Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Rational Design and Construction of Polymers with Large Second-Order Optical Nonlinearities. Synthetic Strategies for Enhanced Chromophore Number Densities and Frequency Doubling Temporal Stabilities

D.-R. Dai [a b], M. A. Hubbard [a b], J. Park [a b], T. J. Marks [a b], J. Wang [a b] & G. K. Wong [a b]

[a] Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, IL, 60208

[b] Department of Physics and the Materials Research Center, Northwestern University, Evanston, IL, 60208

Version of record first published: 22 Sep 2006.

To cite this article: D.-R. Dai , M. A. Hubbard , J. Park , T. J. Marks , J. Wang & G. K. Wong (1990): Rational Design and Construction of Polymers with Large Second-Order Optical Nonlinearities. Synthetic Strategies for Enhanced Chromophore Number Densities and Frequency Doubling Temporal Stabilities, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 189:1, 93-106

To link to this article: http://dx.doi.org/10.1080/00268949008037225

Mol. Cryst. Liq. Cryst., 1990, Vol. 189, pp. 93–106
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Rational Design and Construction of Polymers with Large Second-Order Optical Nonlinearities. Synthetic Strategies for Enhanced Chromophore Number Densities and Frequency Doubling Temporal Stabilities

D.-R. DAI, M. A. HUBBARD, J. PARK and T. J. MARKS†

Department of Chemistry and the Materials Research Center

and

J. WANG and G. K. WONG†

Department of Physics and the Materials Research Center, Northwestern University, Evanston, IL 60208

(*Received February 19, 1990*)

The performance characteristics of poled polymeric second harmonic generation materials are crucially dependent upon achieving high number densities of constituent chromophore entities and on maintaining poling-induced microstructural acentricity. This article reviews recent progress toward these goals. Systems discussed include chromophore-functionalized polyphenylene ether macromolecules with second harmonic coefficients (d_{33}) as high as 65×10^{-9} esu, $T_g \approx 173°C$, and with superior temporal stability of poling-induced chromophore orientation. Also discussed are strategies for simultaneously poling and diepoxide cross-linking chromophore-functionalized poly(*p*-hydroxystyrene). The result is a significant improvement in the temporal stability of chromophore orientation. Finally, two approaches to chromophore immobilization are presented which involve highly cross-linkable epoxy matrices. In the first, chromophore molecules are embedded in a matrix which is simultaneously poled and thermally cured. In the second, a functionalized high-β chromophore is synthesized for use as a cross-linking matrix component.

INTRODUCTION

Amorphous polymers in which molecular chromophore constituents have been aligned with a strong electric field (poled) represent a promising approach to

materials with large second-order optical nonlinearities.[1] Such materials combine the processability, mechanical strength, and typically excellent transparency characteristics of glassy organic polymers with the almost infinite molecular tailorability and high non-resonant nonlinearities of organic π-electron nonlinear optical (NLO) chromophores. The poling achieves acentricity of the chromophore/polymer microstructure in a way that can be adjusted with the magnitude of the electric field and which is not dependent upon the capricious packing forces of crystal lattices. Nevertheless, substantial barriers remain to be surmounted before optimum materials will be available.

For a non-interacting ensemble of NLO chromophores under the influence of an electric field, simple molecular gas theoretical models (equations (1), (2))[2] argue that the frequency doubling efficiency, as expressed by the second harmonic coefficient d_{33}, will be linearly dependent on the chromophore number density

$$d_{33} = -\tfrac{1}{2}Nf^{2\omega}f^{\omega}f^{\omega}\beta_{zzz}L_3(p) \tag{1}$$

$$p = \frac{f^{\circ}\mu E_p}{kT} \tag{2}$$

(N) and the molecular second-order nonlinearity quantized in the dipole moment direction (β_{zzz}). Under most conditions, d_{33} will also be linearly dependent upon the chromophore dipole moment (μ) and the magnitude of the poling field (E_p). In equations (1) and (2), the f's are local field factors and L_3 is the third-order Langevin function. Early chromophore-polymer materials based upon "doping" NLO chromophores into glassy polymer matrices[2] suffered from the low chromophore number densities that could be achieved before phase separation[3] occurred. In addition, poled glassy polymers are not at thermodynamic equilibrium, and the physical aging/structural relaxation processes that such systems undergo[4] leads to randomization of poling-induced preferential chromophore orientation. For the chromophore-doped materials, relaxation is rapid and second harmonic generation (SHG) efficiency is generally rather short-lived.[5] A first step toward ameliorating such effects has been to covalently bind NLO chromophores to selected polymer carriers.[6-9] Initial work in this Laboratory[6] focussed upon functionalized polystyrene and poly(*p*-hydroxystyrene) systems (Figure 1). These materials provide greatly enhanced chromophore number densities, greater SHG temporal stability (the tethering chromophore molecules to massive polymer chains greatly restricts reorientational mobility), improved stability with respect to contact poling-induced dielectric breakdown (presumably a consequence of the restricted microstructural mobility), and enhanced chemical stability (chromophore molecules are more strongly bound within the matrix).[6,7] It was found that contact poling fields as large as 1.8 MV/cm and d_{33} values as high as 19×10^{-9} esu (greater than the corresponding coefficient for $LiNbO_3$[10]) could be achieved.[6b] Considerably enhanced SHG temporal stabilities were also observed.[6,7]

With these results as a background, the purpose of the present article is to summarize recent efforts in this Laboratory to achieve even higher chromophore number densities and greater chromophore immobilization subsequent to electric

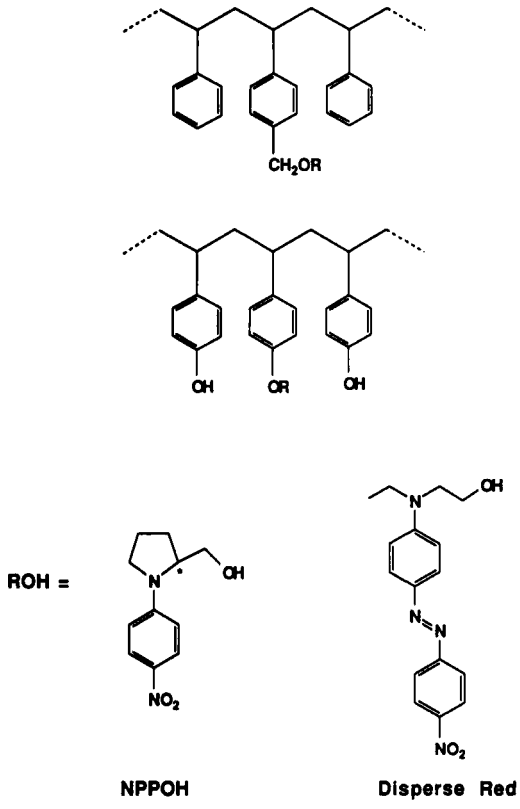


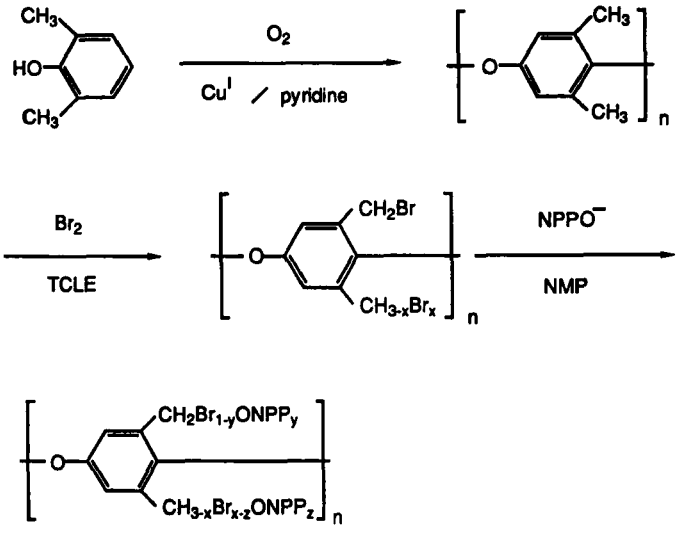
FIGURE 1 Structures of NLO chromophore-functionalized polystyrene and poly(*p*-hydroxystyrene) macromolecules.

field poling. We first describe a macromolecular material with greater than one chromophore moiety per polymer repeat unit and with a very high glass transition temperature (T_g—one index of polymer chain mobility).[11] We then describe two approaches to chromophore immobilization in which thermal cross-linking chemistry is effected in concert with electric field poling. In two cases, we also compare contact to corona poling methodologies and results. The latter technique offers larger (but not precisely known) electric poling fields as well as far greater resistance to dielectric breakdown.[8,12]

POLYPHENYLENE ETHER-BASED FREQUENCY DOUBLING POLYMERS

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a high-strength, amorphous engineering thermoplastic with $T_g \approx 205–210°C$ and good film-forming characteristics.[13] For the present experiments, PPO was prepared by oxidative coupling of 2,6-dimethylphenol and was purified as described elsewhere[14] (Scheme I; M_n = 27,000). Bromination[15] in refluxing tetrachlorethane affords materials (PPO-Br_x) with functionalization levels on the order of 1.6–1.8 Br/repeat unit (predominantly

SCHEME I



methyl bromination) as ascertained by elemental analysis and 400 MHz ^{1}H NMR. N-(4-nitrophenyl)-S-prolinoxy (NPPO-, Figure 1) was chosen as a model chromophore substituent since the optical properties of NPPOH have been extensively characterized[15] and since it is readily amenable to $\lambda = 1.064$ μm NLO experiments. Reaction of PPO-Br_x with $NPPO^-$ (from NPPOH + NaH) in dry N-methylpyrrolidone (NMP) affords the chromophore-functionalized polymer (PPO-NPP_x; Scheme I; 1.4 - 1.6 NPPO/repeat unit; $T_g \approx 173$°C) after precipitation with acetone, washing with H_2O, Soxhlet extraction with MeOH, and vacuum drying. Polymer films were cast onto ITO-coated conductive glass from triply-filtered NMP solutions in a class 100 laminar-flow clean hood. The solvent was then slowly evaporated at 80°C, and the resulting films dried *in vacuo* at 150–170°C for 24 h. These PPO-NPP films have excellent transparency characteristics (*vide infra*; $\lambda_{max} = 405$ nm as a film; 405 nm as a solution in NMP), adhere tenaciously to glass, and are impervious to most organic solvents.

Contact poling of the PPO-NPP films was carried out at 160–170°C with 1.2 MV/cm fields using aluminum electrodes and techniques described previously.[6] After cooling the film to 300 K, the field was maintained for an additional 1.5 h. Corona poling was carried out at 180–190°C (30 min) using a needle-to-film distance of 1.0 cm and a +4 kV potential. After the film had cooled to room temperature, the field was maintained for an additional 1.5 h. Second harmonic data were acquired at 1.064 μm in the p-polarized geometry using the instrumentation and calibration techniques described previously.[6] Second harmonic coefficients (d_{33} values) were calculated from the angular dependence of the second harmonic intensity and the equations of Jerphagnon and Kurtz for uniaxial materials, assuming additionally that $d_{31} = d_{24} = d_{15} = d_{33}/3$.[17] We have previously verified this latter assumption for other poled, chromophore-functionalized polymers.[7a]

In Table I are set out compositional and d_{33} data for representative PPO-NPP films. Assuming approximate additivity of PPO and NPPOH densities, it can be seen that the present chromophore number densities are substantial compared to typical guest-host NLO materials ($N \lesssim 2 \times 10^{20}/cm^3$) and to many chromophore-functionalized polymers (ca. 8-15 $\times$ $10^{20}/cm^3$).[6-8] For comparative purposes, note that the corresponding N value for crystalline NPPOH is 37 $\times$ $10^{20}/cm^3$.[16a] In regard to SHG efficiency, the present d_{33} values are also rather large, with the corona-poled datum of 65 $\times$ 10^{-9} esu comparing favorably with the largest values reported to date for any poled chromophore/polymer system.[6-8] A slight but reproducible decline in d_{33} on increasing the chromophore functionalization level from 1.4 to 1.6 is also observed. This may well reflect unfavorable chromophore aggregation effects, although these are not obvious in uv-visible spectra. In viewing the present d_{33} data, note also that $\mu_z\beta_{zzz}$ for NPPOH, 300 $\times$ 10^{-30} cm^5D/esu at λ = 1.064 μm,[16b] is relatively small. Considerably larger d_{33} values may be achievable with PPO and substituent chromophores having higher $\mu\beta$ values (e.g., $\mu_z\beta_{zzz}$ = 1090 $\times$ 10^{-30} cm^5D/esu for Disperse Red 1 at λ = 1.356 μm[18]).

The temporal characteristics of contact-poled and corona-poled PPO-NPP_x NLO properties are illustrated in Figures 2A and 2B, respectively. As has been noted previously for other chromophore-functionalized NLO polymers,[5] the present $d_{33}(t)$ data cannot be fit to a single exponential. This suggests that greater than one rate process is operative (e.g., different reorientation rates in matrix regions having free volume greater than or less than a certain threshold value[4c]). More satisfactory fits of the present $d_{33}(t)$ data are found for a phenomenological biexponential expression (equation (3)), and derived τ_1, τ_2 values are given in Table I. The τ_2 for the contact-poled PPO-NPP_x film appears to be the largest value

$$d_{33} = Ae^{-t/\tau_1} + Be^{-t/\tau_2} \quad (3)$$

reported to date and corresponds to a degradation in d_{33}, after the initial, rapid decay, of less than 10% of 50 days (Figure 2a). Such decay processes are expected to be additionally moderated in systems with hydrogen bonding, cross-linking (*vide infra*), and more massive chromophores. We reported elsewhere that poled (PS)O-NPP film τ_1 and τ_2 values are significantly reduced as contact poling fields are

TABLE I

Second-Harmonic Coefficients and Temporal Stability Data for NPP-Functionalized Poly(2,6-Dimethyl-1,4-Phenylene Oxide).

Functionalization Level[a]	NPPO Number Density, $10^{20}/cm^3$	Poling Method	d_{33} 10^{-9} esu[b]	r_1 days[c]	r_2 days[d]
1.4	~22	Contact	13	0.9	412
1.4	~22	Corona	65	0.3	39
1.6	~26	Corona	55		

[a]NPPO groups per PPO repeat unit.
[b]At λ = 1.064 μm; measured at 25°C within 0.5 h of poling.
[c]Short-term SHG decay constant from a least-squares fit to Equation (3). Data taken at 25°C.
[d]Long-term SHG decay constant from a least-squares fit to Equation (3). Data taken at 25°C.

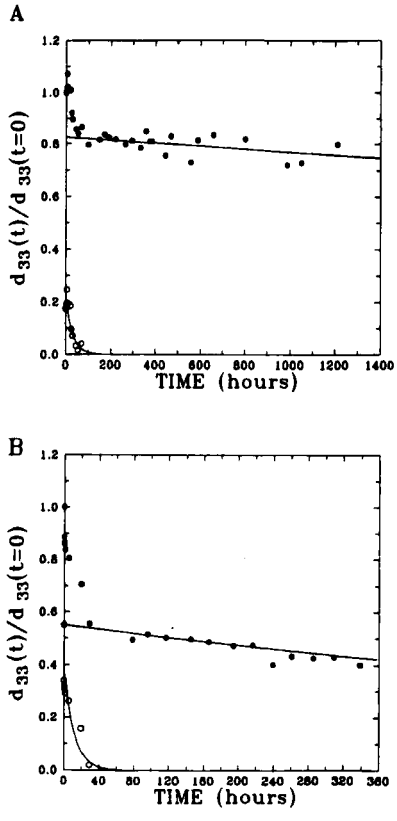
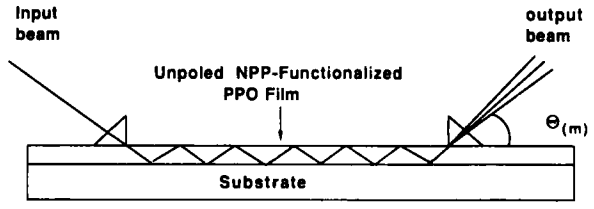


FIGURE 2 (A) Temporal characteristics of the second harmonic coefficient of a PPO-NPP film (1.4 NPP moieties per repeat unit) contact-poled at 1.2 MV/cm. Decay data taken at 25°C. The solid lines show the two exponential components of the least-squares fit to equation (3). (B) Temporal characteristics of the second harmonic coefficient of a corona-poled PPO-NPP film (1.4 NPP moieties per repeat unit). Decay data taken at 25°C. The solid lines show the two exponential components of the least-squares fit to equation (3).

increased,[7a] i.e., the system is driven further from thermodynamic equilibrium. The present $d_{33}(t)$ data for the corona-poled film are in accord with this trend (Figure 2B) in that both τ_1 and τ_2 are significantly diminished when higher poling fields are used.

Preliminary waveguiding experiments have been performed on several PPO-NPP films to better define their optical properties. A planar waveguide configuration consisting of air/film/glass layers was used (Figure 3). The waveguide modes were excited with a He-Ne laser (0.633 μm) using prism coupling techniques with SF6 glass (n = 1.797) prisms as couplers. The refractive index of the films was determined from the coupling angles of the various waveguide modes using standard procedures.[19] For a 1.4 μm thick, unpoled PPO-NPP film (1.4 NPP functionalization level), two TE modes are observed. The coupling angles for these modes (TE_0 and TE_1) are measured to be 29.6° and 25.1°, respectively. From these angles, a refractive index of 1.584 ± 0.001 is then calculated. The refractive index of a

WAVEGUIDE FABRICATION WITH CHROMOPHORE-FUNCTIONALIZED POLYMERS



$$2kn_F d\cos\Theta_{INT} - 2\Phi_{AIR} - 2\Phi_{SUB} = 2m\Pi$$

$$d = 1.40 \text{ microns}$$

$$\Theta_{(0)} = 29.62 \qquad n_F = 1.5844$$
$$\Theta_{(1)} = 25.07 \qquad n_F = 1.5847$$

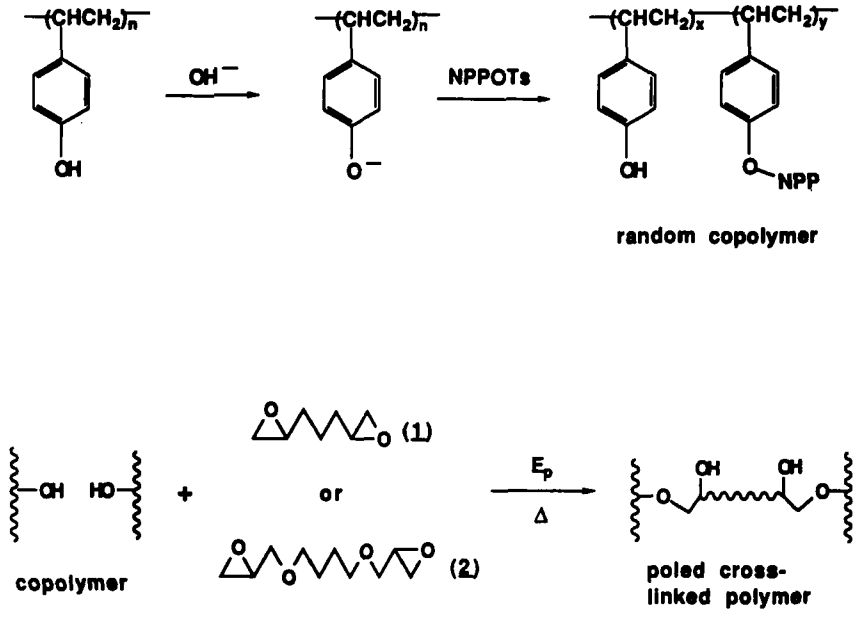
FIGURE 3 Schematic diagram of a PPO-NPP planar waveguide.

neat PPO film is similarly determined to be 1.580 ± 0.001 at 0.633 μm. Measurements of scattering loss have been carried out with an output coupling prism. By measuring the output intensity as a function of the separation between the input and output coupling prisms, a loss coefficient of $\alpha < 1$ dB/cm is estimated for both the PPO-NPP and PPO films.

SHG TEMPORAL STABILIZATION VIA CROSS-LINKING. STUDIES WITH CHROMOPHORE-FUNCTIONALIZED POLYMERS.[20]

Poly(*p*-hydroxystyrene) ($M_w \approx 6{,}000$; $T_g \approx 155°C$) was functionalized with NPP (16% of phenol rings) as shown in Scheme II. The product was purified by repeated benzene precipitation from THF solutions and filtration through a short silica gel column. Purity was verified by elemental analysis, 400 MHz ^{1}H NMR, and FT-IR spectroscopy. In the aforementioned class 100 clean hood, 1-2 μm (PS)O-NPP films were cast onto ITO-coated conductive glass from multiply-filtered THF solutions also containing measured quantities of 1,2,7,8-diepoxyoctane (**1**) or 1,4-butanediol diglycidyl ether (**2**, Scheme II). Optimum thermal cross-linking conditions were established by independent experiments in which the process was monitored by FT-IR spectroscopy of films cast on KBr plates. Cross-linking is accompanied by disappearance of the epoxy ring vibrational mode at 907–913 cm^{-1} and the simultaneous appearance of an ether C-O stretching transition at 1040–1048 cm^{-1}.[22] The (PS)O-NPP/1,2 films were partially cured at 100°C for 1 h under inert atmosphere and then at 100°C/10^{-4} torr for 24 h. As ascertained by FT-IR spectroscopy, this procedure effects partial cross-linking as well as removal of final traces of solvent and other volatiles which may deleteriously plasticize the polymer matrix.

SCHEME II



The annealed (PS)O-NPP films were next corona poled (+3.0 - +4.0 KV; 1.0 cm needle-to-film distance) at 180°C for 1 h. For optimum polymer/diepoxide stoichiometries (*vide infra*), such thermal conditions induce high degrees of cross-linking, while as mentioned above, corona poling provides higher electric fields than contact poling techniques without facile dielectric breakdown. The poled (PS)O-NPP/1,2 films were cooled to room temperature and physically aged for 1 h prior to removal of the corona field. These films are insoluble in common organic solvents and far more resistant to cracking than noncross-linked films. Excellent transparency characteristics are illustrated by the successful fabrication of a waveguide of the type described above for PPO-NPP films.[21]

Second harmonic coefficients of the (PS)O-NPP/1 films were measured at 1.064 μm using the instrumentation and calibration techniques described above. No SHG was observed for unpoled specimens. SHG decay data were fit by least-squares techniques to the phenomenological biexponential expression of equation (3). In Table II are set out d_{33}, τ_1, τ_2 data for (PS)O-NPP films as a function of cross-linking methodology. It can be seen that the present corona-poled d_{33} values are generally higher than previously achieved for contact-poled (PS)O-NPP samples at comparable or higher functionalization levels[6,7] and are also higher than values observed for cross-linked guest-host systems (*vide infra*). This is to be expected if equations (1) and (2) apply. Equally important, Table II shows that SHG efficiency

TABLE II

Second-Harmonic Coefficients and Decay Parameters for Corona-Poled NPP-Functionalized Poly(p-hydroxystyrene) Films as a Function of Cross-Linking[a]

Cross-Linking Agent	Stoichiometry Diepoxide/OH[b]	d_{33} 10^{-9} esu[c]	τ_1 days[d]	τ_2 days[e]
None	—	8.8	26	30
None	—	8.6[f]	36[f]	26[f]
 (1)	0.50	7.0	79	100
 (2)	0.25	3.8	18	74
	0.50	5.5	20	53
	0.75	2.1	11	51
	1.00	1.4	9	46

[a]Films poled at 180°C unless otherwise indicated.
[b]Equivalents diepoxide cross-linking agent per equivalent available phenol OH.
[c]At λ = 1.064 μm.
[d]Short-term SHG decay constant from a least-squares fit to Equation (3). Data taken at 25°C.
[e]Long-term SHG decay constant from a least-squares fit to Equation (3). Data taken at 25°C.
[f]Poled at 150°C.

is not adversely affected by the cross-linking process. In regard to d_{33} temporal stability, Figure 4, compares the effects of simultaneously corona poling and cross-linking (PS)O-NPP with 0.5 equivalents 1/available phenol OH group to two films poled in an essentially identical manner but not cross-linked. The increase in SHG

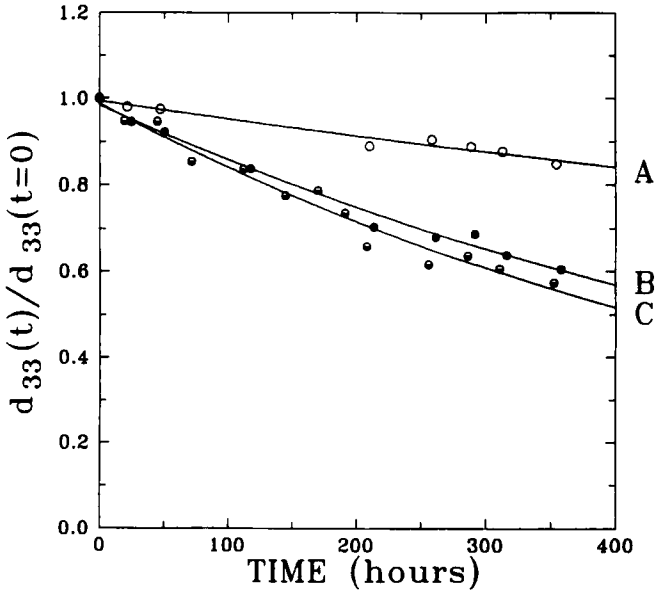


FIGURE 4 Temporal characteristics of the second harmonic coefficient, d_{33}, for corona poled (PS)O-NPP films. A. Simultaneously poled (180°C) and cross-linked with 0.50 equiv. 1,2,7,8-diepoxyoctane/phenol OH; B. Poled at 180°C; C. Poled at 150°C. The solid lines are least-squares fits to equation (3), yielding the parameters in Table II.

temporal stability is clearly evident and translates into 3.0-fold and 3.3-fold increases in τ_1 and τ_2, respectively.

The effect of the epoxy cross-linking/densification process[23] on chromophore mobility will be a complex function of cross-linking temperature, stoichiometry, and diepoxide reagent. Figure 5 shows the effect on the $d_{33}(t)$ τ_2 parameter of varying the stoichiometric ration of cross-linking agent for constant poling conditions. It can be seen that τ_2 rises to a maximum at relatively low diepoxide/available phenol OH ratios, then declines at higher diepoxide ratios. FT-IR spectroscopy reveals residual, unreacted epoxide functionalities (incomplete cross-linking) at the higher 2/OH ratios, and it is not unexpected that dangling, half-reacted epoxide sidechains would have a plasticizing effect on the chromophore/polymer matrix. At 2/OH ratios greater than ca. 0.5, the matrix becomes opaque after casting and curing, indicating phase separation. This results in a decrease in the measured d_{33} values. Differences in τ_1, τ_2 parameters for matrices cross-linked by **1** and **2** (Table I) are tentatively ascribed to differences in the chain flexibility of these diepoxide reagents.

SHG TEMPORAL STABILIZATION VIA CROSS-LINKING. CHROMOPHORES EMBEDDED IN EPOXY MATRICES.[6d,24]

To determine if NLO chromophores can be immobilized in highly cross-linked matrices, experiments were carried out in which the high-β molecules 4-(dimethylamino)-4′-nitrostilbene (DANS, **3**) and Disperse Orange 1 (DO1, **4**) were dis-

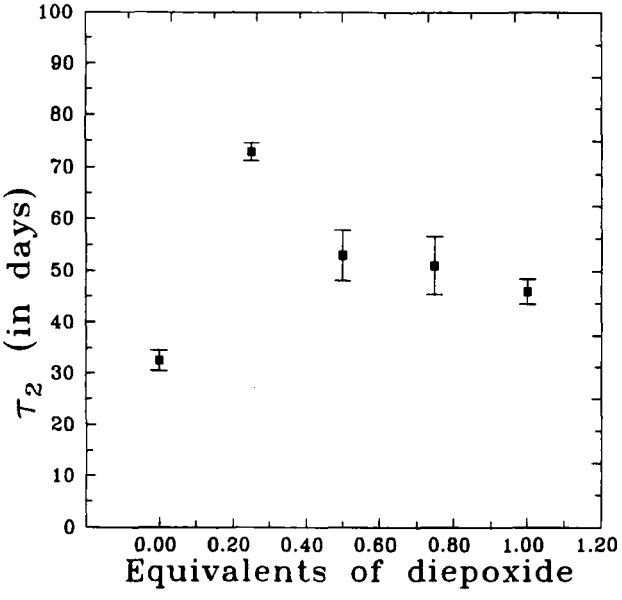
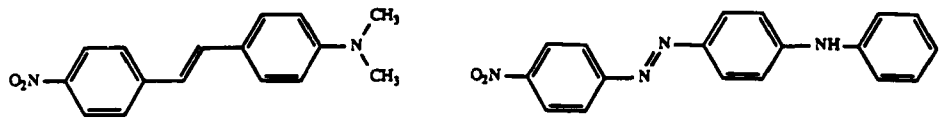


FIGURE 5 Long-term decay parameters (τ_2, equation (3)) for d_{33} of (PS)O-NPP films simultaneously corona poled and cross-linked with the indicated equivalents 1,4-butanediol diglycidyl ether/equivalents available phenol OH.



3 4

persed in an optical grade epoxy resin, which was then simultaneously poled and thermally cured. In these experiments, acetone or dichloromethane solutions of the chromophores were stirred with the epoxy resin and the solvent stripped from the solution *in vacuo*. The chromophore-doped resin was next thoroughly mixed (vortex mixer using glass beads) with the appropriate quantity of amine cross-linker and the resulting fluid introduced between transparent ITO glass electrodes using capillary action (to exclude air bubbles). The separation between the electrodes was maintained at 15–150 μm with Teflon or Mylar foil spacers. Partial crosslinking of the matrix at 80°C prior to poling was necessary to avoid dielectric breakdown. Poling fields of $2 \times 10^4 - 6 \times 10^5$ V/cm were then gradually applied and maintained for measured periods of time at 80–150°C. Films were cooled to room temperature prior to removal of the field.

Second harmonic coefficients of the poled films were determined at 1.064 μm using the instrumentation and data analysis procedures described above. Typical d_{33} values at zero time were found to be in the range 0.1 - 1.0 $\times$ 10^{-9} esu.[24a] Such magnitudes agree well with those expected for the chromophore number densities

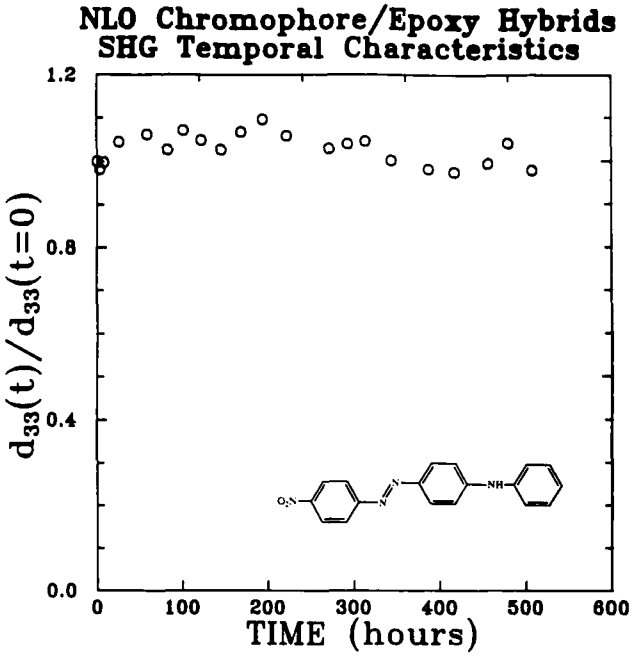
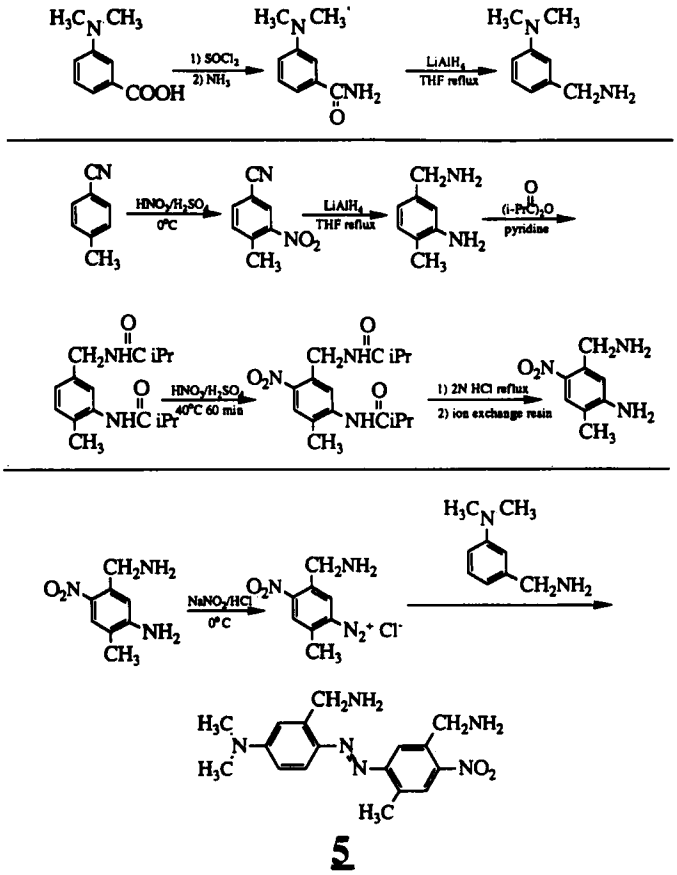


FIGURE 6 Temporal characteristics at room temperature of the second harmonic coefficient, d_{33}, of epoxy films containing Disperse Orange 1 (**4**) and simultaneously poled and cured at 150°C.

employed ($N = 0.4 - 1.9 \times 10^{19}$ cm^3, assuming literature $\mu\beta_{zzz}$ values and the applicability of an isolated chromophore, molecular gas description of the field-induced chromophore orientation process (equations (1), (2)).

The SHG temporal characteristics of the chromophore/epoxy matrices are strongly dependent upon the thermal cross-linking conditions. Thus, in poling field/temperature cycling experiments carried out as a function of curing time, the decay rate of d_{33} following removal of the field gradually declines as the cross-linking process[23] effects increasing degrees of chromophore immobilization.[24a] After very long curing times at 80°C, fitting of $d_{33}(t)$ to equation (3) yields $\tau_1 = 7$, $\tau_2 = 72$ days for the DANS-doped epoxy matrix and $\tau_1 = 8$, $\tau_2 = 142$ days for the DO1-doped epoxy matrix. The lower d_{33} decay rate of the latter matrix is presumed to reflect a slower reorientation time for the more massive DO1 chromophore. As shown in Figure 6, simultaneous curing and contact poling of a DO1-doped matrix at *150°C* yields a more stable NLO material for which only minor decay in d_{33} can be detected over a period of many days.

SCHEME III



5

While the above approach succeeds in effective NLO chromophore immobilization, it suffers from the low chromophore number densities which can be achieved. An attractive alternative strategy would be to construct a cross-linkable matrix in which one active component was a high-β chromophore molecule. Simultaneous poling and thermal cross-linking would then lead to an acentric matrix with a very high NLO chromophore number density. One approach to such a chromophore molecule is illustrated in Scheme III.[24b,c] The synthesis of target molecule **5** has recently been achieved and poling/cross-linking experiments are now in progress.

CONCLUSIONS

The recent results reported here considerably expand the available synthetic approaches to constructing poled polymeric frequency doubling materials with enhanced SHG efficiency and temporal stability. In particular, we have demonstrated that it is possible to assemble chromophore-functionalized polymers with greater than one chromophore substituent per monomer subunit, with d_{33} values as high as 65×10^{-9} esu, with T_g values as high as 173°C, and with improved temporal stability, and with good transparency characteristics at $\lambda = 0.633$ μm. We have also shown that chromophore-functionalized polymers can be simultaneously poled and cross-linked to significantly retard the rate of chromophore disorientation following electric field poling. Finally, NLO systems based upon highly cross-linkable epoxy matrices are shown to be viable candidates for both improved SHG temporal stability and improved frequency doubling efficiency.

Acknowledgments

This research was supported by the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR8821571) and by the Air Force Office of Scientific Research (Contract AFOSR-86-0105).

References

1. (a) J. Messier, F. Kajar, P. Prasad and D. Ulrich, eds. "Nonlinear Optical Effects in Organic Polymers," Kluwer Academic Publishers: Dordrecht, 1989.
   (b) G. Khanarian, ed. "Nonlinear Optical Properties of Organic Materials," *SPIE Proc.*, 1989, **971**.
   (c) A. J. Heeger, J. Orenstein and D. R. Ulrich, eds. "Nonlinear Optical Properties of Polymers;" *Mats. Res. Soc. Symp. Proc.*, 1988, **109**.
   (d) D. S. Chemla and J. Zyss, eds. "Nonlinear Optical Properties of Organic Molecules and Crystals," Vols. 1, 2; Academic Press: New York, NY, 1987.
   (e) C. S. Willand and D. J. Williams, *Ber Bunsenges Phys. Chem.*, 1987, **91**, 1304–1310.
   (f) J. Zyss, *J. Mol. Electronics*, 1985, **1**, 25–56.
   (g) D. J. Williams *Angew. Chem. Intl. Ed. Engl.*, 1984, **23**, 690–703.
2. (a) K. D. Singer, J. E. Sohn and S. J. Lalama, *Appl. Phys. Lett.*, 1986, **49**, 248–250.
   (b) K. D. Singer, M. G. Kuzyk and J. E. Sohn, *J. Opt. Soc. Am. B*, 1987, **4**, 968–975.
3. C. Ye, N. Minami and T. J. Marks, unpublished observations.
4. (a) L. C. E. Struik, "Physical Aging in Amorphous Polymers and Other Materials"; Elsevier: Amsterdam, 1978.
   (b) J. G. Victor and J. M. Torkelson, *Macromolecules*, 1987, **20**, 2241–2250.

(c) W.-C. Yu, C. S. P. Sung and R. E. Robertson, *Macromolecules*, 1988, **21**, 355–364, and references therein.
5. (a) H. L. Hampsch, J. Yang, G. K. Wong and J. M. Torkelson, *Macromolecules*, 1988, **21**, 526–528.
(b) H. L. Hampsch, J. Yang, G. K. Wong and J. M. Torkelson, *Polymer Commun.*, 1989, **30**, 40–43.
(c) H. L. Hampsch, J. M. Torkelson, S. J. Bethke and S. G. Grubb, *Appl. Phys. Lett.*, 1990, **67**, 1037–1041.
6. (a) C. Ye, T. J. Marks, Y. Yang and G. K. Wong, *Macromolecules*, 1987, **20**, 2322–2324.
(b) C. Ye, N. Minami, T. J. Marks, J. Yang and G. K. Wong, in reference 1c, pp. 263–269.
(c) C. Ye, N. Minami, T. J. Marks, J. Yang and G. K. Wong, *Macromolecules*, 1988, **21**, 2901–2904.
(d) M. A. Hubbard, N. Minami, C. Ye, T. J. Marks, J. Yang and G. K. Wong, in reference 1b, pp. 136–143.
7. (a) C. Ye, N. Minami, T. J. Marks, J. Yang and G. K. Wong, in reference 1a, pp. 173–183.
(b) D. Li, N. Minami, M. A. Ratner, C. Ye, T. J. Marks, J, Yang and G. K. Wong, *Synthetic Metals*, 1989, **28**, D585–D593.
8. K. D. Singer, M. G. Kuzyk, W. R. Holland, J. E. Sohn, S. J. Lalama, R. B. Commizzoli, H. E. Katz and M. L. Schilling, *Appl. Phys. Lett.* 1988, **53**, 1800–1802.
9. (a) M. Eich, A. Sen, H. Looser, D. Y. Yoon, G. C. Bjorklund, R. Twieg and J. D. Swalen, in reference 1b, pp. 128–135.
(b) M. Eich, A Sen, H. Looser, G. C. Bjorklund, J. D. Swalen, R. Twieg and D. Y. Yoon, *J. Appl. Phys.*, 1989, **66**, 2559–2567.
10. d_{31} for $LiNbO_3 = 14.2 \times 10^{-9}$ esu.[1f]
11. D. Dai, T. J. Marks, J. Yang, P. M. Lundquist and G. K. Wong, *Macromolecules*, 1990, **23**, 1891–1894.
12. (a) R. B. Comizzoli, *J. Electro. Soc.*, 1987, **134**, 424–429, and references therein.
(b) M. A. Mortazavi, A. Knoesen, S. T. Kowel, B. G. Higgins and A. Dienes, *J. Opt. Soc. Am. B*, 1989, **6**, 733–741.
13. D. Aycock, V. Abolins and D. M. White, in "Encyclopedia of Polymer Science and Technology," Wiley: New York, 1988, Vol. 13, pp. 1–30, and references therein.
14. D. M. White, *J. Org. Chem.*, 1969, **34**, 297–303.
15. I. Cabasso, J. Jagur-Grodzinski and D. Vofski, *J. Appl. Polym. Sci.*, 1974, **18**, 1969–1986.
16. (a) J. Zyss, J. F. Nicour and M. Coquillay, *J. Chem. Phys.*, 1984, **81**, 4160–4167.
(b) M. Barzoukas, D. Josse, P. Fremaux, J. Zyss, J. F. Nicoud and J. Morely, *J. Opt. Soc. Am. B*, 1987, **4**, 977–986.
17. J. Jerphagnon and S, K. Kurtz, *J. Appl. Phys.*, 1970, **41**, 1667–1681.
18. K. D. Singer, J. E. Sohn, L. A. King, H. M. Gordon, H. E. Katz and C. W. Dirk, *J. Opt. Soc. Am. B*, 1989, **6**, 1339–1351.
19. P. K. Tien, *Appl. Optics*, 1971, **10**, 2395–2413.
20. J. Park, T. J. Marks, J. Yang and G. K. Wong, *Chemistry of Materials*, 1990, **2**, 229–231.
21. J. Park, T. J. Marks, J. Yang and G. K. Wong, manuscript in preparation.
22. (a) L. V. McAdams and J. A. Gannon, in "Encyclopedia of Polymer Science and Engineering," Wiley: New York, 1986, Vol. 6, pp. 322–382, and references therein.
(b) E. Mertzel and J. L. Koenig, *Adv. Polym. Sci.*, 1985, **75**, 74–112.
23. (a) J. G. Kloosterboer, *Advan. Polym. Sci.*, 1988, **84**, 3–61.
(b) E. G. Oleinik, *Advan. Polym. Sci.*, 1986, **80**, 49–99.
(c) K. Dusek, *Advan. Polym. Sci.*, 1986, **78**, 1–59.
(d) B. A. Rozenberg, *Advan. Polym. Sci.*, 1986, **75**, 73–114.
(e) R. J. Morgan, *Advan. Polym. Sci.*, 1985, **72**, 1–43.
24. (a) M. A. Hubbard, T. J. Marks, J. Yang and G. K. Wong, *Chemistry of Materials*, 1989, **1**, 167–169.
(b) Communicated in part at the 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec. 1989.
(c) M. A. Hubbard, T. J. Marks, J. Yang and G. K. Wong, manuscript in preparation.