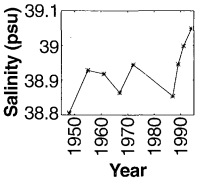

Fig. 5. Observed temporal trend in Aegean Sea salinities, 1948 to 1994. Data points are averages below 500 m in the years for which observations are available.

The intrusion of Aegean waters has changed appreciably the deep distributions of all properties in the eastern Mediterranean. There have been reports of inverted temperature gradients recently in sediments just below the water interface (*14*). The lifting of deep waters has brought nutrient-rich waters closer to the surface, so that in some areas seasonal mixing might bring extra nutrients into the euphotic layer, enhancing biological production. By the same mechanism, density in the so-called Levantine intermediate water layer—that is, the waters feeding the subsurface outflow through the Sicilian Passage into the western Mediterranean (*4*, *5*)—should have increased, enhancing water exchange through the passage. Salinity may also be affected, which could influence deep water production in the western Mediterranean and possibly beyond.

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Chromophores with Strong Heterocyclic Acceptors: A Poled Polymer with a Large Electro-Optic Coefficient

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Syntheses of a series of conjugated donor-acceptor chromophores, based on a strongly electron-withdrawing heterocyclic acceptor, have led to compounds with large second-order optical nonlinearities. Incorporation of one of these chromophores into polycarbonate at 20 percent weight loading yielded, after poling at 150 volts per micrometer, a polymer film with an electro-optic coefficient, r_{33}, of 55 picometers per volt at 1.313 micrometers. This value is roughly twice that of lithium niobate. A variant of one of these chromophores exhibited improved thermal stability as needed for use in polymers with higher glass transition temperatures. The chromophore was soluble in common organic solvents, had a scalar product of the dipole moment, μ, and the molecular first hyperpolarizability, β (corrected for dispersion), of roughly 5000×10^{-48} electrostatic units, and showed less than 10 percent decomposition after heating for 20 minutes in air and at 200°C in an inert organic solvent.

Materials that exhibit the electro-optic effect have refractive indices that can be modulated by application of an external electric field (*1*, *2*). Such materials can be used for a variety of telecommunications and signal processing applications that require light to be modulated or routed within a fiber optic network (*3*). The promise of organic poled polymers with electro-optic coefficients (r_{33}) that surpass those of inorganic crystals such as lithium niobate, whose r_{33} is 30.8 pm/V (*4*) at telecommunication wavelengths of 1.3 and 1.5 μm, has provided the impetus for the development of highly nonlinear chromophores (*3*). In poled polymers, the electro-optic coefficient is proportional to $\mu\beta$, the scalar product of the dipole moment μ and the molecular first hyperpolarizability β.

Recent studies show that for conjugated organic donor-acceptor polyene dyes, there is a specific degree of polarization and concomitant bond length alternation, BLA (the difference between the average lengths of adjacent carbon–carbon bonds), in the ground state of the molecule that is required to optimize $\mu\beta$ (*5*). This point is reached when there is the correct combination of donor and acceptor strengths for a given conjugated π-electron bridge structure (*6*). Beyond this point, stronger donors or acceptors, which lead to increased polarization, can attenuate $\mu\beta$ (*6*, *7*). Most molecules examined to date, such as stilbene and diphenylpolyene donor-acceptor compounds, are not sufficiently polarized to optimize $\mu\beta$. Here, we report the synthesis of a series of chromophores, based on a strong heterocyclic acceptor, that have large molecular optical nonlinearities. One such chromophore has led to a polymer film with an electro-optic coefficient roughly twice that of lithium niobate (*4*).

In an attempt to develop molecules with large values of $\mu\beta$, we synthesized and characterized a series of chromophores based on a very strong acceptor, [3-(dicyanomethylidene)-2,3-dihydrobenzothiophen-2-ylidene-1,1-dioxide] (*8*), which contains two strong electron withdrawing groups, the dicyanomethylidene group and the sulfone group. A commercially available dye, Foron Blue (*8*), incorporating this acceptor has been examined for applications involving anomalous dispersion and phase-matched generation of second harmonics (*9*), but to our knowledge this acceptor has not been used in dyes for electro-optic applications. Accordingly, we reacted 3-(dicyanomethylidene)-2,3-dihydrobenzothiophene-1,1-dioxide (*8*) with (4-*N*,*N*-dimethylamino)phenyl-(CH=CH)$_n$ CHO or with (5-piperidyl)-thio-

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phen-2-yl-$(CH{=}CH)_nCHO$ (where n is defined in Fig. 1) and (4-*N*,*N*-di-*n*-butylamino)phenyl-$(CH{=}CH)_2CHO$ under Knoevenagel conditions (*10*) and characterized the compounds by ^1H nuclear magnetic resonance (NMR), ultraviolet visible spectroscopy, elemental analysis, and mass spectroscopy. The visible absorption maxima, values of $\mu\beta$ measured by electric field–induced second harmonic generation, EFISH, and dispersion-corrected $\mu\beta(0)$ values for compounds in the series **1[*n*]** to **3[*n*]** (as well as for 4-*N*,*N*-dimethylamino-4′-nitrostilbene, **4**, a standard reference compound) are given in Table 1. The compounds in the series **1[*n*]** have large molecular optical nonlinearities and are more nonlinear [comparing $\mu\beta(0)$ values] than either the compounds in series **2[*n*]** with the weaker thiobarbituric acid acceptor (*11*) or the compounds in series **3[*n*]** with the stronger piperidinothiophenyl donor (*12, 13*). We speculate that the unusual decrease in $\mu\beta$ upon going from series **1[*n*]** to **3[*n*]** is a consequence of the latter being too polarized or having too little BLA for β to be optimized in dichloromethane.

To our knowledge, a poled polymer heavily loaded with a covalently attached stilbene chromophore exhibiting an r_{33} value of 34 pm/V measured at 1.3 μm has the largest electro-optic coefficient reported (*14*). We were interested to see if the large molecular nonlinearities in series **1[*n*]** would lead to large electro-optic coefficients in poled polymers. Therefore, we synthesized a highly soluble di-*n*-butyl analog of **1[2]**, **5**, in order to incorporate it into polycarbonate thin films at a reasonably high concentration for poled polymer studies. Compound **5** is slightly more nonlinear than **1[2]** (Table 1). A polycarbonate (PC) film containing 20 weight % of **5** was spin-coated onto a glass substrate coated with indium tin oxide, and a thin film of gold was deposited on top of the polymer as the second electrode. The chromophore-PC composite was poled at 80°C with an applied field of 150 V/μm. After the sample was cooled to ambient temperature, the electro-optic coefficient was determined at 1.313 μm with modulated ellipsometry (*15*). The poled chromophore-PC composite yielded an r_{33} value of 55 pm/V, which is substantially greater than previously reported values for poled polymers (*16*).

The visible near-infrared spectrum of **5** illustrates an important feature that we have observed in several chromophores that are highly polarized and exhibit large values of $\mu\beta$. Dye **5** and related dyes show a very sharp low-energy absorption edge relative to conventional chromophores such as the common azo dye Disperse Red 1 (compound **7** in Fig. 1), as is illustrated in Fig. 2. Thus, although chromophore **5** has an absorption maximum at 770 nm, even in relatively concentrated solutions (0.06 M), there is 98.3% transmission at 1.3 μm (in a 1-cm cuvette). We estimate from this measurement (assuming a linear scaling of chromophore absorption with concentration, to a concentration higher by a factor of 7) that the intrinsic optical loss in the polymer (0.4 M in dye) described above that is attributable to chromophore absorption would be roughly 0.6 dB/cm at 1.3 μm. Furthermore, measurements as a function of the static phase shift between *S* and *P* waves showed that the electro-optic coefficient had essentially no imaginary component (<1%), and therefore modulation of the dye's absorption at 1.3 μm by the applied field was negligible. This observation provides further evidence that a polymer loaded with **5** (even at 20% by weight) has negligible absorption at the measurement wavelength.

A polymer sample kept at room temperature retained 85% of the initial value of the electro-optic coefficient 100 hours after poling and gave the same value after 300 hours, which demonstrates good thermal stability at room temperature. However, we expect that the low glass transition temperature (T_g) of the polymer (~80°C) will preclude its use in commercial devices. It would be necessary to use a polymer with a significantly higher T_g to improve the long-term temporal stability of the poling-induced alignment of the chromophore, and thus the chromophore itself must be sufficiently stable to survive the poling and processing conditions above T_g. Examination of the absorption spectrum of **5** before and after heating in methylnapthalene (an inert solvent with a high boiling temperature) at 150°C in air indicated that after 20 min (adequate time for the poling procedure) there was significant (~40%) decomposition of the chromophore. We have found that substitution of thiophene for an

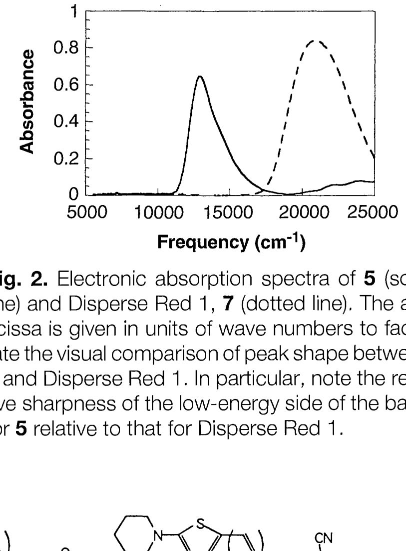

Fig. 2. Electronic absorption spectra of **5** (solid line) and Disperse Red 1, **7** (dotted line). The abscissa is given in units of wave numbers to facilitate the visual comparison of peak shape between **5** and Disperse Red 1. In particular, note the relative sharpness of the low-energy side of the band for **5** relative to that for Disperse Red 1.

Table 1. Absorption maxima (λ_{max}) and $\mu\beta$ and $\mu\beta(0)$ values [in 10^{-48} electrostatic units (esu)], determined by EFISH at 1.907 μm, in dichloromethane, for selected compounds shown in Fig. 1. For $\mu\beta$, the error in the measurements is estimated to be ±20%. The $\mu\beta$ values have not been corrected for the electronic deformation contribution to the EFISH signal. The static $\mu\beta(0)$ values were estimated with the use of the two-level model (*18*). The application of this simple model to compounds with absorption maxima in the vicinity of the second harmonic wavelength may not provide a very reliable estimate of $\mu\beta(0)$. Therefore, for compounds with absorption maxima >700 nm, the values listed should be considered only as estimates of the static nonlinearity.

Compound	λ_{max} (nm)	$\mu\beta$ (10^{-48} esu)	$\mu\beta(0)$ (10^{-48} esu)
1[0]	590	1,100	600
1[1]	676	3,300	1,450
1[2]	744	10,500	3,500
2[1]*	572	1,780	1,050
2[2]	604	3,900	2,100
3[0]	618	450	240
3[1]	726	2,050	740
3[2]	834	10,000	1,900
4	430	640	350
5	770	13,500	3,900
6	744	15,000	5,000

*The same compound has been measured previously and gave a value of 1457 × 10^{-48} (*11*), in good agreement with the values reported here.

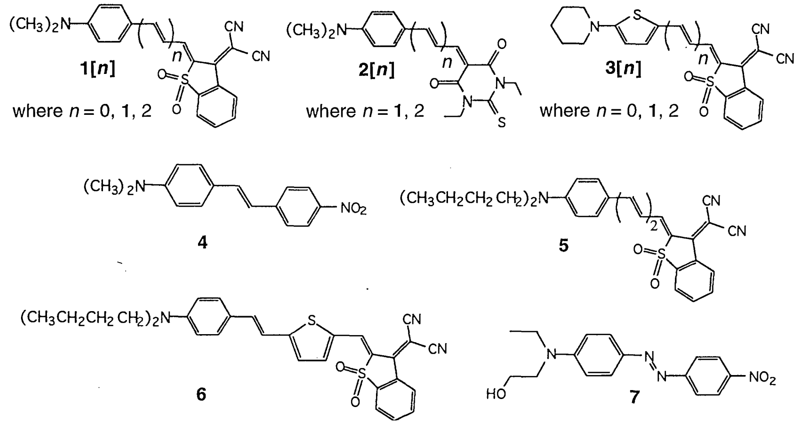

Fig. 1 . Molecular structures of donor-acceptor chromophores used here.

olefinic double bond in the π-electron bridge could lead to significant improvement in the thermal stability of the chromophore without a sacrifice of its optical nonlinearity (*17*).

Accordingly, we synthesized **6,** in which one of the double bonds in the polyene bridge was replaced by a thiophene ring, by a reaction analogous to that used for **5** and characterized the compound by ^{1}H NMR and elemental analysis. Interestingly, **6** retained the excellent solubility observed for **5** and had a similar absorption maximum in the visible spectrum. EFISH measurements indicated that **6** was somewhat more nonlinear than **5**, as seen in Table 1. Compound **6** showed no significant decomposition after heating in methylnaphthalene at 150°C for 20 min (less than 5%) and less than 10% decomposition after heating at 200°C for 20 min. Thus, these results suggest that it is possible to develop chromophores with high optical nonlinearity and adequate thermal stability and to permit their incorporation into high-T_g polymers.

Our results suggest that the [3-(dicyanomethylidene)-2,3-dihydrobenzothiophen-2-ylidene-1,1-dioxide] acceptor is sufficiently powerful to lead to very large values of $\mu\beta$ for several extended dialkylaminophenyl-substituted chromophores. In addition, the r_{33} value reported here is significantly larger than any value that has been reported to date for a poled polymer and almost twice that of lithium niobate. Molecules can be synthesized that have not only large nonlinearities but also reasonable stability at 200°C. Although much additional work must be done before commercially viable electro-optic polymers with such large r_{33} values become available, these results show that organic polymers can have substantially larger optical nonlinearities than lithium niobate.

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    $$\Delta\Phi = (\pi/\lambda)\Delta nL = (\pi/\lambda)n^3 r_{33}EL$$

    where λ is the wavelength of light being modulated, L is the propagation distance over which the beam is being modulated, n is the refractive index, and E is the applied external field. Thus, considering the phase change per unit electric field, a useful figure of merit would be $n^3 r_{33}$. For lithium niobate, $n^3 r_{33}$ is ~300 pm/V (*4*) and for a reasonable n of ~1.7 for our polymer, $n^3 r_{33}$ would be ~270 pm/V, similar to the value for lithium niobate. Further considerations show that a figure of merit characterizing high-frequency power consumption is given by $n^3 r_{33}/\varepsilon$ (where ε is the dielectric constant). For electro-optic polymers (*2*), ε is conservatively <6. In contrast, lithium niobate has a value of ε of 28 (*4*); thus, considering the figure of merit for power consumption, the polymer would be much more efficient.
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Chaos and the Shapes of Elliptical Galaxies

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Hubble Space Telescope observations reveal that the density of stars in most elliptical galaxies rises toward the center in a power-law cusp. Many of these galaxies also contain central dark objects, possibly supermassive black holes. The gravitational force from a steep cusp or black hole will destroy most of the box orbits that constitute the "backbone" of a triaxial stellar system. Detailed modeling demonstrates that the resulting chaos can preclude a self-consistent, strongly triaxial equilibrium. Most elliptical galaxies may therefore be nearly axisymmetric, either oblate or prolate.

Information about the three-dimensional shape of a galaxy is lost when the galaxy is projected onto the plane of the sky. This loss of information is acute in the case of elliptical galaxies, whose apparent shapes are elliptical but whose intrinsic shapes could be oblate, prolate, or fully triaxial. Before about 1975, elliptical galaxies were thought to be rotationally flattened oblate spheroids. The discovery that elliptical galaxies rotate much more slowly than does a fluid body with the same shape (*1*) led to the hypothesis that most of these systems are triaxial ellipsoids, with shapes that are maintained by anisotropic velocity dispersions rather than by centrifugal force (*2*). The triaxial hypothesis was supported by the successful construction of self-consistent triaxial models on the computer (*3*). Most of the stars in these numerical models occupied "regular" orbits that respect three isolating integrals, two in addition to the energy; the major families of regular orbits are the short- and long-axis "tubes" and the "boxes" (*4*).

Box orbits are uniquely associated with the triaxial geometry; they densely fill a box- or bow tie–shaped region, and a star on such an orbit passes arbitrarily close to the galaxy center after many oscillations. The time-averaged shape of a box orbit mimics that of the underlying galaxy, and the potential from a star on a box orbit helps to support the triaxial shape of the galaxy as a whole. Box orbits are always found to be strongly populated in the self-consistent triaxial models. They exist only in triaxial potentials with "cores," that is, models in which the density near the center is approximately constant and the corresponding gravitational potential is roughly quadratic in the coordinates (*5*).

Recent Hubble Space Telescope observations of the centers of elliptical galaxies (*6*) reveal that these galaxies almost never have constant-density cores; the stellar density always continues to rise, roughly as a power law, toward the smallest observable radius. In fainter ellipticals, the stellar density ρ increases roughly as $\rho \propto r^{-2}$, whereas for brighter ellipticals the cusp slope is $\rho \propto r^{-1}$ or shallower (*7*). In addition, there is increasingly strong evidence for massive dark objects (MDOs), possibly supermassive black holes, at the centers of many elliptical galaxies (*8*). In the most convincing cases, these central singularities appear to contain as much as 1% of the total mass of the galaxy.

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