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Communications

Poled Polymeric Nonlinear Optical Materials. Enhanced Second Harmonic Generation Stability of Cross-Linkable Matrix/Chromophore Ensembles

Michael A. Hubbard and Tobin J. Marks*

Department of Chemistry and
the Materials Research Center
Northwestern University, Evanston, Illinois 60208

Jian Yang and George K. Wong*

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

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The creation and stabilization of microstructural acentricity is central to the successful design of polymeric materials with large quadratic optical nonlinearities.[1] While significant preferential alignment of chromophore molecules doped into polymer glasses can be achieved by electric field poling,[2] the pronounced temporal instability of such alignment,[3] and hence the temporal instability of second harmonic generation (SHG) characteristics, remains an unsolved problem. These disorientation effects are a natural consequence of the dynamic processes by which glassy polymers undergo physical aging/relaxation to minimum free volume.[4] We recently reported a promising

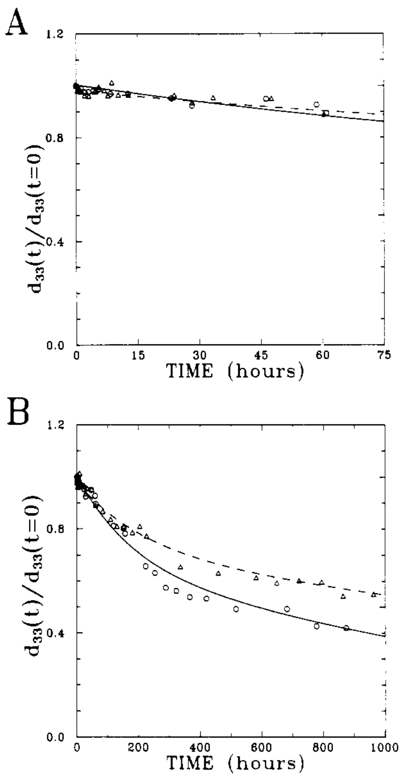

Figure 1. Temporal characteristics at room temperature of the second harmonic coefficient d_{33} for poled NLO chromophore-epoxy films containing 4-(dimethylamino)-4′-nitrostilbene (○) or Disperse Orange 1 (△); (A) short-term decay; (B) long-term decay. Solid lines are the numerical fit to eq 4.

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(1) (a) Heeger, A. J., Orenstein, J., Ulrich, D. R., Eds. Nonlinear Optical Properties of Polymers. *Mat. Res. Soc. Symp. Proc.* **1988**, *109*. (b) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987; Vol. 1 and 2. (c) Willand, C. S.; Williams, D. J. *Ber. Bunsen-Ges Phys. Chem.* **1987**, *91*, 1304–1310. (d) Khanarian, G., Ed. Molecular and Polymeric Optoelectronic Materials: Fundamentals and Applications. *SPIE* **1986**, *682*. (e) Zyss, J. *J. Mol. Electron.* **1985**, *1*, 25–56. (f) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690–703. (g) Williams, D. J., Ed. *Nonlinear Optical Properties of Organic and Polymeric Materials*; ACS Symposium Series; American Chemical Society: Washington, D.C., 1983; Vol. 233.

(2) (a) Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, *49*, 248–250. (b) Small, K. D.; Singer, K. D.; Sohn, J. E.; Kuzyk, M. G.; Lalama, S. J., in ref 1d, pp 150–169. (c) Singer, K. D.; Kuzyk, M. G.; Sohn, J. E. *J. Opt. Soc. Am. B* **1987**, *4*, 968–975. (d) Watanabe, T.; Yoshinga, K.; Fichou, D.; Miyata, S. *J. Chem. Soc., Chem. Commun.* **1988**, 250–251.

(3) (a) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1988**, *21*, 526–528. (b) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Polym. Commun.* **1989**, *30*, 40–43.

(4) (a) Yu, W.-C.; Sung, C. S. P.; Robertson, R. E. *Macromolecules* **1988**, *21*, 355–364, and references therein. (b) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1987**, *20*, 2241–2250. (c) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, 1978.

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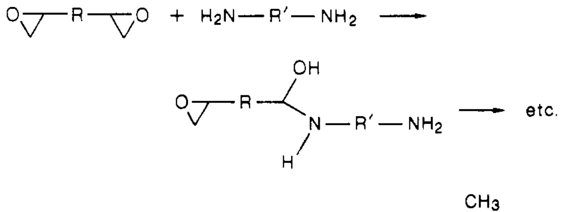
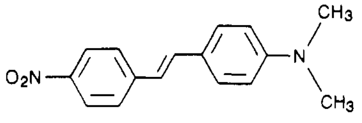
approach to chromophore immobilization in which high-β, nonlinear optical (NLO) chromophores are covalently bound to the backbone of a high-T_g,T_β glassy polymer.[5] We communicate here the development of a second, complementary approach in which a high-β guest chromophore is dispersed in an optically transparent host matrix that can then be simultaneously poled and chemically cross-linked.[6]

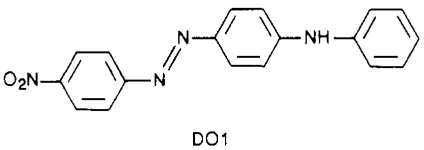
In this work, a two-component optically transparent thermosetting epoxy,[7] EPO-TEK 301-2,[8] was employed as the cross-linkable host matrix. The cross-linking chemistry is of the type shown in eq 1. The high-β molecules 4-



(1)



DANS



DO1

(dimethylamino)-4′-nitrostilbene (DANS) and Disperse Orange 1 (DO1) were chosen as the NLO guest chromophores. These contain no unhindered functional groups which would be expected to readily undergo reaction with the epoxy component of the matrix. Thus, dry acetone or dichloromethane solutions of the chromophores were stirred with the epoxy resin, and the solvent was stripped from the solution under high vacuum. The chromophore-doped epoxy 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 by using capillary action (to exclude air bubbles). The separation between the electrodes was defined by 15–150-μm Teflon or Mylar foil spacers. Partial cross-linking of the matrix at 80 °C prior to poling was found to be necessary to avoid dielectric breakdown.[9] Poling fields of 2×10^4–6×10^5 V/cm were then gradually applied and maintained for measured periods of time at 80 °C. Films were cooled to room temperature prior to removal of the field. SHG measurements at 1064 nm were carried out in the p-polarized geometry using the Q-switched Nd:YAG laser system and calibration techniques described previously.[5,10]

Second harmonic coefficients (d_{33}) of the poled films were estimated from the angular dependence[11] of the second harmonic signal intensity assuming that $^1/_3 d_{33} = d_{31} = d_{24} = d_{15}$. Typical initial d_{33} values were found to be in the range $(0.1–1.0) \times 10^{-9}$ esu. Such magnitudes agree well with those expected for the chromophore number densities 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 (eq 2 and 3).[2,5]

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

$$p = \frac{f^0\mu E_p}{kT} \tag{3}$$

Here μ is the chromophore dipole moment, E_p is the poling field, the f's are local field factors, and L_3 is the third-order Langevin function. No SHG was observed for unpoled samples or for the poled, undoped epoxy matrix.

The temporal characteristics of d_{33} are illustrated for typical poled, maximally cross-linked (as judged by FT-IR studies[12] of identical films heated at 80 °C between KBr plates) chromophore/epoxy matrices over short and long time periods in Figure 1. Most striking is the enhancement in overall SHG temporal stability compared to non-cross-linked guest–host systems.[2,3] As in the case of chromophore-functionalized polymers,[5] the decay data could not be fit to a single exponential. More satisfactory numerical fits to a double exponential (eq 4) are shown in

$$d_{33} = Ae^{-t/\tau_1} + Be^{-t/\tau_2} \tag{4}$$

Figure 1. Such bimodal behavior is plausibly associated with disparate chromophore reorientation rates in regions of free volume above and below a certain critical free-volume threshold.[4a,b,13] Derived fitting parameters for the present $d_{33}(t)$ data are $\tau_1 = 7$, $\tau_2 = 72$ days for the DANS-containing matrix and $\tau_1 = 8$, $\tau_2 = 142$ days for the DO1-containing matrix. A correlation between decay time and chromophore dimensions has been noted previously[3b] and, in the present case, likely reflects the diminished mobility of the more massive DO1 chromophore molecule.

Further insight into the response of chromophore mobility to the matrix cross-linking/densification[7c,13] process is provided by in situ measurements[14] of the SHG signal intensity ($I^{2\omega}$)[15] as a function of temperature, poling field, and matrix curing time. In these experiments, film samples prepared as above were subjected to repeated cycles of curing (88 ± 1 °C) in a poling field, cooling to room temperature, and removal of the poling field. Although detailed numerical analyses of the data are still in progress, two effects are immediately evident in the data (Figure 2). As anticipated from the Boltzmann-like form of eq 2 and 3, decreasing the sample temperature from 360 to 300 K is accompanied by a corresponding increase (ca. 40% is predicted) in $I^{2\omega}$. While such behavior is not unexpected

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(5) (a) Ye, C.; Marks, T. J.; Yang, J.; Wong, G. K. *Macromolecules* **1987**, *20*, 2322–2324. (b) Ye, C.; Minami, N.; Marks, T. J.; Yang, J.; Wong, G. K. *Mat. Res. Soc. Symp. Proc.* **1988**, *109*, 263–269. (c) Ye, C.; Minami, N.; Marks, T. J.; Yang, J.; Wong, G. K. *Macromolecules* **1988**, *21*, 2901–2904.

(6) Communicated in part at the NATO ARW, Polymers for Nonlinear Optics, Nice, France, June 20–24, 1988.

(7) (a) Morgan, R. J. *Adv. Polym. Sci.* **1985**, *72*, 1–43. (b) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 3–61. (c) Oleinik, E. F. *Adv. Polym. Sci.* **1986**, *80*, 49–99. (d) Dušek, K. *Adv. Polym. Sci.* **1986**, *78*, 1–59. (e) Rozenberg, B. A. *Adv. Polym. Sci.* **1986**, *75*, 73–114.

(8) Epoxy Technology Inc., Billerica, MA. From ^{1}H/^{13}C NMR, FT-IR, and mass spectroscopy, we surmise that the epoxy component is the diglycidyl ether of bisphenol A while the hardener consists of one or more polyfunctional aliphatic amines.

(9) (a) Mathes, K. N. In *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1986; Vol. 5, pp 512–593. (b) Blythe, A. R. *Electrical Properties of Polymers*; Cambridge University Press: Cambridge, 1979; Chapter 6. (c) Block, H. *Adv. Polym. Sci.* **1979**, *33*, 93–167, and references therein.

(10) Gu, S. J.; Saha, S. K.; Wong, G. K. *Mol. Cryst. Liq. Cryst.* **1981**, *69*, 287–292.

(11) Jerphagnon, J.; Kurtz, S. K. *J. Appl. Phys.* **1970**, *41*, 1667–1681.

(12) (a) The extent of cure was estimated by monitoring the disappearance with time of the asymmetric epoxy ring stretch at 915 cm^{-1} with respect to the aromatic C═C stretch at 1511 cm^{-1}. (b) Mertzel, E.; Koenig, J. L. *Adv. Polym. Sci.* **1985**, *75*, 74–112.

(13) (a) Yu, W.-E.; Sung, C. S. P. *Macromolecules* **1988**, *21*, 365–371, and references therein. (b) Sung, C. S. P.; Pyun, E.; Sun, H.-L. *Macromolecules* **1986**, *19*, 3922–3929.

(14) (a) Hubbard, M. A.; Minami, N.; Ye, C.; Marks, T. J.; Yang, J.; Wong, G. K. *SPIE Proc.* **1988**, *971*, 136–143. (b) Minami, N.; Marks, T. J., manuscript in preparation.

(15) $I^{2\omega} \sim d_{33}{}^2$.

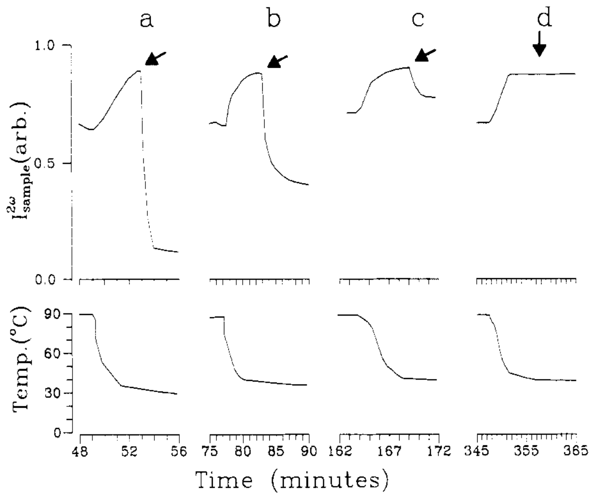

Figure 2. Response of the 532-nm second harmonic signal intensity $I^{2\omega}$ of a Disperse Orange 1-epoxy film to curing time, temperature, and electric poling field. The time ordinate gives total accumulated curing time while the arrows indicate the time of removal of the 4.8×10^4 V/cm poling field. Not shown: The temperature was returned to 88 °C and the poling field reapplied after each experimental sequence.

in more fluid examples (e.g., Figure 2a,b), the relatively rapid response at higher cross-linking levels (Figure 2c,d) indicates significant residual orientational mobility (at least over relatively small angular excursions and at 88 °C—vide infra). For lightly cross-linked samples, removal of the poling field results in a precipitous drop in $I^{2\omega}$, followed by a leveling-off (Figures 2a,b). As the matrix cross-linking process progresses, the magnitude of the room-temperature zero-field decline steadily decreases, and $I^{2\omega}$ at the leveling-off point correspondingly increases. An attractive explanation for this behavior, which is in accord with the bimodal $d_{33}(t)$ data (vide supra), invokes a decreasing component of the free-volume distribution greater than the critical threshold for chromophore reorientation as the degree of matrix cross-linking increases. That $I^{2\omega}$ in Figure 2d responds rapidly to the temperature drop but not to the removal of the poling field can be explained by the closer temperature proximity of the former process to the matrix T_g (ca. 70–75 °C).

These results demonstrate that polymeric frequency-doubling guest–host materials with improved temporal stability can be formed by orienting/immobilizing NLO chromophores within chemically cross-linkable matrices. Moreover, the fluid character of the non-cross-linked precursor solution suggests the possibility of novel processing/fabrication approaches. Beyond the realm of NLO materials, it is evident that such SHG studies also provide valuable information on free-volume and motional characteristics in cross-linkable polymers that complements information accessible via photoisomerization,[4,13] electrochromism,[16] and other probes.[4c,7] Further studies of chemically based NLO chromophore immobilization processes are under way.

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(16) (a) Blumenfeld, F. P.; Chernyakovskii, F. P.; Gribanov, V. A.; Kanevskii, I. M. *J. Macromol. Sci., Chem. Ed.* **1972**, *A6*, 1201–1225. (b) Shchapov, A. N.; Chernyakovskii, F. P.; Kornilov, A. I. *Polym. Sci. USSR* **1984**, *26*, 2322–2328.

Silver Substitution in $Pb_2Sr_2Y_{1-y}Ca_yCu_3O_8$ ($y = 0, 0.25$)

A. C. W. P. James and D. W. Murphy*

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

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The position of Ag directly below Cu in group IB of the periodic table suggests that silver chemistry may provide a route to novel, high-temperature superconductors analogous to the now famous cuprate superconductors. In fact, some 20 years before the discovery of the superconducting cuprates the highly oxidized silver compounds $Ag^+[Ag_6O_8]X^-$ ($X^- = NO_3^-, F^-, BF_4^-$) were shown to be superconducting with transition temperatures of 1.04, 0.3, and 0.15 K, respectively.[1] However, few silver oxides are known because of thermal instability with respect to elemental silver. Compounds with Ag either as a ternary cation as in $AgNbO_3$ or as the active cation would be a source of potentially interesting materials. No cuprates with Ag as a ternary cation have been reported, and substitution of Ag for Cu in $Ba_2YCu_3O_7$ resulted in replacement of no more than 1.5 at. % of Cu by Ag.[3,4]

This communication reports substantial Ag substitution for Cu in $Pb_2Sr_2(Y,Ca)Cu_3O_8$, a class of cuprates with T_c's as high as 70 K, recently discovered by Cava et al.[4] The same series of cuprates was found independently by Subramanian et al.[5] The structure of the prototype cuprate $Pb_2Sr_2YCu_3O_8$ is shown in Figure 1; it contains layers of corner-shared square-pyramidal $[CuO_5]$ units (Cu(2)) similar to those in $Ba_2YCu_3O_7$ separated by a bilayer of edge-shared square-pyramidal $[PbO_5]$ units in turn separated by linear two-coordinate Cu(1) atoms similar to those in $Ba_2YCu_3O_6$. The average oxidation state of copper in $Pb_2Sr_2YCu_3O_8$ is $+^5/_3$, consistent with formal copper oxidation states of +2 in the Cu(2) sheets and +1 for the linearly coordinated Cu(1) atoms. $Pb_2Sr_2YCu_3O_8$ is a semiconductor; superconducting phases are prepared by partial substitution of divalent ions for Y^{3+}, which results in a compensating oxidation of the Cu(2) sheets leaving the overall oxygen stoichiometry and the formal valence of the Cu(1) layers unchanged. The results described below prove that single-phase materials of composition $Pb_2Sr_2YCu_{3-x}Ag_xO_8$ can be prepared for $x \leq 0.55$ and that the silver in these materials occupies the linear Cu(1) sites of the $Pb_2Sr_2YCu_3O_8$ structure. It will be shown that chemical considerations substantially reduce the amount of silver that can be substituted into the superconducting phases $Pb_2Sr_2Y_{1-y}Ca_yCu_3O_8$ ($y \leq 0.5$) but that some Cu/Ag substitution can be achieved with little effect on the superconductivity.

The silver-substituted phases $Pb_2Sr_2YCu_{3-x}Ag_xO_8$ ($0 \leq x \leq 0.55$) were prepared as follows: stoichiometric quantities of $SrCO_3$, Y_2O_3, CuO, and Ag_2O were ground together and heated in air at 840 °C for 24 h with one intermittent

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(1) Robin, M. B.; Andres, K.; Geballe, T. H.; Keubler, N. A.; McWhan, D. B. *Phys. Rev. Lett.* **1966**, *17*, 917.

(2) Cahen, D.; Moisi, Z.; Schwartz, M. *Mater. Res. Bull.* **1987**, *22*, 1581.

(3) Cahen, D.; Schwartz, M.; Reich, S.; Felner, I. *Inorg. Chem.* **1987**, *26*, 3653.

(4) Cava, R. J.; Batlogg, B.; Krajewski, J. J.; Rupp, L. W.; Schneemeyer, L. F.; Siegrist, T.; van Dover, R. B.; Marsh, P.; Peck, Jr., W. F.; Gallagher, P. K.; Glarum, S. H.; Marshall, J. H.; Farrow, R. C.; Waszczak, J. V.; Hull, R.; Trevor, P. *Nature* **1988**, *336*, 211.

(5) Subramanian, M. A.; Gopalakrishnan, J.; Torardi, C. C.; Gai, P. L.; Boyes, E. D.; Askew, T. R.; Flippen, R. B.; Farneth, W. E.; Sleight, A. W. *Phys. C*, in press.