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Journal of Photochemistry and Photobiology A: Chemistry 121 (1999) 133–140

Journal of Photochemistry and Photobiology A:Chemistry

Field-enhanced photodegradation of pyrromethene dye films

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Received 1 June 1998; received in revised form 21 September 1998; accepted 18 November 1998

Abstract

The photodegradation of pyrromethene films, neat and polymer-dispersed, is investigated by measuring the relative photocarrier yield as a function of accumulated 532 mm laser pulses. The rate of reduction in photocarrier production is compared for samples irradiated in the absence and presence of an electric field by utilizing a delayed-photocurrent collection method. Higher bias resulted in higher photocarrier reduction rates: field-enhanced photodegradation. We report the result for polymer-dispersed pyrromethene mixed with dimethylbenzoquinone (electron acceptor) or triphenylamine (electron donor) and vacuum deposited samples. The photocarrier reduction is correlated with the appearance of dark spots, as confirmed by optical microscopy. For these samples, the photocarrier reduction is attributed to intrinsic degrading reaction of dye ions resulting from the optical excitation in the presence of strong electric fields. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Photodegradation; Pyrromethene dye films; Photocarrier production

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1. Introduction

There is a resurgence of interest in organic photoconductors for their potential application in light emitting diodes (LEDs), photodetectors, solar cells, and optical switches [1–7]. Organic semiconductors are attractive as noted by high solubility, chemical and physical stability, and polymerizability. These qualities make such materials appealing from a processing standpoint for utilization in device fabrication. Organic and polymer materials with sensitive optical and electronic response present a very promising alternative to the conventional optoelectronic materials. The concept of ‘plastic optoelectronics’ is very novel and has great future potential.

Limited photostability, however, still poses a problem for many organic photoconductors [8–13]. Recently, the photo-oxidative stability of poly-[2-methoxy,5-(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV), an organic photoconductor sensitive to visible light, was explored as a function of buckminsterfullerene (C_{60}) doping [8]. In those studies, the absorbance at 540 nm was measured as a function of Ar^+ laser (514.5 nm) irradiation time. The addition of C_{60} to MEH-PPV decreased the photo decay rate, stabilizing the MEH-PPV against photo-oxidation. Similar MEH-PPV photostability studies measuring a reduction of photoluminescence with irradiation time have been carried out by Radousky et al. [9]. Such a study showed the photoluminescence reduction rate for samples prepared and irradiated in an oxygen environment exceeded that of samples prepared and measured in an oxygen-free environment. Thus, once again the decrease in the decay rate of an observable (photoluminescence in this case) was attributed to photo-oxidative stability.

In a previous investigation, we determined that pyrromethene dyes, commonly used laser dyes, have potential as visible light photoconductors [2]. The photoconductivity of polymer films doped with these pyrromethene dyes increased upon doping with triphenylamine, a good electron donor. The photoconductivity of pyrromethene/polymer films decreased with laser irradiation time (the number of laser pulses). It was noted that the photocarrier reduction rate for triphenylamine doped samples was less than that for undoped samples. However, the study was somewhat complicated in that the laser irradiation occurred during the

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PII: S1010-6030(98)00446-8

presence of an applied electric field, making it difficult to determine the effect of the electric field on the photocarrier reduction.

In this paper, we report the photocarrier reduction of pyrromethene dyes in the presence and absence of an electric field during laser irradiation by varying the delay time between the laser pulse and the collection field. The higher photocarrier reduction rate for samples irradiated during the applied field is explained by an intrinsic photodegradation process. The photocarrier reduction was also investigated for various compositions by examining films composed of pyrromethene doped polymers and donor/acceptor dopants, as well as vacuum deposited pure pyrromethene films in an ambient atmosphere. Polymer-dispersed pyrromethene/triphenylamine films were also investigated under vacuum in order to determine the photodegradation mechanism for this previously determined promising mixture [2]. The rest of the paper is organized as following: Section 2 discusses the experimental details while Section 3 includes results and discussion. Finally, in Section 4, the main results are summarized.

2. Experimental

2.1. Sample preparation

Preparation of 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene-difluoroborate complex (PM-567) polymer films is discussed in a prior report [2]. Pyrromethene dye/polymer solutions were spin coated onto silicon oxide/indium–tin-oxide coated substrates. The prepared films contained different solid-state concentrations of additive and PM-567. The aim was not to quantitatively compare PM-567/DMBQ/PMMA films with PM-567/TPA/PMMA films, but to obtain a qualitative evidence of photocarrier dynamics or behavior. Neat PM-567 films were also prepared by vacuum deposition onto the SiO_x/ITO coated substrate at a pressure of $\sim 10^{-6}$ Torr. In various samples, thickness varied from 0.4 μm for vacuum deposited films to 1.2 μm for spin coated polymer films. Finally, aluminium thin layers were vacuum deposited at 10^{-6} Torr to serve as current collection and biasing electrodes.

2.2. Photocurrent measurements

The samples were excited by the second harmonic of a Nd-YAG laser (532 nm, 5 ns, 3 Hz, 2.5 mJ/pulse). Collection fields were formed by applying a positive bias to the ITO electrode (anode) such that hole currents were collected at the aluminium cathode. For the experiments conducted with zero bias, a collection field exceeding saturation was applied after delay time $\Delta t = 100$–200 ns, relative to the laser pulse (Fig. 1 (a)). For nonzero bias measurements ($\Delta t < 0$), the collection field was applied prior to laser excitation with adequate duration such that the laser pulse occurs in the middle of the electric field pulse duration (Fig. 1 (b)). In these measurements, the applied voltage acts as both bias and collection field. The magnitude of the collection field is obtained from the asymptotic region of the photocurrent versus field plots (saturation), ensuring the collection of all free carriers. Collection fields varied from 0.7–1.2 MV cm^{-1} for the polymer dispersed samples and 1.90 MV cm^{-1} for the vacuum deposited samples. These extremely high bias collection fields are consistent with those utilized in xerography studies and result in significant decay within a reasonable number of laser pulses.

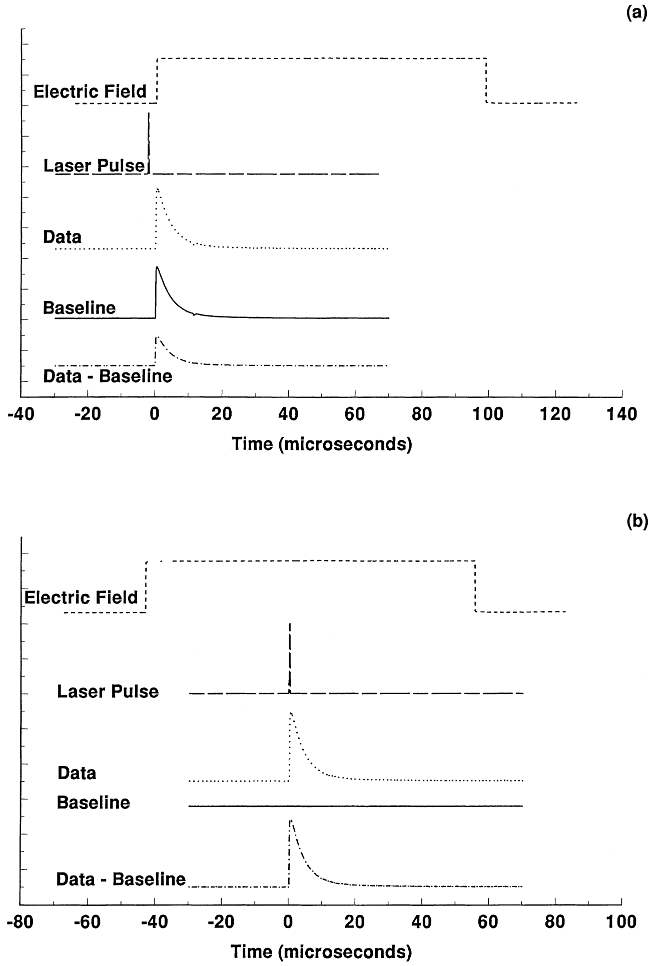

Fig. 1. Timing scheme for (a) delayed, and (b) non-delayed photocarrier measurements.

The laser fluence was varied from 12 to 31 mJ cm^{-2}, respectively, for the above samples. The resulting photocurrent traverses a 50 Ω resistor yielding a transient voltage, captured by a digital oscilloscope (LeCroy 9250) and stored in a personal computer. The experiment is repeated with the laster beam blocked to obtain a background signal. A net transient signal is obtained from the difference of the two signals. A time-integrated signal provides a net charge, which is the photoresponse. The photocarrier reduction rate is simply a derivative of the photoresponse with respect to the number of laser pulses.

2.3. Microscopic analysis

For the PM-567/TPA/PMMA samples, investigation were carried out to probe optical damage for both delayed and non-delayed experiments using microscopy. A stronger laser fluence (36 kJ cm^{-2}) was employed to accelerate the photodegradation, allowing it to be visually conspicuous after 3600 laser pulses. Micrographs were taken with an Olympus BH-2 microscope at 200× magnification.

3. Results and discussion

3.1. Photocarrier reduction

3.1.1. Delayed versus non-delayed collection fields

Fig. 2 (a–c) shows photocurrent plots as a function of accumulated laser pulses for PM-567/TPA/PMMA, PM-567/DMBQ/PMMA and vacuum deposited PM-567 samples, respectively, in an ambient air atmosphere. The TPA doped sample in Fig. 2 (a) shows a ~30% photocurrent decrease for the biased sample and a ~5% decrease for the unbiased sample after 4500 pulses. The photoresponse was normalized to unity and shifted arbitrarily, so as to offset it from the other samples for presentation clarity. The DMBQ sample in Fig. 2 (b) shows a larger disparity between the biased and unbiased samples after only 3000 pulses: ~55% and ~5% decrease, respectively. In order to determine whether the observed photodegradation required a polymer matrix, vacuum deposited samples were also irradiated and exhibited similar behavior (Fig. 2 (c)), i.e. faster photocarrier reduction in the biased samples. Thus, the pool of possible species responsible for this field-enhanced photodegradation may be restricted to the dye, the metal electrode, and possible ambient oxygen. In all samples, the delayed-field (zero bias) photocarrier reduction is noticeably lower than the non-delayed (biased) photocarrier reduction. All three samples differed in dye and/or additive concentration, electric field strength, and laser fluence. Thus, a quantitative cross comparison is not possible. These experiments were conducted primarily to determine if a detectable difference in photocarrier reduction rates exists between the samples irradiated in the presence (non-delay) and absence (delay) of an electric field.

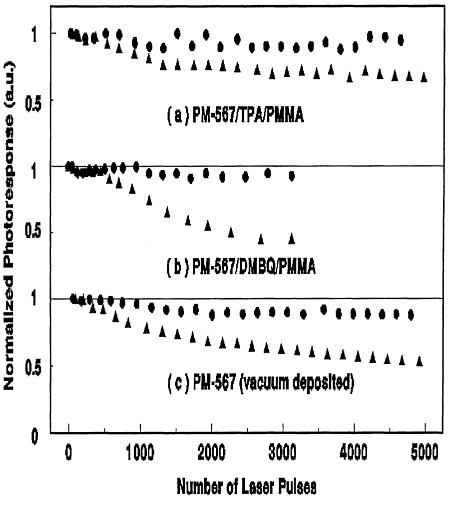

Fig. 2. Photocarrier reduction rate comparison with delayed (circle) and non-delayed (triangle) field collection under high laser fluence. (a) PM-567/TPA/PMMA ($E = 0.91$ MV cm^{-1}, fluence = 15 mJ cm^{-2}, $l = 1.07$ μm), sample (b) PM-567/DMBQ/PMMA sample ($E = 0.70$ MV cm^{-1}, fluence = 13 mJ cm^{-2}, $l = 1.15$ μm), (c) PM-567 vacuum deposited sample ($E = 1.9$ MV cm^{-1}, fluence = 31 mJ cm^{-2}, $l = 0.41$ μm).

Why does the presence of an electric field during irradiation increase the photocarrier reduction rate? One possibility is that biased irradiation leads to an increase in free dye-ions that destructively react with dye molecules (D). Of the dye-ions produced, a certain fraction will undergo recombination and energy relaxation to regenerate the ground state species, while another fraction will undergo dye destruction reactions. Thus in all films including neat PM-567 films, the following mechanism may be operative:

$$^{1}\mathrm{D} + h\nu \rightarrow {}^{1}\mathrm{D}^{*} \tag{1}$$

$$^{1}\mathrm{D}^{*} \rightarrow {}^{3}\mathrm{D}^{*} \tag{2}$$

$$^{3}\mathrm{D}^{*} + \mathrm{D} \rightarrow [\mathrm{D}^{\bullet +} + \mathrm{D}^{\bullet -}] \tag{3}$$

$$[\mathrm{D}^{\bullet +} + \mathrm{D}^{\bullet -}] \rightarrow \mathrm{D}^{\bullet +} + \mathrm{D}^{\bullet -} \tag{4}$$

$$\mathrm{D}^{\bullet +} + \mathrm{D} \rightarrow \text{products} \tag{5}$$

$$\mathrm{D}^{\bullet -} + \mathrm{D} \rightarrow \text{products} \tag{6}$$

In the above reaction scheme, the presence of the field leads to dye polarization, increasing in rate constant of reaction (3) via lowering the activation barrier for ion encounter complex $[\mathrm{D}^{\bullet +}+\mathrm{D}^{\bullet -}]$ formation. In the non-delayed collection field, reaction (3) proceeds much faster than the recombination reaction $^{3}\mathrm{D} + \mathrm{D} \rightarrow 2\mathrm{D}$ resulting in a high yield for the ion encounter complex. In the delayed collection field, the recombination reaction may more effectively compete with reaction (3) during the Δt time delay since no field is applied during this time. This would serve to reduce the ion encounter complex yield relative to that of the non-delayed case. This consequently leads to a greater number of destructive ion-molecule reactions Eqs. (5) and (6) for non-delayed collection fields. Note that reactions between a molecule and its corresponding ion ($\mathrm{A} + \mathrm{A}^{+/-} \rightarrow$ products) may yield new products in contrast to simple charge transport, i.e. $\mathrm{H_2}^{+} + \mathrm{H_2} \rightarrow \mathrm{H_3}^{+} + \mathrm{H}$ and $\mathrm{CH_3F}^{+}$ $\mathrm{CH_3F} \rightarrow \mathrm{CH_3FH}^{+} + \mathrm{CH_2F}$ [14]. Reaction (5) has been postulated for the fading of rhodamine dyes [15]. The increase of electrons and holes in the non-delayed compared to the delayed case may lead to more effective crystallization. This, is turn, may adversely affect the photocarrier generation efficiency. Such is the case for amorphous selenium, in which the photocrystallization has been attributed to hole-electron production, resulting in a change in photoconductivity [16]. Thus, perhaps it is the increase in the initial ion encounter complex yield and the subsequent increase in dye-ions that undergo destructive reaction and/or crystallization that give rise to an increase in the dye photodegradation rate upon irradiation under an applied bias.

Unfortunately, the signal-to-noise (S/N) ratio of the delayed field collection experiments for the polymer samples is much lower than the non-delayed case. There is some ambiguity concerning whether the delayed photocurrent is stable or falling at a very slow rate. However, there is an improvement in the S/N ratio for the vacuum deposited samples for both the non-delayed and delayed field experiments. In these samples, a nonzero decay in the photocurrent is observed in the delayed measurements with increasing number of laser pulses. Thus, even in the absence of an applied field, photodegradation occurs at all levels of laser fluence employed.

3.1.2. Comparison to solid state dye laser photodegradation studies

The photocarrier generation decay observed in this investigation may be compared to photostability studies of PM-567 solid state dye lasers [17–19]. In those studies, a cylindrical rod of 'polymer dispersed PM-567' was side-pumped by the second harmonic of a Nd-YAG laser (532 nm). The efficiency of the lasing output was measured as a function of accumulated laser pulses. The efficiency decreased with accumulated laser pulses, with higher decay rates corresponding to higher pump laser input fluence.

Some steps have been taken to increase the stability of solid state dye laser. For example, Rahn and coworkers [19] enhanced the photostability of PM-567 solutions and solid films by removing singlet oxygen. This was accomplished by evacuating the cell or by the addition of sodium azide, a known quencher the singlet oxygen. Such photostabilization would be effective if the primary mechanism for the observed photodegradation is oxidation via a singlet oxygen. Costela et al. [20] have improved the photostability of rhodamine 6G (Rh6G) by the addition of *n*-propyl-1,8-naphthalimide (NI). *N*-Propyl-1,8-naphtalimide is a good triplet acceptor relative to Rh6G dye. Adding NI to Rh6G in solution or chemically modifying Rh6G such that it is covalently bonded to NI, led to increased photostability. This was attributed to energy relaxation of ^{3}Rh6G* by ^{1}NI, precluding the reaction of ^{3}Rh6G*.

Dyumaev et al. [21] stabilized xanthene dyes (i.e. Rh6G) dispersed in PMMA by adding low-molecular additives (LMAs) such as ethanol and ether. The LMAs are believed to hamper formation of polymer macroradicals undergoing vibrational resonant energy transfer with the polymer macromolecule. For our non-delayed measurements (bias > 0), addition of an efficient energy transfer agent may not be as effective because the presence of a large electric field may ensure that electron transfer is the dominant process. Perhaps for the delayed collection field studies, addition of an energy transfer agent may lead to increased photostability, however, the question remains as to how this would affect CT state formation and subsequent dissociation.

In this study, PM-567 aggregates are directly observed via microscopy and the photodegradation rates in zero field (delayed-collection field data in Fig. 2) are higher than photodegradation rates of molecularly dispersed (solvated) pyrromethene dyes present in solid state dye lasers [14]. The presence of aggregates may lead to an increase or decrease of photostability based upon dye photofading studies [21]. A decrease in the photodegradation rate may be observed if the diffusion of external oxidants/reductants into the interior of the aggregates, i.e. O_2 and H_2O from the ambient atmosphere, is retarded by the size of the aggregates. On the other hand, an increase in the photodegradation rate may be observed if the aggregates bring about an increase in the intersystem crossing (ISC) rate, as in the case of Rh6G dye aggregates [21]. In this case, excitation of the aggregate would yield more reactive triplet states, setting the stage for photodegradation. It should also be noted that due to limited molecular motion in solid films, reactions (5) and (6) would occur only if dye molecules are in close proximity, which is the case for aggregates, but not for molecularly dispersed dye molecules. This would suggest that the primary mechanism of photodegradation in this study is not diffusion of oxidants/reductants, but aggregate-induced ISC.

Assuming a photobleaching number of 1×10^6 photons per molecule [22] and a concentration of 1×10^{-3} M, we obtain an estimate of 43 days for the photobleaching utilizing our value for the maximum fluence of 36 mJ cm^{-2}. The observed photodecay occurs in several minutes, so a solid-solution photobleaching mechanism is not sufficient to explain the decay irrespective of the field strength. Dye aggregation and an applied field each effectively lower the photobleaching number. In making this comparison one must be careful to note the possibility that the two observables, absorption efficiency and photocarrier generation, may possess different sensitivities and dependencies with respect to the true photodegradation, i.e. the actual number of dye molecules destroyed.

3.1.3. Sparse sampling

The signal-to-noise ratio in the non-delayed collection of carriers is much higher than the delayed carriers detection. Low S/N in the latter arises due to the difficulty of integrating the small zero-field transient photocurrent. Also, carrier lifetime limits the photocarrier yield, i.e. the carriers produced during the irradiation relax and recombine. In an attempt to obtain a zero-field result with a stronger S/N ratio, a variation of the non-delay experiment was carried out via a sparse sampling technique. This sampling technique is similar to the non-delay measurements except that the electric field is applied only during sampling (collection) of photocurrent data; otherwise laser irradiation occurs the absence of a field. The data sampling occurs at discrete intervals of ten pulses. For example, the samples are subject to a field for a duration of ten pulses; the average integrated

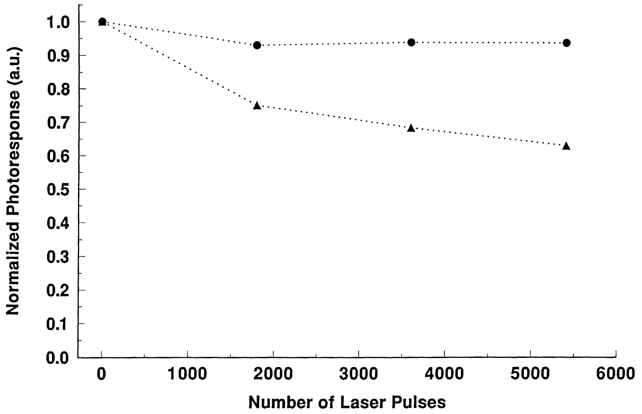

Fig. 3. Photocarrier reduction rate comparison for PM-567/TPA/PMMA. Sampling field (circle) and conventional non-delayed (triangle). ($E = 0.91$ MV cm^{-1}, fluence = 15 mJ cm^{-2}, $l = 1.07$ µm).

photocurrent of these ten pulses yields the photoresponse. Next, the electric field is terminated while the laser delivers ~1800 more pulses. After 1800 pulses, the field is applied again for the duration of ten laser pulses for the second datum. This is repeated for two more 1800 pulse cycles yielding a sequence of data points at 0, 1800, 3600 and 5400 laser pulses. These results are plotted in Fig. 3, yielding results similar to the results of Fig. 2 (a). Since the sampling electric field and the delayed collection field results are about the same, this shows that cycling the field off and on several thousand times does not fatigue the sample in a manner that leads to lower photocurrent. The S/N of the sampling electric field is much higher than that of the delayed field samples, however, the number of data points collected limits the sampling field method. If one collects too many data points, a decrease in the photocurrent is expected since the field is on during laser irradiation for sampling (probing) the photocurrent.

3.1.4. Extrinsic factors

The photocarrier reduction experiments described above have been carried out under an ambient atmosphere. This does not yield information as to whether the photodegradation is intrinsic or extrinsic. In order to determine the relative importance of intrinsic and extrinsic factors responsible for the observed reduction of photocarrier generation, a series of non-delayed collection field experiments were carried out for PM567/TPA/PMMA films with aluminum and gold counter electrodes under ambient atmosphere and vacuum conditions. The results are shown in Fig. 4. Each time decay profile used to generate the Al/vacuum data in Fig. 4 was fit to a single exponential function. The results are shown in Fig. 5 and Table 1. The reduction in photocurrent is primarily due to a decrease in the pre-exponential factor, with very little change in the decay lifetimes. The fact the lifetimes are invariant with respect to the number of excitation pulses suggests that any new traps created via accumulated laser pulses are depleted of charge carriers by the strong

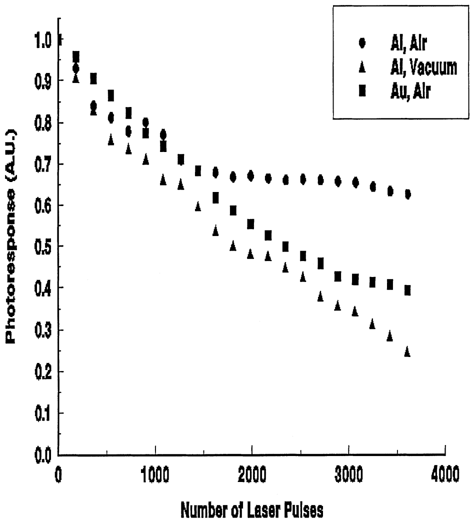

Fig. 4. Photocarrier reduction rate comparison for PM-567/TPA/PMMA/Al (air and vacuum) and PM-567/TPA/PMMA/Au (air). Non-delayed collection field utilized ($E = 1.18$ MV cm^{-1}, fluence = 16 mJ cm^{-2}, $l = 0.68$ µm).

collection fields employed. On a practical note, this mean that the decay maxima may be used instead of the integrated decays in determining the photoresponse. There is little difference in the decay rate of the three samples for the first ~1000 pulses, after which time the Al/air electrode rate decreases. Comparing the Al/air to the Au/air electrodes, the observed difference in photodegradation rates may be attributed to a difference in rates of direct chemical reaction of the metal or to a hole injection rate discrepancy. Laser induced oxidation of metals, known to occur for Al [11,12,23], may be tested by comparing the photocarrier reduction rate of samples containing Al electrodes to those with Au electrodes which are more difficult to oxidize. For the PM-567/TPA/PMMA samples, a negligible difference in the initial

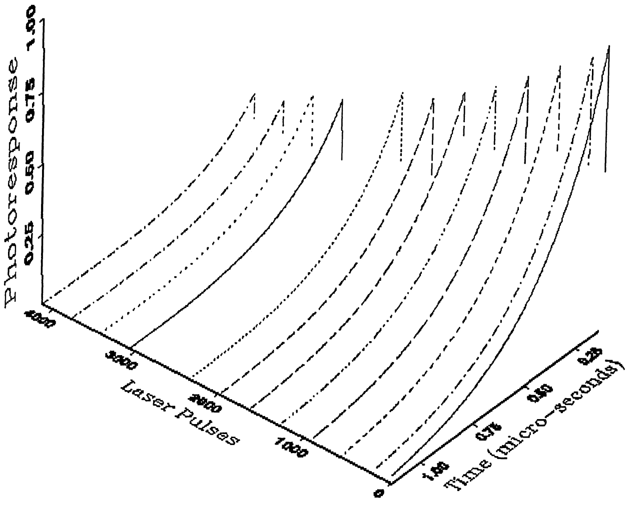

Fig. 5. 3D Photocarrier reduction for PM-567/TPA/PMMA/Al (vacuum) in conditions as given in Fig. 4.

Table 1
Single exponential curve fitting for Al/vacuum samples photoconductivity decay curve

Number of laser pulses	*a*	*b*
0	0.8186	3.3562
180	0.7723	3.4177
560	0.7100	3.4494
900	0.6470	3.5129
1260	0.5810	3.5459
1620	0.5296	3.5995
1980	0.4804	3.7730
2340	0.4632	3.8738
3060	0.3440	3.6549
3420	0.3273	3.7734
3780	0.2546	3.5958
4120	0.2359	3.5991

$f(t) = a\ \exp(-bt)$.

photocurrent reduction rates of Al/air and Au/air electrodes suggests that metal oxidation is not the primary mechanism. In previous organic electroluminescence experiments, several investigators had concluded that physical and chemical change for the metal electrode led to changes at the organic/metal interface resulting in a decreased electroluminescence [10–13]. Although the above argument does not present a strong case for metal oxidation, it is still possible that other mechanisms affecting the organic/metal interface such as the formation of hot spots leading to local rearrangement of ablation, may be operative. The negligible difference in photocarrier reduction rates for Al electrodes in air and vacuum environments and the faster subsequent photodegradation for the vacuum samples for laser pulses exceeding 1000 pulses, suggests that extrinsic photo-oxidation does not play a major role in the photodegradation under an electric field.

These results contrast those for the photoconductivity decrease of poly(2-methoxy-5-[2′-ethylexyloxy]1-,4-phenylvinylene), MEH-PPV [24]. In that study, the photoconductivity of dilute MEH-PPV benzene solutions decreased with the number of 308 nm laser pulses faster for air-saturated than deaerated solutions. This suggests extrinsic photo-oxidation. In that experiment, two possible outcomes were postulated for photo-oxidation prior to conducting the experiment:

1. An increase of photoconductivity due to photo-oxidation induced defects enhancing exciton dissociation in solids [25]. Thus a photoconductivity increase is attributed to an oxygen induced photocarrier generation.
2. A decrease of photoconductivity due to photo-oxidation and its photo-oxidative defects having little influence on exciton dissociation.

In our experiments with PM-567/TPA/PMMA, photocarrier generation decreased with increased exposure of laser pulses for the aerated samples, but not as fast as the deaerated samples. This is consistent with the second mechanism. However, we see that the dominant mechanism does not involve extrinsic oxidation, since the photocarrier reduction rate is higher for the vacuum samples as shown in Fig. 4. As stated earlier, Rahn's observation of PM-567/polymer films are contrary to ours in that he observed an increased photostability upon oxygen removal [19]. Thus, PM-567 photodegradation was primarily attributed to oxygen. The apparent conflict of our results with those reported by Rahn suggests that photo-oxidation via oxygen is not the primary path for photodegradation for biased PM-567/TPA/PMMA samples observed in our system. However, the difference in concentration, field strength, dopant addition, and observables (photocurrent versus fluorescence) may have contributed to this disparity.

The peak power damage threshold for transparent PMMA has been determined [26] to be about 1,000 GW cm^{-2}, which far exceeds the largest peak power utilized in this experiment 36 mJ cm^{-2}, corresponding to a peak intensity of 7.2 MW cm^{-2}. This argument coupled with the visible transparency of PMMA makes it unlikely that direct irradiation of the polymer explains the observed photodegradation. Furthermore, as demonstrated in Fig. 2 (c), the photodegradation of both biased and unbiased films is observed in the absence of a polymer matrix. The strengthens the claim that intrinsic factors, i.e. namely the dye molecules, are primarily responsible for the observed photodegradation.

3.2. *Optical damage*

Fig. 6 shows micrographs (200× magnification) after 3600 laser pulses in the absence and presence of the external bias for PM-567/TPA/PMMA samples. In Fig. 6, the apparent photodarkening occurs to a greater extent in the biased samples. One possibility is that the observed darkening is due to dye photobleaching by oxidation with ambient oxygen. This results in a shortening of conjugation leading to lower visible absorption by the dye which manifests as an increase in the visibility of the aluminum electrode, consistent with solid-state xanthene laser experiments by Gromov [27], in which the transmitted fluence increased as the number of laser pulses accumulated. Another possibility is that the observed photodarkening is due to corrosion of the Al electrode caused by adsorbed dust particles interacting with water and/or oxygen from the atmosphere as in electroluminescence experiments [13]. Once again this would strengthen the argument for similar photodegradation mechanisms for organic electroluminescence and transient photocurrent experiments. Previous organic electroluminescence experiments have shown photodegradation accompanied by dark spots indicative of aluminum corrosion with no change in the Fourier transform infrared spectrum indicative of little or no vinyl oxidation. Fig. 6 is similar to micrographs for organic electroluminescence [10–12]. Furthermore, field irradiated samples show a greater extent of optical degradation, which suggests that the enhanced degradation of the biased samples may be attributed to the same mechanisms as the operational decay of electrolumines-

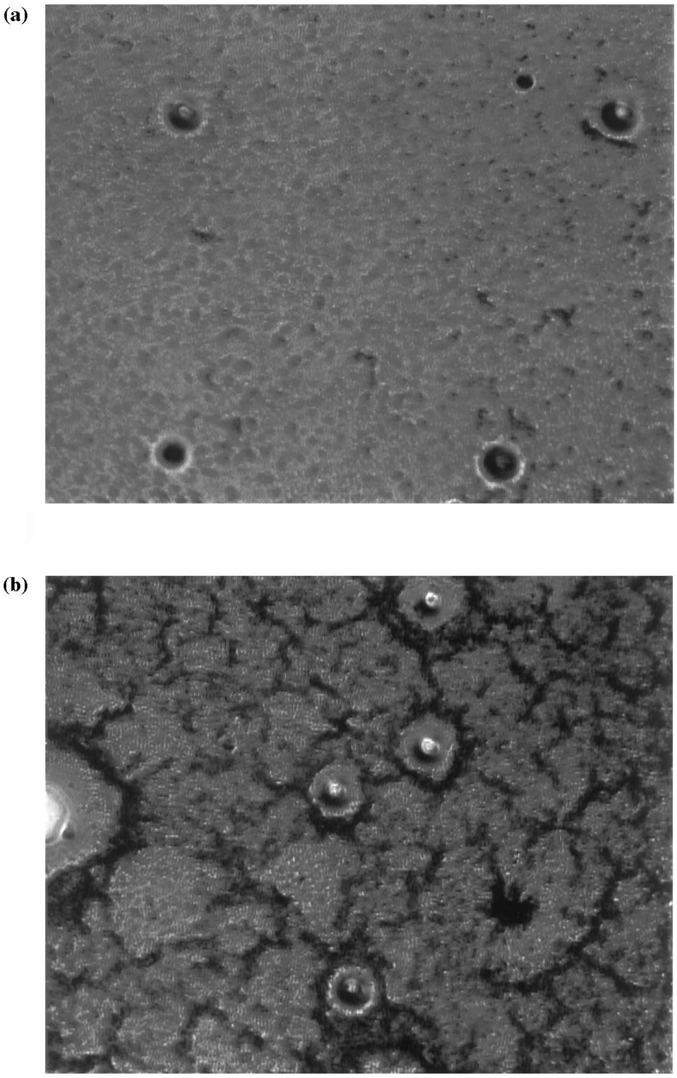

Fig. 6. Micrographs of PM-567/TPA/PMMA sample in ambient air environment after 3600 shots (a) unbiased (b) biased sample ($E = 0.88$ MV cm^{-1}, fluence = 36 mJ cm^{-2}, $l = 0.68$ µm).

cence for organic light emitting devices, in which radiation occurs under a bias. This degradation requires the presence of a field, unlike photobleaching which may occur in the absence of a field.

4. Conclusions

A delayed collection-field technique was employed to compare the decrease in photocurrent with laser irradiation for biased and unbiased organic/dye polymer films. The biased samples exhibited a significantly larger photocarrier reduction compared to the unbiased samples. The field enhanced reduction of photocurrent is attributed to two possible mechanisms: (i) an increase in holes and electrons leading to dye crystallization and/or bulk organic degradative dye ion reactions and (ii) interface effects, in which the metal electrode is altered affecting the hole injection rates. The present results show an increased photodegradation rate upon oxygen removal for biased PM-567 samples containing triphenylamine contrary to previous visible photodegradation work on unbiased PM-567 [19]. Microscopy has revealed that the field-enhanced photodegradation of photocurrent may be correlated to optically induced changes. The similarity of conditions as well as the similar observations of the appearance of dark spots for the present transient photocurrent experiments and previous organic electroluminescence experiments suggests similar photodegradation mechanisms for the two type of experiments. This raises the possibility of employing transient photocurrent measurements to test the electroluminescence photostability of organic samples.

The present experiment is limited in that only photocarrier generation is measured. One problem is the lack of information about the photocarrier generation of the photodegradation products. We are presently designing future experiments to measure both photocarrier generation and fluorescence. Such fluorescence experiments will involve exciting the dye at it's absorption maximum, following irradiation at 532 nm for a specified number of shots. This will give a quantitative measure of dye degradation and define the relationship between the decrease in fluorescence and the decrease in photocarrier generation. Scanning the fluorescence excitation wavelength will allow for a determination of the absorption profile of the photodegradation products to determine if the fluorescence of such products interfere with that of the dye.

Acknowledgements

The authors would like to thank Mr. John Hudak of Cameron Applied Research Center for his technical assistance.

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