

FINAL REPORT ON DEPARTMENT OF ENERGY PROJECT
CONTRACT DE-FG03-92ER45476

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1. Project Title: Photophysical Processes of Triplet States and Radical Ions in Pure and Molecularly Doped Polymers

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2. Principal Project Personnel

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Areas of research include, condensed phase spectroscopy, kinetics and polymer chemistry.

Education includes A.B. degree, Dartmouth College, 1956 and Ph.D. University of Colorado, 1960. Post-doctoral, University of Oregon (Richard M. Noyes)

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Outstanding Teacher at the University of Nevada, 1974.

Publications related to the current project appearing since 1983 are given in the bibliography section at the end of this report.

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3. Other Project Personnel

Graduate Students (Current position, if known, indicated in parentheses)

Ishmael Dawood M. S. degree 1986

Jon A. J. Burrows M. S. degree 1988

Thomas Siu M. S. degree 1988 (Chemistry Instructor, U. S. Naval Academy, Annapolis, MD)

Gregory Haggquist M. S. degree 1988 (Also Ph.D., see below)

William Liebe DEGREE NOT AWARDED

Myra Yuan M. S. degree 1995

Augustine A. Abia Ph.D. degree 1984 (Port Harcourt Univ. Nigeria)

Gregory Haggquist Ph.D. degree 1991 (Lexmar Corporation, Boulder, CO)

Nam-In Jhon Ph.D. degree 1992

Postdoctoral Associates

Norris J. Caldwell Post-doctoral 1984-1986

Dilip Chakraborty Post-doctoral 1986-1989 (Kentucky Department for Environmental Protection)

Franciscek Starzyk Post-doctoral 1987-88 (Institute of Physics, Technical University of Krakow, Poland)

Visiting Faculty Associates

Yong-Tae Park, In residence summers of 1987 and 1988 from Department of Chemistry, Kyungpook National University, Taegu, South Korea

K. Razi Naqvi, In residence 1989-90 from the Institute of Physics, University of Trondheim

Sally Reid Hair, In residence June 1, 1993 to August 15, 1993, on leave from Allegheny College, Meadville, PA.

Visiting Faculty Associates (cont.)

Shinzaburo Ito, In residence June 18, 1993 to July 2, 1993, on leave from the Department of Polymer Chemistry, Kyoto University

Akira Tsuchida, In residence August 1993 from the Division of Polymer Chemistry, Kyoto University

Tapan Ganguly In residence April 1, 1993 to December 1994, on leave from the Indian Association for the Cultivation of Science.

4. Project Overview

A. Specific Project Objectives

Both our past and current objectives are to learn how to control the rate and direction of triplet exciton migration in both pure and molecularly doped polymer systems. Since triplet excimers are efficient traps for migrating excitons, a secondary objective has been to characterize these excimers with a view toward their use as rate modifiers or excited state quenchers.

Our further objectives included those stated above as past and current objectives but with an additional goal. We learned that fluid solutions of many of the nitrogen containing chromophores with which we work produce both radical cations and anions upon excimer laser excitation. We also learned that a phosphorus analogue behaves similarly. At this time the mechanism of charge generation in these systems is not well established but we do know that the electronically excited states and radical ions can potentially interconvert. We wanted to find out whether or not our pure or molecularly doped polymer systems could be used in a step-wise sequence involving light absorption followed by charge generation.

B. Relation of This Project to the DOE Mission

All of our activities are oriented toward the potential end use of polymeric systems in the conversion of light energy to perform various types of useful work. The project therefore contains some of the elements of what is popularly called materials research coupled with the photophysical activities needed to explore the potential utility of these materials in the energy conversion processes which we envision.

C. Project History

- △ U.S. Department of Energy, "Photophysical Studies of Triplet Exciton Processes in Pure Polymer Films," a three year grant initiated July, 1983 having a total budget of \$243,685. Of this amount, \$34,889.25 was spent in indirect costs.
- △ U.S. Department of Energy, "Investigation of Triplet Exciton Processes Occurring in Pure Polymer Films," A three year grant initiated July, 1986 having a total budget of \$285,000. Of this amount, \$23,019.2 was spent in indirect costs.
- △ U. S. Department of Energy, "Photophysical Processes of Triplet Excitons on Polymeric Systems," A three year grant initiated July, 1989 having a total budget of \$276,990. Of this amount, \$46,580.74 was spent on indirect costs.
- △ U. S. Department of Energy, "Photophysical Processes of Triplet States and Radical Ions in Pure and Molecularly Doped Polymers," a three year grant initiated July, 1992 having a total budget of \$276,250.
- △ National Science Foundation, "U.S.-Japan Cooperative Research: Photoinduced Charge Generation in Polymers," April 1, 1993 to September 30, 1995, \$7,875.
[Note that this grant provided funds for the PI to spend a period of five weeks during the summer of 1994 at the University of Kyoto to complete a cooperative research program on polymer photophysics with workers at that institution. Three members of their research group are visited our labs in Reno during 1993 to perform experimental work associated with this project.]

5. Scientific and Technical Content

A. Schedule of Major Research Activities

Here we list the major subtopics which have been addressed since the inception of DOE grant support in 1983.

- △ Characterization of triplet state emission from solid films of various polymers including poly(N-vinylcarbazole), poly[N-((vinylxy)carbonyl)carbazole], poly(2-vinylnaphthalene *alt* methylmethacrylate), poly(3,6-dibromo-N-vinylcarbazole) and poly[4-(N,N-diphenylamino)phenylmethylmethacrylate].
- △ Effect of temperature upon spectroscopic properties of pure and molecularly doped polymers including time resolved spectra and excited state decay kinetics.
- △ Chemical modifications, primarily of the carbazolyl chromophore, to determine the propensity for triplet excimer formation and the bonding mode of triplet excimers.
- △ An evaluation of the binding energies of triplet excimers in pure and molecularly doped polymers.
- △ Computer assisted resolution of complex phosphorescence spectra obtained from solid polymer films.
- △ Use of time resolved transient absorption spectroscopy to characterize long lived excited states in polymer systems and monomeric analogues.
- △ Use of photoselection and optical anisotropy to evaluate mechanisms for energy migration in polymeric systems.
- △ Kinetic and spectroscopic probes of triplet state and ionic pathways following excimer laser excitation of polymers and monomeric analogues.

B. Scientific or technical issues addressed and their significance.

△ The carbazole chromophore has been a favorite subject for our investigations since it displays such a rich array of photophysical activity. It occurred to us, however, that no comparable investigations have ever been carried out on the corresponding chromophore containing phosphorus as the heteroatom rather than nitrogen. One reason for this is that n-alkyl dibenzophospholes are air sensitive and therefore inconvenient for ordinary photophysical investigations. One compound, phenyl dibenzophosphole is not air sensitive and so we have undertaken a photophysical investigation of this compound. Due to the presence of the heavy phosphorus atom emission from the singlet state of this compound is rather weak and triplet state processes dominate. Furthermore, there is a strong tendency for

photoion production from this compound. We have evaluated the excimer forming tendencies of this compound by examining its luminescence properties in inert polymer matrices. The indications are that triplet excimer formation is not efficient in this compound so energy migration in molecularly doped polymers is potentially rapid in this case. In fact, the excited state complexes formed seem to be so weakly bound that naming them excimers is probably misleading. We prefer the term "excited state van der Waals complexes."

Δ The rate of decay of non-excimeric triplet state luminescence from pure or molecularly doped polymer films has an unusual temperature dependence. In every case examined we find that graphs of $\ln k$ versus $1/T$ are discontinuous. At sufficiently low temperatures the slope of these graphs approaches zero but there always exists some temperature, which we call the kink temperature, above which a dramatic increase in slope occurs. In every case, we have been able to link the onset of increased temperature dependence with the formation of triplet excimers. In fact, the slope of the Arrhenius graph above the kink temperature represents the activation energy for triplet excimer formation. When we monitor the excimeric phosphorescence a similar phenomenon is observed but in this case the slope of the Arrhenius graph represents the dissociation of the triplet excimer. If the activation energy for excimer formation represents energy required for bond formation then $E_{act,diss} - E_{act,form}$ represents the bond energy of the excimer. Arrhenius studies of this sort have been carried out for many nitrogen-containing chromophores during these investigations.

Δ In poor solvents it is well known that polymer molecules tend to exclude solvent from the chain units and coil up rather tightly. In good solvents the coils tend to relax forming a more expanded chain. We hypothesized that the rate of intrachain triplet energy migration will depend upon the coil volume and that this can be detected by measuring the rate constant for triplet-triplet annihilation for a polymer in solution. Experiments have been carried out to test this hypothesis. These experiments show that it may be possible to introduce photophysical methods into the study of hydrodynamics of polymer systems.

C. Experimental and theoretical approach taken, techniques used, and resources applied.

Our primary experimental approach involved the usual tools of photophysics including luminescence spectroscopy and kinetics as well as transient absorption spectroscopy and kinetics. Associated with these spectroscopic methods is an array of chemical operations designed to produce samples for testing which are well defined in terms of purity and identity of constituents.

The resources available for dealing with the chemistry of our samples include high field FT-NMR, GC-mass spectrometry, FT-IR and various chromatographic techniques. It should be mentioned that a new 500 MHz NMR spectrometer was recently installed here so that very high resolution NMR studies can now be done. The more conventional laboratory facilities include a vacuum system for degassing samples, an inert atmospheres isolation box for preparing film samples and the usual complement of distillation, sublimation and zone

refining equipment.

Two independent spectroscopic installations were set up in completely separate laboratories to carry out this work. They are distinguished primarily by the time resolution of the equipment available. In both labs sample excitation was accomplished by excimer lasers, although nitrogen laser excitation was often used. Luminescence was detected by SPEX model 1680/B monochromators and either a Hamamatsu R928 or an EMI 9789 photomultiplier. The signals from these photomultipliers were detected using a LeCroy model 9410 digital oscilloscope or a system composed of LeCroy components including a 2323A dual gate generator, and a 6810 waveform recorder. Both of these systems were interfaced with desk top computers for storage and analysis of data.

Most of our spectroscopic work was carried out using a Princeton Instruments diode array spectrometer. This system included a SPEX model 1681C spectrograph a Princeton Instruments IRY-700-S/B diode array, an ST-120 controller and FG-100 and PG-10 pulsers used for triggering, gating and delay setting. Realistic time resolution for this system was 50 ns although the detector can, in principle, resolve signals at 11 ns. To record luminescence spectra with this system one need only enter the gate width and delay desired as well as the number of accumulated scans, usually several hundred. The data were then transferred to the computer and stored. To record transient absorption spectra the experiment was more involved. Here one must create four separate data files. One (bak) is taken in the absence of either laser light or probe light. A second (io) is taken using the probe lamp only. The third (i) is taken using both the probe lamp and the laser (that is in the presence of transients). The fourth (d) is taken using the laser only (to compensate for the presence of emission). The absorbance for each data point was calculated using $A = \log[I_{io} - I_{bak}]/[I_i - I_d]$. We used a xenon arc lamp as the probe in these experiments.

D. Importance of solving the problems being addressed by the research

There are many examples both from pure and applied chemistry which serve as motivations for continued effort on the photophysical properties of polymeric systems. Examples include the photoablation of polymers by laser radiation to produce patterns for microcircuit fabrication and as a technique for the removal of arterial blockages. In addition those who are involved in the development of polymeric liquid crystals, semiconductors, electrochromic and photochromic devices, solar cells and photoconductors are requiring more detailed knowledge about fundamental photophysical processes. Interchromophore energy migration is a fundamental photophysical event and in most of these applications the transfer occurs between chromophores which have no translational freedom and very limited rotational freedom. Furthermore, it is usually true that interchromophore distances are not fixed but vary according to some, usually unknown, distribution function. The fate of triplet excitons generated in such an environment can include radiative or radiationless relaxation, triplet-triplet annihilation and trapping at an excimer forming site. It is also possible that delayed generation of triplets can occur as a result of ion recombination. We viewed our task as determining how and why controllable variables affect the outcome of these various decay channels for excited state species. The controllable variables are the chemical makeup of the chromophores, the mode of polymerization of the polymeric material, the procedures

used to produce solid state samples, and the temperature. The degree to which we succeeded in this activity is determined, in part, by our ability to tell a synthetic chemist which specific features should be incorporated in a given molecule to accomplish predetermined tasks.

6. Project Output

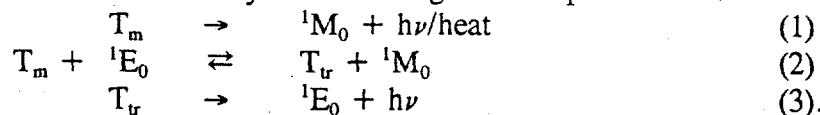
A. Major accomplishments with supporting data and their significance.

There are two areas which we would like to single out as major accomplishments of this project. Both of them involve experimental results which evoked reactions of surprise at their discovery and both proved to be extremely valuable as investigations continued. They also shared the common feature that, in retrospect, perhaps they should not have been so surprising. The first of these was the discovery that at sufficiently low temperatures, the phosphorescence from solid films of poly(N-vinylcarbazole) as well as other polymers changes from excimeric to non-excimeric. We find the same to be true of molecularly doped polymers. The second discovery was that fluid solutions of molecules containing the carbazolyl chromophore produce transient radical cations and anions upon photoexcitation which have lifetimes on the order of tens of microseconds. Furthermore, the recombination of these ions constitutes one mechanism for the production of excimeric luminescence. Details of both of these discoveries will now be described starting with the low temperature work.

Much of the work on low temperature spectra and kinetics of polymer systems is carried out at 77 K because of the obvious advantage of using liquid nitrogen as a coolant. Under these conditions poly(N-vinylcarbazole) (PVCA) and many other polymers produce a phosphorescence spectrum which is totally excimeric in character. Since a closed cycle liquid helium cryostat became available to us, the decision was made to investigate the phosphorescence spectrum of PVCA at lower temperatures. The result was that a structured non-excimeric phosphorescence spectrum of the carbazolyl chromophore is found at 15 K but, as the temperature is raised, the structured emission disappears and is replaced by a broad structureless band displaced to the red with a lambda-max near 500 nm. In this case the zero-zero band of the non-excimeric phosphorescence emission found near 420 nm essentially disappears between 36 and 42 K.

Additional relevant data is in the form of a graph of the log of the rate constant for phosphorescence decay plotted versus $1/T$. A discontinuity in this graph occurs near 36 K. Additionally, the intensity of delayed fluorescence versus $1/T$ exhibits a maximum near 42K. It is crucial to our arguments to observe that the peak of the delayed fluorescence curve, the discontinuity in the Arrhenius graph and the transition from non-excimeric to excimeric emission all occur at essentially the same temperature. We concluded that at sufficiently low temperatures monomeric triplets, symbolized here by T_m , disappear by first order radiative or radiationless deactivation and that the temperature dependence for this process is very small. As the temperature is raised, however, a competing process for removal of triplets becomes available and this is trapping of T_m at excimer forming sites, symbolized by 1E_0 . This process results in the formation of triplet excimers which we symbolize by T_{tr} . The relevant

processes may therefore be described by the following three step scheme-



We further conclude that the initial rise in the delayed fluorescence intensity at low temperature is due to the increased mobility of triplet excitons giving rise to triplet-triplet annihilations. The decrease in delayed fluorescence intensity at even higher temperatures is due to a depletion of these excitons as they become trapped at excimer forming sites. Since a single mechanistic sequence is able to explain all three of these observations in a consistent and rational fashion, we adopted it in all of our subsequent studies of the temperature dependence of photophysical processes in solid polymer films. It should be added that this same sequence works equally well for film samples consisting of small molecules doped into inert polymer matrices.

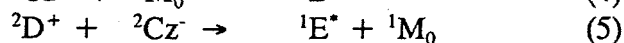
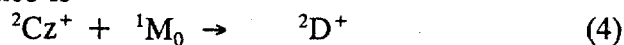
A useful corollary to this discovery is a related one involving the temperature dependence of the excimeric phosphorescence. When the logarithm of the rate constant for excimeric phosphorescence is plotted in Arrhenius fashion a discontinuous graph is obtained once again. In this case it seems clear that at sufficiently low temperatures triplet excimers are relaxing by first order processes but that excimer dissociation can compete with this relaxation as the temperature is raised. Thus, the activation energy for excimer dissociation may be obtained from the temperature dependence of the rate of triplet excimer decay and the activation energy for the formation of triplet excimers may be obtained from the temperature dependence of the rate of non-excimeric triplet decay. The difference between these two quantities provides an upper limit to the bond energy of the corresponding triplet excimer. As a result of this important finding we have been able to make these bond energy determinations for a number of triplet excimers related to polymers of photophysical interest.

The other discovery which we believe has important consequences involves the photoproduction of relatively long-lived radical cations and anions in fluid solutions containing PVCA and related monomeric compounds. This work was prompted by the suggestion that delayed fluorescence in solid films of PVCA is due, at least in part, to ion recombination. This was a surprising suggestion since most workers had thought that such emission was primarily the result of triplet-triplet annihilation. Measuring transient absorption spectra in solid polymer films is extremely difficult due to the necessarily very short optical pathlengths involved and so we decided to carry out a study of PVCA and its monomeric counterparts in fluid solutions at ambient temperature. Earlier work on the transient absorption of photoexcited carbazolyl compounds had been reported for the picosecond and nanosecond time domain using low dielectric solvents. We found that when high dielectric media were used such as ethanol or N,N-dimethylformamide (DMF) it was possible to detect not only triplet state species but also radical cations and anions having lifetimes on the order of tens of microseconds.

In ethanol, for example, an absorption band near 790 nm is indicative of the carbazolyl radical cation based upon earlier assignments by others. Similarly a short wavelength component found near 380 nm is indicative of the radical anion of this chromophore while a band at 420 nm is due to the triplet state. Note that the intensity ratio of the bands at 380 and 420 nm change with a change in delay time proving that two

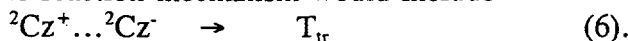
absorbing components are present.

A time resolved delayed emission spectrum of NEC in DMF at ambient temperature shows a distinct change in the nature of the emission spectrum with a change in delay time following the excitation pulse. The emission at a delay time of 1 μ s near 370 nm is due to delayed fluorescence but at longer delay times a second band near 450 nm becomes evident which is due to delayed excimer fluorescence. In a mixed solvent consisting of glycerol/ethanol (90/10) the band near 370 nm is still evident but the delayed excimer fluorescence band near 450 nm is missing. Instead a new emission is found near 500 nm which is typical of excimeric phosphorescence of the carbazoyl chromophore. Thus, in a high viscosity solvent excimeric delayed fluorescence is eliminated and replaced by excimeric phosphorescence. We concluded that the formation of excimeric delayed fluorescence somehow involves a diffusion controlled step. A reasonable candidate for this process is the reaction of a radical cation with a ground state molecule to form a cation dimer. Subsequently this cation dimer can recombine with an anion to form the singlet excimer and a ground state species. Using ${}^2\text{Cz}^+$ and ${}^2\text{Cz}^-$ to symbolize the cation and anion respectively the proposed reaction sequence is

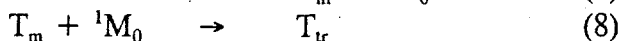
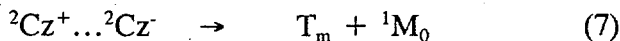


where ${}^2\text{D}^+$ is the cation dimer and ${}^1\text{E}^*$ is the singlet excimer.

The formation of the triplet excimer is apparently a process which does not include a diffusion controlled step since it occurs with some efficiency in a high viscosity medium. We propose that its formation involves ion recombination without going through the cation dimer intermediate. Thus, the reaction mechanism would include



Possibly this occurs in a stepwise fashion-



It is worth reviewing the reasons why formation of the singlet excimer seems to require the prior formation of a cation dimer whereas formation of the triplet excimer can proceed by a direct ion recombination. A back electron transfer can occur even between ions which are not nearest neighbors. When an excited singlet state is formed in such a process its lifetime is usually sufficiently small so that it relaxes to the ground state before any reaction with its ground state partner can occur. In the case of the triplet, the lifetime is usually many orders of magnitude larger so that the opportunity exists for a monomeric triplet to interact with its ground state partner before it relaxes to the ground state. We feel that the important lesson to be learned from these experiments is that a triplet excimer can be formed by direct reaction between a monomeric triplet and a ground state molecule as long as they are found in close proximity. This is why excimeric phosphorescence is a prominent emission from polymers such as PVCA. The ion recombination route which we have identified for triplet excimer formation provides just such a juxtaposition of the triplet and the ground state species.

B. Bibliography of publications emanating from this project.

32. Burkhart, R. D., "Studies on the Nature of Solute Distributions in Molecularly Doped Polystyrene. Triplet-Triplet Absorption of 1,2-Benzanthracene Excited by Nanosecond Laser Pulses," J. Phys. Chem., **1983**, 87, 1566-1577.
33. Burkhart, R. D. "Triplet Emissions from Poly(N-vinylcarbazole) Solid Films at Ambient Temperature Studied in the Microsecond Time Regime Using Pulsed Laser Excitation," Macromolecules, **1983**, 16, 820-824.
34. Abia, A. A. and Burkhart, R. D., "Triplet Excimer Emission from Carbazolyl Chromophores in Polystyrene Matrices," Macromolecules, **1984**, 17, 2739-2744.
35. Burkhart, R. D., Lee, O. Boileau, S. and Boivin, S., "Spectroscopic and Triplet Photophysical Properties of Poly[N-((vinylloxy)carbonyl)carbazole] and its Monomeric Analogue," Macromolecules, **18**, **1985**, 1277-1284.
36. Burkhart, R. D., Dawood, Ishmael, "Computer Assisted Resolution of Phosphorescence Spectra from Solid Films of Poly(N-vinyl carbazole)," Macromolecules, **19**, **1986**, 447-452.
37. Caldwell, N. J., Burkhart, R. D., "Triplet State Absorption and Decay Kinetics of Poly(N-vinylcarbazole) and N-Ethylcarbazole by a Laser Excitation Optical Probe Method, Macromolecules, **1986**, 19, 1653-1658.
38. Burkhart, R. D.; Caldwell, N. J., "The Influence of Chromophore Organization on Triplet Energy Migration in Amorphous Polymer Solids" Polymer Preprints, **1986**, 27, 350-351.
39. Burkhart, R. D.; Boileau, S.; Boivin, S., "A Laser Pulse-Probe Study of Triplet Exciton Processes in Poly[N-((vinylloxy)carbonyl)carbazole] and its Monomeric Analogue", J. Phys. Chem., **1987**, 91, 2189-2193.
40. Burkhart, R. D. "Models for Intramolecular Triplet Exciton Migration Applied to Vinyl Aromatic Polymers", Chem. Phys. Letters, **1987**, 133, 568-573.
41. Burkhart, R. D.; Burrows, J. A. J., "The Influence of Polymer Structure on Triplet Luminescence," Polymer Preprints, **1987**, 28, 66-67.
42. Burkhart, R. D. and Abia, A. A., "Triplet Exciton Migration and Trapping in Molecularly Doped Polystyrene," in Molecular Electronic Devices II, F. L. Carter, Ed., Marcel Dekker, New York (1987) pp. 523-536.
43. Burkhart, R. D.; Haggquist, G. W.; Webber, S. E., "Triplet Photophysical Properties of the Alternating Copolymer of 2-Vinylnaphthalene with Methyl Methacrylate,"

Macromolecules, 1987, 20, 3012-3016.

44. Burkhart, R. D.; Caldwell, N. J., "The Influence of Chromophore Organization on Triplet Energy Migration in Amorphous Polymer Solids," in Photophysics of Polymers, C. E. Hoyle and F. M. Torkelson, Eds., ACS Symposium Series 358, 1987, pp242-251.
45. Burkhart, R. D.; Siu, T. J. K. S. "Kinetic and Spectroscopic Probes to Evaluate the Dimensionality of Triplet Exciton Migration in Polymeric Systems," *Proc. SPIE-Int. Soc. Opt. Eng.*, 1988, 910, 183-185.
46. Park, Y. T.; Kim, Y. D.; Burkhart, R. D.; Caldwell, N. J. "Transient Absorption Spectra of Phenothiazine Derivative in the Vesicle System Containing R²⁺ Complex as a Sensitizer," *Bull. Korean Chem. Soc.* 1988, 9, 84-87.
47. Burkhart, R. D.; Caldwell, N. J.; Haggquist, G. W. "Polystyrene as an Inert Matrix for Photophysical Investigations," *J. Photochem. Photobiol., A, Chem.* 1988, 45, 369-378.
48. Haggquist, G. W.; Burkhart, R. D. "Optical Anisotropy of Phosphorescence from Photoselected Molecules in Polystyrene Matrices," *Chem. Phys. Lett.* 1988, 152, 56-60.
49. Siu, T. J. K. S.; Burkhart, R. D. "Coil Dimensions of Poly(2-vinylnaphthalene) in Solution and Their Influence on Triplet Photophysics," *Macromolecules*, 1989, 22, 336-340.
50. Starzyk, F. C.; Burkhart, R. D. "Triplet Emission from Poly(3,6-dibromo-N-vinylcarbazole): Spectra and Kinetics," *Macromolecules*, 1989, 22, 782-786
51. Chakraborty D. K.; Burkhart, R. D. "Delayed Fluorescence and Delayed Excimer Fluorescence from Fluid Solutions of Poly(2-vinylnaphthalene) in the Nanosecond Time Regime," *Chem Phys. Lett.* 1989, 157, 189-193.
52. Chakraborty D. K.; Burkhart, R. D. "Triplet Photophysical Properties of Poly(2-vinylnaphthalene) and Poly(N-vinylcarbazole) Solid Films in a Low Temperature Regime," *J. Phys. Chem.* 1989, 93, 4797-4802.
53. Burkhart, R. D.; Burrows, A. J.; Haggquist, G. W. "Triplet Photophysics of Polystyrene With and Without Selected Terminating Substituents", *Proc. SPIE-Int. Soc. Opt. Eng.*, 1989, 1054, 130-135.
54. Burkhart, R. D., "Photophysical Studies of Triplet Exciton Processes in Solid Polymers," in *Application of Lasers in Polymer Science and Technology*, J. F.

Fouassier and J. F. Rabek, Eds., CRC Press, Inc.: Boca Raton, FL, 1990; pp 147-160.

55. Burkhart, R. D., "Triplet State Spectroscopy of Polymers," in *Optical Techniques to Characterize Polymers*, H. Bassler, Ed. Elsevier Science Publishers: Amsterdam, 1990; pp 227-275.
56. Chakraborty, D. K.; Burkhart, R. D. "Triplet Photophysical Properties of Poly(N-vinylcarbazole) in Fluid Solutions and in Solid Films in the Submicrosecond Time Regime", *Macromolecules*, **1990**, *23*, 121-126.
57. Burrows, J. A. J.; Haggquist, G. W.; Burkhart, R. D. "End Injection of Triplet Electronic Energy into a Polymer Molecule Using Chromophores Bound at Chain Ends"; *Macromolecules*, **1990**, *23*, 988-997.
58. Chakraborty, D. K.; Burkhart, R. D. "Binding Energies of Triplet Excimers in Poly(N-vinylcarbazole) Solid Films Using Laser Based Kinetic Spectroscopy Between 15 K and 55 K", *J. Phys. Chem.*, **1990**, *94*, 4143-4147.
59. Burkhart, R. D.; Chakraborty, D. K.; Shirota, Y. "Triplet Photophysical Properties of Poly[4-(N,N-diphenylamino)phenylmethacrylate]" *Macromolecules*, **1991**, *24*, 1511-1518.
60. Burkhart, R. D.; Jhon, N. I. "Triplet State Spectroscopy of Pure and Molecularly Doped Polymer Films," *Polym. Mater. Sci. Eng.* **1991**, *64*, 244-245.
61. Burkhart, R. D.; Jhon N. I. "Triplet Excimer Formation of Triphenylamine and Related Chromophores in Polystyrene Films," *J. Phys. Chem.* **1991**, *95*, 7189-7196.
62. Haggquist, G. W.; Burkhart, R. D.; Naqvi, K. R. "Kinetic and Spectroscopic Study of Triplet State and Ionic Pathways in the Laser-Induced Photoexcitation of N-Ethylcarbazole in Fluid Solution," *J. Phys. Chem.* **1991**, *95*, 7588-7594.
63. Burkhart, R. D.; Jhon, N. I.; Boileau, S. "An Investigation of Binding Energies of Triplet Excimers in Carbazolyl-Containing Polymers," *Macromolecules* **1991**, *24*, 9310-6317.
64. Haggquist, G. W.; Burkhart, R. D. "The Influence of Laser Induced Photoion Production in Polymer Photophysics," *Polymer Preprints* **1992**, *33*, 841.
65. Naqvi, K. R.; Haggquist, G. W.; Burkhart, R. D.; Sharma, D. K. "Evaluation of a Squirrel-Cage Photomultiplier Base for Time-Resolved

- Spectroscopy with Low-Repetition Pulses," *Rev. Sci. Instrum.* **1992**, *63*, 5806-5807.
66. Haggquist, G. W.; Burkhart, R. D. "Photophysics of N-Ethylcarbazole in Fluid Solution. Evidence for Solvent Dependence and Triplet Excimer Formation," *J. Phys. Chem.* **1993**, *97*, 2576.
 67. Burkhart, R. D.; Jhon, N. I. "Triplet Excimer-Monomer Equilibria as Structural Probes in Pure and Molecularly Doped Polymers." in *Structure-Property Relations in Polymers*, M. W. Urban and C. D. Craver Eds., Advances in Chemistry Series No. 236, **1993**, pp 599-609.
 68. Ganguly, T.; Burkhart, R. D.; Nelson, J. H. "An Investigation of Triplet States, Radical Ions, and Triplet Excimers Produced by Laser Photoexcitation of Phenylidibenzophosphole in Fluid Solutions and Rigid Matrices," *J. Phys. Chem.* **1994**, *98*, 5670-5678.
 69. Ganguly, T.; Burkhart, R. D. Computer-Assisted Resolution of Transient Absorption Bands in Phenylidibenzophosphole in Fluid Solution. Further Evidence for Triplet Excimers," *Chem. Phys. Lett.* **1994**, *226* 552-558.
 70. Ito, S.; Yamamoto, M.; Liebe, W. R.; Burkhart, R. D.; Wada, Y. "Triplet Excimer Formation of Dibromocarbazole Chromophores in Methacrylate Copolymer Films Measured by Time-resolved Phosphorescence and Transient Absorption Spectroscopy," *J. Phys. Chem.* **1994**, *98* 7608-7612.
 71. Haggquist, G. W.; Burkhart, R. D. "Triplet Photophysics of Multi-chromophoric Molecules. A Study of Poly(N-vinylcarbazole) and meso-2,4-dicarbazolylpentane in Fluid Solutions," *Macromolecules*, **1995**, *28*, 2465-2471.
 72. Tsuchida, A.; Yamamoto, M.; Liebe, W. R.; Burkhart, R. D.; Tsubakiyama, K. "Triplet Energy Migration in Poly(4-methacryloyl benzophenone-co-methyl methacrylate) Films: Temperature Dependence and Chromophore Concentration Dependence," *Macromolecules*, **1996**, *29*, 1589-1594.
 73. Ganguly, T.; Burkhart, R. D. "Some Photophysical Properties of Electronically Excited Phenylidibenzophosphole in Rigid Polymer Matrices," *J. Phys. Chem.* **1997**, *101*, 5633-5639.