

Second-Order Optical Nonlinearity of Novel Methacrylate Polymer with Pendant Disazo Dye Chromophore Containing a Perfluorobutylsulfonyl Group

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Potential applications like optical communications and electrooptics have motivated researchers to flourish the area of nonlinear optics (NLO).^{1–4} To get a large second-order nonlinear optical coefficient (d_{33}), dyes terminated with strong electron-withdrawing and donating groups at both the ends of the molecule separated by a π -electron conjugated system find better position.^{5–9} Efforts are also being made to improve the relaxation behavior of the chromophore after poling. The strong electron-withdrawing nature of the perfluorobutylsulfonyl group has been reported in chromophore design for NLO.^{10–12} In our previous report,¹³ disazo dyes having a perfluorobutylsulfonyl group doped in polycarbonate (PC) and poly(methyl methacrylate) (PMMA) exhibited a large d_{33} value and slow relaxation behavior.

Based on these results, in this note, we wish to report second-order optical nonlinearity of novel methacrylate polymer with pendant perfluorobutylsulfonyl-substituted naphthylene disazo dye.

EXPERIMENTAL

Preparations

4-[4-(Perfluorobutylsulfonyl)phenylazo]-1-naphthylamine (2)

To an 20 ml acetone-water solution containing 750 mg (2 mmol) of 4-(perfluorobutylsulfonyl)aniline **1** was added conc. hydrochloric acid (0.5 ml, 6 mmol). After cooling the solution to 0°C, an aqueous solution (5 ml) of sodium nitrite (138 mg, 2 mmol) was added and stirred for 2 h. To this mixture was added an aqueous buffer solution of acetic acid–sodium acetate of 1-naphthylamine (284 mg, 2 mmol) and stirred for 2 h at –5°C. After the reaction was completed, the resulting precipitate was filtered, rinsed with water and dried. The obtained solid was purified by column chromatography (silica gel, CH₂Cl₂), followed by recrystallization from chloroform–hexane. Yield 50%; mp 114–115°C; ¹H NMR (CDCl₃): δ 4.92 (br s, 2H), 6.86 (d, $J=8.2$ Hz, 1H), 7.55–7.65 (m, 1H), 7.67–7.77 (m, 1H), 7.84 (d, $J=9.4$ Hz, 1H), 8.06 (d, $J=9.4$ Hz, 1H), 8.16 (d, $J=6.7$ Hz,

2H), 8.21 (d, $J=6.7$ Hz, 2H), 9.04 (d, $J=8.2$ Hz, 1H); EIMS (70 eV) m/z (rel intensity) 529 (M⁺; 32), 297 (73), 268 (50), 142 (100), 127 (39), 115 (76).

4-[4-[4-(Perfluorobutylsulfonyl)phenylazo]naphthylazo]-N-ethyl-N-hydroxyethylamine (3)

To an acetone–ethanol–water solution (2.0:1.0:0.5, 30 ml) of 529 mg of **2** (1 mmol) was added conc. hydrochloric acid (0.25 ml, 3 mmol). After cooling the solution between 0 and 5°C, an aqueous solution (5 ml) of sodium nitrite (69 mg, 1 mmol) was added and stirred for 6 h. To this mixture was added an acetone solution (5 ml) of 2-(N-ethylamino)ethanol (350 mg, 2 mmol) and stirred overnight at room temperature. After the reaction was completed, the resulting precipitate was washed with water and dried. The product was purified by column chromatography (silica gel, CH₂Cl₂), followed by recrystallization from chloroform–hexane. Yield 30%; mp 130°C; ¹H NMR (CDCl₃): δ 1.29 (t, $J=6.4$ Hz, 3H), 1.63 (br, 1H), 3.60 (q, $J=6.4$ Hz, 2H), 3.66 (t, $J=4.6$ Hz, 2H), 3.91 (t, $J=4.6$ Hz, 2H), 6.87 (d, $J=7.9$ Hz, 2H), 7.74–7.78 (m, 2H), 7.89 (d, $J=8.8$ Hz, 1H), 8.04 (d, $J=8.8$ Hz, 1H), 8.05 (d, $J=7.9$ Hz, 2H), 8.23 (d, $J=9.0$ Hz, 2H), 8.28 (d, $J=9.0$ Hz, 2H), 9.03–9.05 (m, 2H); ¹⁹F NMR (CDCl₃, ext. CF₃COOH): δ –2.0 (3F), –32.7 (2F), –42.0 (2F), –47.2 (2F); EIMS (70 eV) m/z (rel intensity) 705 (M⁺; 6), 391 (100), 196 (30), 195 (20), 133 (76), 76 (36). Anal. Calcd for C₃₀H₂₄F₉N₅O₃S: C, 51.43%; H, 3.58%; N, 10.27%. Found: C, 51.07%; H, 3.43%; N, 9.93%.

4-[4-[4-(Perfluorobutylsulfonyl)phenylazo]naphthylazo]-N-ethyl-N-(2-methacryloyloxyethyl)amine (4)

To an anhydrous tetrahydrofuran (THF) solution (4 ml) of 254 mg of disazo dye **3** (0.36 mmol) was added triethylamine (250 mg, 2.47 mmol) at –10°C with stirring. To this solution a precooled THF solution (2 ml) of methacryloyl chloride (189 mg, 1.8 mmol) was added in 30 min and stirred for 20 h at room temperature. After the reaction was completed, the product was extracted with dichloromethane and washed with water. The extract was purified by column chromatography (silica gel, CH₂Cl₂). Yield 50%; mp 123–125°C; ¹H NMR (CDCl₃): δ 1.29 (t, $J=7.1$ Hz, 3H), 1.96 (s, 3H), 3.58

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(q, $J=7.1$ Hz, 2H), 3.76 (t, $J=6.7$ Hz, 2H), 4.42 (t, $J=6.7$ Hz, 2H), 5.61 (s, 1H), 6.13 (s, 1H), 6.87 (d, $J=9.6$ Hz, 2H), 7.72–7.79 (m, 2H), 7.88 (d, $J=8.4$ Hz, 1H), 8.04 (d, $J=8.4$ Hz, 1H), 8.05 (d, $J=9.6$ Hz, 2H), 8.22 (d, $J=8.7$ Hz, 2H), 8.25 (d, $J=8.7$ Hz, 2H), 9.00–9.04 (m, 2H); EIMS (70 eV) m/z (rel intensity) 773 (M^+ ; 8), 674 (29), 391 (63), 126 (26), 113 (33), 104 (28), 91 (23), 69 (100).

Co-polymers **P1** and **P2**

Into a polymerization tube were placed 492 mg of methyl methacrylate (4.93 mmol), co-monomer (0.075 mmol) (**4**, 58 mg; **5**,¹⁴ 28.6 mg), 4.5 mg of AIBN (0.0274 mmol), and 0.5 ml of anhydrous dimethylformamide (DMF). The tube was sealed under vacuum and heated with stirring at 60°C for 48 h. The reaction mixture was then cooled and poured into 100 ml of vigorously stirring methanol. The polymer obtained was purified by dissolving in a minimum amount of anhydrous DMF and reprecipitating with methanol. This reprecipitation was repeated three times. The polymer was dried and used for the measurements of SHG. **P1**, 380 mg; **P2**, 460 mg. The amount of dye content was calculated on the basis of the peak integration of the methoxy protons and the aromatic ones in the ¹H NMR spectra of the

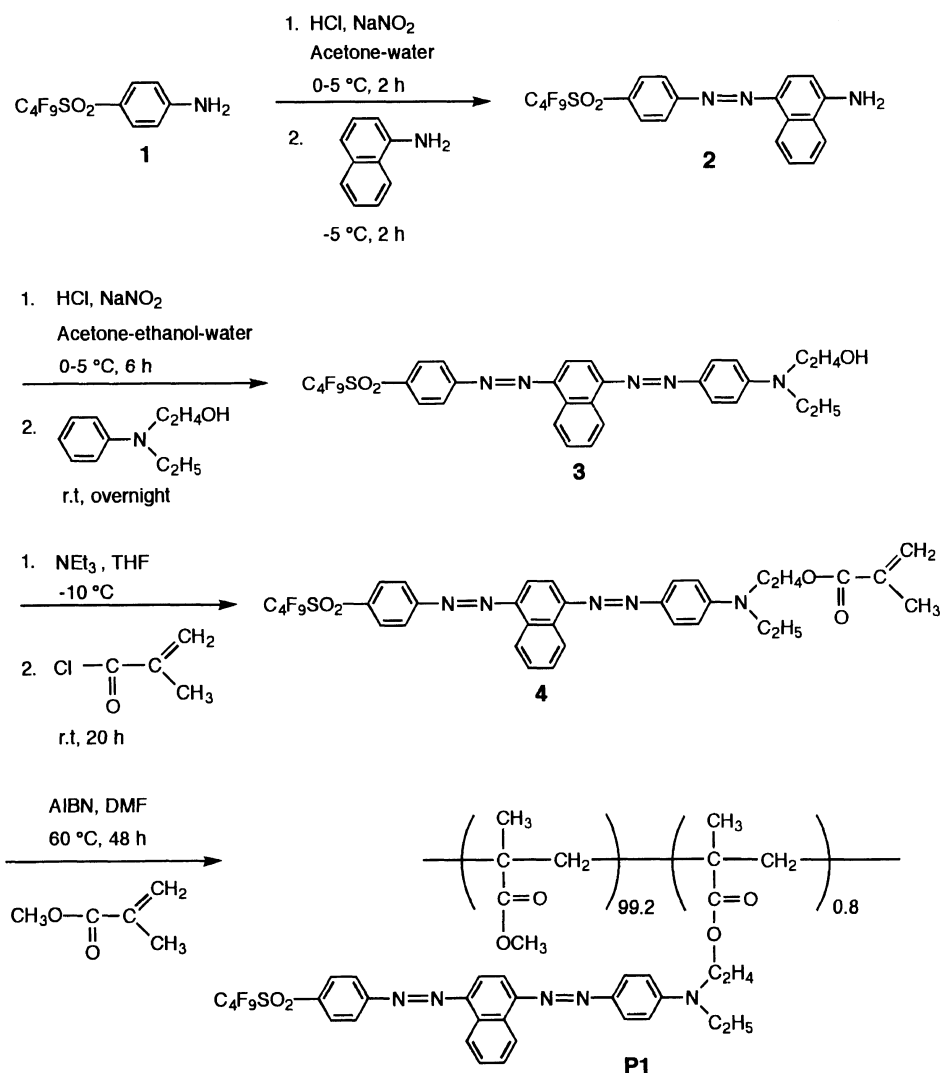
co-polymer. The dye content was calculated as 0.8 mol% for **P1** and 1.0 mol% for **P2**, respectively.

Measurements

Melting points were measured with a Yanagimoto micro melting point apparatus. NMR spectra were taken on JEOL 270-GX and α -400 spectrometers. MS spectra were recorded with Shimadzu QP-1000 and 9020-DF spectrometers. Molecular weights of the co-polymers were measured with a Waters 410 HPLC using PL gel MIXED-B and D (Polymer Laboratories) using chloroform as an eluent.

Preparation of Polymer Films and SHG Measurement

To allow the passage of the laser beam, about 5 mm square of ITO was wet-etched. Co-polymers (**P1** and **P2**) (100 mg) were dissolved in 5 ml of chloroform and spin-coated (600 rpm, 20 s) on the ITO glass and dried under vacuum at room temperature for 10 h. The film was heated by applying an electric current to the ITO glass above the glass transition temperature (T_g) of the co-polymer. A voltage of 6 kV cm⁻¹ was applied to the glass for 2 min. After the heating was stopped, the film was allowed to cool to about 30°C, and the high voltage was turned off. Second harmonic generation



Scheme 1.

(SHG) of the poled polymer films was measured using a rotational Maker fringe method at a fundamental wavelength of 1064 nm using a Nd:YAG laser. The d_{33} values of the samples were compared with the d_{11} value (0.33 pm V^{-1}) of y -cut quartz and evaluated by the curve-fitting method as described in our previous report.¹³ UV spectra were taken on a Hitachi U-4000 spectrophotometer. Refractive indices were determined by a Mizojiri Kogaku DVA-36VWLD ellipsometer. Film thicknesses were measured with a Dektak 3030 surface profile measuring system.

RESULTS AND DISCUSSION

The synthesis of co-polymer **P1** is shown in Scheme 1. The diazotization-coupling reaction of 4-(perfluorobutylsulfonyl)aniline **1**, obtained as described in our paper,¹⁵ with 1-naphthylamine gave azo intermediate **2** in moderate yield. By using acetone-ethanol-water system as the reaction medium, disazo dye **3** was obtained in 30% yield. Co-polymer **P1** was obtained by radical polymerization using AIBN as a radical initiator.

Co-polymer **P2** was also prepared by the same procedure.

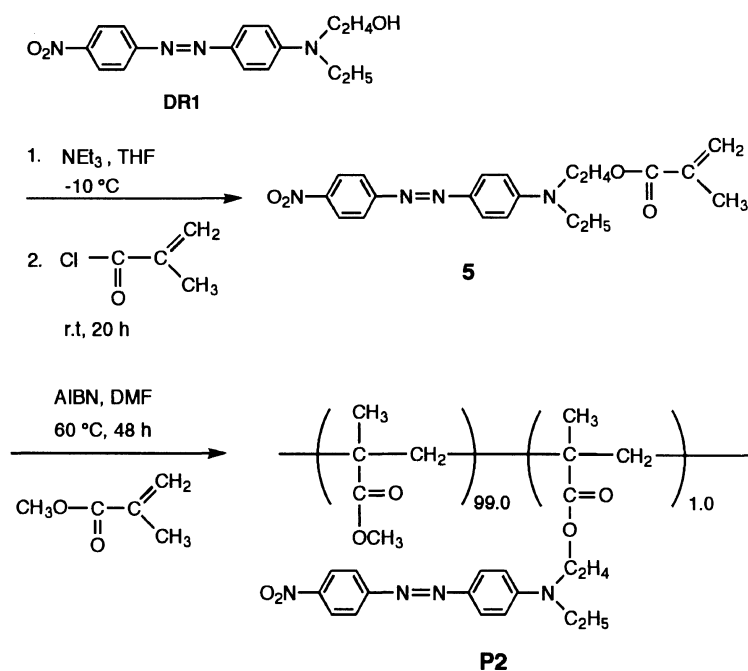
Physical and NLO properties of the co-polymers **P1** and **P2** are summarized in Table I. The T_g 's for both the co-polymers were similar. While for absorption maxima, **P1** was more bathochromic than **P2**. Presence of both, perfluorobutylsulfonyl and naphthylene moieties in the

disazo dye gave bathochromicity to **P1**. Co-polymers **P1** and **P2** showed d_{33} values of 20 and 15 pm V^{-1} respectively. For both the co-polymers **P1** and **P2**, as the absorption coefficients at 532 nm were similar, the contribution of the resonance effect on the d_{33} values also seems to be similar.

Figure 1 shows the changes in absorption spectra of **P1** films before and after poling (0 and 900 h) at 80°C . Absorbance at 544 nm decreased after poling (0 h). After 900 h, the absorbance became similar to that of before poling. No change in the absorption maximum was observed. The decomposition temperature (T_d) of the disazo dye **3** was measured to be 285°C by thermal analysis. The above observations suggested that the chromophore was oriented by corona poling and relaxed without decomposition.

The relaxation behavior of the orientated chromophore is indicated in Figure 2. The films were stored at 80°C throughout the measurements. Compared to the doped system, the co-polymers **P1** and **P2** showed slower relaxation. In case of the two co-polymers, **P1** was more stable than **P2**. This can be attributed to the longer conjugated aromatic skeleton of the chromophore **3** and the rigidity of the perfluorobutylsulfonyl moiety in **P1**.

Thus, methacrylate polymer with pendant disazo dye containing a perfluorobutylsulfonyl group provided better matrix for slower relaxation behavior. The perfluorobutylsulfonyl group having strong electron-withdrawing and rigid nature offered to the linearly shaped



Scheme 2.

Table I. Physical and NLO properties of **P1** and **P2**

Co-polymer	M_w^a	T_g^b	λ_{max}	Film thickness	Refractive index		d_{33}
		°C			nm	μm	
P1	171000	130	544	0.3	1.52	1.49	20
P2	259000	126	490	0.5	1.53	1.49	15

^a Determined by gel permeation chromatography. ^b DSC analysis.

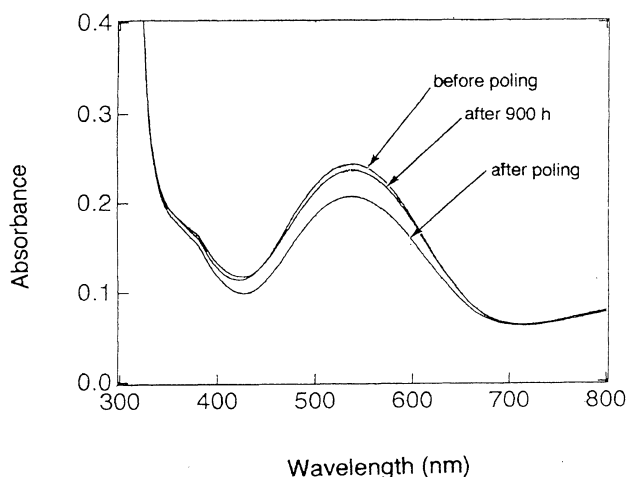


Figure 1. Absorption spectra of co-polymer P1.

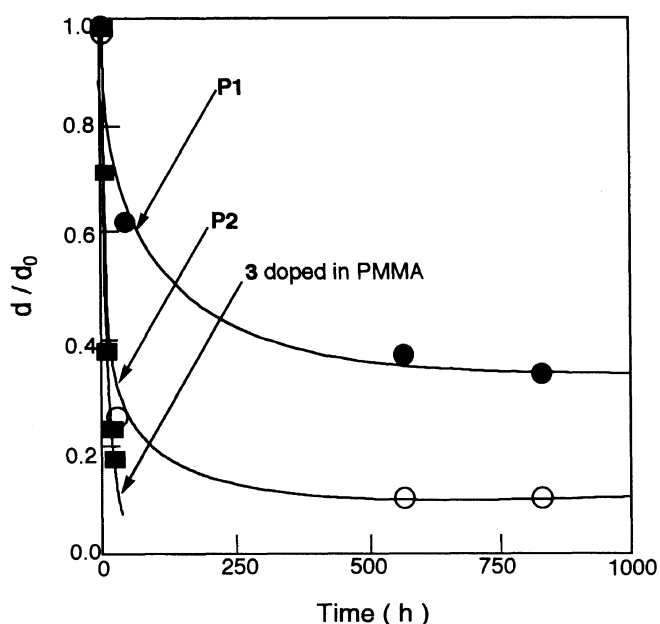


Figure 2. Relaxation behavior of the orientated chromophore at 80°C. The curve represents the % retention (d/d_0).

NLO chromophore along with the presence of π -extended conjugation system in the disazo dye were very effective at enhancing the d_{33} value and also improving the relaxation behavior.

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