Molecular and Macroscopic NLO Properties of Organic Polymers

H. T. MAN,* C. F. SHU, O. ALTHOFF, I. A. McCULLOCH, D. POLIS, and H. N. YOON

Hoechst Celanese Research Division, 86 Morris Avenue, Summit, New Jersey 07901

SYNOPSIS

Two classes of aryltrienes in which the conjugation was incorporated in six-membered rings have been developed. The microscopic nonlinear susceptibility, $\mu\beta$, the product of the dipole moment and the second-order nonlinear susceptibility, of these chromophores were measured using electric field-induced second harmonic generation (EFISH). The chromophores were then copolymerized as side-chain pendant groups in a methacrylate backbone copolymer with methyl methacrylate and their macroscopic electrooptic coefficients, r, were experimentally determined using a reflection technique after electric field poling of the polymers. When compared with 4,4'-N,N-dimethylaminonitrostibene (DANS), these molecules demonstrated electrooptic activities up to three times of DANS, when measured at 1.3 μm. By using a simple two-level free-gas model, the two sets of measurements corresponded closely at low poling fields. At high fields, the simple model breaks down as more detailed poling parameters are required to accurately describe the nonlinear poling effects. The results of the analysis of the high-field poling data will be published separately. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

For an organic molecule to possess large second-order nonlinear susceptibility, it must contain an electron donor and acceptor pair connected by a highly conjugated linkage.[1] Two-ring benzenoidal-type conjugated structures were some of the earliest polymers that showed promising electrooptic activities. One noted example is the 4,4'-N,N-dimethylaminonitrostilbene (DANS),[2] where the electron donor and acceptor groups are amine and nitrostilbene, respectively. One way to increase this nonlinearity is to increase the conjugation length of the linkage. However, for polyphenyl derivatives, the increase of the second-order nonlinear activity with length has been shown to level off rapidly when the number of aromatic rings contained in the molecule exceeds two.[3] This result can be explained by aromatic delocalization energy requirements and the planarity necessity for polarization between the donor and acceptor to be energetically favored.[4] In ad-

dition to increasing the length and planarity to increase conjugation, other studies have focused on bond alternation and aromaticity.[5,6]

For polyene derivatives, since the neutral and charge-separated states consist of similar π-systems of alternating single and double bonds, effective delocalization is realized. Computation studies revealed that the nonlinear activity of polyenes increases rapidly with an increasing number of ethenyl units up to 20, before saturation.[7] However, the simple polyenes suffer from the disadvantage that they can adopt several distinct conformations, especially at high temperatures, such as during some device fabrication steps, making them unsuitable for this kind of application. One way to improve the conformational stability is to incorporate conjugated double bonds into ring systems. In the present study, two classes of aryltrienes with the double bonds incorporated into a six-membered ring were developed that showed increased nonlinear optical (NLO) activity compared to DANS. Compound 2a, shown in Figure 1, is a phenyltriene derivative prepared by the Knoevenagel reaction, as described by Lemke.[8] In compound 2b, the phenyl group was replaced by a heterocyclic group, thiophene, to further reduce
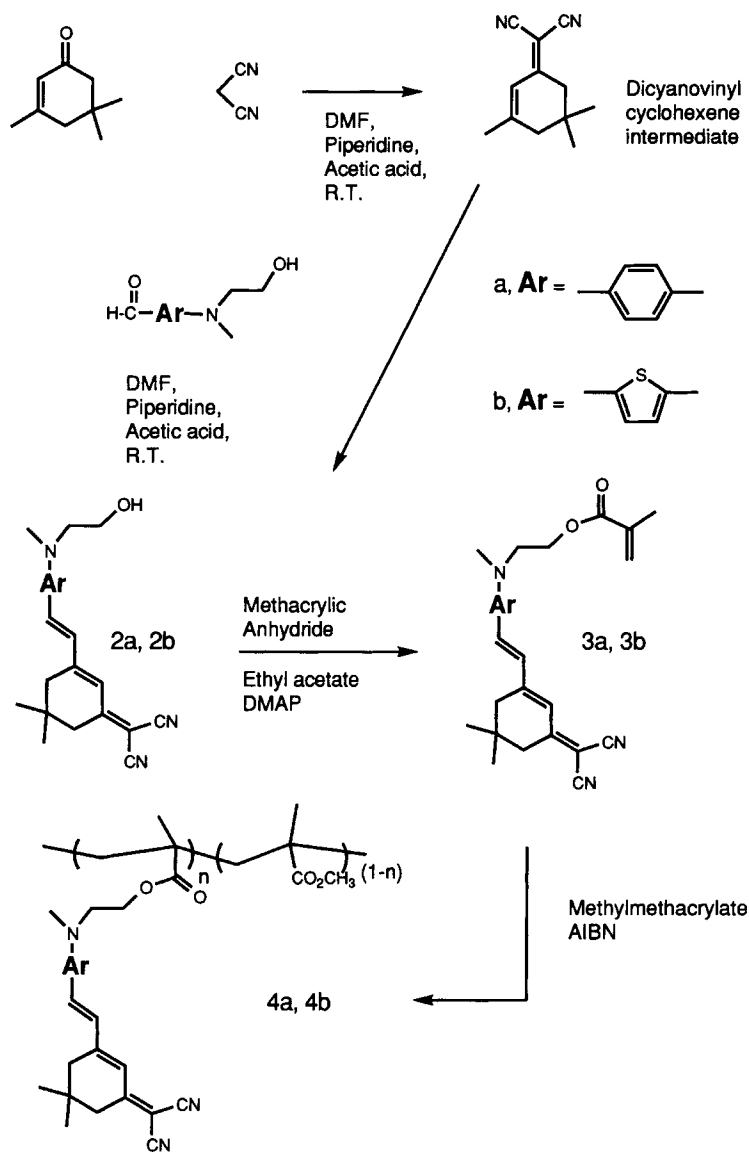

Figure 1   Synthetic scheme for the NLO molecules used in the present study.

the ground-state aromatic stabilization and, hence, to enhance the hyperpolarizability.[9] Also, the high acceptor strength of the dicyanovinyl group that, as an oxo-vinyl substituent of a six-membered ring, has been shown to be significantly more stable than isolated vinylic derivatives.[10,11]

Early studies on poled thin-film nonlinear optical polymers used mainly guest–host systems[12-15] in which the NLO chromophores were dispersed as a polymer solution in poly(methyl methacrylate) (PMMA). More recently, polyimide, which has a much higher glass transition temperature than that of PMMA, was used as the host to increase the poling stability.[16,17] Such guest–host systems, however,

suffer from a number of disadvantages including low chromophore density caused by phase separation at high concentration, opacity, and poor poling characteristics. A similar approach was to dissolve the NLO chromophores in an optically transparent thermosetting epoxy that can be simultaneously poled and cross-linked.[18,19] Due to the increased effective T_g of the cross-linked structure, the stability of these systems is subsequently increased.

Other approaches to prepare stable, highly active NLO polymers utilize chemical bonding of the NLO moieties directly into the polymer matrix. This include incorporating the NLO chromophores in the main chain itself,[20] but, more significantly, attaching

the NLO moieties as side chains on a polymer backbone[2] not only increases the NLO chromophore concentration, but also prevents phase separation as one end of the moiety is permanently bonded to the backbone. Further, by using appropriate spacer groups between the side chain and backbone, sufficient mobility is provided to respond to electrical poling.

In the present study, the microscopic NLO activity of two classes of dicyanovinyl aryltrienes and the DANS molecule were characterized. The quantity, $\mu\beta$, which is the product of the ground-state dipole moment, μ, and the molecular second-order hyperpolarizability, β, of the chromophores, were measured for all three molecules using electric field-induced second harmonic generation (EFISH).[21] The chromophores were then copolymerized as side-chain pendant groups in a methacrylate backbone copolymer with MMA in a 50/50 mol ratio resulting in isotropic polymers with glass transition temperatures (T_g) of above 140°C. These polymers were fabricated into thin films and electrically poled and their macroscopic electrooptic coefficients along the poling direction, r_{33}, measured using a simple reflection technique[22] at 1.3 μm wavelength.

EXPERIMENTAL

Synthesis

Figure 1 illustrates the synthetic scheme for polymers **4a** and **4b**. The DANS polymer was synthesized as reported.[2] Compound **1a**, 4-N-(2-hydroxyethyl)-N-methylaminobenzaldehyde was purchased from Riedel de Haan. Compound **1b**, 5-N-(2-hydroxyethyl)-N-methyl amino-2-thiophenecarboxaldehyde, was prepared by reaction of 5-bromo-2-thiophenecarboxaldehyde with hydroxyethyl methylamine.[23]

The "hexatriene" alcohols were synthesized by a two-step knoevenagel condensation first to form the dicyanovinyl cyclohexene derivative and, second, this intermediate with compounds **1a** or **1b** to form **2a** and **2b**, respectively. The cyclohexene intermediate was synthesized from isophorone and malonitrile in DMF with a catalytic amount of piperidine in acetic acid at room temperature. On recrystallization from isopropanol/water, the material is quite pure (> 99.8 in some cases).

The alcohols were synthesized under the same conditions as was the cyclohexene derivative being recrystallized from isopropanol/water to give materials of purity > 97%. The methacrylates were synthesized by direct reaction of the alcohols with methacrylic anhydride in ethyl acetate containing triethylamine and a catalytic amount of dMAP. Yields were typically high (95%+ with purity identical to the starting alcohol). Polymerization-grade monomer was obtained by column chromatography on a silica gel using methylene chloride eluant. Copolymers **4a** and **4b** were prepared by free-radical polymerization of the methacrylate with AIBN as described previously.[24]

EFISH

At the fundamental wavelength of 1600 nm, the second harmonic signal generated was sufficiently away from the optical absorption of the polymers that resonant enhancement complications were minimized. The optical design of the experimental setup is shown in Figure 2. A tunable pulsed dye laser, pumped by a injection-seeded YAG laser, was used to produce 639 nm wavelength, which was then combined with the doubled YAG from the dye laser pump source at 532 nm in a parametric mixer to generate the 1600 nm pulses.

The molecules studied were dissolved in a suitable solvent and placed between two glass windows aligned at a slight angle to produce Maker fringes[25,26] upon translation. This assembly was placed between two stainless-steel electrodes, through which an electric field was supplied by a high-voltage pulse generator to align the molecules in a perpendicular direction to the optical beam. The second harmonic generated at 650 nm was detected by photomultiplier tubes and boxcar-averaged. The ratio of this signal over a concurrent reference measurement on a quartz plate was measured to minimize laser power fluctuations. All measurements were calibrated using published quartz values. To take into account the local field effects and interactions, measurements on each sample were repeated through a range of concentrations and extrapolated to infinite dilution[27] to obtain the molecular hyperpolarizability. The Onsager[28] model for the local field correction was used in the analysis of the measured data.

Poling

The characterization of the macroscopic electrooptic properties of glassy polymers require that they be electrically poled to induce asymmetry, a property that is required by the third-order tensorial properties of the second-order NLO response. The procedure for electric poling of NLO polymers using fixed electrodes has been previously described[29] and

Nd:YAG   SEED LASER

S H G   0.532 μm   DYE LASER   0.639 μm

1.06 μm

Parametric Mixer

QUARTZ REFERENCE   FILTER 1.6 μm

P M T   MONOCHR.   1.6 μm

P M T   MONOCHR.   1.6 μm

BOXCAR   MOTION CONTROL   H V   SAMPLE CELL
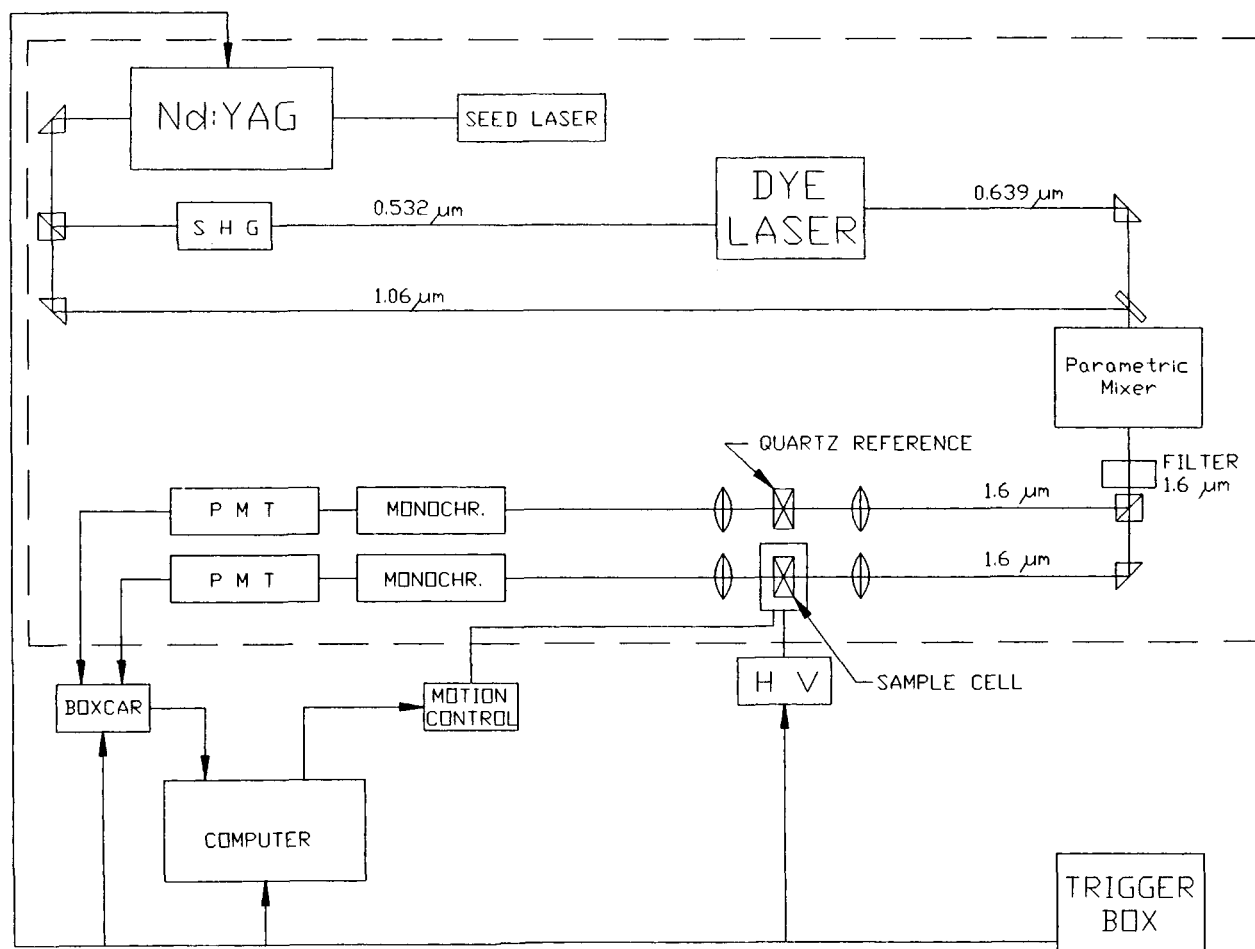
COMPUTER

TRIGGER BOX

Figure 2   Schematic representation of the apparatus for the EFISH experiment.

summarized as follows: The polymer, dissolved in a suitable solvent, was first spin-coated onto an indium–tin–oxide (ITO)-coated glass slide and dried at above the glass transition temperature. The resulting thickness of the films were of the order of a few microns. The ITO glass served as one of the two electrodes for poling; the other was in the form of a thermally deposited gold layer of approximately 0.15 μm on top of the polymer film. The poling procedure involved heating the sample to close to the T_g when a poling field was applied across the electrodes for a period of time sufficient for alignment equilibrium to be reached. The waveform characteristics of the poling and relaxation of poling depend on many intrinsic and extrinsic factors that include orientation mechanisms, NLO chromophore concentration, molecular weight, method of chromophore incorporation, and poling field strength.[30] The time taken for equilibrium to be attained is particularly sensitive to the poling temperature. In situ poling experiments on a number of similar side-chain copolymers[29] revealed that poling equilibrium occurred after about 1 min at the DSC determined T_g. The time used in the present poling procedure was typically 5 min. Additional poling times were used to confirm that no noticeable increase in electrooptic coefficient were observed. The sample was then cooled to room temperature before removing the electrical field, thus locking in the alignment. The time taken to cool down to room temperature typically took 30 min.

Electrooptic Characterization

The electrooptic coefficient of the poled film was measured at 1.3 μm wavelength using a simple reflection technique.[22] Figure 3 depicts the experimental setup. A laser beam is incident on the back of the glass substrate at an angle θ. It propagates through the substrate, the ITO layer, and the polymer and is back-reflected at the top gold electrode. The polarization of the input beam is at 45° to the
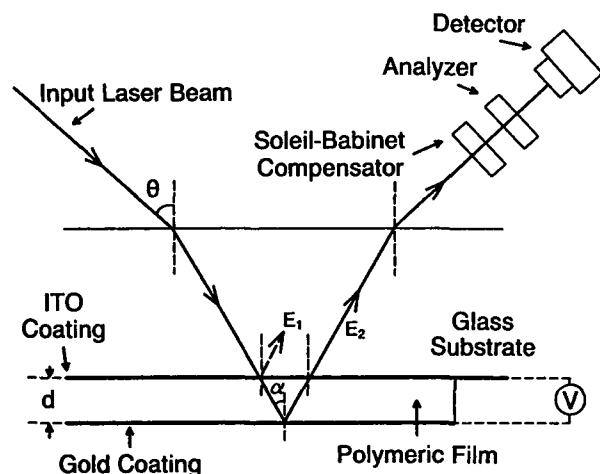
Figure 3 Optical configuration for r measurement by the reflection technique.

plane of incidence so that the parallel (p-wave) and perpendicular (s-wave) components of the optical field are equal in amplitude. The reflected beam propagates through a Soleil-Babinet compensator and an analyzer. When a modulating voltage, V_m, is applied across the electrodes, the phase angles of the s- and p-waves are retarded, to different degrees, by the electrooptically induced refractive index change. This results in a modulation of the polarization in the reflected beam and is converted into intensity modulation of the laser beam by the output analyzer. This modulation is measured using a photodiode through a lock-in amplifier. By measuring this intensity and the use of the approximations $n_e \cong n_0 \cong n$, where n_e and n_0 are the refractive indices, respectively, along and perpendicular to the poling direction, and $r_{33} = 3r_{31}$, where r is the electrooptic tensor and subscripts 3 and 1 represent directions, respectively, perpendicular and parallel to the film, the electrooptic coefficient can be obtained by the following expression:

$$ r_{33} = \frac{3\lambda I_m \sqrt{(n^2 - \sin 2\theta)}}{4\pi V_m I_c n^2 \sin 2\theta} \quad (1) $$

where I_m is the amplitude of the modulation, and I_c, the dc intensity of the output beam.

RESULTS AND DISCUSSION

The results of the EFISH measurements are summarized in Table I. Meaningful comparisons at a single frequency between molecules with different absorption peaks require resonant enhancement ef-

fects to be minimized because it greatly affects the measured value. The $\mu\beta$ value at 1.3 μm is calculated by approximating that β arises largely from terms involving the first excited state.[1] When the molecular susceptibility, β, is dominated by the change in the dipole moment between the ground and the first excited electronic states along the molecular x-axis,[1]

$$ \beta_{xxx}(-2\omega; \omega, \omega) $$
$$ = \frac{e^3 |\mu_{01}|^2 (\mu_{11} - \mu_{00})}{\hbar^2} \frac{3\omega_0^2}{(\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)} \quad (2) $$

where μ_{01} is the transition moment between the ground and excited states; μ_{00}, and μ_{11}, ground- and excited-state dipole moments, respectively; and $\hbar\omega_0$, the first excited-state energy.

The expected values of the macroscopic electrooptic coefficient, r, from the poled polymeric films of the corresponding copolymers at 1.3 μm, can be deduced from the measured microscopic β values by taking the Boltzmann average of the molecular polarization[31]:

$$ r = \frac{2}{n^2 \varepsilon} N\beta \left(\frac{\varepsilon(n^2 + 2)}{(n^2 + 2\varepsilon)} \right) \left(\frac{n^2 + 2}{3} \right)^2 \left\{ \frac{p}{5} - \frac{p^3}{105} \right\} $$
$$ p = \frac{\varepsilon_p (n^2 + 2)}{(n^2 + 2\varepsilon)} \frac{\mu E_p}{kT} \quad (3) $$

where N is the number density of molecules; ε, the static dielectric constant; ε_p, the dielectric constant at the poling temperature; n, the index of refraction; E_p, the poling field; μ, the molecular dipole moment; and kT, the Boltzmann constant.

Figure 4 shows the measured r constant for the three polymers as a function of poling fields for up to 100 V/μm, although measurements as high as

Table I   Results of EFISH Measurements

Chromophore	DANS	**2a**	**2b**
Absorption peak	450 nm	518 nm	550 nm
Solvent	DMSO	DMSO	Dioxane
$\mu\beta$ (1600 nm)			
($\times 10t^{-48}$ esu)	610	1410	1940

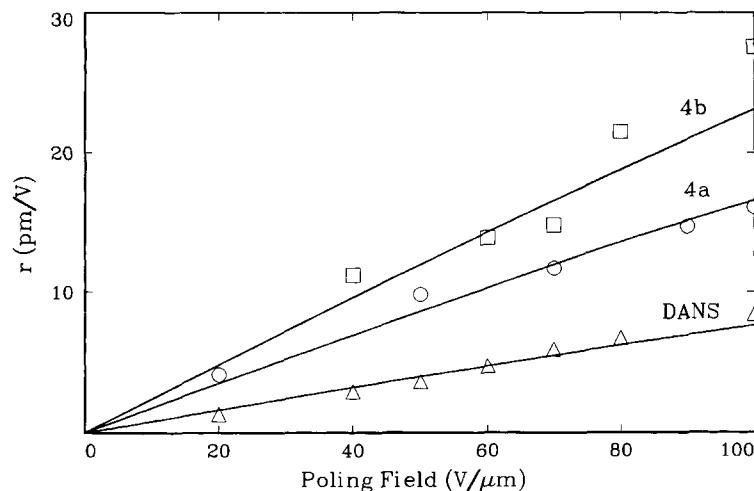| Polymer	DANS	**4a**	**4b**
T_g (°C)	135	148	153
n	1.630	1.668	1.716

Electrooptic Activity of NLO Polymers
vs. Poling Field

Figure 4 Electrooptic activity vs. poling field.

200 V/μm were also collected (see below). The lines represent the r values theoretically calculated by eq. (3) using β values from Table I. At these low fields, the correlation between the measured and calculated values is remarkably accurate considering the simplicity of the models used.

At higher fields, however, the experimental data, not shown here, deviates from the theoretical curve if the above analysis is used. Field-induced liquid crystalline formation has been put forward to explain this discrepancy.[32] This theory predicts that a field-induced phase transition to the nematic phase for isotropic materials occurs when a strong electric field is applied to a side-chain polymer with π-conjugated acceptor–donor molecules as pendant groups. This subsequently leads to enhancement in the polar order and thus to a larger nonlinear susceptibility than is predicted by the simpler isotropic model. The use of the relation of $r_{33}/r_{31} = 3$ in eq. (1) also requires modification for higher fields. It has been previously observed that from experimentally measured values of the SHG coefficient, d_{ij}, for poled NLO polymer films, this ratio often exceeded the theoretical value of 3,[33,34] although this deviation is not yet well established because of the low accuracy of these measurements. A simple model was also suggested[35] to explain the observation of $r_{33}/r_{31} > 3$ in epoxy copolymer planar waveguides, although theoretical understanding of experimental results from the high-field poling of side-chain NLO polymers has yet to be published.

CONCLUSIONS

Two classes of aryltrienes in which isolated double-bond problems associated with different molecular conformations is solved by incorporating the conjugation into six-membered rings have been developed. These molecules showed up to three times the electrooptic activity of DANS, measured at 1.3 μm. The microscopic nonlinear susceptibility, $\mu\beta$, of all three chromophores, and the macroscopic electrooptic coefficients, r, of their corresponding side-chain copolymers with MMA, were experimentally determined using, respectively, EFISH and the reflection technique. By using a simple two-level free-gas model, the two sets of measurements corresponded remarkably well at low poling fields. At high fields, however, the simple model breaks down as more detailed poling parameters are required to more accurately describe the effect of poling. The results of the analysis of the high-field poling data will be published separately.

REFERENCES

1. D. S. Chemla and J. Zyss, Eds., *Nonlinear Optical Properties of Organic Molecules and Crysatals*, Academic Press, New York, 1987.
2. R. DeMartino and H. Yoon, U.S. Pat. 4,808,332 (1989).
3. L. T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman,

G. Rikken, and C. W. Spangler, *J. Phys. Chem.,* **95,** 10643 (1991).

4. S. R. Marder, D. N. Beratan, and L. T. Cheng, *Science,* **252,** 103 (1991).
5. K. Y. Wong, A. K. Y. Jen, V. P. Rao, K. Drost, and R. M. Mininni, *SPIE Symp. Proc.* **1775,** 74 (1993).
6. S. Marder, J. Perry, B. Tiemann, C. Gorman, S. Gilmour, S. Biddle, and G. Bourhill, *J. Am. Chem. Soc.,* **115,** 2524 (1993).
7. J. O. Morley, V. J. Docherty, and D. Pugh, *J. Chem. Soc. Perkin Trans. II,* 1351 (1987).
8. R. Lemke, *Synthesis,* 359 (1974).
9. C. W. Dirk, H. E. Katz, and M. L. Schilling, *Chem. Mater.,* **2,** 700 (1990).
10. M. L. Schilling, H. E. Katz, and D. I. Cox, *J. Org. Chem.,* **53,** 5538 (1988).
11. H. E. Katz, M. P. Bohrer, D. A. Mixon, J. Alonzo, J. Markham, J. E. Sohn, and D. I. Cox, *J. Appl. Polym. Sci.,* **40,** 1711 (1990).
12. K. D. Singer, J. E. Sohn, and S. L. Lalama, *Appl. Phys. Lett.,* **49,** 248 (1986).
13. G. R. Meridith, J. G. Van Dusen, and D. J. Williams, *Macromolecules,* **15,** 1385 (1988).
14. C. H. L. Hampsch, Y. Yang, G. K. Wong, and T. K. Torkelson, *Macromolecules,* **21,** 526 (1988).
15. H. E. Katz, C. W. Dirk, M. L. Schilling, K. D. Singer, and J. E. Sohn, *Mater. Res. Soc. Symp. Proc.,* **109,** 127 (1988).
16. J. W. Wu, J. F. Valley, S. Ermer, E. S. Binkley, J. T. Kenney, G. F. Lipscomb, and R. Lytel, *Appl. Phys. Lett.,* **58,** 225 (1991).
17. K. Y. Wong and A. K-Y. Jen, *J. Appl. Phys.,* **75,** 3308 (1994).
18. M. A. Hubbard, T. J. Marks, J. Yang, and G. K. Wong, *Chem. Mater.,* **1,** 167 (1989).
19. M. Eich, B. Reck, D. Y. Yoon, C. G. Willson, and G. C. Bjorklund, *J. Appl. Phys.,* **66,** 2141 (1989).
20. W. Kohler, D. R. Robello, P. T. Dao, C. S. Willand, and D. J. Williams, *J. Chem. Phys.,* **93,** 9157 (1990).
21. C. G. Bethea, *Appl. Opt.,* **1447,** 14 (1975).
22. C. C. Teng and H. T. Man, *Appl. Phys. Lett.,* **56,** 1734 (1989).
23. F. A. Mikhailenko and L. I. Shevchuk, *Chem. Heterocycl. Compd.* (English Translation), **10,** 1151 (1974).
24. T. M. Leslie, C. F. Shu, K. Blatter, R. DeMartino, and F. Battito, U.S. Pat. 5,187,234 (1993).
25. P. D. Maker, R. W. Terhune, M. Nisenoff, and C. M. Savage, *Phys. Rev. Lett.,* **8,** 21 (1962).
26. J. Jerphagnon and S. K. Kurtz, *J. Appl. Phys.,* **41,** 1667 (1970).
27. K. D. Singer and A. F. Garito, *J. Chem. Phys.,* **75,** 3572 (1981).
28. L. Onsager, *J. Am. Chem. Soc.,* **58,** 1456 (1936).
29. H. T. Man and H. N. Yoon, *Adv. Mater.,* **4,** 159 (1992).
30. C. L. Hoffman, H. T. Man, and G. G. Fuller, *Acta Polym.,* **44,** 39 (1993).
31. K. D. Singer, M. G. Kuzyk, and J. E. Sohn, *J. Opt. Soc. Am.,* **B4,** 968 (1987).
32. C. P. J. M. van der Vorst and S. J. Picken, *J. Opt. Soc. Am.,* **B7,** 320 (1990).
33. E. Eich, R. Reck, D. Y. Yoon, C. G. Wilson, and G. C. Bjorklund, *J. Appl. Phys.,* **66,** 3241 (1989).
34. E. Eich, G. C. Bjorklund, and D. Y. Yoon, *Polym. Adv. Technol.,* **1,** 189 (1990).
35. S. Herminghaus, B. A. Smith, and J. D. Swalen, *J. Opt. Soc. Am.,* **B8,** 2311 (1991).