Photocurrent and optical limiting studies of C_{60} films and solutions

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Photocarrier generation efficiency (PGE) and reverse saturable absorption (RSA) measurements have been conducted on fullerene (C_{60})/polymethyl methacrylate (PMMA) thin films and C_{60}/toluene solutions. The photocarrier generation has been measured at 330 and 532 nm for various concentrations and electron donor/acceptor addition. The photocarrier generation yield for 330 nm traversed a maximum with increasing concentration which was not observed for 532nm excitation. This concentration dependence is explained via electron-hole pair dissociation. A large enhancement of photocarrier generation was observed in the case of triphenylamine addition to C,,. Fullerene solutions containing electron donors and acceptors demonstrated optical limiting with a vertical shift in the transmittance versus fluence optical limiting plots. This vertical shift could not account for the optical limiting profile of C_{60}/dimethylbenzoquinone samples.

1. Introduction

The photoconductivity of buckminster fullerene, C_{60}, films (neat and polymer dispersed), has been studied by many researchers [1–6] owing to its potential application in various areas of technology. Such studies have shown that the photoconductive response of C_{60} thin films extends from the ultraviolet to the visible regime. Fullerene thin films may lead to the development of solid-state optoelectronic devices. In contrast to neat films, it was determined that the polymeric environment may be important to the stabilization of electron transfer products [3]. This increases the likelihood that C_{60}-based optoelectronic devices will utilize C_{60}-doped polymers. One process that competes with photocarrier generation in C_{60} films at high laser fluence is that of secondary photon absorption of singlet and triplet states [2, 7–9], as illustrated in figure 1. This two-photon absorption leads to reverse saturable absorption (RSA): increasing absorbance for increasing light fluence. This

is because σ_S and σ_T are larger than σ_O. It has been known that fullerene/toluene solutions are reverse saturable absorbers [10, 11]. These RSA materials may be exploited for the development of new optical limiting devices for safety use. Practical device fabrication would necessitate the development of such materials in the solid-state form, e.g. thin films or substrates [12]. In the above scheme triplet charge transfer state dissociation competes with secondary photon absorption ($S_2 \leftarrow S_1$ and $T_2 \leftarrow T_1$) responsible for RSA.

Introduction of electron donor/acceptor additives may facilitate CT state formation/dissociation and hence affect the photocarrier generation and RSA efficiencies [2, 6, 7, 13, 14]. In the experiments reported here, perturbation of the above mechanism by the introduction of additives was studied in a systematic way. The measurement of optical limiting behaviour (via transmitted

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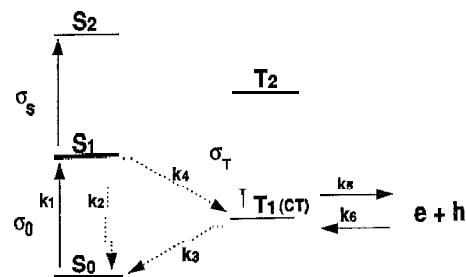
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Figure 1. Jablonski diagram of C_{60} excited state dynamics.

light fluence) of solution samples and the photocarrier generation of solid-state (polymer doped) samples was carried out in order to understand the role of various donor/acceptor additives.

2. Experiment
2.1. *Material and sample preparation*

Purified fullerene (99.9% C,,) was obtained from Fullerenes Enterprises. Polymethyl methacrylate (PMMA) as well as the dopants, triphenylamine (TPA), N,N,N',N'-tetramethyl-p-phenylenediamine (TMPDA), 1,4-dinitrobenzene (DNB), 2,6-dimethyl-1,4-benzoqui-none (DMBQ), 7,7,8,8-tetracyano-quinodimethane (TCNQ) were acquired from Aldrich Chemical Company.

For photocarrier measurements, coating solutions were prepared by dissolving C_{60} (10–70 mg), dopants (0 or 50mg) and PMMA (360 mg) in 3 ml of a 7 : 3 (volume : volume) 1-chloronaphthalene/tetrachloroe-thane (TCE) solvent mixture. According to Ruoff *et al.* [15], the solubility of C_{60} in toluene is 10 times less than the solubility in l-chloronaphthalene. Since PMMA is insoluble in l-chloronaphthalene, TCE was added in the aforementioned 7 : 3 volume ratio. In contrast to the blue C_{60}/toluene solution, the C_{60}/1-chloronaph-thalene/TCE solution has a brownish appearance. The solution is spin coated onto a SiO_x/indium-tin-oxide/glass substrate and allowed to air dry for several hours before undergoing 335 hours of degassing under vacuum (10^{-6} Torr). Afterwards an aluminium electrode is deposited at 10^{-6} Torr vacuum condition.

For optical limiting studies, the solution is prepared by dissolving C_{60} and various dopants in toluene. Although C_{60} is less soluble in toluene than chloronaph-thalene, a toluene solvent mixture was utilized, because photodarkening was observed for chloronaph-thalene/C_{60} solutions with 532nm light at a fluence of $45 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, consistent with previous accounts of photodarkening [16,17].

2.2. *Transient photocurrent measurements*

Figure 2 shows a schematic of the apparatus used for transient photocurrent measurements, similar to that used in our previous report [18]. The photocurrent measurements were performed with 330nm laser pulses generated by doubling the output of a dye laser Continuum ND6000 system (5 ns, 0·38 mJ pulse-r) and 532nm laser pulses from the second harmonic of the Nd: YAG laser (5 ns, 1·00 mJ pulse-'). These pulses irradiated DC-biased (O-120 V) C_{60}/PMMA thin films (~ 1 μm) for photocarrier generation studies. The resulting photocurrent signal traversed a 50 Ω load resistor and the voltage signal was amplified by a
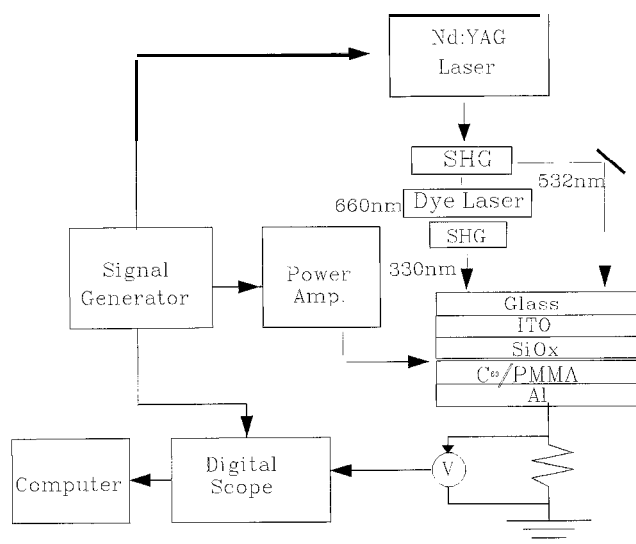

Figure 2. Schematic view of transient photocurrent apparatus.

preamplifier (Stanford Research Systems Model SR 250). The signal was acquired using a digital oscilloscope (LeCroy 9350) and stored in a personal computer. The photoresponse was defined as the peak photocurrent observed in the voltage versus time profile. This was done in contrast to using the time integral of the photocurrent, because the photocurrent did not decay back to zero within reasonable observation time, thus precluding time integration. The relative photocarrier generation efficiency (PGE), a quantity proportional to the number of carriers produced per photon absorbed, was determined by dividing the photoresponse by absorbance. The absorbance was measured using a Shimadzu-2100 UV-visible spectrometer. This normalization procedure accounts for variations in film thickness and concentration. For these films the absorbance at 330nm is much larger than the absorbance at 532nm as expected [14].

2.3. *Reverse saturable absorption measurements*

For optical limiting measurements C_{60}/toluene solutions were placed in 1 cm cuvettes, with an energy meter downstream to measure the transmitted light energy, 6. The $\mathscr{E}_0$ value was obtained by measuring the transmitted light intensity for a cuvette containing pure toluene devoid of C_{60} and dopants for the same 532nm laser power (10–500 $\text{mJ cm}^{-2} \text{ pulse-}^{1}$). The transmitted energy was measured by a Melles-Griot Broadband Power/Energy meter after 20 laser pulses. The laser energy was increased and the procedure repeated such that each laser energy sweep yielded an array of $\mathscr{E}$ and $\mathscr{E}_0$ values. This laser energy ramping was repeated in the reverse sweep direction yielding a second independ-

ent array of $\mathscr{E}$ and $\mathscr{E}_0$ values. The transmittance values of the two arrays $(\mathscr{E}/\mathscr{E}_0)$ at the same laser energy were averaged to yield the final transmittance. Great care was taken to avoid photodegradation of the sample. This was verified by comparing the magnitudes of transmittance for both arrays, and noting no significant differences between transmitted energies for corresponding array elements (those with the same incident energy).

3. Results and discussion
All solutions demonstrated photocarrier production at both 330 and 532nm as well as a decrease in transmittance for increasing light intensity: optical limiting.

3.1. Optical limiting donor/acceptor dependence
The optical limiting results for fullerene/toluene solutions devoid of dopants show a dramatic decrease in transmittance for an increase in laser fluence, consistent with previous studies [10, 11]. The transmittance versus laser fluence profiles are shown in figure 3 for several C_{60}/toluene solutions with various dopants: namely TPA, DNB and DMBQ. When the data are scaled to the same transmittance (41·39%), at the lowest fluence no differences in optical limiting behaviour are detected, except in the case of DMBQ addition. Dimethylbenzoquinone affects the optical limiting process by perturbing the quantum state photophysics. Further experiments are currently being conducted to understand this better. Prior to this experiment it was hypothesized that dopant addition would promote more CT state formation accompanied by either little exciton dissociation (leading to enhanced optical limiting ability) or more CT state dissociation, leading to reduced optical

limiting ability. The results show that dopant addition does not alter the optical limiting ability for these materials in the absence of an external applied field. If the samples were biased, then perhaps significant differences would have been observed. This postulate is based on the field dependence of C_{60} PGE investigated in our previous work on pyrromethene dyes [18], as well as new data on the field dependence of PGE detailed in the next section of this report. The complexity of carrying out an external-field (biased) optical limiting experiment precluded us from obtaining results for comparison in this paper. We attempted to carry out such an experiment, but the laser damage threshold was reduced, upon the application of an electric field, leading to photodamage of the sample for medium laser fluences.

One major motivation for doping optical limiters with donor/acceptors is to expand the wavelength range of optical limiting. Heflin et al. [19] have doped C_{60}/xylene solutions with tetraphenylporphine, resulting in the extension of the optical limiting region beyond 750nm wavelength region. Tetraphenylporphine forms a charge transfer complex with C_{60} which possesses an absorption tail longer than pure C_{60} solutions. The resulting wavelength extension is important for the development of broadband optical limiters. In addition to wavelength extension, our results show that dopant addition does not adversely affect the optical limiting behaviour in the absence of an applied field.

Following the development employed by Li [11], these transmittance versus fluence results could be simulated from a PC-based computer program. The simultaneous differential equations that govern the populations
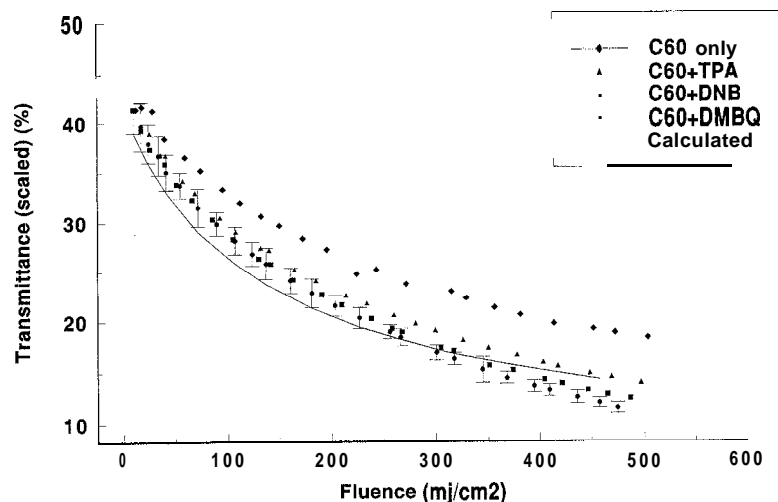

Figure 3. Reverse saturable absorption. Transmittance versus fluence in millijoules per square centimetre. 2·5 mg of C_{60} and 100 mg of (TPA, DNB, DMBQ) in 7 ml toluene. Laser intensity (lo-500 mJ cm^{-2} pulse^{-1} for 532nm). Data shifted such that transmittance at lowest energy is identical with C_{60} toluene transmittance.

of S_0, S_1 and T_1 are (notation taken from figure 1):

$$\frac{\partial S_0}{\partial t} + - \frac{\sigma_0 I}{h\nu} S_0 + k_2 S_1 + k_3 T_1 \qquad (1)$$

$$\frac{a\,s}{at}\,\dot{} = \frac{\sigma_0 I}{h\nu} S_0 - (k, + k_4) S_1 \qquad (2)$$

$$\frac{\partial T_1}{\partial t} = k_4 S_1 - k_3 T_1 . \qquad (3)$$

The depth (z) dependence of the irradiance is given by:

$$\frac{\partial I}{\partial z} = - - (\sigma_0 S_0 + \sigma_s S_1 + \sigma_T T_1) I \qquad (4)$$

The program utilizes a set of nested loops for independent variables z and t, in which the pathlength is divided into small slices dz (thin slice approximation) and the pulse is divided into time slices dt. Since z and t are fixed for each loop iteration, the numerical integration may be carried out for ordinary differential equations instead of partial differential equations. The results of the simulation are shown in figure 4 and agree well with the data. The simulation ignores the charge production/recombination processes: $CT(T_1) \rightleftarrows e + h$, and yet fits the data. This is further evidence that the charge production rate (k_5) is negligibly slow in the absence of an external field.

3.2. Photocarrier generation efficiency

The photocarrier generation efficiency exhibited a dye concentration dependence at 330 and 532nm as well as a dopant composition dependence for the 532 nm studies. By definition, the PGE is the photoresponse per absorbed photon. This implies a concentration normalization, such that one might expect the PGE to be concentration independent. However, the observed PGE is not concentration independent, and this dependence will be explained by electron-hole pair separation theory [20] in the next section.

3.2.1. Concentration variation

In figure 4 the PGE concentration dependence is presented for two wavelengths over the range of field strengths. For the 330nm studies a PGE concentration maximum is observed: an intermediate concentration (40mg) yields the largest PGE value. This is similar to the concentration maximum observed for the pyrromethene dyes in previous studies [21]. The 532 nm studies do not exhibit a concentration maximum, but do show a monotonic increase in PGE with increasing concentration. How does one explain these observations?

An explanation may be found in the electron-hole pair (EHP) dissociation theory discussed by Kuvshinskij *et al.* [20], who also observed similar behaviour for
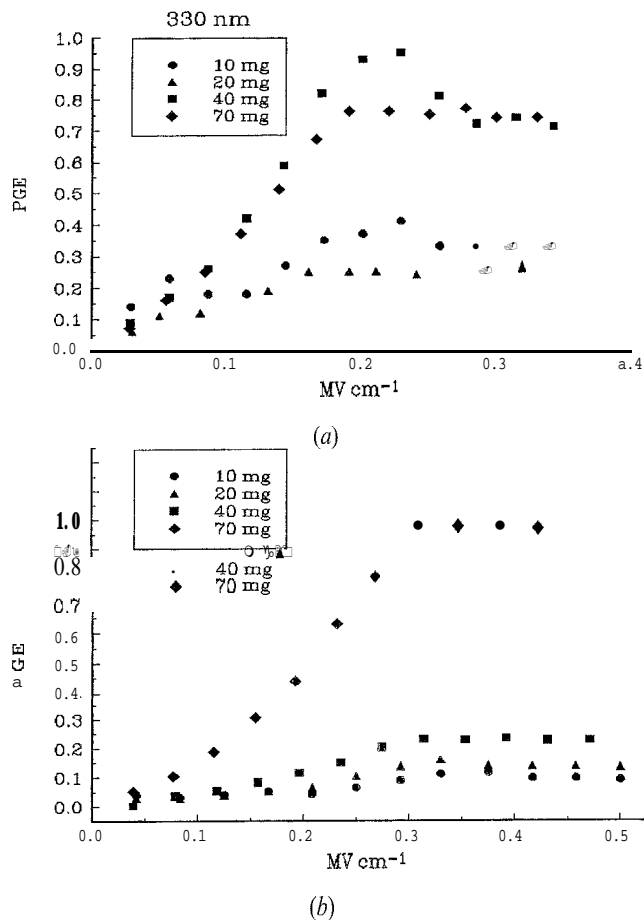

Figure 4. Relative photocarrier generation efficiency (PGE) for C_{60}/PMMA films with varying concentration: (a) PGE from photoresponse normalized to absorbance @ 330 nm, 0·38 mJ pulse-1; b PGE from photoresponse normalized to absorbance @ 532 nm, 1·0 mJ pulse^{-1}. Films consist of 10–70 mg C_{60} and 360mg PMMA.

Rhodamine 6G-doped poly-N-epoxyproplycarbazole. This theory states that crucial to charge dissociation is the electron jump distance (R,) in the n-type electron accepting medium and the hole jump distance (R,) in the p-type electron donating medium. The PGE dependence on this factor is:

$$PGE \propto R_n R_p \exp\left(-\frac{R_n}{\alpha_n} - \frac{R_p}{\alpha_p} \right) \qquad (5)$$

where a, and α_p are the electron and hole localization distance on C_{60} and PMMA respectively. The jump distances are inversely proportional to the cube root of n/p concentrations. Thus, R_n is proportional to $[C_{60}]^{-1/3}$ and R_p is proportional to [PMMA]$^{-1/3}$.

Since we are primarily varying $[C_{60}]$, we will assume [PMMA] = constant such that the PGE variation with

$[C_{60}]$ may be described by:

$$PGE \propto [C_{60}]^{(-1/3)} \exp\left(-\frac{[C_{60}]^{(-1/3)}}{\alpha_{C_{60}}} \right). \qquad (6)$$

Even though our PGE measurements are obtained via integration of hole carriers, the above expression is valid for describing this PGE dependence on $[C_{60}]$ variation.

The 330nm PGE concentration dependence is described via equation (6) as follows. As the concentration is increased from a nominally low value, the exponential term predominates yielding a rise in PGE with concentration. At higher concentrations the exponential term varies only slightly such that the pre-exponential term dominates leading to a dampening of PGE at higher concentrations. This predicted low-high-low PGE variation with increasing concentration is observed at 330nm with the 40mg C_{60} sample yielding the highest PGE.

At 532 nm the PGE only increases with concentration. This may be attributed to the expected higher electron affinity (reduction potential) for 330 nm excited C_{60} than for 532nm excited C,,. The lower electron affinity at 532nm should lead to a larger localization radius α_{C60}, which in turn leads to a more sensitive exponential factor, which should dominate over a larger concentration range. For example, $e^{-1/5x}$ grows faster than $e^{-1/x}$ for increasing x.

Both wavelengths also show PGE saturation: $\sim 0.2\,\text{MV cm}^{-1}$ for 330nm and $\sim 0.3\,\text{MV cm}^{-1}$ for 532 nm. Once again these observations may be rationalized via electron-hole pair dissociation theory in the formalism of Onsager [22]. Since α_{C60} is larger for 532 than 330 nm, the thermalization distance (R_0) between the geminate electron-hole pair is expected to be smaller for 532nm. A smaller thermalization distance results in a higher saturation field strength, which is consistent with observation. Figure 5 summarizes the theoretical scenario for the observed concentration dependence.

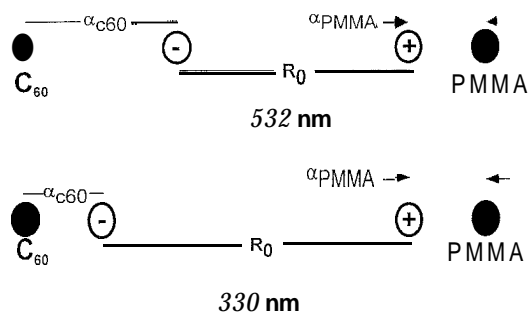As mentioned earlier in the experimental section, the PGE was obtained by a normalization procedure in which the photoresponse is divided by the absorbance at the excitation wavelength (330nm). The intent was to correct for differences in film thickness and concentration. This was tested by comparison with a second normalization procedure in which the photoresponse data were normalized to the product of film thickness and concentration of C,,. For both normalization procedures virtually the same PGE profile was obtained yielding the same trend in PGE versus dye concentration. Slight differences in the absorbance normalized and thickness-concentration normalized results may be due to the C_{60}/PMMA films not forming true molecular solutions, leading to slight differences in measured and predicted absorbencies.

3.2.2. Donor/acceptor dependence

Figure 6 shows the PGE dependence on electron donors/acceptors. Saturation occurs at a field strength in the range 0·4 to 0·5 MV cm^{-1} which implies all the available free carriers are collected. Only TPA addition led to an increase in the PGE. This is consistent with the formation of a strong excited charge transfer complex between TPA and C_{60}, a good electron donor and a good electron acceptor respectively [22]. The addition of several electron donors (TMPD) and electron acceptors (DMBQ, DNB, and TCNQ) did not affect the PGE to the same degree as TPA, although a noticeable difference exists among various additives. A similar trend was observed for films composed of pyrromethene dyes and these additives [18]. It has been observed that TMPD is a better quencher of $C_{60}(T_1)$ than TPA in solution due to the relative magnitude of the oxidation potentials $(E^0(\text{TPA}) = 0.85\ \text{V},\ E^0(\text{TMPD}) = 0.14\ \text{V})$ [23]. This is to say, the photoelectron transfer rate from TMPD to C_{60} occurs faster than photoelectron transfer from TPA to C_{60}; thus one might predict TMPD/C_{60} mixtures produce more photocarriers than TPA/C_{60} mixtures. However, our data show otherwise. The inequivalence of PGE and photoelectron transfer rate may be responsible for the observed discrepancy: in the solid state, in which the present PGE experiments are conducted, photoelectron transfer is only one factor of several that contributes to PGE. One must also consider the competing relaxation processes as well as migration of the carriers to electrodes (trapping). In our previous work on pyrromethene dyes [18] it was noted that a large enhancement of PGE following TPA addition was attributed to the large reorganization energy associated with the geometry change of neutral TPA to its radical cation. The addition of some electron acceptors actually led to a slight decrease in PGE. This raises a question about the photophysical scheme presented in the introduction: why does TPA addition affect photocarrier generation more than the optical limiting behaviour?

Figure 5. Molecular schematic of electron-hole pair dissociation for PMMA/C60 films at 330 and 532nm excitation.
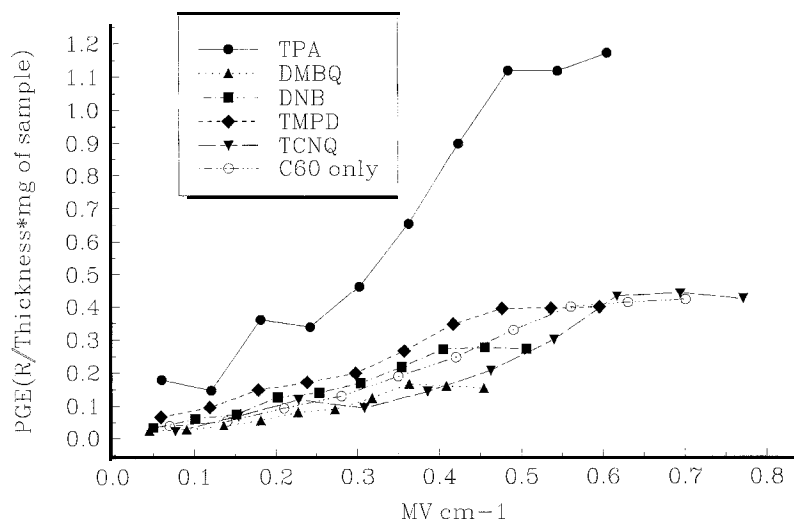
Figure 6. Relative photocarrier generation efficiency with donor/acceptor addition. PGE is determined by normalizing the photoresponse to the product of thickness and mass of C_{60} @ 532 nm, 1·00 mJ pulse-'. Films consist of 40mg C_{60}, 360mg PMMA and 50 mg respective additives.

One reason may be due to the different experimental conditions of the RSA and PGE experiments. In the PGE experiments the samples were subjected to an electric field, whereas the optical limiting studies were carried out in a zero field. It would be better to compare RSA and PGE of the same sample under the application of an electric field. However, as noted earlier, laser damage problems occurred when these C_{60}/PMMA films were irradiated during application of an electric field. The electric field not only affects CT state production (minor field dependence) but also CT state dissociation (strong field dependence). This is easily rationalized since the CT state lifetime is very long in the absence of a field, even in the presence of dopants, such that the dissociation into free carriers happens at a much slower rate than secondary photon absorption. On the other hand, large electric fields may increase the exciton dissociation rate to the degree that it may perturb secondary photon absorption, the process responsible for optical limiting.

Previous studies with dimethylaniline (electron donor) dopant added to C_{60}/PMMA films have shown an increase in the intersystem crossing (ISC) efficiency compared with undoped films [2]. Thus, there was hope that TPA addition would increase the ISC efficiency and be manifest as a perturbation in optical limiting behaviour. For C_{60} at 532 nm the $S_2 \leftarrow S_1$ absorption cross-section is larger than the $T_2 \leftarrow T_1$ absorption cross-section, but the lifetime of the S_1 state is smaller than that of T_1 [11]. These two competing processes preclude the dominance of either transition such that the optical limiting behaviour will not significantly change upon

increasing the ISC rate, and hence a small dependence on the dopant is observed.

4. Conclusions

The addition of triphenylamine (TPA) to C_{60}-doped polymethyl methacrylate films significantly improves the photocarrier generation efficiency. However, when corrected for initial absorbance differences, there is no appreciable change in the optical limiting behaviour of C_{60}/PMMA films upon the introduction of electron donors/acceptors in the absence of an applied electric field, with the exception of DMBQ addition. The difference in experimental conditions for the RSA and PGE experiments may be responsible for the apparent inconsistency: the RSA experiments were conducted in zero field, whereas the PGE results were carried out under strong electric fields. For both ultraviolet and visible light the PGE varies with concentration. The concentration dependence of PGE is explained by electron-hole pair dissociation theory.

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