# Nonlinear Optical Polymers: Discovery to Market in 10 Years?

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Systems that use light as a carrier of information offer the possibility of extremely high speed processing, transmission, and storage of data. Many such photonic systems require high-performance nonlinear optical (NLO) materials (*1*, *2*), particularly those exhibiting second-order NLO effects, which occur only in molecules and materials lacking a center of symmetry (*1*). Certain conjugated organic molecules have been known to exhibit substantial second-order optical nonlinearities, and recently, successful approaches to optimization of these properties by rational modification of molecular structure have been demonstrated. However, achieving the required noncentrosymmetric order has in the past been a major obstacle to the synthesis of materials with large nonlinearities because the large majority of nonchiral organic compounds crystallize in centrosymmetric space groups.

The method most widely used to artificially achieve noncentrosymmetry, and the one closest to commercialization, is the poled-polymer approach. If dipolar NLO species are dissolved in a polymer and subjected to a large electric field while at or above the temperature at which the polymer becomes rubbery (its glass transition temperature, $T_g$), the interaction of the dipole with the field causes the dipolar species to align, to a certain extent, in the direction of the applied field. If the polymer is cooled back to the glassy state with the field applied, then the field-induced noncentrosymmetric alignment can be frozen in place, yielding a material with a second-order optical nonlinearity (*3*). However, this thermodynamically unstable alignment quickly decays in polymers such as poly(methylmethacrylate), resulting in a greatly reduced nonlinearity.

As a result, it was recognized that if polymers could be designed that would more effectively lock the aligned molecules in place, even at elevated temperatures, and if more highly nonlinear molecules could be incorporated, a valuable new technology could flourish. In comparison to inorganic crystal-based electrooptic devices, organic polymer devices have the potential for lower power, higher speed switching and, in addition, could be less expensive to manufacture because polymeric devices are amenable to automated mass production.

For applications in which the electrooptic polymers are used as interconnects on integrated circuits, the polymer must have extremely high thermal stability (because it will have to survive several soldering steps during processing, as well as high operational temperatures) but only modest nonlinearity. In contrast, for some applications that demand high sensitivity and low power consumption, such as spatial light modulation, moderate thermal stability is adequate, but large nonlinearity is essential. Accordingly, it is possible to categorize research on poled polymers according to two goals: (i) synthesis of polymers with large nonlinearities (electrooptic coefficient greater than 30 pm/V) that have long-term thermal stability at 85°C and (ii) polymers with moderate nonlinearity that are stable at high temperatures (≥ 300°C ) for short periods and 150°C for long periods.

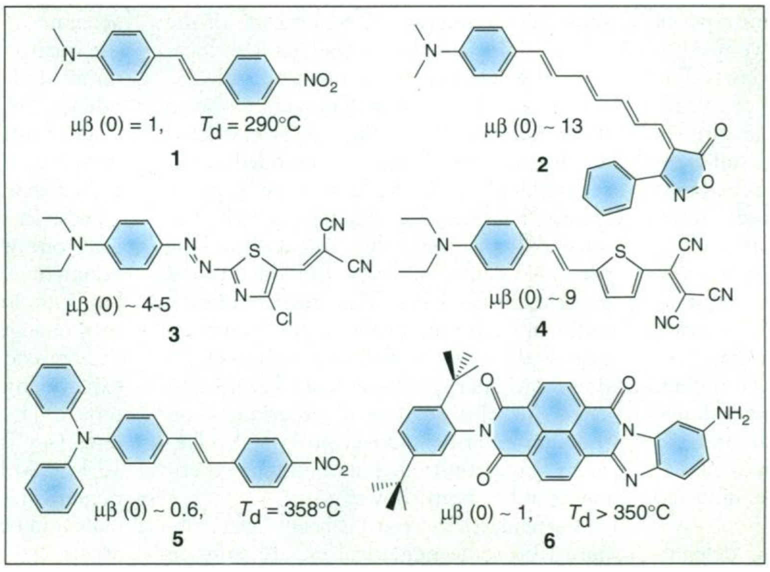

**Fig. 1.** Structures of nonlinear chromophores, with μβ(0) values (normalized to that for DANS) and, in some cases, decomposition temperature, $T_d$.

In poled polymers, the nonlinearity scales directly with the scalar product of the dipole moment, μ and the frequency-normalized hyperpolarizability β(0). In the mid-1980s, state-of-the-art NLO molecules typically had aromatic π-electron systems (such as benzenes and stilbenes), end-capped with electron-donating groups (such as *N*,*N*-dimethylamino) and electron-withdrawing groups (such as nitro). Thus, a donor-acceptor molecule that was considered to be quite nonlinear at that time was 4-*N*,*N*-dimethylamino-4'-nitrostilbene (DANS) (**1**, Fig. 1) for which μβ(0) ~350 × $10^{-48}$ electrostatic units. In general, attempts to increase the magnitude of the nonlinearity focused on using stronger donor and acceptor endgroups (*4*) and increasing the length between the donor and the acceptor (by increasing the number of double bonds, for example) (*5*). In 1991, it was shown that there is an optimal combination of donor and acceptor strengths—and thus, ground-state polarization—required to maximize μβ(0) for a given conjugated bridge, and that beyond this point, increased donor-acceptor strength (or further ground-state polarization) leads to a diminution of the nonlinearity (*6*). More recently it was shown that β(0) could be correlated (*7*) with a molecular structural parameter, the bond length alternation (BLA) (the difference in length between adjacent carbon-carbon bonds), that can be tuned systematically and measured experimentally.

In donor-acceptor–substituted polyenes, BLA is related to the relative contribution of neutral and charge-separated resonance structures describing the molecule, which in turn is dependent on the donor-acceptor strength. Molecules with aromatic ground states (for example, those containing benzene rings, as in DANS) will tend to be more bond length alternated (and less polarized) for a given donor and acceptor pair than a simple polyene of comparable length. This is attributable to a large energetic price associated with the loss of aromaticity in the benzene rings upon polarization. As a result, molecules with donors and acceptors that are sufficiently strong to reach the point where β(0) is maximized, for stilbene-like bridges, have not been synthesized. It was therefore necessary to develop synthetic design strategies to tune the degree of BLA in the π-electron system between the donor and acceptor in order to

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optimize $\beta(0)$. Two key advances have been made in this regard. First, it has been shown that for molecules that have a bridge that loses aromaticity upon polarization, but also have an acceptor that gains aromaticity upon polarization, such as the 3-phenyl-5-isoxazolone compound (**2**) or analogous thiobarbituric acid derivatives, the magnitude of the BLA in the polyene bridge is reduced, and large enhancements of the $\mu\beta(0)$ product—in one case, roughly 40 times that for DANS—can be realized (*8*). Second, it was shown that for molecules in which benzene rings were replaced with heterocyclic rings, such as a thiazole [as in **3** (*9*)] or a thiophene [such as in **4** (*10*)], that have less aromatic stabilization energy, nonlinearities approaching 10 times that of DANS could be obtained. If high concentrations of molecules such as **2** through **4** could be incorporated into poled polymers, with excellent alignment that is maintained over long periods of time, then the resulting materials would have persistent electrooptic figures-of-merit much higher than inorganic materials, such as lithium niobate.

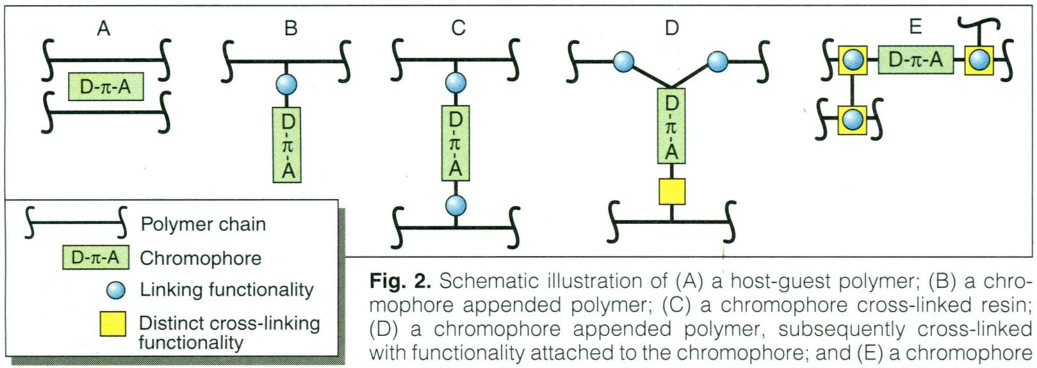

**Fig. 2.** Schematic illustration of (A) a host-guest polymer; (B) a chromophore appended polymer; (C) a chromophore cross-linked resin; (D) a chromophore appended polymer, subsequently cross-linked with functionality attached to the chromophore; and (E) a chromophore containing main chain prepolymer, subsequently cross-linked with an additive, that reacted with functionality in the prepolymer chain.

Researchers have adopted two approaches to improving the long-term stability of molecular alignment in poled polymers. First, several groups have used polymers with very high glass transition temperatures as host matrices (Fig. 2A). The rationale is that if the $T_g$ of the polymer is roughly 150° to 200°C above the ultimate operating temperature, decay of the alignment would be negligible over the device lifetime. This was first demonstrated with a commercial polyimide and NLO chromophore (*11*) and more recently with a highly nonlinear chromophore, **4**, leading to a large poled-polymer electrooptic coefficient (*12*). Moreover, the semiconductor industry was already accustomed to using polyimide as photoresists for and in the packaging of integrated circuitry; thus, for integrated optics applications, it may be possible for polyimide-based electrooptic polymers to be easily incorporated into devices. The motion of chromophores in polymer matrices might be further restricted if the chromophore is covalently attached at one or more sites to the polymer (Fig. 2B) (*13*).

In related approaches, various methods of cross-linking (Fig. 2, C through E) have been used and yield materials with exceptional stability and minimal loss of NLO coefficients (*14–16*). In these systems, the cross-linking process can take place at temperatures under 200°C; however, in the high-$T_g$ polymer approach, the minimum poling temperature being seriously considered is 225° to 250°C, and for the integrated optics applications, poling temperatures in excess of 350°C may be necessary. The latter thermal requirements are extremely demanding for organic molecules, and for chromophores with extended conjugation, stability even at 200°C is nontrivial.

Accordingly, one active avenue of research is to identify chromophores that are both highly nonlinear and thermally robust. Some earlier "rules of thumb" about factors that lead to chromophore thermal instability have recently been shown to be inaccurate. For example, it was generally believed that in the common dye Disperse Red-1, whose structure is similar to DANS, the nitro group was the weak point for thermal decomposition. However, it was recently shown that the alkyl amino functionality was the culprit and that for many chromophores with amino donors, replacement of the alkyl functionality on the nitrogen with an aryl group (like phenyl) could improve the thermal stability dramatically (by over 65°C relative to DANS in the case of **5**) (*17*). In other studies, it was shown that for molecules containing a thiophene bridge, rather than a simple polyene bridge, it was possible to achieve excellent thermal stability without a major sacrifice of optical nonlinearity. Thus, it was recently demonstrated that chromophore **4** could be poled at 220°C to yield a polymer that retained 80% of its initial electrooptic coefficient even after 600 hours at 120°C (*12*).

It has also been shown that fused-ring structures lead to respectable nonlinearities and high thermal stability. For example, in **6**, the functionality that is responsible for imparting the nonlinearity is intrinsically similar to that found in polyimides. Although its nonlinearity is modest [$\mu\beta(0)$ roughly equal to that of DANS] compared with some of the other compounds shown in Fig. 1, thermal stability in excess of 350°C was reported (*18*). Thus, these results demonstrate that large molecular nonlinearities and high thermal stability can be achieved in organic chromophores, and by careful design, chromophores with both of these important attributes can be obtained.

Our understanding of second-order NLO materials has advanced dramatically over the past several years. In particular, there now exist strategies for the optimization of molecular second-order nonlinearities, as well as for improving the thermal stability of NLO chromophores. Poled polymers with nonlinearities as large as state-of-the-art inorganic materials have now been reported, and systematic approaches to locking in this nonlinearity at high temperatures have been demonstrated. Nonlinearities much larger than those realized to date are achievable if we can build the "best of the bests" all into one system. If so, then the great promise of organic materials for second-order NLO applications will be realized. One thing is certain: The window of opportunity for organic electrooptic materials is narrow; if they are to make a technological impact, commercial materials, devices, and systems will have to be available within 3 to 5 years. The race is on.

### References

1. P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers* (Wiley, New York, 1991).
2. S. R. Marder, J. E. Sohn, G. D. Stucky, Eds., *Materials for Nonlinear Optics: Chemical Perspectives* (ACS Symposium Series, vol. 455, American Chemical Society, Washington, 1991).
3. K. D. Singer, J. E. Sohn, S. J. Lalama, *Appl. Phys. Lett.* **49**, 248 (1986).
4. H. E. Katz *et al.*, *J. Am. Chem. Soc.* **109**, 6561 (1987).
5. M. Barzoukas, M. Blanchard-Desce, D. Josse, J.-M. Lehn, J. Zyss, *Chem. Phys.* **133**, 323 (1989).
6. S. R. Marder, D. N. Beratan, L.-T. Cheng, *Science* **252**, 103 (1991).
7. C. B. Gorman and S. R. Marder, *Proc. Natl. Acad. Sci., U.S.A.* **90**, 11297 (1993).
8. S. R. Marder *et al.*, *Science* **263**, 511 (1994).
9. C. W. Dirk, H. E. Katz, M. L. Schilling, L. A. King, *Chem. Mater.* **2**, 700 (1990).
10. P. Rao, A. K.-Y. Jen, K. Y. Wong, K. J. Drost, *Chem. Commun.* 1993, 1118 (1993).
11. J. W. Wu *et al.*, *Appl. Phys. Lett.* **58**, 225 (1991).
12. K. Y. Wong and A. K.-Y. Jen, *J. Appl. Phys.*, in press.
13. J. T. Lin, M. A. Hubbard, T. J. Marks, W. Lin, G. K. Wong, *Chem. Mater.* **4**, 1148 (1992).
14. M. A. Hubbard, T. J. Marks, W. Lin, G. K. Wong, *ibid.*, p. 965.
15. C. Xu *et al.*, *Macromolecules* **25**, 6714 (1992).
16. C. Xu *et al.*, *ibid.*, p. 6716.
17. C. R. Moylan *et al.*, *J. Am. Chem. Soc.* **115**, 12599 (1993).
18. R. F. Shi, M. H. Wu, S. Yamada, Y. M. Cai, A. F. Garito, *Appl. Phys. Lett.* **63**, 1173 (1993).