

Singlet and Triplet Excited State Behaviors of C₆₀ in Nonreactive and Reactive Polymer Films

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The excited state behavior of C₆₀ has been investigated in polystyrene (PS) and poly(9-vinylcarbazole) (PVCz) polymer films. Picosecond and nanosecond laser flash photolysis techniques are employed to probe the transient absorption properties of singlet and triplet excited states in nonreactive (PS) and reactive (PVCz) microenvironments. In PS film, the absorption properties and lifetimes of these excited states are very similar to those observed in solutions. Encapsulation of C₆₀ with PS results in the suppression of excited state self-quenching processes. Excited state charge transfer complex formation dominates in PVCz film. The absence of long-lived electron transfer products indicates that the charge separation in PVCz film is short-lived.

Introduction

The photophysical, photochemical, and photoelectrochemical behaviors of fullerenes, C₆₀ and C₇₀, in homogeneous and heterogeneous media (e.g., in organic solvents,^{1–17} cyclodextrins,¹⁸ polymers,^{19–23} Langmuir–Blodgett films,²⁴ artificial membranes,²⁵ solid surfaces,²⁶ thin films,²⁷ and colloidal semiconductor suspensions²⁸) have been the focus of many recent research efforts. Of particular interest is the photophysical study of fullerene-doped polymer films.^{19–22} Such doped polymer films have been shown to possess photoconductive properties. Moreover, the long-lived triplet excited state and absorption in the visible make fullerenes suitable for solar energy conversion. In order to employ fullerenes for any such practical applications, it is important to understand the reaction pathways with which they might undergo photochemical changes in heterogeneous media such as polymers.

One convenient method of developing photoactive polymers is to incorporate photoactive guest molecules in a polymer film via electrostatic or hydrophobic interactions. The type and degree of interaction with the polymer can significantly influence the excited state properties of the photoactive guest molecule. Various aspects of photochemical processes in polymers have been presented in recent reviews.^{29–33} The polymeric environment is also useful for effecting and controlling photochemical processes more efficiently than can be accomplished in homogeneous solutions.

Enhanced photoconductivity in C₆₀-doped polymers has been attributed to the formation of excited charge transfer products.^{19,20} The photoinduced charge transfer between excited C₆₀ and a conducting polymer such as poly(3-octylthiophene) has been reported to occur on the subpicosecond time scale.³⁴ The fast recombination has been found to be a major limiting factor in extending the lifetime of charge transfer products. Neutral polymers such as poly(methyl methacrylate) have been shown to stabilize electron transfer products formed in a photochemical reaction between C₆₀ (or C₇₀) and dimethylaniline.²¹ Electron transfer products have also been identified in UV-excited poly(vinylcarbazole) solutions containing C₆₀.²³ Efforts are also being made to copolymerize C₆₀ with styrene.³⁵ Interaction of C₆₀ with the functional groups of a polymer can be a crucial factor in controlling the excited state charge transfer. In view

of these important aspects of the polymeric environment in controlling the photochemistry of dopant, we have now compared the excited state behavior of C₆₀ in a neutral (polystyrene) and reactive (poly(9-vinylcarbazole)) polymeric environment. The transient absorption measurements which elucidate the behavior of excited C₆₀ in PS and PVCz are presented.

Experimental Section

Materials and Sample Preparation. The purified C₆₀ sample (99.99%) was obtained from SES Research, Houston, TX. Poly(9-vinylcarbazole) (mol wt 92 100) was obtained from Aldrich, and polystyrene (mol wt 63 000) was obtained from Polysciences Inc. The polymer solution containing C₆₀ was prepared by either dissolving desired amounts of C₆₀ and polymer in benzene or mixing concentrated solutions of C₆₀ (in toluene) and the polymer (in CH₂Cl₂). The resultant mixture (0.1 mL solution containing 100 nmol of C₆₀ and 160 nmol of the polymer) was applied to a quartz plate (9 × 12 mm²). After the polymer film was dried in air, the glass slide was transferred to an optical cell and, when necessary, the cell was connected to a vacuum line for 3–5 h for the purpose of degassing. The evacuated sample cell containing C₆₀-doped polymer film sample was closed with a vacuum-tight Ace stopcock before disconnecting from the vacuum line. The films thus prepared were stable and transparent, although in the case of PVCz films opacity due to crystallization of the polymer was encountered. In such cases, care was taken to probe only the transparent portion of the film. All experiments were carried out at room temperature (296 K).

Optical Measurements. Absorption spectra were recorded with a Perkin-Elmer 3840 diode array spectrophotometer. The spectra were corrected for background scatter by using blank quartz plates.

Picosecond laser flash photolysis experiments were performed with 355 nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (output 2–3 mJ/pulse, pulse width ~18 ps). The white continuum picosecond probe pulse was generated by passing the fundamental output through a D₂O/H₂O solution. The output was fed to a spectrograph (HR-320, ISDA Instruments, Inc.) with fiber optic cables and was analyzed with a dual diode array detector (Princeton Instruments, Inc.) interfaced with an IBM-AT computer. The details of the experimental setup and its operation are described elsewhere.³⁶ Time zero in these

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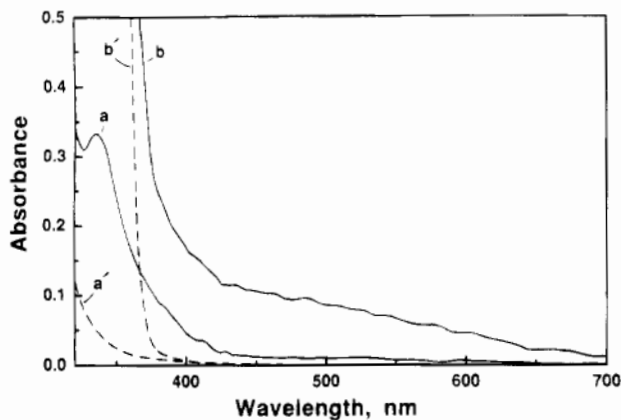


Figure 1. Absorption spectrum of C_{60} -doped polymer films: (a) polystyrene and (b) poly(vinylcarbazole) films cast on a quartz plate. Samples of C_{60} (100 nmol) and polymer (160 nmol) were spread over an area of ~ 1 cm². The absorption spectra of undoped polymer films (a') polystyrene and (b') poly(vinylcarbazole) vs air are also shown.

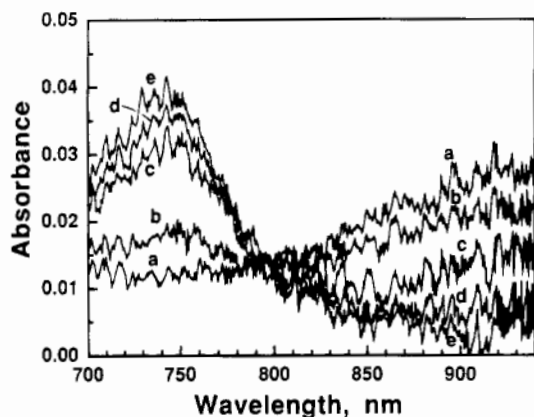


Figure 2. Time-resolved difference absorption spectra of singlet and triplet excited states of C_{60} -doped PS film. The spectra were recorded following the 355 nm laser pulse excitation of C_{60} (100 nmol) in PS film (C_{60} :polymer ratio was 1:1.6) at time intervals of (a) 0, (b) 300, (c) 11500, (d) 1900, and (e) 4900 ps.

experiments corresponds to the end of the excitation pulse. All the lifetimes and rate constants reported in this study have an experimental error of $\pm 5\%$.

Nanosecond laser flash photolysis experiments were carried out with a Laser Photonics PRA/Model UV-24 nitrogen laser system (337 nm, 2 ns pulse width, 2–4 mJ/pulse) with a front face excitation geometry. A typical experiment consisted of a series of 2–3 replicate shots per single measurement. The average signal was processed with an LSI-11 microprocessor interfaced with VAX-3400 computer. Details of the experimental set up can be found elsewhere.³⁷

Results and Discussion

Absorption and Emission Characteristics. The absorption spectra of C_{60} in PS and PVCz films are shown in Figure 1, a and b, respectively. The absorption characteristics of undoped PS and PVCz films (vs air) are shown in Figure 1 as spectra a' and b', respectively. While PS exhibits little absorption in the 300–350 nm region, PVCz shows significant absorption below 360 nm. C_{60} incorporated in the PS film is found to retain all the characteristic absorption bands with a sharp absorption peak at 336 nm and a broad absorption in the 500–600 nm region. In the case of PVCz films the absorption band in the visible is rather broad (400–650 nm). The absorption in the visible is significantly increased in C_{60} -doped PVCz films. These changes in the absorption characteristics indicate charge transfer interac-

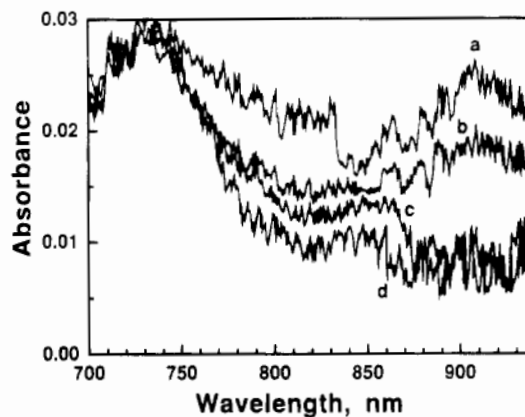


Figure 3. Time-resolved difference absorption spectra of singlet and triplet excited states of C_{60} -doped PVCz film (C_{60} , 100 nmol; C_{60} :polymer ratio, 1:1.6). The spectra were recorded following the 355 nm laser pulse excitation at time intervals of (a) 0, (b) 400, (c) 1150, and (d) 4900 ps.

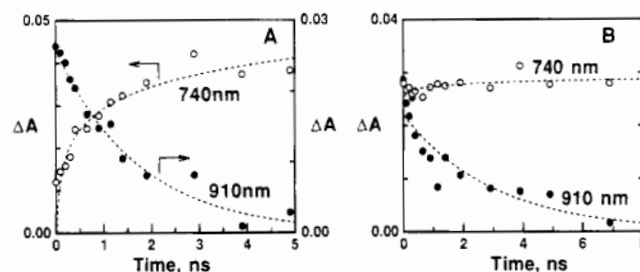


Figure 4. Transient absorption decay recorded at 910 (●) and 740 nm (○): (A) C_{60} -doped PS film and (B) C_{60} -doped PVCz film. (Experimental conditions are same as in Figures 2 and 3, respectively.)

tion between C_{60} and PVCz. Note that below 360 nm PVCz absorbs strongly, and hence, the spectra of C_{60} cannot be well resolved. Similar increased absorption in the visible band of the absorption spectrum has been observed as a result of charge transfer interaction between amines and fullerenes.^{17,18} Such a charge transfer interaction between the carbazole group and C_{60} can be important in altering the properties of the host polymer as indicated by the improved photoconductivity of PVCz films.¹⁹

Picosecond Laser Flash Photolysis Experiments. In order to probe the singlet and triplet excited state behavior of C_{60} in PS and PVCz films, time-resolved difference absorption spectra were recorded immediately following 355 nm laser pulse excitation (pulse width 18 ps) of C_{60} in the respective polymer films. Time-resolved absorption spectra of the transients generated in these polymer films are shown in Figures 2 and 3. The spectral region of 700–960 nm was chosen because both excited singlet (920 nm) and triplet (740 nm) states of C_{60} absorb in this region. The absorption time profiles at 740 and 910 nm are shown in Figure 4.

(a) *In Polystyrene Film.* The absorption characteristics of $^1C_{60}^*$ and $^3C_{60}^*$ in PS film are similar to those observed in various nonpolar solvents.^{2–9} The isosbestic point observed at 790 nm (Figure 2) suggests that there are only two transient states which contribute to the absorption in the 700–960 nm region. The decay of $^1C_{60}^*$ at 910 nm closely matches the growth of $^3C_{60}^*$ at 740 nm (see the absorption time profiles shown in Figure 4A). The lifetime of $^1C_{60}^*$ measured from these kinetic traces was 1.2 ns. This value of the singlet lifetime is similar to that in aromatic solvents (e.g., benzene or toluene^{3a,4a,7}) and poly(methyl methacrylate) film ($\tau = 1.2$ ns).²¹ These observations suggest that the host polymer, PS, is nonreactive and did not alter the excited state properties of C_{60} .

Similarly, experiments carried out with C₇₀-doped PS films exhibit no major changes in the excited state properties of C₇₀.

(b) *In Poly(vinylcarbazole) Film.* The photochemical events in PVCz film doped with C₆₀ were probed by recording time-resolved transient absorption spectra following the 355 nm laser pulse excitation (Figure 3). The yields of both singlet and triplet excited states in PVCz film are lower than in PS film. More significantly the changes in the absorption bands at 910 and 740 nm with time are different than in PS film. The growth in the transient absorption at 740 nm due to intersystem crossing was absent in PVCz film.

The absorption at 910 nm decays cleanly with first-order kinetics. The lifetime of ¹C₆₀* measured from this decay is 825 ps, which is shorter than that observed in the PS film. This shorter lifetime of ¹C₆₀* suggests quenching of uncomplexed singlet excited state by PVCz. During the period of 3 ns most of the singlet excited state (910 nm absorption) is found to decay while the absorption at 740 nm remains unchanged (Figure 4B). If PVCz film is nonreactive, one would see a growth in the 740 nm band as a result of excited triplet formation. The isosbestic point observed in PS film at 790 nm is also absent in PVCz film. The difference in the absorption features of the transients in Figures 2 and 3 indicates the reactive nature of carbazole group of the host polymer in complexing with C₆₀ and its influence on the photochemical events in the subnanosecond time domain. The prompt appearance of this band suggests that the formation of an excited charge transfer complex is completed within the laser pulse duration of 20 ps.

It is evident from Figure 3 that either the triplet excited charge transfer complex between C₆₀ and carbazole and/or the electron transfer products formed following the laser excitation contribute to the absorption in the 700–750 nm region. It has been reported earlier^{2c,9a,17} that C₆₀⁻ has a strong absorption in the IR with maxima at 950 and 1075 nm. Since we do not see any increasing absorption at wavelengths greater than 900 nm during the time period of 0–5 ns, we cannot ascribe this difference to the formation of charge transfer products. Therefore, the absorption in the 700–750 nm region must be due to triplet excited charge transfer complex (i.e., ³[C₆₀:PVCz]*). The absence of absorption growth in the 740 nm region further shows that the intersystem crossing in ¹[C₆₀:PVCz]* complex occurs more rapidly than in uncomplexed ¹C₆₀*. Formation of ³[C₆₀-dimethylaniline]* complex in poly(methyl methacrylate) film was also found to yield similar changes in the transient absorption spectra.²¹ It has been shown by Sension *et al.*¹⁷ that the formation of [DMA^{•+}:C₆₀⁻] ion pairs in solution occurs on a time scale of 1–2 ps. Similarly, photoinduced charge separation in the subpicosecond time scale has been reported in C₆₀-doped poly(3-octylthiophene).³⁴ If the charge transfer products are formed in a subpicosecond time scale, the width of the laser pulse (18 ps) in the present experiments does not allow us to resolve the contribution of C₆₀⁻ to the spectra recorded immediately after the laser pulse excitation.

Nanosecond Laser Flash Photolysis. The transient absorption spectra recorded following 337 nm laser pulse excitation of degassed PS and PVCz films containing C₆₀ are shown in Figures 5 and 6, respectively.

(a) *In Polystyrene Film.* ³C₆₀* in the PS film exhibits absorption maxima at 360, 400, and 750 nm (Figure 5). These absorption features are similar to those reported earlier for triplet excited fullerenes in toluene and benzene solutions.^{2–9} The similarity between the spectra recorded at 4.7 and 131.2 μs indicates that no other long-lived transients are formed following the 337 nm laser excitation. Thus fullerene molecules, when incorporated in a polymer film such as PS, retain their native

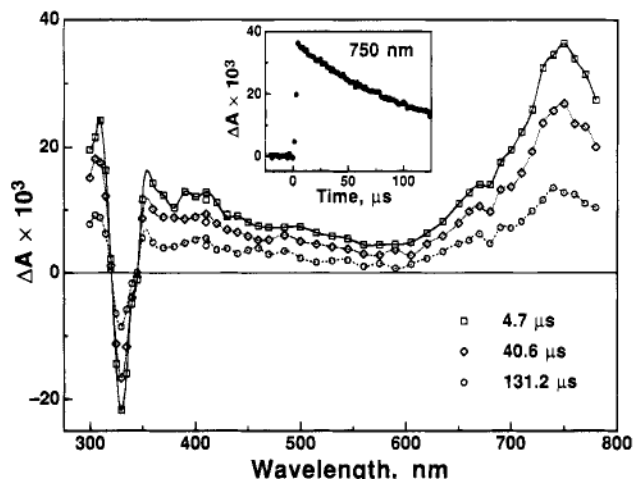


Figure 5. Time-resolved difference absorption spectra of triplet excited state of C₆₀ in PMMA film. The spectra were recorded following the 337 nm laser pulse excitation of C₆₀ (100 nmol) in PS film (C₆₀:polymer ratio was 1:1.6) at time intervals of (a) 4.7, (b) 40.6, and (c) 131.2 μs. The insert shows the decay profile of the transient at 750 nm.

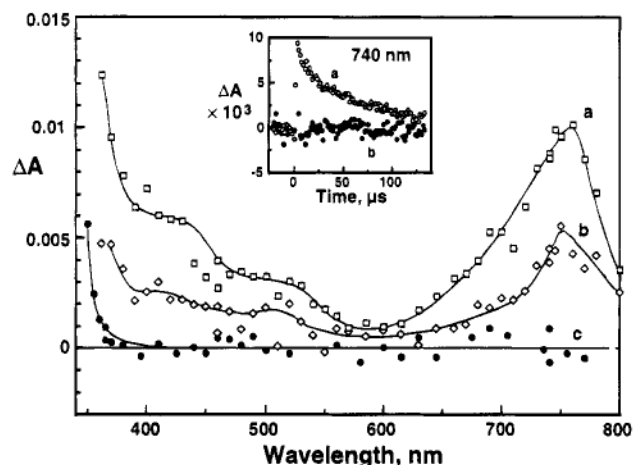


Figure 6. Time-resolved difference absorption spectra of triplet excited state of C₆₀ in PVCz film. The spectra were recorded following the 337 nm laser pulse excitation of C₆₀ (100 nmol) in PMMA film (C₇₀:polymer ratio was 1:1.6) at time intervals of (a) 3.1 and (b) 39.1 μs. Spectrum c was recorded 39.1 μs after the 337 nm laser pulse excitation of undoped PVCz film. The insert shows the absorption-time profiles at 740 nm: (a) PVCz film doped with C₆₀ (○) and (b) undoped PVCz film (●).

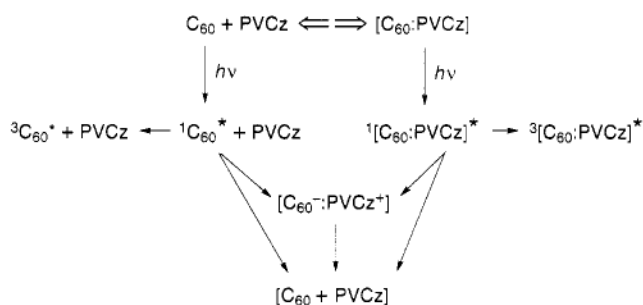
photoactivity, and they are quite stable to laser irradiation in an inert atmosphere.

The lifetime of triplet excited state in the degassed PS films was found to be 136 μs. This value is significantly higher than the triplet lifetime observed in solution (10–50 μs). It has been shown that in organic solvents self-quenching processes such as T–T annihilation and ground state quenching dominate the deactivation of the triplet excited states of C₆₀ and C₇₀.^{4a,10b} The longer triplet lifetime observed in the PS film shows that C₆₀ molecules are isolated as a result of being entrapped within the polymer network. Thus, polymer encapsulation is a convenient approach to suppress the self-quenching process and increase the lifetime of triplet excited C₆₀.

When equilibrated in air, the triplet excited state exhibits shorter lifetime as a result of quenching by O₂. This quenching process proceeds via an energy transfer mechanism resulting in the formation of singlet oxygen, the details of which can be found elsewhere.^{2d,38,39}

(b) *In Polyvinylcarbazole Film.* The transient absorption spectra recorded following 337 nm laser excitation of PVCz

SCHEME 1



film containing C_{60} are shown in Figure 6. The spectrum recorded immediately after the laser flash (spectrum a in Figure 6) closely match the spectral features of the ${}^3C_{60}^*$. This absorption band arises from both complexed and uncomplexed C_{60} triplet excited state. The absorption–time profile at 740 nm indicates two different decay lifetimes for the decay of the excited triplet. The shorter lifetime component which arises mainly from the triplet excited charge transfer complex has a lifetime of 35 μ s. The longer lifetime component which arises from the uncomplexed ${}^3C_{60}$ has a lifetime of 77 μ s. It should be noted that the spectral features of these two transients (complexed and uncomplexed forms of ${}^3C_{60}^*$) essentially remained the same during the time scale of triplet decay.

PVCz also absorbs significantly in the ultraviolet. UV excitation of PVCz in a polar solvent such as benzonitrile has been shown to yield the cation radical, $PVCz^{+\bullet}$, with characteristic absorption around 740 nm.^{23,40} However, no such transients were seen when blank film of PVCz film was subjected to UV excitation. The transient absorption spectrum recorded with undoped PVCz film is shown as spectrum c in Figure 6. The absorption–time profiles of undoped and C_{60} -doped PVCz films are also shown in the insert of Figure 6. These results indicate the contribution of photoproducts resulting from PVCz excitation to be negligible under the experimental conditions employed in these experiments. It should be noted that in all these experiments the excitation was carried out with low intensity laser pulse (~ 2 mJ/pulse).

Photochemistry of C_{60} in PVCz Film. The possible photochemical reactions which lead to the charge separation in the C_{60} -doped PVCz film are summarized in Scheme 1.

Both the complexed and uncomplexed forms of fullerenes are capable of undergoing photoinduced electron transfer process in the PVCz film. It has been recently shown that photoinduced reduction of C_{60} by PVCz can be carried out in polar solvents.²³ It should be noted that in solutions the complexation between C_{60} and PVCz is weak, and most of the electron transfer quenching occurs via diffusion-controlled processes. Alternatively, photoionization of PVCz in polar solvents also yields $PVCz^{+\bullet}$ and solvated electrons. These solvated electrons in turn could react with C_{60} to yield $C_{60}^{\bullet-}$. However, the mechanism of charge transfer product formation is likely to be different in polymer films. In the case of PVCz film most of the C_{60} in PVCz exists as a charge transfer complex because of the high concentration of carbazole groups. This fact is supported by the appearance of a charge transfer band in the absorbance spectrum (Figure 1). In our earlier quenching experiment of ${}^3C_{60}^*$ with dimethylaniline in a poly(methyl methacrylate) film, we were able to characterize electron transfer products.²¹ It was concluded that uncomplexed C_{60} was responsible for the net electron transfer and that the polymer matrix stabilized the electron transfer products. However, in the present case the major fraction of the excited state quenching and charge separation occurs within the charge transfer complex. The fast

recombination within the complex is likely to be the reason for not observing long-lived products in the C_{60} –PVCz system. Similar fast recombination of charge transfer products has also been noted in C_{60} –amine complexes¹⁷ and C_{60} -doped poly(3-octylthiophene).³⁴ The time-resolved transient absorption experiments described here thus provide an insight into the excited state behavior of C_{60} in a reactive and nonreactive polymeric environment.

Conclusions

Polystyrene and poly(vinylcarbazole) films doped with C_{60} are photoactive, but the interaction between the host polymer and dopant controls the excited state behavior of the C_{60} molecule. The singlet and triplet excited states of C_{60} in a polystyrene film have spectral features similar to those observed in aromatic solvents. Self-quenching processes are greatly suppressed as a result of polymer encapsulation. In PVCz films the charge transfer complexation between C_{60} and the host polymer controls the excited state behavior.

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References and Notes

- (1) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991**, *91*, 1213 and references therein.
- (2) (a) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. J. *J. Phys. Chem.* **1991**, *95*, 11. (b) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886. (c) Arbogast, J. W.; Foote, C. S.; Kao, M. J. *Am. Chem. Soc.* **1992**, *114*, 2277. (d) Krasnovsky, Jr., A. A.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 6013. (e) Foote, C. S. *Top. Curr. Chem.*, in press. (f) Arbogast, J. W.; Foote, C. S.; Kao, M. J. *Am. Chem. Soc.* **1992**, *114*, 2277.
- (3) (a) Ebbesen, T. W.; Tanigaki, K.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *181*, 501. (b) Tanigaki, K.; Ebbesen, T. W.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *185*, 189.
- (4) (a) Dimitrijević, N. M.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 4811. (b) Samanta, A.; Kamat, P. V. *Chem. Phys. Lett.* **1992**, *199*, 635.
- (5) (a) Hung, R. R.; Grabowski, J. J. *J. Phys. Chem.* **1991**, *95*, 6073. (b) Hung, R. R.; Grabowski, J. J. *Chem. Phys. Lett.* **1992**, *192*, 249.
- (6) (a) Kajiji, Y.; Nakagawa, T.; Suzuki, S.; Achiba, Y.; Obi, K.; Shibuya, K. *Chem. Phys. Lett.* **1991**, *181*, 100. (b) Terazima, M.; Hirota, N.; Shinohara, H.; Saito, Y. *J. Phys. Chem.* **1991**, *95*, 6490. (c) Terazima, M.; Sakurada, K.; Hirota, N.; Shinohara, H.; Saito, Y. *J. Phys. Chem.* **1993**, *97*, 5447. (d) Kato, T.; Kodama, T.; Shida, T.; Nakagawa, T.; Matsui, Y.; Suzuki, S.; Shiromaru, H.; Yamauchi, K.; Achiba, Y. *Chem. Phys. Lett.* **1991**, *180*, 446.
- (7) (a) Palit, D. K.; Sapre, A. V.; Mittal, J. P. *Indian J. Chem., Sect. A* **1992**, *31*, F46. (b) Palit, D. K.; Sapre, A. V.; Mittal, J. P.; Rao, C. N. R. *Chem. Phys. Lett.* **1992**, *195*, 1. (c) Palit, D. K.; Ghosh, H. N.; Pal, H.; Sapre, A. V.; Mittal, J. P.; Seshadri, R.; Rao, C. N. R. *Chem. Phys. Lett.* **1992**, *198*, 113. (d) Ghosh, H. N.; Pal, H.; Sapre, A. V.; Mittal, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 11722.
- (8) (a) Bensasson, R. V.; Hill, T.; Lambert, C.; Land, E. J.; Leach, S.; Truscott, T. G. *Chem. Phys. Lett.* **201**, 326. (b) Bensasson, R. V.; Hill, T.; Lambert, C.; Land, E. J.; Leach, S.; Truscott, T. G. *Chem. Phys. Lett.* **206**, 197.
- (9) (a) Biczok, L.; Linschitz, H.; Walter, R. I. *Chem. Phys. Lett.* **1992**, *195*, 339. (b) Zeng, Y.; Biczok, L.; Linschitz, H. *J. Phys. Chem.* **1992**, *96*, 5237. (c) Steren, C. A.; Levsten, P. R.; Van Willigen, H.; Linschitz, H.; Biczok, L. *Chem. Phys. Lett.* **1993**, *204*, 23.
- (10) (a) Sibley, S. P.; Argentine, S. M.; Francis, A. H. *Chem. Phys. Lett.* **1992**, *188*, 187. (b) Sibley, S. P.; Argentine, S. M.; Francis, A. H. *Chem. Phys. Lett.* **1992**, *188*, 187. (c) Fraelich, M. R.; Weisman, R. B. *J. Phys. Chem.* **1993**, *97*, 11145. (d) Nadochenko, V. A.; Vasil'ev, I. V.; Denisov, N. N.; Rubtsov, I. V.; Lobach, A. S.; Moravskii, A. P.; Shestakov, A. F. *J. Photochem. Photobiol. A: Chem.* **1993**, *70*, 153. (e) Nadochenko, V. A.; Vasil'ev, I. V.; Denisov, N. N.; Rubtsov, I. V.; Lobach, A. S.; Moravskii, A. P.; Shestakov, A. F. *J. Photochem. Photobiol. A: Chem.* **1993**, *70*, 153. (f) Haynes, D. R.; Tokmakoff, A.; George, S. M. *Chem. Phys. Lett.* **1993**, *214*, 50.
- (11) (a) Wang, Y.; Cheng, L.-T. *J. Phys. Chem.* **1992**, *96*, 1530. (b) Wang, Y. *J. Phys. Chem.* **1992**, *96*, 764.

- (12) (a) Levanon, H.; Meiklyar, V.; Michaeli, A.; Michaeli, S.; Regev, A. *J. Phys. Chem.* **1992**, *96*, 6128. (b) Levanon, H.; Meiklyar, V.; Michaeli, S.; Gamliel, D. *J. Am. Chem. Soc.* **1993**, *115*, 8722. (c) Michaeli, S.; Meiklyar, V.; Schulz, M.; Möbius, K.; Levanon, H. *J. Phys. Chem.* **1994**, *98*, 7444. (d) Goudsmit, G.-H.; Paul, H. *Chem. Phys. Lett.* **1993**, *208*, 73.
- (13) (a) Guldi, D. M.; Hungerbühler, H.; Janata, E.; Asmus, K.-D. *J. Phys. Chem.* **1993**, *97*, 11258. (b) Guldi, D. M.; Hungerbühler, H.; Janata, E.; Asmus, K.-D. *J. Chem. Soc., Chem. Commun.* **1993**, 84. (c) Guldi, D. M.; Hungerbühler, H.; Wilhelm, M.; Asmus, K.-D. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1391. (d) Guldi, D. M.; Neta, P.; Asmus, K.-D. *J. Phys. Chem.* **1994**, *98*, 4617. (e) Guldi, D. M.; Huie, R.; Neta, P.; Hungerbühler, H.; Asmus, K.-D. *Chem. Phys. Lett.* **1994**, *223*, 511.
- (14) (a) Schell-Sorokin, A. J.; Mehran, F.; Eaton, G. R.; Eaton, S. S.; Viehbeck, A.; O'Toole, T. R.; Brown, C. A. *Chem. Phys. Lett.* **1992**, *195*, 225. (b) Bhyrappa, P.; Paul, P.; Stinchcombe, J.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 11004.
- (15) (a) Dimitrijević, N. M. *Chem. Phys. Lett.* **1992**, *194*, 457. (b) Dimitrijević, N. M.; Fessenden, R. W.; Kamat, P. V. *J. Phys. Chem.* **1993**, *97*, 615.
- (16) Sension, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanov, W. J.; McGhie, A. R.; McCauley, Jr., J. P.; Smith, A. B.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 6075.
- (17) Sension, R. J.; Szarka, A. Z.; Smith, G. R.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1991**, *185*, 179.
- (18) (a) Andersson, T.; Nilsson, K.; Sundhal, M.; Westman, G.; Wennerström, O. *J. Chem. Soc., Chem. Commun.* **1992**, 604. (b) Dimitrijević, N. M.; Kamat, P. V. *J. Phys. Chem.* **1993**, *97*, 7623.
- (19) Wang, Y. *Nature* **1992**, *356*, 585.
- (20) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474.
- (21) Gevaert, M.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 9883.
- (22) Keepler, R. G.; Cahill, P. A. *Appl. Phys. Lett.* **1993**, *63*, 1552.
- (23) Watanabe, A.; Ito, O. *J. Chem. Soc., Chem. Commun.* **1994**, 1285.
- (24) (a) Obeng, Y. S.; Bard, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 6279. (b) Wang, Y.; Kamat, P. V.; Patterson, L. K. *J. Phys. Chem.* **1993**, *97*, 8793.
- (25) (a) Hwang, K. C.; Mauzerall, D. *J. Am. Chem. Soc.* **1992**, *114*, 9705. (b) Hungerbühler, H.; Guldi, D. M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1993**, *115*, 3386.
- (26) Gevaert, M.; Kamat, P. V. *J. Chem. Soc., Chem. Commun.* **1992**, 1470.
- (27) Miller, B.; Rosamilia, J. M.; Dabbagh, G.; Tycko, R.; Haddon, R. C.; Muller, A. J.; Wilson, W.; Murphy, D. W.; Hebard, A. F. *J. Am. Chem. Soc.* **1991**, *113*, 6291.
- (28) (a) Kamat, P. V. *J. Am. Chem. Soc.* **1991**, *113*, 9705. (b) Kamat, P. V.; Bedja, I.; Hotchandani, S. *J. Phys. Chem.* **1994**, *98*, 9137.
- (29) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: New York, 1985.
- (30) Gopidas, K. R.; Kamat, P. V. *J. Phys. Chem.* **1990**, *94*, 4723.
- (31) Farid, S.; Martic, P. A.; Daly, R. C.; Thompson, D. R.; Specht, D. P.; Hartman, S. E.; Williams, J. L. R. *Pure Appl. Chem.* **1979**, *51*, 241.
- (32) Kalyansundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987; p 255.
- (33) Kamat, P. V.; Fox, M. A. In *Lasers in Polymer Science and Technology: Applications*; Fouassier, J.-P., Rabek, J. F., Eds.; CRC Press: Boca Raton, FL, 1990; Vol. II, pp 185–202.
- (34) Kraabel, B.; Lee, C. H.; McBranch, L. D.; Moses, D.; Sarciftci, N. S.; Heeger, A. J. *Chem. Phys. Lett.* **1993**, *213*, 389.
- (35) Hawker, C. J. *Macromolecules* **1994**, *27*, 4836.
- (36) Ebbesen, T. W. *Rev. Sci. Instrum.* **1988**, *59*, 1307.
- (37) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330.
- (38) Black, G.; Dunkle, E.; Dorko, E. A.; Schlie, L. A. *J. Photochem. Photobiol. A: Chem.* **1993**, *70*, 147.
- (39) Scurlock, R. D.; Martire, D. O.; Ogilby, P. R.; Taylor, V. L.; Clough, R. L. *Macromolecules* **1994**, *27*, 4787.
- (40) Taniguchi, Y.; Nishina, Y.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1646.