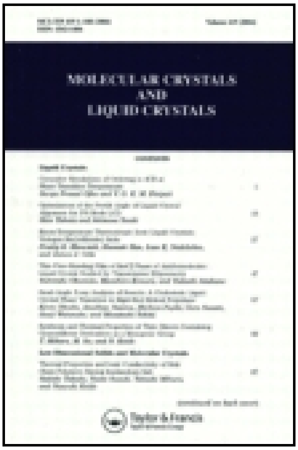

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Nonlinear Optical Responses of a Polarized Stilbene Side Chain Liquid Crystalline Polyacrylate

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A 100 μm film of a side chain liquid crystal polyacrylate (**P-10**) containing a $(CH_2)_{10}$ spacer chain and a 4-dimethylaminostilbene-4′-carboxylic ester mesogen was measured to have degenerate four wave mixing efficiencies at 532 nm 24 times that of a 1 cm cell of carbon disulfide and 0.16 times that of a 90 μm film of 1.25 weight percent 4-dimethylamino-4′-nitrostilbene (**DANS**) in poly(methyl methacrylate) [PMMA]. The second harmonic generation efficiency of **P-10** at 1064 nm on a molecular basis was 0.18 times that of **DANS** in PMMA.

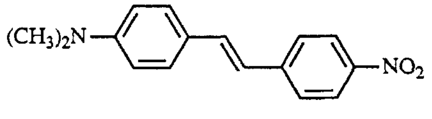
Keywords: Stilbene, polyacrylate, SHO, DFWM

INTRODUCTION

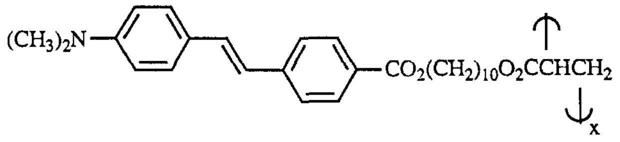
Organic polymers with donor-acceptor substituted aromatic structures are of interest due to large second-order nonlinear optical coefficients $\chi^{(2)}$,[1-4] and ease of fabrication into thin films. Two approaches have been used to incorporate the structure of choice into the nonlinear optical (NLO) material. One approach has the active NLO structure dissolved in a polymer film, such as 4-dimethylamino-4′-nitrostilbene (**DANS**) doped into poly(methyl methacrylate). Films of such dyes oriented by DC electric fields in glassy polymers have $\chi^{(2)}$ values greater than those of inorganic crystals.[5-7] However, the initial $\chi^{(2)}$ values of **DANS** in PMMA are not temporally stable due to relaxation of the polymer glass and of the solute toward an equilibrium isotropic state.[8,9] Greater temporal stability has been achieved by incorporation of **DANS**-like structures as side chains of glassy polymers.[10] Further improvement in temporal stability is expected in this second approach when the NLO structure is the mesogen of a polymer liquid crystal (LC) which will retain anisotropic structure indefinitely. LC copolymers with dyes in the side chains have higher order parameters than dyes dissolved in LC polymers.[11] Numerous side chain polymers have been prepared for second order NLO applications,[2,3,12–14] but many of the structures are proprietary, and most of them probably do not have liquid crystal phases. Some of these polymers have been tested as frequency doubling and waveguide devices.[15–18]

Somewhat less is known about the structural requirements of organic materials for $\chi^{(3)}$. Polymers with long conjugated π-electron systems and heteroaromatic ladder polymers have shown the largest $\chi^{(3)}$ values.[19] Calculations on simple polyenes indicate that donor and acceptor substituents such as those on **DANS** should enhance nonresonant $\chi^{(3)}$.[20] Third harmonic generation has been reported for copolymers of methyl methacrylate and acrylates containing structures analogous to **DANS**.[21]

We describe here preliminary degenerate four wave mixing (DFWM) and second harmonic generation (SHG) experiments on films of a side chain liquid crystal polymer **P-10** and on films of **DANS** in PMMA for comparison.



DANS



P-10

EXPERIMENTAL

Preparation and properties of **P-10** and related polymers are reported elsewhere.[22] The sample used for film preparations had M_n = 13,300, M_w/M_n = 14, and 2% residual monomer by GPC, and had thermal transitions of T_g = 79°C and T_i = 128°C. The phase transitions are broad and can be observed after the first DSC scan only after the highly viscous mesophase has been annealed. The type of mesophase has not been identified yet, but the polarizing microscopic texture suggests a low degree of order.

The **P-10** sample for DFWM was a 100 μm thick film contained in an area 1 cm × 2.5 cm with a lead spacer designed for a solution infrared spectroscopy cell, sandwiched between two microscope slides, annealed in a vacuum oven under slight pressure at 140°C, and cooled to room temperature over 2 h to form a low-scattering, slightly birefringent, yellow polymer glass. The **DANS** sample for DFWM was a 90 μm film on a 1 mm microscope slide prepared by evaporation of a chloroform solution of a 1.25 weight percent dispersion of **DANS** in PMMA and drying in air for 2 days. The average film thickness was calculated from measurements of the thicknesses of the coated and the uncoated glass slide with a micrometer caliper. Without magnification the **DANS** sample appeared orange and nonscattering. Examination with a polarizing microscope revealed small crystals of **DANS** dispersed in the PMMA and a low concentration of **DANS** dissolved in the PMMA.

The **P-10** sample for SHG was prepared by filtering a 10% weight/volume solution of the polymer in 1,4-dioxane through a 0.5 μm filter and spin coating the filtrate onto a 2.5 cm × 2.0 cm sheet of indium tin oxide (ITO) coated glass. The glass was cleaned by washing with sulfuric acid, *n*-amyl alcohol, and isopropyl alcohol with water rinses after each washing step. The film was dried under vacuum before poling. Its thickness of 1.5 μm and its number density of polymer repeat units were calculated from the weight, area, and density (1.155 g/cm^3, measured by pycnometry). The film was covered with a second sheet of ITO-coated glass, and wires were cemented to each of the conductive surfaces with electrically conductive epoxy resin (Zymet SL 100-ZX). On a microscope hot stage the film was heated above its isotropization temperature for 10 min, and a DC electric field of 800 kV/cm was applied. The sample was cooled at 0.2°C/min to a temperature 5°C below T_i, maintained there for 24 h, and then cooled quickly to room temperature before the field was turned off. The SHG experiments were performed after the sample had been kept at room temperature for 3 days. After poling the sample was clear at the center with small ripples near the edges, and the transmittance of plane-polarized light through the sample at an acute angle depended strongly on the direction of polarization, indicating homeotropic alignment of the long axis of the stilbene. This same effect was observed qualitatively 8 months after poling.

The **DANS** in PMMA sample for SHG measurements was prepared similarly by spin coating a 1,4-dioxane solution of 1.0 weight percent **DANS** in PMMA onto ITO-coated glass. The thickness of the orange, transparent film was calculated to be 7 μm from its weight, area, and density. The sample was heated on a microscope hot stage to 120°C at 10 deg/min, annealed at 120°C (T_g of PMMA = 105°C) for 2 h, and then poled with voltage slowly increased to 400 V (570 kV/cm) and held at 400 V for 2 h. The sample cooled slowly to room temperature with the field on. No microscopic changes in the sample were observed during this procedure. Unlike the sample used for DFWM, there was no sign of **DANS** crystals in the film at 400× magnification. Apparently the solution of **DANS** in PMMA stayed homogeneous during rapid evaporation of dioxane in the spin coating process, and **DANS** crystallized out of PMMA during slow evaporation of chloroform in the preparation of the DFWM sample. In plane-polarized light the sample still appeared ordered 8 months after poling.

RESULTS AND DISCUSSION

$\chi^{(3)}$ was measured by DFWM using a frequency-doubled, mode-locked Nd:YAG laser (Quantel Model YG571C) producing single 20 ps pulses at 532 nm. The pulses were split into two pump beams and a probe beam. The pump beams were focused to an area of about 1 mm^2 and crossed at an angle of 6° in the samples with incident intensities in the range 1.0–10.0 GW/cm^2. The probe beam exactly counterpropagated to one of the pump beams with incident intensities in the range 0.02–0.13 GW/cm^2, and the signal beam emerged from the sample exactly counterpropagating to the second pump beam. The two pump beans were σ-polarized, and the probe beam was p-polarized, so that $\chi^{(3)}_{xyyx}$ was measured. The temporal overlap of the three input pulses was adjusted using optical delay lines, and the quantitative measurements were made when all three pulses were coincident in the material.

The magnitude of $\chi^{(3)}$ for the polymer films was determined relative to a 1 cm reference cell containing CS_2 under the same experimental conditions.[23] The preliminary data are not corrected for self-focusing in the CS_2 sample. A much shorter pathlength of CS_2 is needed to avoid self-focusing. The $\chi^{(3)}_{xyyx}$ data corrected for sample absorbance, number densities of the samples, and molecular third order responses are given in Table I. The **P-10** and **DANS** films possess $\chi^{(3)}$ greater than that of the CS_2 sample by factors of 24 and 145. The extinction coefficients, also given in Table I, show that the films have considerable absorption at the wavelength of the experiment, and the measured values of $\chi^{(3)}$ may be enhanced by band-edge effects.

SHG experiments on **P-10** and on **DANS** in PMMA were performed with a modelocked Nd:YAG laser producing 20 ps single pulses at 1064 nm. The absolute conversion efficiency was determined by measuring the ratio of the 532 and the 1064 nm signal intensities and applying corrections for the relative responses of the monochromator and photomultiplier tube to the two wavelengths. The angular dependence of the conversion efficiency for the **P-10** sample was similar to that of earlier reports[6] of dye/polymer films with minimum response at incident angle $\theta = 0°$ from normal and increasing response to $\theta = 60°$, but the coherence length could not be calculated because no series of Maker fringes was observed.[24] The coherence length of a similar polymer was reported to be about 5 μm.[25]

The conversion efficiency of the **P-10** sample was measured as a function of input intensity at an angle of $\theta = 50°$, and the results are shown in Figure 1 and Table II. Absolute efficiencies approached 10^{-7}, which are typical values for organic polymer films. At this time we have no independent measurements of the sample order parameters to judge how well the samples were aligned. Fewer SHG experiments were performed on the **DANS** sample, but preliminary experiments

TABLE I

DFWM $\chi^{(3)}$ values and extinction coefficients

Sample	$\chi^{(3)}_{xyyx}$ (esu)[b]	N (10^{20} cm^{-3})[c]	Rel. molecular response	α (cm^{-1} at 532 nm)
CS_2[a]	7.6×10^{-14}	129	1	
DANS	$1.1 \pm 0.4 \times 10^{-11}$	0.33	1.1×10^4	165
P-10	$1.8 \pm 0.7 \times 10^{-12}$	14.6	23	25

[a] N. P. Xuan, J.-L. Ferrier, J. Gazengel, and G. Rivoire, *Opt. Commun.*, **51**, 433 (1984).

[b] Estimated errors due to uncertainties of the interaction length in CS_2 and to random errors in measured scattering efficiencies.

[c] Number density of chromophores.

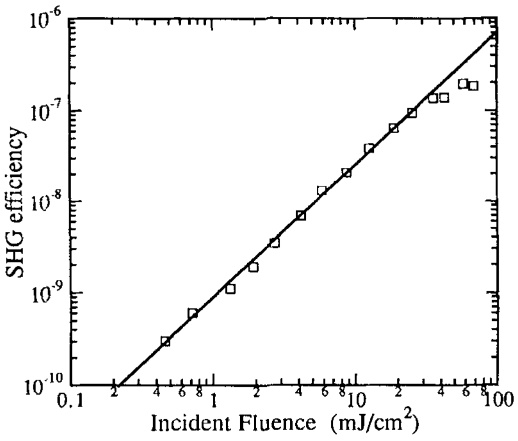


FIGURE 1 SHG efficiency of a film of P-10 as a function of input intensity at $\Theta = 50°$.

TABLE II

SHG coefficients

Sample	Relative $\chi^{(2)}$	N (10^{20} cm^{-3})	Relative d_{33}
DANS	1	0.27	1[a]
P-10	2.1	14.6	0.18

[a] Absolute values are reported to be 1.5×10^{-9} esu (Reference 6) and 2×10^{-9} esu (Reference 9).

indicated the conversion efficiency was less than that of the **P-10** sample. Corrected for path length and number density the molecular contribution d_{33} to $\chi^{(2)}$ of the polarized stilbene of **P-10** is less than that of **DANS**, qualitatively what is expected for substitution of the strongly electron-withdrawing nitro group of **DANS** with a moderately electron-withdrawing carboxylic ester group.

After hundreds of laser pulses at either 532 nm or 1064 nm all samples showed visible damage in the form of black spots, bleached spots, or cracking of the film. All data reported were obtained at exposures well below the damage threshold.

In conclusion, optically clear thin films of a new liquid crystal polymer (**P-10**) containing a polarized stilbene side chain, and of **DANS** in PMMA have been shown to exhibit strong picosecond DFWM responses at 532 nm and strong picosecond SHG responses at 1064 nm. The DFWM responses of the **P-10** and the **DANS** samples are about two and three orders of magnitude less respectively than those of the best polymers with long conjugated main chains ($\chi^{(3)}$ about 10^{-9} esu).

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REFERENCES

1. D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, **23**, 690 (1984).
2. R. N. DeMartino, E. W. Choe, G. Khanarian, D. Haas, T. Leslie, G. Nelson, J. Stamatoff, D. Stuetz, C. C. Teng and H. Yoon, in *Nonlinear Optical and Electroactive Polymers*; P. N. Prasad and D. R. Ulrich, Eds. (Plenum Press, New York, 1988).
3. G. R. Mohlmann and C. P. J. M. van der Vorst, in *Side Chain Liquid Crystalline Polymers*; C. B. McArdle, Ed. (Blackie and sons, Glasgow, U.K., 1989), pp 330–356.
4. G. J. Bjorklund, R. W. Boyd, G. Garter, A. F. Garito, R. S. Lytel, G. R. Meredith, P. Prasad, J. Stamatoff and M. Thakur, *Appl. Optics*, **26**, 227 (1987).
5. G. R. Meredith, J. G. Van Dusen and D. J. Williams, *Macromolecules*, **15**, 1385 (1982).
6. K. D. Singer, J. E. Sohn and S. J. Lalama, *Appl. Phys. Lett.*, **49**, 248 (1986).
7. D. J. Williams, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, D. S. Chemla and J. Zyss, Eds. (Academic, Orlando, FL: 1987), vol. 1, pp 405–536.
8. H. L. Hampsch, J. Yang, G. K. Wong and J. M. Torkelson, *Macromolecules*, **21**, 526 (1988).
9. H. L. Hampsch, J. Yang, G. K. Wong and J. M. Torkelson, *Polym. Commun.*, **30**, 40 (1989).
10. D.-R. Dai, T. J. Marks, J. Yang, P. M. Lundquist and G. K. Wong, *Macromolecules*, **1990**, 23, 1891 and references therein.
11. H. Ringsdorf and H.-W. Schmidt, *Makromol. Chem.*, **185**, 1327 (1984).
12. A. C. Griffin, A. M. Bhatti and R. S. L. Hung, in *Nonlinear Optical and Electroactive Polymers*; P. N. Prasad and D. R. Ulrich, Eds. (Plenum, New York, 1988), pp 375–391.
13. T. M. Leslie, R. N. DeMartino, E. W. Choe, G. Khanarian, D. Haas, G. Nelson, J. B. Stamatoff, D. E. Stuetz, C.-C. Teng and H.-N. Yoon, *Mol. Cryst. Liq. Cryst.*, **153**, 451 (1987).
14. J. E. Sohn, K. D. Singer, M. G. Kuzyk, W. R. Holland, H. E. Katz, C. W. Dirk, M. L. Schilling and R. B. Comizzoli, in *Nonlinear Optical Effects in Organic Polymers*; J. Messier, F. Kajzar, P. Prasad and D. Ulrich Eds. (Kluwer, Dordrecht, 1989), pp 291–297.
15. R. Lytel, G. F. Lipscomb, J. Thackara, J. Altman, P. Elizondo, M. Stiller and B. Sullivan, in *Nonlinear Optical and Electroactive Polymers*; P. N. Prasad and D. R. Ulrich, Eds. (Plenum, New York, 1988), pp 415–426.
16. J. I. Thackara, G. F. Lipscomb, M. A. Stiller, A. J. Ticknor and R. Lytel, *Appl. Phys. Lett.*, **52**, 1031 (1988).
17. J. C. Altman, P. J. Elizondo, G. F. Lipscomb and R. Lytel, *Mol. Cryst. Liq. Cryst.*, **157**, 515 (1988).
18. A. Buckley and J. B. Stamatoff, in *Nonlinear Optical Effects in Organic Polymers*; J. Messier, F. Kajzar, P. Prasad and D. Ulrich, Eds. (Kluwer, Dordrecht, 1989), pp 325–336.
19. D. R. Ulrich, *Mol. Cryst. Liq. Cryst.*, **160**, 1 (1988).
20. J. W. Wu, J. R. Heflin, R. A. Norwood, K. Y. Wong, O. Zamani-Khamiri, A. F. Garito, P. Kalyanaraman and J. Sounik, *J. Opt. Sci. Am. B*, **6**, 707 (1989).
21. S. Matsumoto, T. Kurihara, K. Kubodera and T. Kaino, *Mol. Cryst. Liq. Cryst.*, **182A**, 115 (1990).
22. M. Zhao, M. Bautista and W. T. Ford, *Macromolecules*, in press.
23. J. L. Oudar, *J. Chem. Phys.*, **64**, 446 (1977).
24. J. Jerphagnon and S. K. Kurtz, *J. Appl. Phys.*, **41**, 1667 (1970).
25. M. Amano, T. Kaino, F. Yamamoto and Y. Takeuchi, *Mol. Cryst. Liq. Cryst.*, **182A**, 81 (1990).