Photostability of electro-optic polymers possessing chromophores with very efficient amino donors and cyano-containing acceptors

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The photostability of various electro-optic active guest–host polymers, doped with chromophores that possess very efficient cyano-containing acceptors and dialkyamino- or diarylamino-benzenes, and also their extended thiophene analogs as bridging structures, has been investigated over a broad wavelength range in the near infrared and the visible.   A variation of over 2 orders of magnitude was found in the probability that an absorbed photon will lead to a photodegraded chromophore.   The most photostable chromophore contained a tricyanovinyl acceptor and a diarylaminobenzene bridge unit.   © 2001 Optical Society of America

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1. INTRODUCTION

Polymers have been shown to have a promising future in photonics.[1–5]   For example, in electro-optics applications modulation with >100 GHz bandwidth has been demonstrated, and modulation with half-wave voltages approaching 1 V has been reported.[1,5]   The origin of the large, fast nonlinearities used is the tailored and designed chromophores that are dispersed and oriented in a polymer host.   Usually these chromophores are chemically bonded to the polymer backbone for enhanced concentration and orientational stability.[6,7]   The chromophore structures consist of an electron-donor and an electron-acceptor group at opposite ends of the molecule, separated by an electron transporting bridge structure that facilitates electron delocalization.   This structure typically results in the formation of a strong charge-transfer state characterized by a large permanent molecular dipole moment, a large transition moment for excitation by incident light to the first excited state, and a large first hyperpolarizability.   Usually, the stronger the charge-transfer state, the larger the shift of the charge-transfer peak toward the infrared, and usually the larger the second-order nonlinearity one can expect after efficiently orienting the chromophores.

The design of such molecules to optimize various important parameters has been an important task for the last decade.[6,7]   For poled polymers the initial emphasis has been on large dipole moments and first-order hyperpolarizability because both were needed for making media with large macroscopic second-order nonlinearities.[6,7]   Other important criteria have been the stability of the molecular alignment against temperature, and chemical stability, etc.[8–10]   This has led to the development of state-of-the-art polymers with both large nonlinearities and impressive thermal and chemical stability.   Some of the most promising polymers developed to date contain cyano groups and aniline bridge structures.[11–13]   Recently, yet another important parameter has been added to the requirement list; namely, photochemical stability.[14–17]   The absorption of photons by molecules under illumination for long periods of time leads to changes of their chemical structure that cause them to lose their nonlinearity.   This effect is referred to as photodegradation.
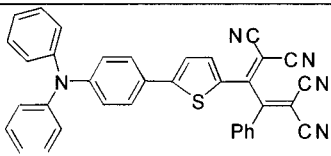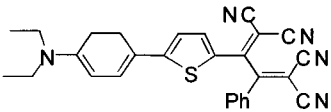
Table 1. Compounds Studied
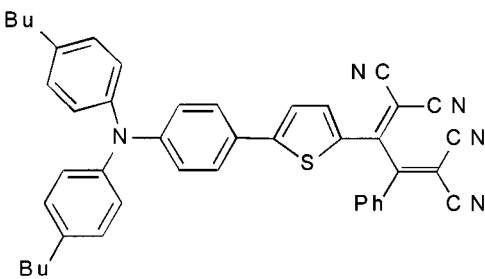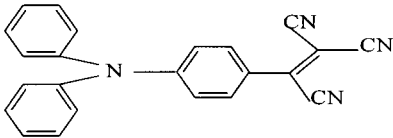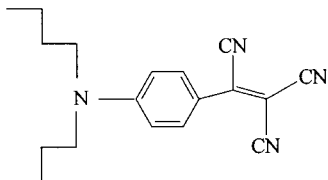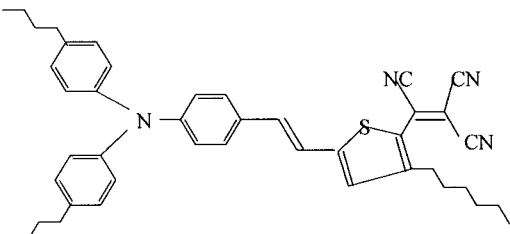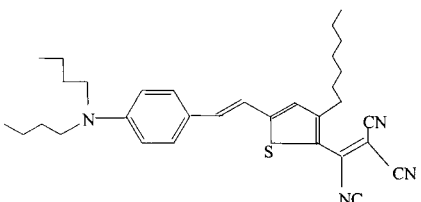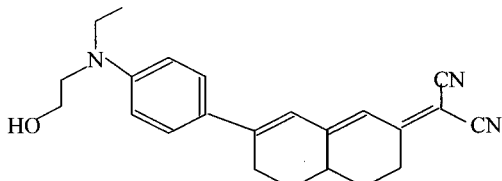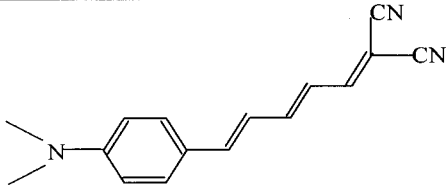
Symbol[a]	Chromophore	λ_{max} (nm)	B (543 nm, 2.28 eV)	B (633 nm, 1.96 eV)
1 ◇		575	3×10^6	8×10^6
2 ▽		595	5×10^6	8×10^6
3 △		600	1×10^6	2×10^6
4 ✕		520	1×10^7	1×10^8
5 ○		525	2×10^7	1×10^8
6 □		635	4×10^5	5×10^5
7 +		680	5×10^5	7×10^5
8 ●		510	6×10^5	2×10^6

Table continues

Table 1. (Continued)

Symbol[a]	Chromophore	λ_{max} (nm)	B (543 nm, 2.28 eV)	B (633 nm, 1.96 eV)
9 ▲		505	6×10^5	1×10^6

[a]Symbols and numbers used in figures.

The photodegradation of various chromophore families has been reported recently, including stilbenes and azobenzenes.[14–24] For example it has been shown that stilbene-based chromophores degrade very quickly because of the attack on the central stilbene bridge carbon bond by oxygen in the presence of light absorption in the main absorption band.[19,21,22] Azobenzenes are more stable, especially when antioxidant groups are incorporated into the chromophore structure.[20,22–24] The systematic wavelength dependence of photodegradation has been identified, and the range of stability for a large spectrum of bridge structures and donor and acceptor groups has been probed.

In this paper a hitherto unexplored class of chromophores based on dialkyaminobenzenes or diarylaminobenzenes, and also their extended thiophene analogs as bridging structures, is examined for photostability. Because of their key role in producing strong charger transfer states, the current studies are focused on electron acceptors based on cyano-containing groups, such as the dicyanovinyl, tricyanovinyl, and tetracyanobutadienyl.[11–13] In fact, some of the compounds studied here have been determined to have not only very large nonlinearities but also high thermal stability. For nine such chromophores the figure of merit (FOM) for photostability was measured as a function of wavelength in the near infrared up to 1.3 μm.

2. EXPERIMENTAL DETAILS

The synthesis and characterization of the chromophores investigated here have been discussed in the literature.[11–13] The nine chromophores investigated are listed in Table 1 along with the location of their absorption maxima. (The individual absorption spectra are shown in Figs. 2, 4, and 6.) All spectra were recorded with a two-way apparatus using an identical substrate and an undoped polymer cover-layer film of similar thickness as a reference.

These chromophores were incorporated as guest molecules in a poly(methyl methacrylate) polymer host matrix with a typical 5% weight loading. The polymers were dissolved in cyclopentanone and then spin coated onto the substrate (fused silica) with a standard photoresist spinner. The films were a few micrometers thick.

Note that, to provide a uniform and reproducible illumination on the polymer film, the opposite side of each substrate was coated with a thin aluminum film into which round holes 50–250 μm in diameter were fabri-

cated photolithographically, prior to the polymer spin-coating procedure. (Illumination was then performed always onto the aluminum side, through the hole, the substrate, and then the doped polymer.)

The experiments are based on the following model for the photodegradation process.[25] Assuming a single dominant excited charge-transfer state with a well-defined absorption spectrum, the absorption of a photon raises the molecule from the ground state to this excited state. Normally the deexcitation returns the molecule to its ground state. However, a small fraction of the excited molecules undergoes a geometrical or chemical change and returns to a different ground state, one in which the electro-optical activity is greatly reduced or even zero. As a result the concentration of the electro-optic active molecules is decreased, and the magnitude of the corresponding charge-transfer absorption line is also decreased. By measuring the absorption in the tail of this spectral line, where it is assumed that the photoproduct absorption may be neglected, the rate of loss of the electro-optic active species can be measured.

Whether a single excited state dominates the process and whether there is a single photodegradation channel, i.e., a single (dominant) final state, can be tested by monitoring the absorption spectrum as a function of illumination time. Previous studies on stilbenes and azobenzenes have shown multiple contributing excited states and multiple decay channels.[19–21] However, in the present collection of chromophores, there are several in which the charge-transfer absorption band is well separated spectrally from other absorption features (that are usually located in the blue to near-UV region). One example is the chromophore **3**, *N,N*-di(4-butylamino)phenyl-thiophene-5[1,3(1,4-bis-dicyano-3-phenyl)butyldiene] in Table 1. Its absorption spectrum (Fig. 1) was measured at different time intervals when the film was illuminated with red light at $\lambda = 633$ nm in air. Note that initially all of the spectra pass through essentially a single point called an isobestic point. This usually implies that there is a transfer of oscillator strength from a single line in the visible to single or to multiple absorption lines deep in the UV. Since no additional peaks are observed for early times, the photodegradation products are likely to be short molecules whose excitation spectrum lies below 400 nm. This implies that there is only one charge-transfer state participating in the degradation process, similar to the case found previously in azobenzenes under a nitrogen atmosphere.[20,23] This is contrary to the previous cases in which no isobestic point was observed, when
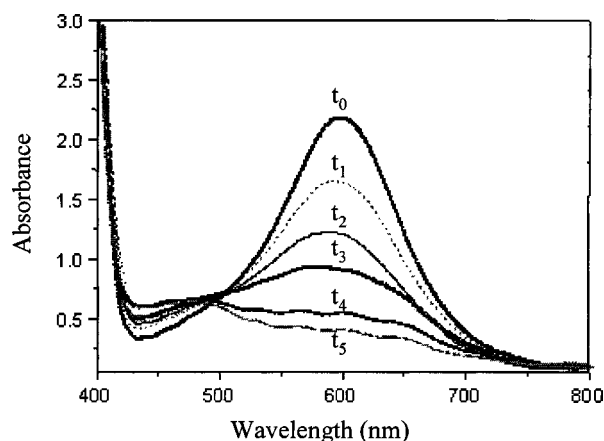
Fig. 1. Evolution of the absorption spectrum of compound **3** with time, under 0.16 W/cm^2 irradiation at 633 nm. Note the presence of an isobestic point around 475 nm. The illumination times are $t_0 = 0$ min, $t_1 = 15$ min, $t_2 = 30$ min, $t_3 = 90$ min, $t_4 = 300$ min, and $t_5 = 600$ min.

there were multiple decay pathways with different decay times. One should then conclude that in the present case, there is only one pathway for significant degradation. Therefore, the photodegradation of chromophores with charge-transfer bands well separated from the UV region, like many of those studied here, could involve only a single excited state in the early stages. However, a new spectral peak does begin to grow at ~475 nm that eventually shifts the isobestic point to shorter wavelengths for times in excess of 90 min. This 475-nm spectral line takes only a small fraction of the initial oscillator strength associated with the charge-transfer state.

The wavelength-dependent photostability measurements are relatively straightforward and have been described in detail elsewhere.[20,23] Radiation of a specific wavelength, ranging from 450 to 1064 nm (and in some cases to 1320 nm), irradiates a well-defined region of a thin film of the polymer-chromophore sample. (We used a number of different lasers for that task including He–Ne at 633 and 544 nm, pulsed Nd:YAG at 1060 and 1320 nm, Ti–sapphire in the 750–900-nm range, and Ar and He–Cd for the shorter wavelengths from 530 down to 450 nm. Data at each wavelength were taken in the linear regime, in conditions where the observed changes were linear with respect to the photon flux used.) The change in the transmission in the tail of the dominant charge-transfer band was measured as a function of time. The initial slope in the film transmission versus time (i.e., versus the integrated photon flux) directly gives the photostability FOM B/σ. Here B is the number of absorption events needed, on average, to photodegrade a single chromophore molecule, and σ is the molecular absorptivity at the wavelength λ of the incident radiation. The effective lifetime of the chromophores is then $\tau = B/\sigma n$, where n is the photon flux.

3. WAVELENGTH DEPENDENCE OF THE FIGURE OF MERIT

We choose to separate the chromophores that we have studied into three groups. Chromophores **1–3**. Each

have a tetracyanobutadienyl group in the acceptor and a benzenethiophene bridge between the donor and acceptor. Chromophores **4–7**. Each have a tricyanovinyl group as the acceptor and a benzene as part of the bridging structure. Finally, two miscellaneous chromophores, **8** and **9**. Both have a dicyanovinyl group at the acceptor end and either a polyene or a fused polyene as the bridge. In each case the order was chosen for increasing wavelength in the charge-transfer state, which is usually an indicator of increasing electro-optic activity.

A. Chromophores with the Tetracyanobutadienyl Acceptor Group
For the three chromophores containing the tetracyanobutadienyl group at the acceptor end, the linear absorption spectra, shown in Fig. 2, are similar. They all peak between 570 and 600 nm. The spectrum of compound **1**, with a diphenylamino group as the donor, is marginally broader than **2** and **3**, and the absorption tail at long wavelengths is also more pronounced for **1**.

The plots of the measured FOM B/σ are shown in Fig. 3. The variation with wavelength is typical of that found previously for other electro-optic chromophores.[20–24] The FOM rises from its minimum value at the peak of the ab-
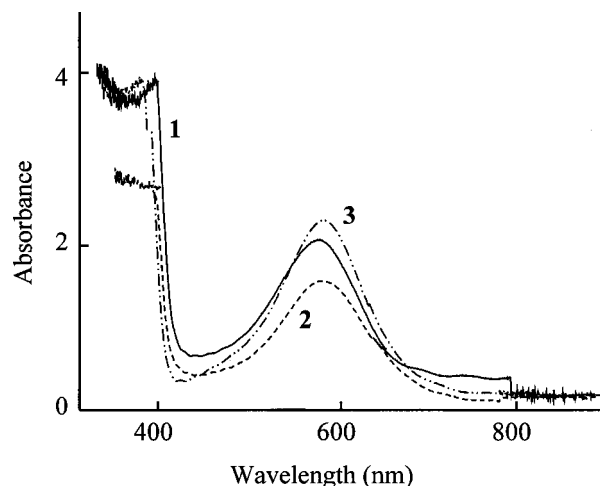

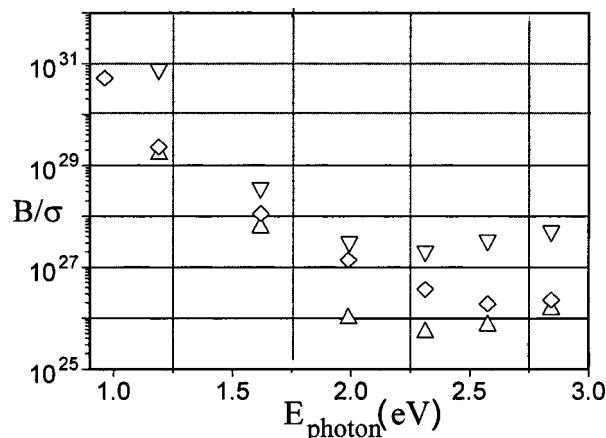Fig. 2. Absorption spectra of thin films of compounds **1–3**.

Fig. 3. Photostability figure of merit (FOM) B/σ as a function of exciting photon energy as measured in air for guest–host polymers **1–3**. Diamond, **1**; inverted triangle, **2**; triangle, **3**.

sorption toward both the infrared and UV regions of the spectrum. It has been shown for azobenzenes and stilbenes that this increase in B/σ toward the near IR is due to the variation in σ with wavelength and that B is, in comparison, approximately a constant.[22,23] This leads to the minimum in B/σ at the absorption peak and the dramatic increase with increasing wavelength. At wavelengths in the vicinity of 1300 nm this trend is no longer observed, and B/σ levels off and in some cases has been found to decrease relative to its 1064-nm value.[22,23] This behavior, which has been attributed to the generation of singlet oxygen, was also found in this study.

The value of the molecular absorptivity was estimated from the measured absorption spectra and from the concentration of guest chromophores. The values of B deduced from B/σ and σ are listed in Table 1 at two neighboring wavelengths: 544 nm (2.28 eV) and 633 nm (1.96 eV). The estimated uncertainty is a factor of two.

The compound with diethylamino as the donor group consistently exhibits the highest FOM. Note, however, from Table 1 that chromophore **2** has the same value of B as **1**, despite having a smaller B/σ: This is a consequence of the smaller absorptivity per molecule of compound **2**, as indicated by the relative absorption spectra in Fig. 2. This reinforces the conclusion that it is both B and σ that are important for long lifetimes against photodegradation.

The third compound, with *N,N*-dibutylphenylamino donor groups, is the least photostable. This result was unexpected and shows the complexity of this photostability case. This instability may be due to the benzyl hydrogen atoms on the donor group that are sensitive to light illumination and tend to generate reactive H radicals to degrade the nonlinear optical chromophores. It is interesting to compare the values of B obtained at 544 and 633 nm. Despite the uncertainty in this parameter of a factor of two, nevertheless there is a consistent trend that the value of B closer to the UV (544 nm) is always smaller than that closer to 633 nm, which indicates that there may be additional contributions from degradation processes at lower wavelengths (higher energies). Note that for compound **3**, for which the absorption spectrum was measured as a function of illumination time, the two values of B obtained at 544 and 633 nm agree to within the experimental uncertainty, as expected from those measurements obtained for **1** and **2**.

B. Chromophores with the Tricyanovinyl Acceptor Group

The chromophores containing the tricyanovinyl group are separated into two groups, the first containing just an aminobenzene bridge (**4** and **5**), and the others with a longer benzenethiophene stilbene bridge (**6** and **7**).

The *N,N*-diphenylaminobenzene and *N,N* dibutylaminobenzene 4-tricyanovinyl compounds **4** and **5** are among the most stable studied to date. (The only exception found previously was the azobenzene Disperse Red 1, with a methacrylate antioxidant group grafted on, which acts as an antioxidant.[24]) Both compounds have almost identical absorption spectra (Fig. 4) and a similar variation in the FOM versus wavelength (Fig. 5). The long wavelength value of B is more than an order of magnitude

larger than any of the other chromophores reported here. Note that the value of B in both cases increased dramatically from 544 to 633 nm, which indicates that multiple excited states, presumably located at higher energies, are involved in the process. The large increase in B at 633 nm implies that the strong charge-transfer excited states at 520 nm are the more stable.[19,21] This coupled with the narrow spectral width of the absorption spectra (Fig. 4) is a good prognosis for excellent photostability in the communications bands if no additional effects occur at still longer wavelengths.

The rest of the tricyanovinyl group consists of compounds **6** and **7**. They have more extensive conjugated electron pathways between the donor and acceptor groups that result in absorption peaks moved toward the IR relative to compounds **4** and **5**. Their absorption peaks are at 620 and 680 nm, respectively (see Fig. 4). As shown in Fig. 5, the FOM are among the smallest discussed here.

Note that both bridge structures, i.e., for **6** and **7**, contain a stilbenelike carbon double bond that was found in the classical stilbene chromophore DANS to be the primary cause for the lack of photostability in the presence of oxygen.[19,21,22] In fact the B values are similar for **6** and **7**, and comparable to the values observed in other

Fig. 4. Absorption spectra of thin films of compounds **4–7**.

Fig. 5. Photostability figure of merit (FOM) B/σ as a function of exciting photon energy as measured in air for guest–host polymers **4–7**. X, **4**; open circle, **5**; open square, **6**; plus, **7**.
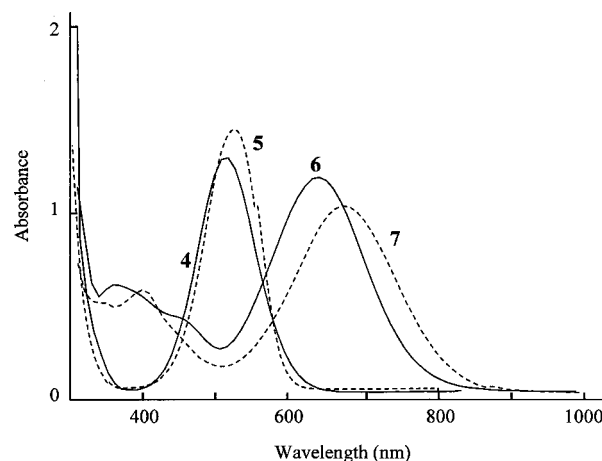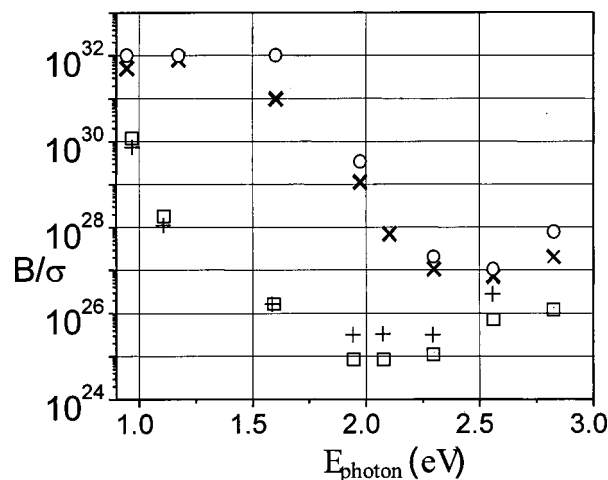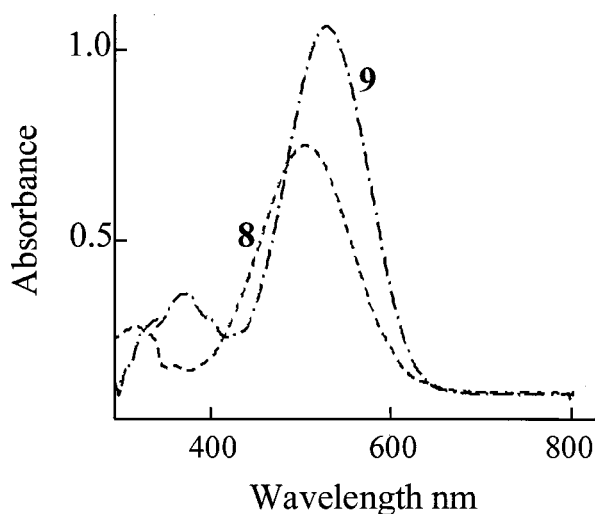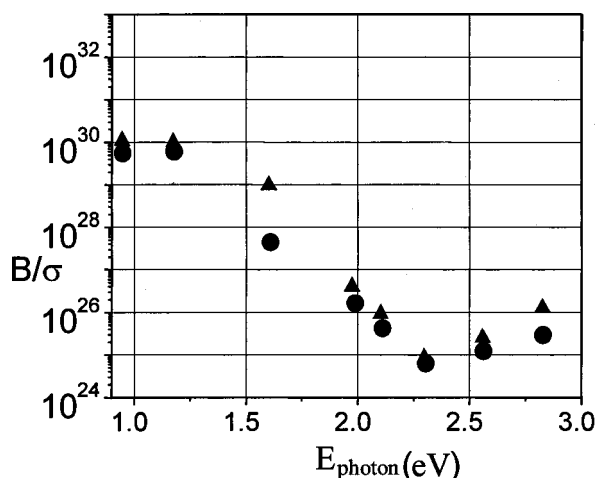
Fig. 6.   Absorption spectra of thin films of compounds **8–9**.

Fig. 7.   Photostability figure of merit (FOM) B/σ as a function of exciting photon energy as measured in air for guest–host polymers **8–9**.   Filled circle, **8**, filled triangle, **9**.

stilbenes.   Comparing the results for compounds **5** and **7** that have the same electron acceptor and donor groups, the large difference between their photostabilities must arise from the different bridging structures used.   From a chemical perspective, the weak link is the stilbene bond, which is known to undergo *trans-cis* isomerization, or photo-oxidation of the central carbon double bond, or both.

C.   Chromophores with Dicyanovinyl Acceptor Groups
For the last two cases, **8** and **9**, the electron acceptor consists of a dicyanovinyl group.   However, that is the only thing these two chromophores have in common.   Nevertheless, although their bridge structures and their donors are quite different, many of their optical properties are similar due to similar donor–acceptor and effective conjugation lengths.   For example, their absorption spectra are quite similar (Fig. 6).   This is also the case for their photodegradation FOM (Fig. 7) and their value of B.   This is perhaps surprising because compound **9** has multiple carbon double bonds along its backbone, whereas **8**

has a much more rigid structure, and **9** would have been expected to be much less photostable.

4.   DISCUSSION

It has recently been shown that σ in the long wavelength tail of the absorption line for many chromophores varies as $\exp[-(E_{phot} - hc/\lambda_{max})/E_0]$, where λ_{max} is the wavelength at which the absorption due to the charge-transfer state peaks.[22,23,26]   Here E_0 is a constant that varies with both the host polymer and the chromophore, and the smaller the E_0, the spectrally narrower is the tail of the absorption spectrum.   That is, E_0 is a broadening term that influences how far out into the IR the serious problem of degradation may affect.   This behavior typically reflects the degree of inhomogeneous broadening of the system.   Therefore, the FOM will have the form

$$B/\sigma = B/\sigma_0 \exp[(E_{phot} - hc/\lambda_{max})/E_0]$$
$$= D_0 \exp(E_{phot}/E_0).$$

Here D_0 is the lifetime of the chromophore per unit of photon flux.   It is believed to depend primarily on the details of the molecular structure, in contrast to E_0, which is related to the inhomogeneous broadening of the absorption line and which depends on the interaction of the chromophore with the polymer host.   Under these assumptions the parameters D_0 and E_0 should be independent of the wavelength, and it is convenient to characterize the wavelength dependence of B/σ in the near IR by these two parameters.

The variation of B/σ of a representative sampling (**4**, **6**, and **9**) of the guest–host polymers studied here in their long wavelength tail is shown in Fig. 8.   Clearly this equation is well satisfied in these cases and in fact is a useful approximation in all of the cases studied.   The results are summarized in a plot of D_0 versus E_0 in Fig. 9.   As was noted before for azobenzenes, there is a clustering of E_0 around 0.1 eV ($E_0 \cong 0.1 \pm 0.01$ eV) that implies that the inhomogeneous broadening is comparable in all of these polymers in poly(methyl
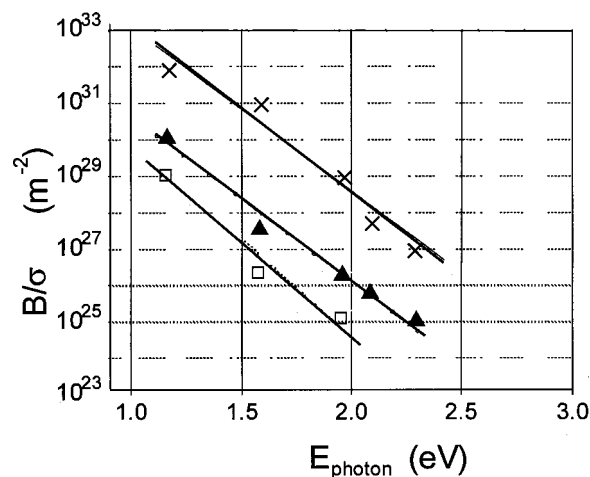
Fig. 8.   Photostability figure of merit (FOM) B/σ as a function of exciting photon energy for $\lambda > \lambda_{max}$ as measured in air for guest–host polymers **4**, **6**, and **9**.   The straight lines indicate the quasi-linear variation in the log of the FOM with E_{photon} over this wavelength range.   X, **4**; open square, **6**; filled triangle, **9**.
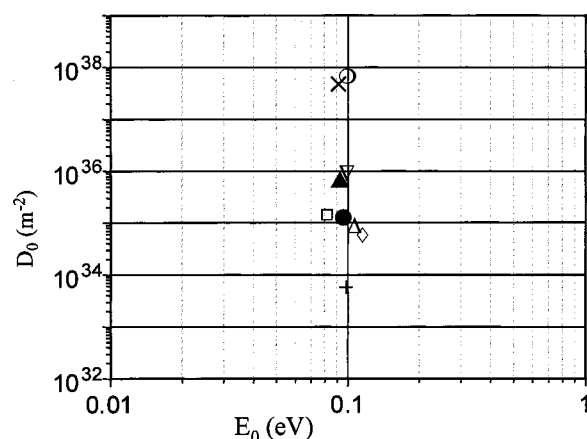
Fig. 9.   Parameters D_0 and E_0 for all nine compounds.   Diamond, **1**; inverted triangle, **2**; triangle, **3**; *X*, **4**; open circle, **5**; open square, **6**; plus, **7**; filled circle, **8**; filled triangle, **9**.

methacrylate).[22–23]   However, there is a large spread in the values of D_0, i.e., 4 orders of magnitude.   Clearly compounds **4** and **5** are the most photostable ($D_0 \cong 7 \times 10^{37}\,\mathrm{m}^{-2}$), and **7** ($D_0 \cong 7 \times 10^{33}\,\mathrm{m}^{-2}$) is the least photostable.   The other compounds have values in the range $D_0 \cong 10^{35}\text{–}10^{36}\,\mathrm{m}^{-2}$.

The most photostable compounds have a few features in common.   First, they are the only two chromophores that have a simple benzene bridge structure, so that *trans-cis* isomerization is not a potential photodegradation mechanism.   Furthermore, they both have a tricyanovinyl electron-acceptor group.   However, other compounds with different bridge structures were also investigated with the same tricyanovinyl group, and those compounds had much lower photostability.   Furthermore, we note that compounds **1** and **2** have similar electron-donor end groups, but reduced photostability as compared with **4** and **5**.   Although obviously the situation is a complex one, the implication is that it is the benzene bridging group that has led to the improved photostability of compounds **4** and **5**.   However, the price for this increased stability is a shorter conjugation path and hence a reduced second-order nonlinearity as compared with, for example, compounds **1** and **2** or **6** and **7**.   Another overall conclusion that can be drawn is that the number of cyano moieties in the electron-acceptor group does not have a large effect on the photostability.

It is relatively straightforward to estimate the electro-optic chromophore lifetime $\tau = B/\sigma n$.   For polymers **3** and **4** the projected lifetimes at 1064 nm are 2–3 weeks for continuous illumination of 1 mW in a waveguide cross section of 10 $\mu\mathrm{m}^2$.   This is well short of the best case of ~1 year reported previously for the azobenzene DR1 with an attached methacrylate group.   Note however that the addition of this antioxidant improved the photostability of DR1 by two orders of magnitude, and it would be worthwhile to graft an antioxidant onto chromophores **3** or **4**.   At the other end of the scale in the present investigation, compound **7** will last less than 1 hour!

5.   SUMMARY

The photostability of a number of electro-optic chromophores incorporated as guest molecules in a poly

(methyl methacrylate) polymer matrix was investigated in the visible and near-IR regions of the spectrum.   The focus here was on compounds that contained benzene bridging structures and cyano-contaning electron-acceptor groups.   The general wavelength dependence of the FOM B/σ established previously for other electro-optic active polymers was also observed here: Namely, the B/σ is a minimum at the peak of the charge-transfer absorption band and then increases exponentially with decreasing photon energy in the near IR.   As observed previously in other polymers, at 1320 nm this trend no longer holds, and B/σ is reduced, probably due to the generation of singlet oxygen.   Clearly data at longer wavelengths, in the main telecommunication optical band around 1550 nm, are needed, but the need for longer laser illumination times has prohibited experimental access to such data until now.

The most photostable polymers are characterized by benzene bridges and tricyanovinyl electron-acceptor groups.   For these cases, only about 10 out of a milliard photo-excitations of the charge-transfer state lead to degradation of the electro-optic active chromophore.   More complex bridges between the electron-donor and -acceptor groups in general resulted in reduced photostability.   It did not appear that the number of cyano moieties making up the electron acceptor affected significantly the photostability.

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