N92-22476

NONLINEAR OPTICAL POLYMERS FOR ELECTRO-OPTIC SIGNAL PROCESSING

Geoffrey A. Lindsay
Polymer Science Branch Head, Code 3858
Chemistry Division, Research Department
Naval Weapons Center, China Lake, CA 93555

ABSTRACT

Photonics is an emerging technology, slated for rapid growth in communication systems, sensors, imagers and computers. Its growth is driven by the need for speed, reliability and low cost. New nonlinear polymeric materials will be a key technology in the new wave of photonic devices. Electron-conjugated polymeric materials offer large electro-optic figures of merit, ease of processing into films and fibers, ruggedness, low cost and a plethora of design options. Several new broad classes of second-order nonlinear optical polymers have been developed at the Navy's Michelson Laboratory at China Lake, California. Polar alignment in thin film waveguides was achieved by electric-field poling and Langmuir-Blodgett processing. Our polymers have high softening temperatures and good aging properties. While most of the films can be photobleached with ultraviolet (UV) light, some have excellent stability in the 500 - 1600 nm range, and UV stability in the 290 - 310 nm range. The optical nonlinear response of these polymers is subpicosecond. Electro-optic switches, frequency doublers, light modulators and optical data storage media are some of the device applications anticipated for these polymers.

INTRODUCTION

Recently, there has been immense interest in second-order nonlinear optical polymer (NLOP) films[1] because of their large nonlinear optic coefficients, and the ease of casting thin films on many substrates. NLOP can be spin-cast into optical waveguides using conventional microlithographic equipment. These new polymers are under development for applications in electro-optical modulators,[2] switches,[3] waveguides[4] and optical interconnects.[5]

Electric-Field Poling. A useful process for imparting the second-order NLO property is electric field poling.[6] A polymer containing dyes (i.e., chromophores) which have large dipole moments,[1a] is heated and poled near the glass transition temperature (Tg), then cooled below the Tg while still applying the electric field. After the external field is removed, a net alignment of dipole moments can remain essentially locked in the film for years as long as the temperature of the film remains well below any solid state transition, such as the glass-rubber transition (Tg). This imparts a noncentrosymmetry to the film which is necessary for frequency doubling (i.e., the thin film's ability to generate second harmonic light when a laser beam is transmitted through it)[7], and the Pockels effect (i.e., its ability to change index of refraction as a function of an electric field applied across the film).

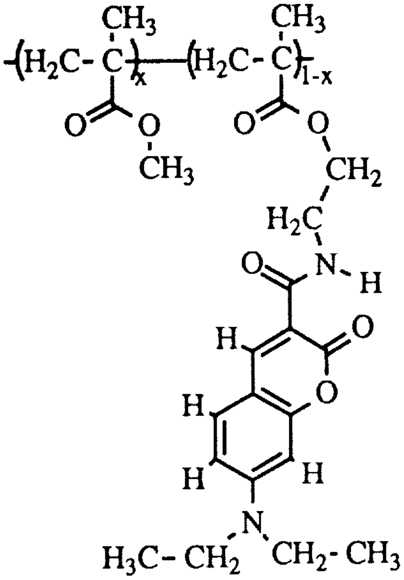
Langmuir-Blodgett Processing. Another technique for fabricating polar films is Langmuir-Blodgett (LB) processing. There are several good reference books on LB technology.[8] Simply stated, an organic compound is floated on a liquid, usually water, and a solid substrate is dipped through the air-water interface depositing a single molecular layer per stroke on the substrate. Eastman Kodak researchers have built up a micron-thick, NLOP film of optical high quality.[9] Turn-key, computer-automated LB troughs are available from many commercial suppliers. Appendix I briefly reviews LB film deposition. The Naval Weapons Center chemistry laboratory has a NIMA LB trough equipped with two compartments such that multilayer films, alternating $(AB)_n$ times, can be deposited automatically.

Developments in the NLOP Field. The development of nonlinear optical polymers has been rapidly evolving over the last eight years. The earliest materials investigated were the guest-host systems comprised of a dye (chromophore) dissolved in a glassy polymer matrix, such as Disperse Red #1 dissolved in poly(methyl methacrylate).[10] These mixtures exhibit second-order optical nonlinearity, but it slowly decays over a period of months. Soon investigators found that if the dye is chemically attached to the polymer backbone, the stability of the poled films is greatly enhanced. Many laboratories have reported novel sidechain NLOP compositions[11]in which the chromophores are attached at one site, pendent to the polymer backbone. The sidechain polymers are easy to process, and most of the research effort has focused on this class of NLOP. Attaching chromophores along a polymer backbone so that they form the backbone of the polymer is another interesting configuration which may yield processable polymers with a higher concentration of chromophoric material (the active nonlinear optical component). Developments in each of these types of NLOP will be described in the following sections. Another approach which will not be covered are the crosslinked NLOP. This class of NLOP are formed by carrying out a chemical reaction (the crosslinking reaction) in the presence of an electric field. Crosslinked NLOP promise to yield films which are more thermally stable; however, in practice, they are very difficult to process into films which have low scattering losses

THREE CLASSES OF NONLINEAR OPTICAL POLYMERS

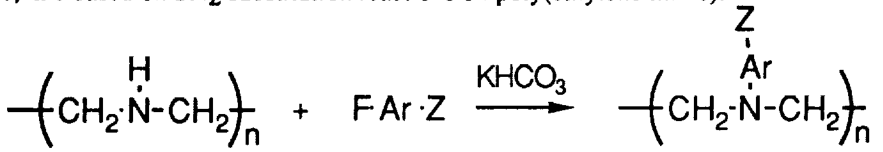
1. Sidechain NLOP. The first sidechain polymers made in our laboratory were designed for Langmuir-Blodgett (LB) deposition.[12] These polymers were based on the stilbazolium chromophore which has one of the largest second-order nonlinear coefficients due in part to the formal positive charge on the picolinium group. Due to migration of the charges, these polymers can not be aligned by electric field poling, but LB deposition gives a high degree of polar order. Thin LB films of these polymers can be easily patterned when exposed to UV light to form optical gratings and holograms. A patent application has been filed.[13]

Quite a large number of sidchain polymers were developed in our laboratory which have no charges, hence are ideal candidates for electric-field poling.[14] Most of the sidechain polymers developed in our laboratory are described in references 11e through 16. One of the sidechain polymers, with which we have the most experience, is based on the coumarin chromophore:



This NLOP is quite fluorescent and very photo stable. The damage threshold at 532 nm is about 60 GW/cm[2] for short pulses.[14c] We have prepared a sidechain polymer with a glass transition temperatures of 170° C, and polymers with even higher thermal stability are under development. A patent application has been submitted.[15]

Several new sidechain polymers under development in our laboratory, which have not yet been reported in the scientific literature, are based on SN_2 substitution reactions on poly(ethylene imine):



$$-\left(CH_2\text{-}\overset{H}{N}\text{-}CH_2\right)_n + F\text{-}Ar\text{-}Z \xrightarrow{KHCO_3} -\left(CH_2\text{-}\overset{\overset{Z}{Ar}}{N}\text{-}CH_2\right)_n$$

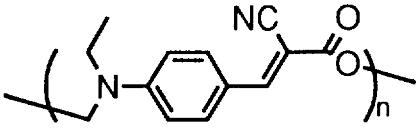
where FArZ is a group containing an aromatic ring system with at least one electron accepting group (Z) attached para to fluorine. Hence, a large dipole moment results because the amine is an excellent electron donating group. Since the amine lies in the backbone, a high density of chromphores is possible.

Another potentially useful chromophore, 4-nitrocinnamylidene, developed by Prof. Sam Huang at the Univ. of Connecticut, was converted to a novel sidechain NLOP by our group. The nitrocinnamylidene chromophore is nearly "water white" in the visible region of the spectrum.

We have been designing synthetic polypeptides which can form ordered monolayers at the air-water interface. We have synthesized novel, chromophore-substituted polypeptides designed for self-organization (in beta-sheet conformations). These polymers are prepared by derivatization of preformed polypeptides, and by polymerization of derivatized amino acids. An invention disclosure has been submitted.[16]

Sidechain NLOP are very attractive for many applications, and still hold the record for degree of alignment and NLO figures of merit. They also may be crosslinked by various techniques to give higher stability.

2. Isoregic Mainchain NLOP. The configuration of chromophores attached head-to-tail along a polymer backbone is called the isoregic mainchain configuration. Isoregic NLOP have been of interest, in part, because it was proposed that for chemically connected dipoles compared to the unconnected case, the propensity to align in an electric field is greatly enhanced due to larger molecular dipole moments.[17] One example of an isoregic polymer prepared in our laboratory is shown below[18]:



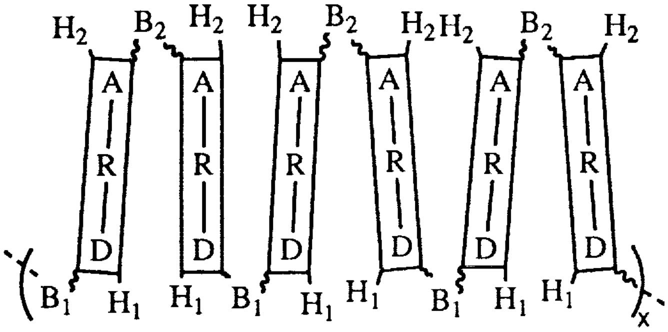
This polymer is completely soluble in common solvents, is amorphous, has a glass transition temperature of 105° C, and can be polarized by electric-field poling.

The isoregic configuration offers the possibility of aligning the chromophores by mechanically stretching the polymer. However, one must find a technique to induce all of the dipoles in the mainchains to point in the same direction, or else they will cancel each other even if the chains are aligned.

We remain bullish about the possibilities for isoregic NLOP. We describe our progress in publications listed in reference (18). We have submitted a patent application.[19] Our current interests in this area, in collaboration with other laboratories, include: a) poling in a supercritical fluid to plasticize the polymers (D. Soane at U.C. Berkeley), and 2) growing polymers from a surface in one direction to effect a perfect polar alignment (C. Martin at U. Colorado).

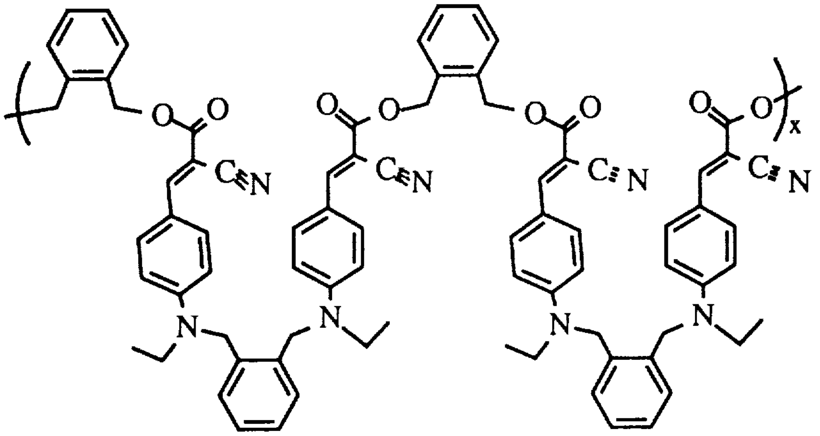
3. Syndioregic Mainchain NLOP. Our laboratory was the first to explore the head-to-head (syndioregic) configuration. If the syndioregic backbone is viewed in the extended conformation, the dipole moments appear to cancel each other out. However, we felt it might be possible to cause the backbone to wrinkle into a rigid, folded conformation by selecting proper groups for local molecular interactions.

It is clear from molecular models that one can place bridging groups (B) and other "helper" groups (H) between rigid, syndioregic chromophores (ARD) that will encourage the backbone to fold.



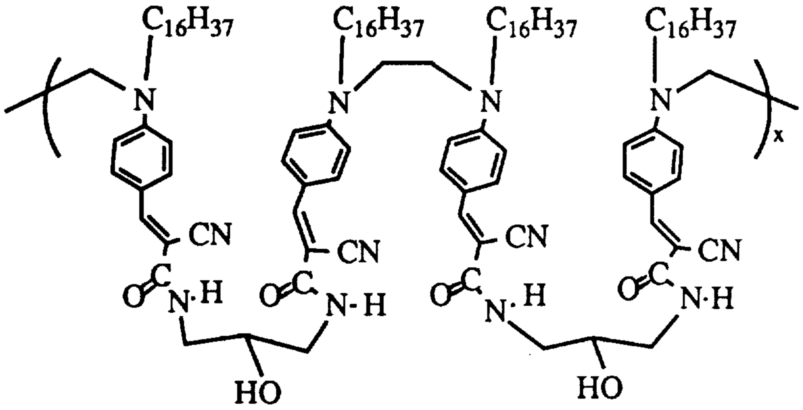
There would be two molecular processes involved in forming the final solid state conformation. One process would be the folding of the chromophoric groups relative to their immediate neighbors along the backbone, and the other process would be the placing of the entire polymer chain relative to neighboring polymer chains. The folded polymer may act as a rigid ensemble whose dipole moment is the sum of the constituent chromophores. However, during electric field poling, the folding of the chromophores should also be influenced by the applied electric field.

We are now in the process of synthesizing new syndioregic polymers with rigid bridging groups and high glass transition temperatures, such as the polymer shown below:



Preliminary samples of this polymer have glass transition temperatuers of about 150° C, and are soluble in many common solvents. Electric field poling of thin films is now underway. Eliminating the methylene groups on the xylyl bridges will further increase the glass transition temperature.

By placing hydrophilic and hydrophobic groups in the right places, one can also design syndioregic polymers for LB deposition:



We have made these and other syndioregic polymers films which have nonlinear optical properties (as measured by second harmonic generation).[20] Several of these polymers can be patterned by UV etching/bleaching. The patent application is in process.[21]

KEY PROPERTIES AND APPLICATIONS

Temporal Response. The response time of NLOP has been shown to be sub-picosecond.[14c] This is essential for rapid switching in hybrid electro-optic computers, and sensor protection against lasers. We have identified many applications for missile systems involving signal modulation and laser beam deflection.

Holographics. NLOP can be processed on conventional photolithography equipment. While most of the NLOP films can be photobleached with ultraviolet (UV) light, some have excellent stability in the 500 - 1600 nm range, and UV stability in the 290 - 310 nm range. Chromophores can be tailor-made to absorb light in certain regions of the spectrum, and to be transparent in others. This means that a grating can be etched by exposing the NLOP through a mask in the absorbing region, while the grating spacing is designed to diffract light in a nonabsorbing region. The concept of three dimensional images stored in high density in NLOP has not yet been developed, but it offers many exciting possibilities, such as electro-active (switchable) holograms.

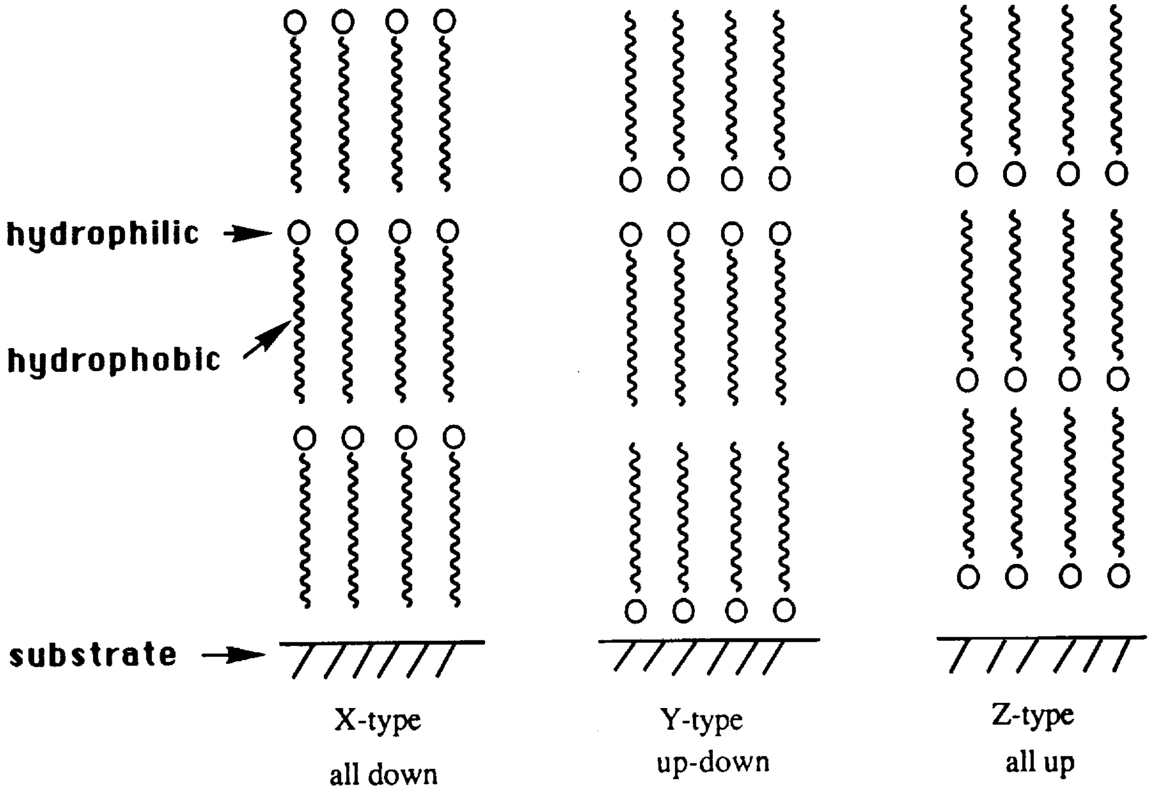
Mach-Zehnder Interferometer. A major applications focus for NLOP materials has been optical signal modulation. There have been several reports of modulation rates in the range of 20 to 40 GHz. NLOP have the advantage of low dielectric constants and high electro-optic coefficients compared to conventional materials such as lithium niobate.

ACKNOWLEDGEMENT

The author gratefully acknowledges the sponsorship of the Office of Naval Research, and his research colleagues at the Naval Weapons Center who prepared and characterized the nonlinear optical polymers: Dr. John Fischer, Dr. Ronald Henry, Dr. James Hoover, Dr. Robert Kubin, Dr. Michael Seltzer and Dr. John Stenger-Smith.

APPENDIX I. Langmuir-Blodgett (LB) Film Deposition

Multilayer LB films can be formed in three different configurations, as depicted on the next page. Historically, these are called "X"-, "Y"-, and "Z"-type films, where X is made by depositing always on the down-stroke, Z is made by depositing always on the up-stroke, and Y is made by alternating up- and down-strokes. For the case in which the large dipole moment of the sidechain chromophore is normal to the polymer backbone (and the backbone is in the plane of the air-water interface), all-up or all-down films will be polarized, and the up-down films will not be polarized (dipoles in adjacent layers cancel out). The Y configuration is thermodynamically more stable; and, sometimes X and Z configurations spontaneously rearrange in the solid state to form the Y configuration. Hence, one may interleave a sidechain chromophoric polymer with an optically inert spacer layer (having little dipole moment) and arrive at a stable, polarized film in the Y configuration.



---

[1] a) D. J. Williams, *Angew. Chem. Int. Ed. Engl.*, 23, 690 (1984);
b) D.S. Chemla and J. Zyss, Eds., Vol. 1, *Nonlinear Optical Properties of Organic Molecules and Polymeric Materials* (Academic, New York, 1987);
c) A.F. Garito, K.Y. Wong and O. Zamani-Khamiri, in *Nonlinear Optical and Electroactive Polymers*, P.N Prasad and D. R. Ulrich, Eds. (Plenum, 1988).

[2] G.H. Cross, A. Donaldson, R.W. Gymer, S. Mann, N.J. Parsons, D.R. Haas, H.T. Man and H.N. Yoon, *SPIE Proc.* **1177**, 79 (1989).

[3] P. Kaczmarski, J.-P. Van de Capelle, P.E. Lagasse, R. Meynart, *IEE Proc.* **136, Pt. J** (3), 152 (1989).

[4] M.J. McFarland, K.K. Wong, C. Wu, A. Nahata, K.A. Horn, J.T. Yardley, *SPIE Proc.* **993**, 26 (1988).

[5] C.A. Eldering, S.T. Kowel, P. Brinkley, N. Matloff, T. Schubert, R. Gosula, *SPIE Proc.* **1151**, 72 (1989).

[6] a) K.D. Singer, M.G. Kuzyk, W.R. Holland, J.E. Sohn, S.L. Lalama, R.B. Comizzoli, H.E. Katz, M.L.Schilling, *Appl. Phys. Lett.* **53**(19), 1800 (1988);
b) M.A. Mortazavi, A. Knoesen, S.T. Kowel, B.G. Higgins, A. Dienes, *J. Opt. Soc. Am. B* **6**(4), 733 (1989);
c) C.P.J.M. van der Vorst, S.J. Picken, *J. Opt. Soc. Am. B*, 7(3), 320 (1990).

[7] Y.R. Shen, "The Principals of Nonlinear Optics," John Wiley & Sons, NY, 1984.

[8] a) G. L. Gaines, *Insoluble Monolayers at Liquid-Gas Interfaces*, Interscience: New York, 1966;
b) G. G. Roberts, *Langmuir-Blodgett Films*, Plenum Press: New York, 1990.

[9] T. Penner, et al., *SPIE Proceedings*, **1064**, San Diego, CA, July 25, (1991).

---

[10] K.D. Singer, J.E. Sohn, and S.J. Lalama, *Appl. Phys. Lett.* **49**, 248 (1986).

[11] a) E.W. Choe, U.S. Patent 4,755,574, Jul. 5, 1988;
b) R. N. DeMartino, U.S. Patent 4,757,130, Jul. 12, 1988;
c) P. LeBamy, et al., *SPIE Proc.* **682**, 56 (1986);
d) A.C. Griffin, *SPIE Proc.* **682**, 65 (1986);
e) T.J. Marks, U.S. Patent 4,935,292, Jun. 19, 1990;
e) K.D. Singer, M.G. Kuzyk, W.R. Holland, J.E. Sohn, S.L. Lalama, R.B. Comizzoli, H.E. Katz and M.L.Schilling, *Appl. Phys. Lett.*, **53**(19), 1800 (1988);
f) L..M. Hayden, G.F. Sauter, F.R. Ore, P.L. Pasillas, J.M. Hoover, G.A. Lindsay and R.A. Henry, *J. Appl. Phys.*, **68**(2), 456 (1990).

[12] a) "New Hemicyanine Dye-Substituted Polyethers as Nonlinear Optical Materials," R. C. Hall, G. A. Lindsay, S. T. Kowel, L. M. Hayden, B. L. Anderson, B. G. Higgins, P. Stroeve, and M. P. Srinivasan, *SPIE Proceedings.*, **824**, 121-124 (1988);
b) "Optically Nonlinear Films of Amphiphilic Polymers: Synthesis, Langmuir-Blodgett Deposition, and Optical Measurements," Robert C. Hall, Goeffrey A. Lindsay, Brian Anderson, Stephen T. Kowel, Brian G. Higgins, and Pieter Stroeve, *Mat. Res. Soc. Symp. Proc.*, **109**, 351-356 (1988);
c) "Quadratically Enhanced Second Harmonic Generation in Polymer-Dye Langmuir-Blodgett Films," B. L. Anderson, R. C. Hall, B. G. Higgins, G. A. Lindsay, P. Stroeve, and S. T. Kowel, *Synthetic Metals* , **28**(3), D683-688 (1989);
d) "Second Harmonic Generation in Langmuir-Blodgett Multilayers of Stilbazolium Chloride Polyethers," B. L. Anderson, J. M. Hoover, G. A. Lindsay, B. G. Higgins, P. Stroeve, and S. T. Kowel, *Thin Solid Films* , **179**, 413 (1989).

[13] "NEW HEMICYANINE DYE-SUBSTITUTED POLYETHERS AS NONLINEAR OPTICAL MATERIALS," R. C. Hall and G. A. Lindsay, Navy Case No. 73112 (Oct 1990).

[14] a) "Second-Order Nonlinear Optical Measurements in Guest-Host and Side-Chain Polymer," L. M. Hayden, G. F.Sauter, F. R. Ore, P. L. Pasillas, J. M. Hoover, G. A. Lindsay, and R. A. Henry, *J. Appl. Phys.* **68**(2), 456-465 (1990);
b) "Synthesis and Second-Order Nonlinear Optical Properties of New Coumaromethacrylate Copolymers," R. A. Henry, J. M. Hoover, A. Knoesen, S. T. Kowel, G. A. Lindsay, and M. A. Mortazavi, *Mat. Res. Soc. Symp. Proc.* **173**, 601-606 (1990);
c) "Generation of 315 nm Femtosecond Pulses using a Poled Copolymer Film," D.R. Yankelevich, A. Dienes, A. Knoesen, R.W. Schoenlein, C.V. Shank, and G.A. Lindsay, *CLEO Proceedings*, (postdeadline paper) 602 - 603 (1991).

[15] "FUNCTIONAL AND POLYMERIZABLE COUMARIN DYES FOR COUMARIN DYE-SUBSTITUTED POLYMERS WHICH EXHIBIT NONLINEAR OPTICAL PROPERTIES," G. A. Lindsay, R. A. Henry, and J. M. Hoover, Navy Case No. 72263 (Oct 89).

[16] "NONLINEAR OPTICAL POLYPEPTIDES," G.A. Lindsay, et al., Navy Case No. 73086 (Sept 90).

[17] C.S. Willand and D.J. Williams, *Ber. Bunsenges. Phys. Chem.*, **91**, 1304 (1987).

[18] a) "Nonlinear Optical Polymer with Chromophoric Main Chain," J. D. Stenger-Smith, J. W. Fischer, R. A. Henry, J. M. Hoover, G. A. Lindsay, and L. M. Hayden, *Makromol. Chem., Rapid Commun.* **11**, 141 (1990);
b)"A New Nonlinear Optical Polymer with Mainchain Chromophore," J. D. Stenger-Smith, J. W. Fischer, L. M. Hayden, R. A. Henry, J. M. Hoover, G. A. Lindsay, *A.C.S., Polymer Preprints*, **31**(1), 375 (1990);
c)"Recent Synthetic Developments in Mainchain Chromophoric Nonlinear Optical Polymers," J.D. Stenger-Smith, J.W. Fischer, R.A. Henry, J.M. Hoover and G.A. Lindsay, *Proceedings of the 15th Biennial Polymer Division Symposium* Nov.(1990);
d) "Poly[(4-*N*-ethylene-*N*-ethylamino)-a-cyanocinnamate]: A Non-linear Optical Polymer with a Chromophoric Mainchain. 1. Synthesis and Spectral Characterization," J. D. Stenger-Smith, J. W. Fischer, R. A. Henry, J. M. Hoover, M. P. Nadler, R. A. Nissan, and G. A. Lindsay, *J. Poly. Sci.: Part A: Polym. Chem.*, **29**, 1623-

1631 (1991).

19 "MAIN CHAIN CHROMOPHORIC POLYMERS WITH SECOND ORDER NONLINEAR OPTICAL PROPERTIES," A. Chafin, J. W. Fischer, R. A. Henry, J. M. Hoover, G. A. Lindsay, and J. D. Stenger-Smith, Navy Case No. 72224 (Sep 89).

20 a) "Langmuir-Blodgett Multilayers of Fluorinated , Mainchain Chromophoric, Optically Nonlinear Polymers," J.M. Hoover, R.A. Henry, G.A. Lindsay, C.K. Lowe-Ma, M.P. Nadler, S.M. Nee, M.D. Seltzer, and J. D. Stenger-Smith, *Am. Chem. Soc. Polymer Preprints*, 32(1), 197 (1991);

b)"A New Class of Mainchain Chromophoric Nonlinear Optical Polymers," G.A. Lindsay, R.A. Henry, J.M. Hoover, R.F. Kubin, and J. D. Stenger-Smith, SPIE Proceedings, Dallas, TX, May 8-10 (1991), also reprinted in the Proceedings of the 38th Sagamore Army Materials Research Conference, Watertown, MA, Sept, 10-12 (1991);

c) "Syndioregic Mainchain Polymers for Nonlinear Optical Applications," G.A. Lindsay, J.W. Fischer, R.A. Henry, J.M. Hoover, R.F. Kubin, M.D. Seltzer and J.D. Stenger-Smith, Am. Chem. Soc Polymer Preprints, (Special 40th Anniversary Issue) Philadelphia, PA, June 3-5, (1991);

d) "New Syndioregic, Mainchain, Nonlinear Optical Polymers and their Ellipsometric Characterization," G.A. Lindsay, S.F. Nee, J.M. Hoover, J.D. Stenger-Smith, R.A. Henry, R.F. Kubin, *SPIE Proceedings*, **1064**, 24-26 July (1991).

21 "NEW ACCORDIAN MAIN-CHAIN POLYMERS," G. A. Lindsay, J. W. Fischer, R. A. Henry, J. D. Stenger-Smith, J. M. Hoover, Navy Case No. 72857 (Jun 90).