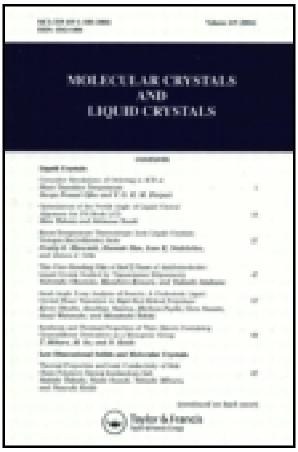

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SECOND-ORDER OPTICAL NONLINEARITIES IN PERFLUOROALKYLSULFONYL SUBSTITUTED AZO DYES

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Abstract The second-order nonlinear optical coefficients d_{33} (-2ω:ω,ω) of polymer films doped with novel azo dyes, which have a perfluoroalkylsulfonyl group as an electron acceptor and an extended π-electron conjugated system, are determined by second-harmonic generation (SHG) measurements. Thin polycarbonate (PC) film doped with 4-(4-(4-perfluorobutylsulfonylphenylazo) naphthylazo)-N-ethyl-N-hydroxyethylaniline showed a large d_{33} value, 67 pm/V, at a wavelength of 1064 nm. The decay of the d_{33} values was slow due to the stability of the molecular arrangement in a polymer matrix at high temperature. In addition, a side-chain nonlinear optical polymer with this novel disazo dye is synthesized and the decay of d_{33} values is estimated.

INTRODUCTION

Recently many kinds of nonlinear optical materials have been studied for their applications to electrooptical systems.[1, 2] Organic nonlinear optical materials are shown to exhibit a higher potential than inorganic materials because of a faster response and a larger nonlinear optical susceptibility.[3-5] In terms of the molecular properties of the material, the intramolecular charge transfer and extended π-electrons through the π-electron-conjugated system cause large optical nonlinearities at the molecular level. In order to obtain a large second-order nonlinear optical material, the electron donor-acceptor substitution is absolutely necessary for a π-electron-conjugated system.

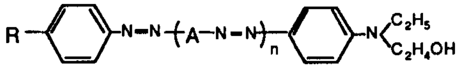
A perfluoroalkylsulfonyl group is predicted to be a strong electron acceptor. The substituent constant (σ_p) from Hammett's rule,[6] which accounts for the donor-acceptor interactions, is considerably larger for a perfluoromethylsulfonyl group than a nitro group.[7] A perfluoroalkylsulfonyl group is thought to have an excellent solubility and some chemical modification for cross-linking achieving a stability of molecules. To extend a π-electron-conjugated system, an insertion of another azo chromophore is an effective method for the enhancement of d_{33} values of a monoazo dye.[8] In this study, the d33 values for polymer films doped with novel azo dyes which have a perfluoroalkylsulfonyl group and an extended π-electron system are determined by second-harmonic generation (SHG) measurements and the stability of these molecular arrangements in polymer matrices is investigated.[9] For an attempt to get a long term stability of the second-order nonlinear property, a polymethylmethacrylate (PMMA) copolymer containing this novel disazo dye in the side-chain, was synthesized.

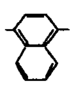
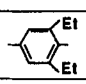
EXPERIMENTAL

Structures of the novel optical nonlinear materials synthesized by us and DR1 are shown in Table I. The materials were purified by column chromatography, and characterized by ^{1}H-NMR, ^{19}F-NMR and electron impact mass spectrometry (EIMS). These materials were dispersed into polymer matrices, PC and PMMA, and dissolved in chloroform. Concentrations of the materials were 4 mol% and 2 mol% for PC and PMMA, respectively. Side-chain polymers (PDC3, PDR1) including DC3 and DR1 were synthesized. Thin films were spin-coated from these solutions onto the glass side of ITO glass. To allow the passage of the laser beam, about 5 mm square of ITO was wet-etched. The thickness of the samples was about 1 μm, as measured by the Dektak 3030 surface profile measuring system. The absorption spectra were measured by a HITACHI U-4000 spectophotometer. Using the Mizojiri Kogaku ellipsometer (DVA-36VWLD), the refractive indices were determined.

A corona-poling method was applied to arrange the dye molecules in this study. First, the samples were heated by sending an electric current to ITO about the glass transition temperatures (Tg) of the polymers, which were 110 °C for PMMA, 150 °C for PC, and 120 °C for side-chain polymers. A 6 kV/cm voltage was applied to the sample

TABLE 1 Structure of novel azo dyes and the d33 values of polymer films doped with dyes



	n	R	A	d_{33} (pm/V) at 1.064 μm	
				PC	PMMA
DR1	0	NO_2	—	—	38
MC1	0	$C_4F_9SO_2$		—	28
DC1	1	H		35	31
DC2	1	NO_2		50	31
DC3	1	$C_4F_9SO_2$		67	33
DC4	1	C_4F_9S		63	32
DC5	1	NO_2		23	29
DC6	1	$C_4F_9SO_2$		43	34

for two minutes at the Tg's of the polymers. After the heating was stopped, the sample was allowed to cool to about 30 °C, and the high voltage was turned off.

After the poling procedure was completed, the d_{33} values of polymer films doped with novel compound dyes were evaluated using a rotational SHG Maker fringe method with fundamental wavelengths of 900-1550 nm obtained by optical parametric oscillator (Spectra-Physics, MOPO-730). The nonlinear optical susceptibility d_{33} of samples was compared with the d_{11} value (0.33 pm/V, 1064 nm) of y-cut quartz. The d_{33} values are evaluated by the curve-fitting method as follows:[10, 11]

$$P_{2\omega} = (512\,\pi^3)\, T\, d^2 p^2 P_\omega^2 f_a, \tag{1}$$

where P is the light intensity for fundamental (subscript ω) and second-harmonic (2ω) frequencies, T is a transmission factor, d is the second-order nonlinear optical coefficient, p is a projection factor, and f_a is an absorption factor:

$$f_a = \frac{[1-\exp(-\alpha_{2\omega}\, l/2)]^2/4 + (\Delta\psi)^2 \exp(-\alpha_{2\omega}\, l/2)}{(n_{2\omega}^2 - n_\omega^2 - k_{2\omega}^2)^2 + (2n_{2\omega} k_{2\omega})^2}, \tag{2}$$

where n and k are the real and imaginary parts of refractive indices, respectively, α is the linear absorption coefficient at 2ω, $\Delta\Psi$ is the phase mismatch between the fundamental and harmonic frequencies, and l is the sample thickness.

Exposing these samples at 50 °C and 80 °C in air, the d_{33} decay of the samples was observed.

RESULTS AND DISCUSSION

Absorption spectra of the PMMA films doped with several dyes are shown in Fig. 1. Between a nitro and a perfluorobutylsulfonyl group, big differences of absorption maxima were not observed in mono and disazo dyes. Comparing DR1 with the absorption peak at about 490 nm, DC2 and DC3 indicate that the absorption peaks shift to red. The shift of the peak to longer wavelengths indicates that these samples must have an extended π-electron-conjugated system. The peak with the longest wavelength (570 nm) was observed for DC3. The d_{33} values of polymer films doped with several azo dyes at 1064 nm are shown in Table I. In PMMA system, significant difference between monoazo dyes and disazo dyes was not observed. In the PC films doped with dyes, the corona-poling was not successful due to the sublimation of monoazo dyes at 150 °C. The largest d_{33} value, 67 pm/V, was obtained for DC3 having a perfluorobutylsulfonyl group as an electron acceptor. The d_{33} value of DC6 was 43

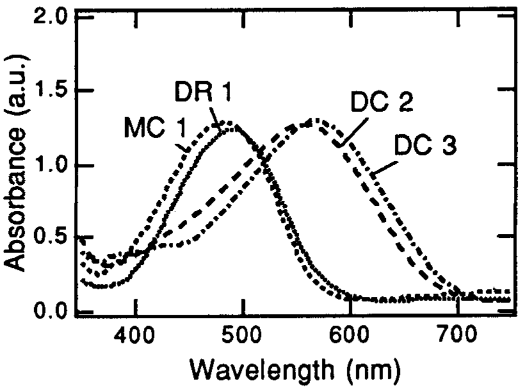


FIGURE 1 The absorption spectra of PMMA films doped with several dyes

pm/V. These d33 values of DC3 and DC6, which contain a perfluorobutylsulfonyl group, are larger than those of DC2 and DC5, which have a nitrogroup. A similar tendency of the d33 values, although showing smaller differences among those, is obtained for the PMMA-doped films. The absorption coefficients of DC2 and DC3 were almost the same at 532 nm, because the absorption peaks are located at the close wavelength, respectively, as shown in Fig. 1.

In order to investigate a resonance effect, the dispersion property of d33 values was evaluated. At absorption region, the d33 values were large and dispersion curve was similar to absorption curve (Fig. 2). A nonresonant d33 value was 8 pm/V for PMMA film doped with DC3.

The stability of molecules arranged in polymer matrices was investigated between a perfluoroalkylsulfonyl group and a nitro group. One example of the decay of the d33

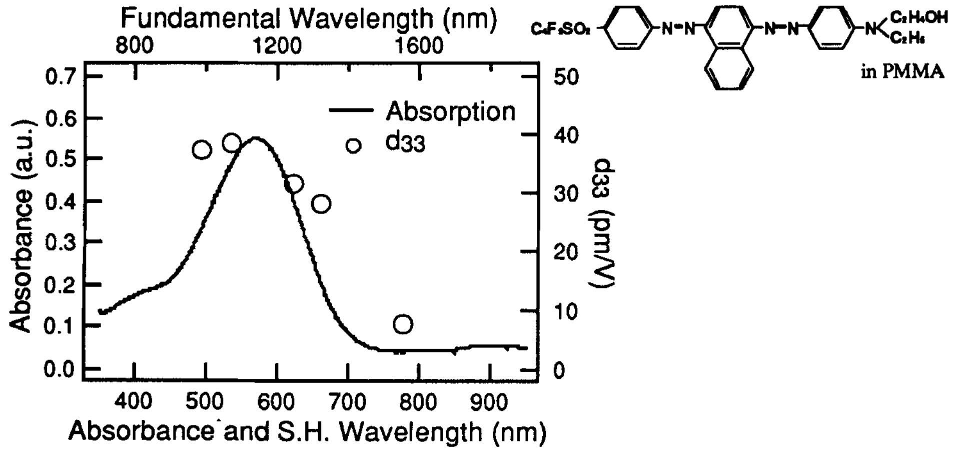


FIGURE 2 Absorption spectrum and the d33 values of the PMMA film doped with DC3

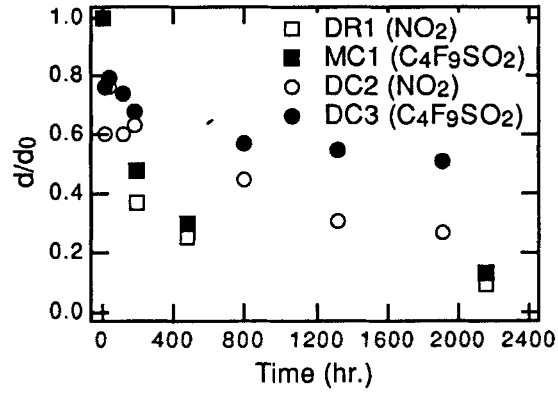


FIGURE 3 The decay of PC films doped with several dyes at 50 °C

values is shown in Fig. 3, which shows the decay of the PC films doped with dyes at 50 °C. The d33 values after poling are normalized. In this case, the decay of the d33 values of DC3 is found to be over 50 % after 2000 hr. At 2000 hr, the d33 value of DC3 is the largest, and the d33 values of MC1 and DC3 are larger than those of DR1 and DC2. This tendency of the decay is similarly displayed for other matrices at other temperatures. Furthermore, the decay of the PC films doped with dyes is less than that of the PMMA films. The tendency of the decay phenomenon may be due to both the molecule's length and the electron acceptor group. The Tg's of PC or PMMA films doped with several dyes at low concentrations were almost of the same temperature. Since the decay rate of MC1 and DC3 having a perfluoroalkylsulfonyl group is slower than that of DR1 and DC2 having a nitro group, we presume that it is hard for a larger substituent to move through polymer matrices.

The decay of the d33 values of the side-chain polymers, (PDC3, PDR1), were

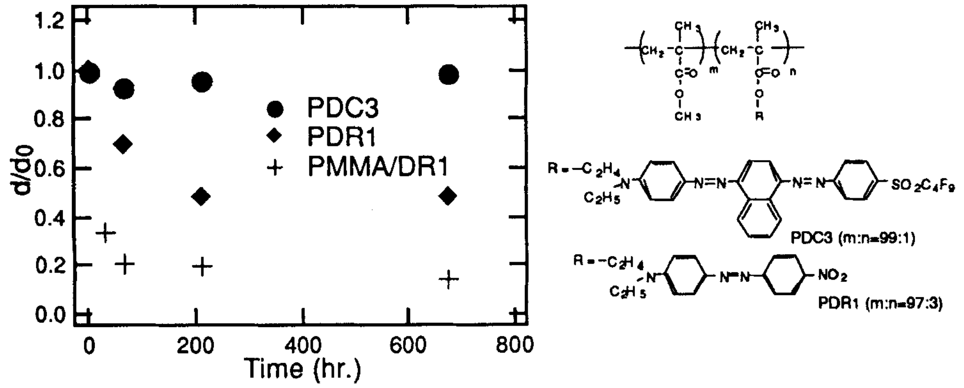


FIGURE 4 The decay of side-chain polymer films at 50 °C

investigated. The decay of the polymers at 50 °C is shown in Fig. 4. The d33 values of PDC3 almost did not change until 600 hr., and those of PDR1 decreased to 50 %. This result may be explained by a different size between DC3 and DR1. The decay of the d33 values of PC film doped with DC3 at 50 °C after 600 hr. was found to be about 60 %, as shown in Fig. 3, however, that of the side-chain polymer, PDC3 was unchanged on the same condition. The superior stability of the second-order nonlinear property of the side-chain polymer including a disazo dye having a perfluoroalkylsulfonyl group was achieved.

CONCLUSIONS

In conclusion, the second-order nonlinear optical coefficients of polymer films doped with the novel disazo dyes are determined by second-harmonic generation measurements at wavelengths of 900- 1550 nm. These thin films showed large second-order nonlinear optical coefficients, with the largest d33 value of 67 pm/V for the polycarbonate film doped with 4 mol% 4-(4-(4-perfluorobutylsulfonylphenylazo) naphthylazo)-N-ethyl-N-hydroxyethylaniline. In addition, the decay of the d33 values of the materials in the above system are slower in comparison with similar molecules having a nitro group. Thus, it appears that the perfluoroalkylsulfonyl group is more effective than a nitro group in terms of the large optical nonlinearity and the stability of molecular arrangement. The stability of the d33 values is improved by means of attaching a disazo dye having a perfluoroalkylsulfonyl group to PMMA.

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