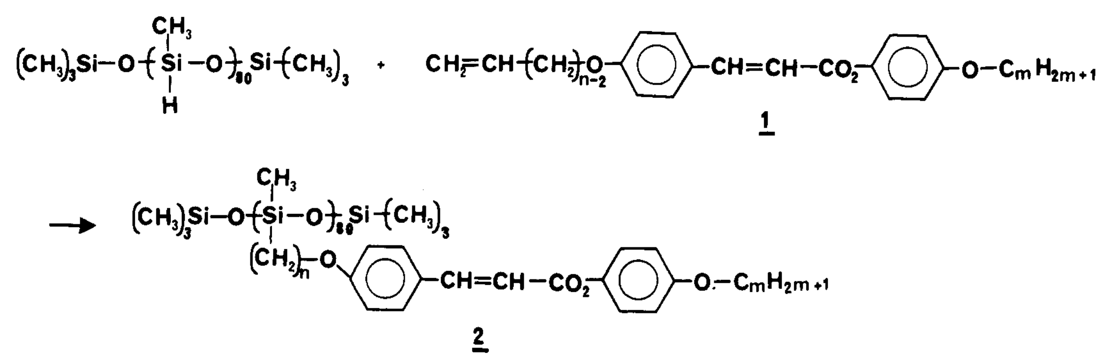
Scheme I



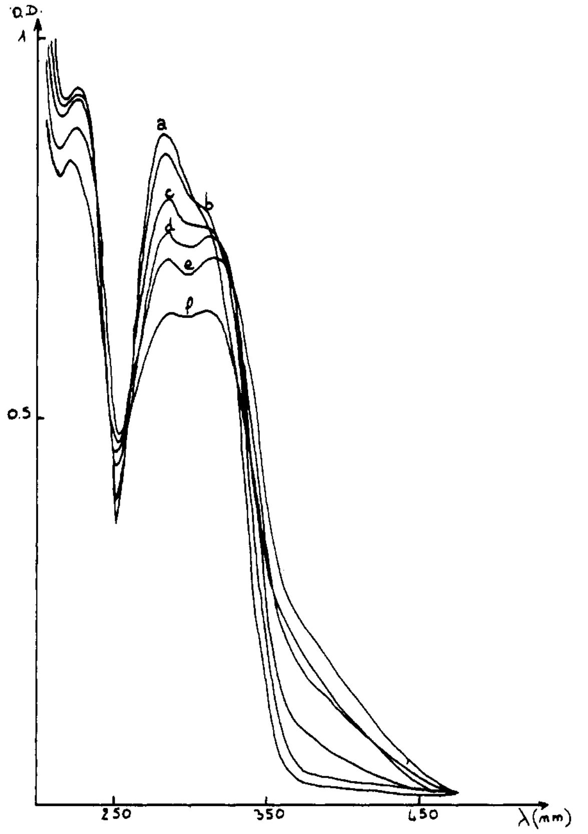


Figure 1. Changes in the UV spectra of polysiloxane **2d** upon irradiation for (a) 0, (b) 5, (c) 15, (d) 30, and (e) 45 min and (f) photo-cross-linked film after washing with dichloromethane.

well-known tendency of side-chain polysiloxanes to give smectic C phases.[9]

For photo-cross-linking procedures, the polymers (**2**) were cast as thin films on the outside of a 1-mm quartz cell by coating from dichloromethane solutions. The resulting films were annealed for several minutes in the liquid-crystalline phase and then cooled to the glassy state. UV light irradiation (Hanovia low-pressure mercury lamp) of the thin films of **2** resulted in modifications of their UV spectra (Figure 1), IR spectra (decrease of the IR absorbance at 1650 cm^{-1} due to the conjugated carbon-carbon double bonds), and phase-transition temperatures (for compound **2d** changes in the S_C to isotropic transition temperatures upon irradiation are the following: (a) 0 min, T = 133 °C; (b) 5 min, T = 122-125 °C; (c) 15 min, T = 115-120 °C; (d) 30 min, T = 109-116 °C; (e) 60 min, T = 104-113 °C). The cross-linking was tested by washing the films after irradiation by immersing the quartz cell for a few minutes in dichloromethane, drying, and then recording the UV spectra (Figure 1, curve f). The photochemical process leading to the cross-link formation might be postulated to be similar to the one put forward in chemically related photoresist materials: photochemical 2 + 2 dimerization of the photosensitive cinnamate groups.[11a,b,d] Work is in progress to confirm the postulated mechanism.

In conclusion, a new procedure has been described for the synthesis of liquid-crystalline side-chain polysiloxane elastomers that consists of the photo-cross-linking of thin films made with mesomorphic side-chain polysiloxanes possessing a phenyl cinnamate group as mesogenic part. Utilization of this procedure to the creation of insoluble and eventually macroscopically oriented organic thin films made with ferroelectric liquid-crystalline side-chain polysiloxanes[9c,13d,14] of interest for various applications is now in progress, and results will be published shortly.

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Squarylium Dye-Doped Polymer Systems as Quadratic Electrooptic Materials

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Large bulk third-order nonlinear optical susceptibilities, $\chi^{(3)}$, have been reported in conjugated polymers such as polydiacetylene,[1] polythiophene,[2] polyacetylene,[3] and polybisbenzthiazoles.[4] Conjugated polymers have been the main focus of organic $\chi^{(3)}$ research because of the potential

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Table I. Quadratic Electrooptic Thin-Film Solid Solution $\chi^{(3)}{}_{1133}(-\omega,0,0,\omega)$ Results[28] Compared to Third Harmonic Generation (λ_0 = 1.064 μM) of PTS–PDA Solution, THG (λ_0 = 1.908 μm) of a β-Carotene Solution, and DFWM (λ_0 = 602 nm) of Hexathiophene[a]

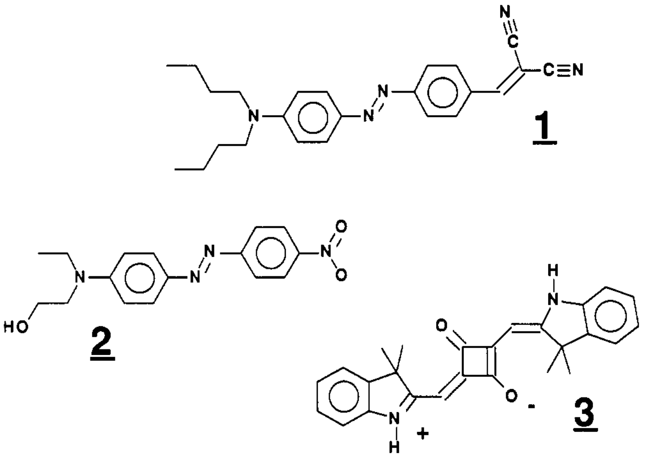
compd	wt %	λ_{max}, nm	$10^{14}\lvert\mathrm{Re}[\bar{\chi}^{(3)}]\rvert_{1133}$, esu	$10^{34}\lvert\mathrm{Re}[\bar{\gamma}]\rvert_{1133}$, cm^7/esu^2	$10^{34}\lvert\mathrm{Re}[\bar{\gamma}]\rvert_{1111}$, cm^7/esu^2
1	7.5	526[21]	40	29	(87)
2	7.5	491[21]	12	7.1	(21)
3	1.0	657.5[21]	13	68	(204)
PTS–PDA[1,26]	≈1.4	≈465	≈5[b]	(1.2)	3.6
β-carotene[33]		452		(37)	110
hexathiophene[29]		429		(33)	100

[a] The results in parentheses are those converted for the difference in isotropic average between QEO and the DFWM and THF processes (for THG or DFWM vs QEO: $\bar{\chi}^{(3)}{}_{1111}(-3\omega,\omega,\omega,\omega) = \bar{\chi}^{(3)}{}_{1111}(-\omega,\omega,-\omega,\omega) = 3\bar{\chi}^{(3)}{}_{1133}(-\omega,0,0,\omega)$). [b] $\lvert\bar{\chi}^{(3)}{}_{3\omega}\rvert_{1111}$. The corresponding QEO value ($\chi^{(3)}{}_{1133}$) would be ≈1.7×10^{-14} esu.

ease of fabrication of wave guides, and the highly oriented materials mentioned above permit access to a nonisotropic bulk $\chi^{(3)}$ component that is 5 times[5] larger than that from an isotropic solution of molecules. However, it is likely that isotropic, polarization-independent materials will be more useful for initial device fabrication, so the apparently large susceptibilities reported for oriented polymers may be less relevant. The polymeric materials mentioned above are also fairly intractable, though some progress has been made toward solubilization of polythiophene.[6] Also, experimentally derived molecular exciton lengths of 30–40 Å in polydiacetylene[7,8] suggest that extremely long conjugation lengths are not necessary to maximize the microscopic third-order nonlinear susceptibility, γ.

Early studies have focused on third-order nonlinearities of small molecules in nonviscous solutions. Nitrobenzene[9,10] and other[11-14] small molecules have been studied, both neat and in solution. Only recently has there been the use of viscous matrices such as glasses and polymers, primarily in an effort to eliminate orientational contributions.[15-18] Except for these few studies, third-order nonlinear properties of bulk materials made of solid-state solutions of discrete molecules are being largely ignored. Presented here are results that show that solid-state polymer solutions of discrete molecules could be very competitive with the isotropic third-order susceptibilities of conjugated polymers and could offer a most attractive avenue for easy materials optimization. Results are presented for the quadratic electrooptic process and compared to materials measured by other processes.

Scheme I



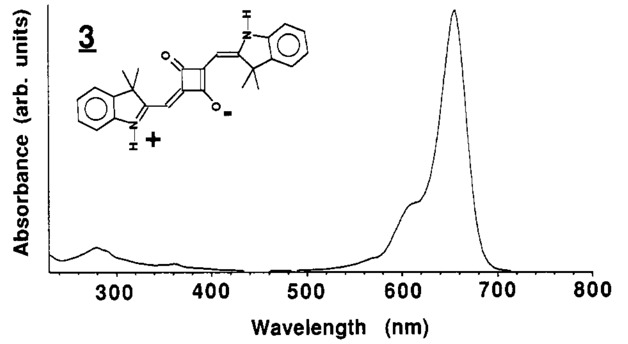


Figure 1. Electronic spectrum of 3 in methylene chloride solution.

Reported in Table I are the bulk and microscopic third-order nonlinear quadratic electrooptic[19-21] (QEO) susceptibilities for three dye–PMMA materials.[22,23] This QEO measurement has been shown to give the fast electronic contribution because of the polymer-impeded dye

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(5) Wagniere, G. *J. Chem. Phys.* **1982**, *76*, 473–480. The isotropic average of third-order nonlinear susceptibilities depends on which rotational invariant one is sampling. For THG, the rotational invariant is *xxxx*, and the isotropic average is given by $^1/_{15}[(\mathbf{P}\cdot\mathbf{E}_1)(\mathbf{E}_2\cdot\mathbf{E}_3) + (\mathbf{P}\cdot\mathbf{E}_2)(\mathbf{E}_1\cdot\mathbf{E}_3) + (\mathbf{P}\cdot\mathbf{E}_3)(\mathbf{E}_1\cdot\mathbf{E}_2)]$, where $\mathbf{E}_1$, $\mathbf{E}_2$, and $\mathbf{E}_3$ are the three optical vector fields, and $\mathbf{P}$ is the induced polarization vector. Expanding, collecting terms, and assuming a one-dimensionally anisotropic molecule yield $^1/_5 P_x E_{1x} E_{2x} E_{3x}$. For QEO, the rotational invariant being sampled is *xxyy* and the corresponding expression is $^1/_{30}[4(\mathbf{P}\cdot\mathbf{E}_1)(\mathbf{E}_2\cdot\mathbf{E}_3) - (\mathbf{P}\cdot\mathbf{E}_2)(\mathbf{E}_1\cdot\mathbf{E}_3) - (\mathbf{P}\cdot\mathbf{E}_3)(\mathbf{E}_1\cdot\mathbf{E}_2)]$. Expanding, collecting terms, and applying the one-dimensional molecule approximation yield $^1/_{15} P_x E_{1x} E_{2x} E_{3x}$. Thus, the QEO nonlinearity is 3 times smaller than for THG.

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(21) Note that the λ_{max}'s reported in the previous two references were not obtained directly from the dye–PMMA films. All spectral measurements reported here (except in Figure 1) were obtained directly from the dye–PMMA films. Also note that the refractive index used in ref 19 to calculate $\chi^{(3)}$ from the electrooptic coefficient, *s*, was 1.52 for molecule 2, while n = 1.50 was used for all data reported here.

(22) Compound 1 was prepared as previously reported: Schilling, M. L.; Katz, H. E.; Cox, D. I. *J. Org. Chem.* **1988**, *53*, 5538–5540. Compound 2 is available from Aldrich Chemical Co. and was purified by extracting into methanol, filtering, and reducing the filtrate. Compound 3 was prepared by reaction of squaric acid and 2,3,3-trimethylindolenine using a general procedure: Sprenger, H.-E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 553–554. The dye–PMMA films were spun from a 65:35 mixture of propylene glycol methyl ether acetate (PGMEA)–γ-butyrolactone onto ITO glass. Two such films were placed face-to-face and briefly heated above the T_g under compression to effect an optical contact. The electrooptic coefficient was measured in a Mach-Zehnder interferometer as described in ref 19. Compounds 1 and 2 were measured with a HeNe probe at 633 nm, while compound 3 was measured with a Kr$^+$ laser at 799 nm.

(23) Dirk, C. W.; Kuzyk, M. G. Manuscript to be submitted to *J. Chem. Phys.*

motion, as assayed by an EFISH orientation study.[24] The QEO susceptibility was further shown[19,20] to be comparable to third harmonic[18] results.

Structures of the molecules measured are shown in Scheme I.

These results[25] are compared to the third harmonic generation (THG) results of Kajzar and Messier on a solution of soluble PTS–polydiacetylene in DMF.[1,26] Considering the bulk results, given a fundamental wavelength λ_0 of 1.064 μm (ν_0 = 9398 cm^{-1}) for THG, PTS–PDA ($\lambda_{\max} \approx 465$ nm, $\nu_{\max} \approx 21\,500$ cm^{-1}) has a two-photon resonance at 18 800 cm^{-1} ($|\nu_{\max} - 2\nu_0| \approx 2700$ cm^{-1}), while a three-photon resonance is at 28 200 cm^{-1} ($|\nu_{\max} - 3\nu_0| \approx 6700$ cm^{-1}). These are relative only to the first excited state. For **1** ($|\nu_{\max} - \nu_0| \approx 3200$ cm^{-1}), **2** ($|\nu_{\max} - \nu_0| \approx 4570$ cm^{-1}), and **3** ($|\nu_{\max} - \nu_0| \approx 2700$ cm^{-1}), the difference between the QEO probe, ν_0, and the nearest excited-state frequency, $\nu_{\max}$, is no smaller than the closest THG multiphoton resonance with PTS–PDA. Thus, to a first approximation,[27] the resonance enhancements for **1**, **2**, and **3** will be roughly similar to that from Kajzar and Messier's PTS–PDA THG measurement. The isotropic average for the THG process is 3 times larger than for the QEO process ($[\bar{\chi}^{(3)}{}_{1111}]_{\mathrm{THG}} = 3[\bar{\chi}^{(3)}{}_{1133}]_{\mathrm{QEO}}$).[5] The PTS–PDA result[1] has been converted (Table I) to make it comparable to the QEO results presented here. Extrapolating their data to 100%, Kajzar and Messier[1] predict a bulk real isotropic susceptibility, Re $\bar{\chi}^{(3)}{}_{3\omega}$, of -800×10^{-14} esu (-270×10^{-14} esu when converted for the difference in isotropic averages between THG and QEO). It can be concluded that a QEO material comparable to PTS–PDA (in isotropic solution) could be made by making a more concentrated polymer solution of **3**. This bulk $\chi^{(3)}$ will still be smaller than the largest bulk $\chi^{(3)}$'s of $\approx 10\,000 \times 10^{-14}$ esu achieved in oriented conjugated polymers, but it would likely represent the largest isotropic value ever achieved on a solution of discrete molecules.

It should be noted that the microscopic QEO third-order nonlinearity, γ, of **3** is quite large.[28] Comparing this value to the degenerate four-wave mixing (DWFM) solution value for hexathiophene[29] and the THG solution value for β-carotene (Table I) shows that even though **3** has a much shorter conjugation length, it possesses a γ of very similar magnitude. The values of γ for hexathiophene and β-carotene are less enhanced[27] by dispersion (for β-carotene $|\nu_{\max} - 3\nu_0| \approx 6400$ cm^{-1}, for hexathiophene $|\nu_{\max} - \nu_0| \approx 6700$ cm^{-1}) than is the QEO γ for **3**, but the extremely narrow excitation of **3** (Figure 1) means that this susceptibility is undamped[30] and that the linear absorption will be quite low over a broad spectral region in the visible and near-IR regions. The linear absorptions for β-carotene[31] and hexathiophene[29] are considerably broader.

The comparisons of the QEO γ of **3** presented here suggest it to be among the largest third-order optical nonlinearities. However, this assessment comes from comparisons between compounds assayed by different third-order optical processes. Given that all of the nonlinearities are purely electronic, the nonlinearities still differ through dispersion. Also, as a consequence of dispersion, for different processes, two- and three-photon resonances can contribute to different extents, depending on the relative difference in energies between one- and two-photon states. These complications can make the strict comparisons of third-order nonlinearities measured from different processes somewhat tenuous.

At 1%, compound **3** is at its solubility limit in PMMA when spun from PGMEA–γ-butyrolactone. Concentrations of **3** as high as 17 wt % have recently been obtained when spun from solvents such as 1,2-dichloroethane or 1,1,2-trichloroethane, though the film surfaces are presently too poor (0.1–0.2-μm ripples in a 2–3-μm film) to permit a QEO measurement. Other very soluble squarylium dye derivatives are available,[32] and the alternative exists for chemically attaching the dye to the polymer backbone, thus permitting even higher dye concentrations. The dye concentration dependence of $\chi^{(3)}$ has been shown to be linear,[20] so, keeping in mind the above caveats about comparison of processes, a 20% solution of **3** should produce a QEO γ comparable in magnitude to a THG γ of 100% PTS–PDA used by Kajzar and Messier.

The squarylium moiety is particularly advantageous because, being a cyanine dye, it possesses intense isolated electronic absorptions (Figure 1), which will permit near-resonant use. Meredith et al. have shown that aza (=N—) replacement of methines (=CH—) in cyanine dyes can lead to significant improvements in the THG γ.[33] While most cyanine dyes will display poor solubility in polymers because of the need to dissolve a counterion as well as the cationic dye, the zwitterionic squarylium cyanines circumvent this. Bulky counterions will facilitate the cyanine dye solubility but also represent additional volume the dye could have occupied; thus, higher net concentrations should be achievable by using the squarylium moiety. Appropriate aza modification to the squarylium topology followed by chemical attachment to glassy polymers could produce materials comparable or perhaps superior to polydiacetylenes, at least with regard to the QEO process.

In conclusion, we report an unusually large third-order quadratic electrooptic nonlinearity for a squarylium dye molecule. At least with regard to the QEO process, it should be possible to prepare bulk QEO materials with large third-order nonlinearities. The predominantly electronic response from the QEO process[20,24] suggests that this material class could be useful for other third-order processes. The magnitude of the third-order nonlinearity of these materials, as supplied by other third-order processes, remains to be determined.

Acknowledgment. We would like to thank H. Ling and E. Chandross for careful reading of this paper.

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[27] This presumes consideration of only the first excited state and the simple approximation $1/(|\omega_{\max} - \omega|)^{-3}$, where ω is taken as ν_0, $2\nu_0$, or $3\nu_0$.

[28] QEO γ uncertainties are thought to be ±10–20% on the basis of the known experimental uncertainties (i.e., concentration, refractive indices, the measured electrooptic coefficient, etc.). This does not consider the relatively poorly quantified errors from orientational contributions, artifacts such as electrostriction, electrode attraction, and heating, etc. A detailed analysis of errors and other contributions to QEO are provided in ref 20.

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