J = 7.6 Hz, 2H), 3.65 (t, J = 6.0 Hz, 2H), 3.90 (q, J = 6.0 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 8.6 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 735 (M^+; 3), 321 (60), 253 (100), 223 (84), 104 (58), 76 (50), 69 (58), 57 (80); UV (EtOH) 484 nm (ε 37000).

4-[4-(Perfluorohexylsulfonyl)phenylazo]-*N*-(8-hydroxyoctyl)-*N*-octylaniline (5d): Yield 46%; mp 78—79 °C; ^{1}H NMR ($CDCl_3$) δ = 0.90 (t, J = 6.7 Hz, 3H), 1.24—1.37 (m, 20H), 1.57—1.65 (m, 5H), 3.37—3.41 (m, 4H), 3.65 (q, J = 6.7 Hz, 2H), 6.69 (d, J = 9.1 Hz, 2H), 7.89 (d, J = 9.1 Hz, 2H), 8.00 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 819 (M^+; 4), 223 (73), 156 (32), 135 (43), 120 (35), 119 (40), 92 (45), 69 (100), 57 (64); UV (EtOH) 490 nm (ε 37000).

Synthesis of Monomers 6—9. To a THF solution (10 ml) of a NLOphore (1 mmol) and triethylamine (0.7 ml) was added a THF solution (5 ml) of methacryloyl chloride (523 mg, 5 mmol) at 0 °C and stirred overnight. After the reaction was completed, the mixture was poured into water and extracted with dichloromethane. After evaporation of the solvent, the product was purified by column chromatography (SiO_2, CH_2Cl_2). The physical and spectral data are given below.

4-(4-Nitrophenylazo)-*N*-ethyl-*N*-[2-(methacryloyloxy)ethyl]-aniline (6a): Yield 49%; mp 70—71 °C; ^{1}H NMR ($CDCl_3$) δ = 1.27 (t, J = 7.0 Hz, 3H), 1.94 (s, 3H), 3.55 (q, J = 7.0 Hz, 2H), 3.74 (t, J = 6.2 Hz, 2H), 4.38 (t, J = 6.2 Hz, 2H), 5.60 (s, 1H), 6.11 (s, 1H), 6.82 (d, J = 9.0 Hz, 2H), 7.85—7.96 (m, 4H), 8.32 (d, J = 9.0 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 382 (M^+; 13), 283 (100), 133 (45).

4-[4-(Perfluorobutylsulfonyl)phenylazo]-*N*-ethyl-*N*-[2-(methacryloyloxy)ethyl]aniline (6c): Yield 45%; mp 98—99 °C; ^{1}H NMR ($CDCl_3$) δ = 1.27 (t, J = 7.1 Hz, 3H), 1.94 (s, 3H), 3.56 (q, J = 7.1 Hz, 2H), 3.75 (t, J = 6.2 Hz, 2H), 4.38 (t, J = 6.2 Hz, 2H), 5.60 (s, 1H), 6.11 (s, 1H), 6.83 (d, J = 9.2 Hz, 2H), 7.92 (d, J = 9.2 Hz, 2H), 8.02 (d, J = 8.5 Hz, 2H), 8.11 (d, J = 8.5 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 619 (M^+; 16), 521 (63), 520 (100), 237 (88), 133 (36), 69 (36).

4-[4-(Perfluorohexylsulfonyl)phenylazo]-*N*-ethyl-*N*-[2-(methacryloyloxy)ethyl]aniline (6d): Yield 36%; mp 103—105 °C; ^{1}H NMR ($CDCl_3$) δ = 1.27 (t, J = 7.3 Hz, 3H), 1.94 (s, 3H), 3.56 (q, J = 7.3 Hz, 2H), 3.75 (t, J = 6.1 Hz, 2H), 4.38 (t, J = 6.1 Hz, 2H), 5.60 (s, 1H), 6.11 (s, 1H), 6.83 (d, J = 9.2 Hz, 2H), 7.93 (d, J = 9.2 Hz, 2H), 8.02 (d, J = 8.5 Hz, 2H), 8.11 (d, J = 8.5 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 719 (M^+; 8), 621 (16), 620 (67), 237 (100), 133 (39), 69 (46).

4-[4-(Perfluorooctylsulfonyl)phenylazo]-*N*-ethyl-*N*-[2-(methacryloyloxy)ethyl]aniline (6e): Yield 61%; mp 123—124 °C; ^{1}H NMR ($CDCl_3$) δ = 1.27 (t, J = 7.0 Hz, 3H), 1.94 (s, 3H), 3.56 (q, J = 7.0 Hz, 2H), 3.75 (t, J = 6.1 Hz, 2H), 4.38 (t, J = 6.1 Hz, 2H), 6.00 (s, 1H), 6.11 (s, 1H), 6.83 (d, J = 9.1 Hz, 2H), 7.91 (d, J = 9.1 Hz, 2H), 8.02 (d, J = 8.5 Hz, 2H), 8.11 (d, J = 8.5 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 819 (M^+; 2), 721 (10), 237 (100), 133 (40), 69 (49).

4-[4-(Perfluorohexylsulfonyl)phenylazo]-*N*-[2-(methacryloyloxy)ethyl]-*N*-octylaniline (7d): Yield 40%; mp 66—67 °C; ^{1}H NMR ($CDCl_3$) δ = 0.89 (t, J = 7.4 Hz, 3H), 1.29—1.40 (m, 12H), 1.94 (s, 3H), 3.45 (q, J = 7.4 Hz, 2H), 3.75 (t, J = 6.1 Hz, 2H), 4.37 (t, J = 6.1 Hz, 2H), 5.59 (s, 1H), 6.10 (s, 1H), 6.81 (d, J = 9.3 Hz, 2H), 7.91 (d, J = 9.3 Hz, 2H), 8.01 (d, J = 8.5 Hz, 2H), 8.16 (d, J = 8.5 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 803 (M^+; 3), 223 (31), 113 (100), 69 (72).

4-[4-(Perfluorohexylsulfonyl)phenylazo]-*N*-ethyl-*N*-]8-(methacryloyloxy)octyl]aniline (8d): Yield 52%; mp 53—54 °C; ^{1}H NMR ($CDCl_3$) δ = 0.89 (t, J = 7.6 Hz, 3H), 1.29—1.35 (m, 12H), 1.94 (s, 3H), 3.45 (q, J = 7.6 Hz, 2H), 3.75 (t, J = 6.1 Hz, 2H), 4.37 (t, J = 6.1 Hz, 2H), 5.60 (s, 1H), 6.10 (s, 1H), 6.81 (d, J = 9.0 Hz, 2H), 7.91 (d, J = 9.0 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H), 8.11 (d, J = 8.4 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 803 (M^+; 3), 237 (100), 133 (26), 69 (54).

4-[4-(Perfluorohexylsulfonyl)phenylazo]-*N*-[8-(methacryloyloxy)octyl]-*N*-octylaniline (9d): Yield 55%; ^{1}H NMR ($CDCl_3$) δ = 0.90 (t, J = 7.1 Hz, 3H), 1.29—1.37 (m, 24H), 1.94 (s, 3H), 3.36—3.41 (m, 4H), 4.14 (t, J = 6.7 Hz, 2H), 5.55 (s, 1H), 6.10 (s, 1H), 6.70 (d, J = 9.2 Hz, 2H), 7.89 (d, J = 9.2 Hz, 2H), 8.00 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 8.7 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 887 (M^+; 35), 886 (61), 885 (51), 787 (40), 786 (35), 704 (44), 703 (41), 607 (27), 606 (29), 224 (25), 223 (20), 69 (100), 56 (42).

Synthesis of MMA Copolymers 10—13. To an ampoule were placed DMF (1.2 ml), dye monomer (0.06 mmol), methyl methacrylate (394 mg, 3.94 mmol), and AIBN (6.56 mg, 0.04 mmol). The ampoule was sealed under vacuum and heated at 60 °C for 2 h. The mixture was then poured into methanol (300 ml). The resulting precipitate was filtered. The precipitate was dissolved in DMF and poured into methanol again. The precipitation-dissolving process was repeated 3 times. Yields: **10a** (300 mg), **10c** (220 mg), **10d** (350 mg), **10e** (400 mg), **11d** (300 mg), **12d** (100 mg), **13d** (350 mg).

Preparation and Poling Procedure of NLOphores Doped in PMMA. The NLOphore was dissolved in a chloroform solution of PMMA at room temperature. The solution was filtered (0.5 μm), put on an ITO glass, spin-coated (1000 rpm, 20 s), and dried overnight under vacuum. The film was poled (6.0 kV, 2 min) under heating (120 °C). The film was cooled to room temperature under poling. The applied high voltage was then removed.

Preparation and Poling Procedure of Pendanted MMA Copolymers. The polymer was dissolved in chloroform at room temperature. The solution was filtered (0.5 μm), put on an ITO glass, spin-coated (1000 rpm, 20 s), and dried overnight under vacuum. The film was poled (6.0 kV, 2 min) under heating (120 °C). The film was cooled to room temperature under poling. The applied high voltage was then removed.

Second Harmonic Generation (SHG) Measurement. SHG of the film was measured by a Maker fringe method using a Q-switched Nd : YAG laser (λ = 1064 nm). A 1 mm-thick piece of y-cut quartz (d_{11} = 0.33 pm V^{-1}) was used as a reference. The second-order NLO coefficient (d_{33}) was determined by mean-square methods using the relationship of the second-harmonic light intensity and an incident angle of the poled film, as described in our previous paper.[14]

This work was partially supported by Saiziroh Endoh Foundation.

References

1) a) T. Watanabe, M. Amano, and S. Tomaru, *Jpn. J. Appl.*

Phys., **33**, L1683 (1994); b) K. Izawa, N. Okamoto, and O. Sugihara, *Jpn. J. Appl. Phys.*, **32**, 807 (1993); c) M. Amano and T. Kaino, *J. Appl. Phys.*, **68**, 6024 (1990); d) C. W. Dirk, H. E. Katz, M. L. Schilling, and L. A. King, *Chem. Mater.*, **2**, 700 (1990).

2) a) C.-F. Shu, W. J. Tsai, J.-Y. Chen, A. K.-Y. Jen, Y. Zhang, and T.-A. Chen, *J. Chem. Soc., Chem. Commun.*, **1996**, 2279; b) S. R. Marder, L.-T. Cheng, B. G. Tiemann, A. C. Friedli, M. Banchard-Desce, J. W. Perry, and J. Skindhøj, *Science*, **163**, 511 (1994).

3) F. Pan, M. S. Wong, V. Gramlich, C. Bosshard, and P. Günter, *J. Am. Chem. Soc.*, **118**, 6315 (1996).

4) a) Y. Kubo, T. Takaba, and S. Aramaki, *Chem. Lett.*, **1997**, 255; b) Y. Kubo, S. Aramaki, Y. Okamoto, and T. Murayama, *J. Chem. Soc., Chem. Commun.*, **1995**, 969.

5) S. M. LeCours, H.-W. Guan, S. G. DiMagno, C. H. Wang, and M. J. Therien, *J. Am. Chem. Soc.*, **118**, 1497 (1996).

6) a) J. Abe and Y. Shirai, *J. Am. Chem. Soc.*, **118**, 4705 (1996); b) N. Nemoto, J. Abe, F. Miyata, M. Hasegawa, Y. Shirai, and Y. Nagase, *Chem. Lett.*, **1996**, 851.

7) J. L. Ouder and D. S. Chemla, *J. Chem. Phys.*, **66**, 2664 (1977).

8) a) D. Yu, A. Gharavi, and L. Yu, *Appl. Phys. Lett.*, **66**, 1050 (1995); b) C.-K. Park, J. Zieba, C.-F. Zhao, B. Swedek, W. M. K. P. Wijekoon, and P. N. Prasad, *Macromolecules*, **28**, 3713 (1995); c) D. Yu and L. Yu, *Macromolecules*, **27**, 6718 (1994); d) D. R. Robello, P. T. Dao, J. S. Schildkraut, M. Scozzafava, E. J. Urankar, and C. S. Willand, *Chem. Mater.*, **7**, 284 (1994); e) J. A. F. Boogers, P. T. A. Klaase, J. J. de Vlieger, D. P. W. Alkema, and A. H. A. Tinnemans, *Macromolecules*, **27**, 205 (1994); f) J. A. F. Boogers, P. T. A. Klaase, J. J. de Vlieger, D. P. W. Alkema, and A. H. A. Tinnemans, *Macromolecules*, **27**, 197 (1994); g) C. Xu, B. Wu, O. Todorova, L. R. Dalton, Y. Shi, P. M. Ranon, and W. H. Steier, *Macromolecules*, **26**, 5303 (1993); h) P. M. Ranon, Y. Shi, W. Steier, X. Xu, B. Wu, and L. R. Dalton, *Appl. Phys. Lett.*, **62**, 2605 (1993); i) Y. Shi, P. M. Ranon, W. H. Steier, C. Xu, B. Wu, and L. R. Dalton, *Appl. Phys. Lett.*, **63**, 2168 (1993); j) C. Xu, B. Wu, M. W. Becker, L. R. Dalton, P. M. Ranon, Y. Shi, and W. H. Steier, *Chem. Mater.*, **5**, 1439 (1993); k) M. A. Mitchell, M. Tomida, A. B. Padias, H. K. Hall, Jr., H. S. Lackritz, D. S. Robello, C. S. Willand, and D. J. Williams, *Chem. Mater.*, **5**, 1044 (1993); l) W. Köhler, D. R. Robello, C. S. Willand, and D. J. Williams, *Macromolecules*, **24**, 4589 (1991); m) W. Köhler, D. R. Robello, P. T. Dao, C. S. Willand, and D. J. Williams, *J. Chem. Phys.*, **93**, 9157 (1990).

9) a) P. Boldt, G. Bourhill, C. Bräuchle, Y. Jim, R. Kammler, C. Müller, J. Rase, and J. Wicheren, *J. Chem. Soc., Chem. Commun.*, **1996**, 793; b) V. Pushkara, Y. M. Cai, and A. K.-Y. Jen, *J. Chem. Soc., Chem. Commun.*, **1994**, 1689.

10) M. Ahlheim, M. Barzoukas, P. V. Bedworth, M. Blanchard-Desce, A. Fort, Z.-Y. Hu, S. R. Marder, J. W. Perry, C. Runser, M. Staehelin, and B. Zysset, *Science*, **271**, 335 (1996).

11) N. Nemoto, F. Miyata, Y. Nagase, J. Abe, M. Hasegawa, and Y. Shirai, *Chem. Mater.*, **8**, 1527 (1996).

12) C. R. Moylan, R. D. Miller, R. J. Twieg, K. M. Betterton, V. Y. Lee, T. J. Matray, and C. Nguyen, *Chem. Mater.*, **5**, 1499 (1993).

13) J. Jerphagnon and S. K. Kurtz, *J. Appl. Phys.*, **41**, 1667 (1970).

14) a) B. Joglekar, K. Shibata, H. Muramatsu, M. Matsui, K. Hirota, M. Hosoda, and K. Tai, *Polym. J.*, **29**, 184 (1997); b) K. Hirota, M. Hosoda, B. Joglakar, M. Matsui, and H. Muramatsu, *Jpn. J. Appl. Phys.*, **32**, L1811 (1993).