

Energy Transfer Processes in Solar Energy Conversion
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This program involves the experimental and theoretical study of optically induced electron transfer and electronic excitation transport in systems with complex structures. The focus is to obtain an understanding of the intimate interplay among intermolecular interactions, structure, and dynamics. A combination of picosecond transient grating experiments, time resolved fluorescence depolarization experiments, conventional optical spectroscopy, and statistical mechanical theory is being employed to elucidated fundamental aspects of processes which are important in the conversion of solar energy to usable forms of energy.

We are continuing to address the very important problem of electron back transfer following optically induced donor to acceptor electron transfer. In a system in which there are donors (low concentration) and acceptors (high concentration) randomly distributed in solution, optical excitation of a donor can be followed by transfer of an electron to an acceptor. Once electron transfer has occurred, there exists a ground state radical cation (D^+) near a ground state radical anion (A^-). Since the thermodynamically stable state is neutral ground state D and A, back transfer will occur. The electron will back transfer from A^- to D^+ to regenerate the neutral species. In liquid solution, back transfer competes with separation by diffusion. Separated ions are extremely reactive and can go on to do useful chemistry.

The purpose of the experimental and theoretical work we are pursuing in this area is to understand the dynamics of the combined forward and back transfer processes. While the forward transfer process is relatively straight forward to study using time resolved fluorescence quenching, the back transfer process requires the application of a method which is sensitive to the ground state ion concentrations. We have previously shown that picosecond transient grating experiments can

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probe the electron back transfer process. Recently we have conducted the first comprehensive study by using tunable picosecond dye lasers to probe the back transfer dynamics. It is very important to use a tunable source to test the results for complications which can arise if the ions have optical absorptions at the experimental wavelengths. By combining measurements at several wavelengths on a variety of samples with different acceptor concentrations, we can obtain a complete description of the dynamics of the combined forward and back transfer processes.

Previously we have developed a theoretical description of this problem which involves a infinite series of terms. This series, when calculated to convergence, is an exact solution to the model problem. One of the assumptions of the model is that excluded volume can be ignored, i. e. the molecules can be considered point particles. We have now proven theoretically that for all accessible concentrations, this is a valid assumption. While the theory we have is exact, it requires a great deal of computer computation to actually calculate the experimental results. We have recently developed an approximate solution to this problem. The approximation is being tested against our exact series solution. The preliminary results indicate that it is extremely accurate. It is a type of mean field approximation which tremendously reduces the theoretical complexity. This will greatly facilitate comparison to experiment.

The new theoretical approach may prove important for another reason. In the experimental and theoretical work, we have considered solid solutions (glasses). Thus there is no molecular spatial diffusion. The new theoretical approach seems mathematically tractable enough to permit the inclusion of diffusion into the problem. This will allow the very important competition between spatial separation of the ions and electron back transfer to be understood in detail.

We have also been conducting experiments and theoretical studies on electronic energy transport in systems with complex structures. Recently we have devoted considerable effort to the nature of energy transport among chromophores attached to polymers. The structure for flexible polymer chains (freely jointed chains) results in a highly nonrandom distribution of chromophores. The positions of the chromophores are correlated. For an isolated chain in solid or liquid

solution, the result is a clustered energy transport system in which transport can be extremely efficient. In polymer blend systems (solid solutions of one type of polymer in another polymer) microphase separation can occur. In a microphase separated system, there are microscopic domains of one type of polymer chain in the host material, the other type of polymer. If the phase separated chains contain chromophores, extremely fast excitation transport can occur in a system which over all does not have a high average chromophore concentration.

To understand the relationship between polymer structure and energy transport, we have developed the first detailed theoretical description of transport between chromophores end tagged on short polymer chains. The normal models of polymer structure, which assumes Gaussian statistics, can not be applied to very short chains. Gaussian statistics arise from the statistics of infinite random walks, i. e. infinite (very long) polymer chains. However, for short chains it was necessary to develop detailed models of the end-to-end distribution of distances. More than that, to realistically calculate the energy transfer, it was necessary to include in the model the chromophore and the nature of the chemical linkage which attaches it to the polymer. The results are very interesting and will serve as a guide to future experiments and the design of transport systems.

In our previous work on polymer chains tagged with chromophores, we examined miscible blends, i. e. no phase separation. We are now obtaining the first results on non-miscible blends. In these systems phase separation occurs at very low concentrations of the tagged chains in the host polymer. Using the very sensitive time resolved fluorescence depolarization methods that we have developed, we are studying the nature of energy transport for very low concentrations of tagged coils (isolated chains) and for higher concentrations in which phase separation occurs. The onset of microphase separation results in a very dramatic increase in the rate of energy transport. Different concentrations of tagged chains and different methods of preparation of the samples can result in producing a wide variety of microdomain structures. These different structures are different clustered energy transport systems. Control of the phase separation can provide tailored clustered energy transport systems.

Publications Supported by the Department of Energy

1. "The Influence of Orientational Fluctuations on Electron Transfer in Systems of Donor-Acceptor Pairs," R. P. Domingue and M. D. Fayer, *J. Phys. Chem.* 90, 5141 (1986).
2. *"Picosecond Transient Grating Experiments on Hydrogenated Amorphous Silicon: Models for Surface Quenching," Vincent J. Newell and M. D. Fayer, *The Second International Conference on Unconventional Photoactive Solids* (Plenum Publishing, New York, 1987).
3. "Quantitative Determination of the Radius of Gyration of Poly(Methyl Methacrylate) in the Amorphous Solid State by Time-Resolved Fluorescence Depolarization Measurements of Excitation Transport," K. A. Peterson, M. B. Zimmt, S. Linse, R. P. Domingue, and M. D. Fayer, *Macromolecules* 20, 168 (1987).
4. "Determination of the Ensemble Average Conformation of Isolated Polymer Coils in Solid Blends Using Electronic Excitation Transport: Theory and Experiment," K. A. Peterson, M. B. Zimmt, S. Linse, and M. D. Fayer, *Photophysics of Polymers*, ACS Symposium Series 358, Eds: C. E. Hoyle and J. M. Torkelson, (1987).
5. "Short Chain Polymer Statistics and the Relationship to End to End Electronic Excitation Transport: Random Walks with Variable Step Lengths," M. B. Zimmt, K. A. Peterson, and M. D. Fayer, *Macromolecules*, accepted (1987).
6. "Electronic Excitation Transport in Restricted Geometries," Kristen A. Peterson, Alan Stein, and M. D. Fayer in *Molecular Dynamics in Restricted Geometries*, Eds. J. Klafter and J. M. Drake (John Wiley & Sons, New York), 1987.
7. "Fluorescence Depolarization of Chromophores in Polymeric Solids," K. A. Peterson, M. B. Zimmt, M. D. Fayer, Y. H. Jeng, and C. W. Frank, submitted, *Macromolecules* (1987).
8. "Theoretical Description of Electron Transfer and Back Transfer for Donors and Acceptors Randomly Distributed in Solid Solution", R. Dorfman, Y. Lin, R. P. Domingue, and M. D. Fayer, *J. Chem. Phys.*, in preparation (1987).
9. "Optically Induced Electron Transfer and Back Transfer Among Donors and Acceptors in Solid Solution: Picosecond Transient Grating Experiments", R. Dorfman, M. B. Zimmt, J. Bauman, R. P. Domingue and M. D. Fayer, *Chem. Phys. Lett.*, in preparation (1987).
10. "Electron Transfer and Back Transfer Among Donors and Acceptors in Solid Solution: A Detailed Comparison of Theory and Experiment", R. Dorfman, Y. Lin, M. B. Zimmt, and M. D. Fayer, *J. Chem. Phys.*, in preparation (1987).

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