Grenoble, is also gratefully acknowledged. The assistance of the technical establishments at AERE and ILL during the course of this work was invaluable.

Registry No. Polystyrene, 9003-53-6; neutron, 12586-31-1.

References and Notes

(1) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(2) Edwards, S. F. *Proc. Phys. Soc., London* **1966**, *88*, 265.
(3) Muthukumar, M.; Edwards, S. F. *J. Chem. Phys.* **1982**, *76*, 2720.
(4) Daoud, M.; Jannink, G. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 973.
(5) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(6) de Gennes, P.-G. *Isr. J. Chem.* **1975**, *14*, 154.
(7) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587.
(8) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 594.
(9) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(10) Brochard, F. *J. Phys. (Les Ulis, Fr.)* **1983**, *44*, 39.
(11) Schaefer, D. W.; Joanny, J. F.; Pincus, P. *Macromolecules* **1980**, *13*, 1280.
(12) Schaefer, D. W. *Polymer* **1984**, *25*, 387.
(13) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley: New York, 1969.
(14) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(15) Whittington, S. G. *Adv. Chem. Phys.* **1982**, *51*, 1.
(16) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(17) de Gennes, P.-G. *Phys. Lett. A* **1972**, *38A*, 339.
(18) des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, 281.
(19) Wilson, K.; Kogut, J. *Phys. Rep.* **1974**, *12C*, 77.
(20) Farnoux, B.; Boue, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P.-G. *J. Phys. (Les Ulis, Fr.)* **1978**, *39*, 77.
(21) Chu, B. In "Scattering Techniques Applied to Supramolecular and Non-equilibrium Systems" Chen, S.-H., Chu, B., Nossal, R., Eds.; Plenum: New York, 1981.
(22) Debye, P. *J. Phys. Colloid Chem.* **1947**, *57*, 18.
(23) Edwards, S. F. *Proc. Phys. Soc., London* **1965**, *85*, 613.
(24) Edwards, S. F. *J. Phys. A: Math. Gen.* **1975**, *8*, 1670.
(25) Edwards, S. F.; Jeffers, E. F. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1020.
(26) Edwards, S. F.; Singh, P. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1001.
(27) Cotton, J. P.; Farnoux, B.; Jannink, G. *J. Chem. Phys.* **1972**, *57*, 290.
(28) Cotton, J. P.; Farnoux, B.; Jannink, G.; Ober, R. *J. Appl. Crystallogr.* **1974**, *7*, 189.
(29) Richards, R. W.; Maconnachie, A.; Allen, G. *Polymer* **1981**, *22*, 189.
(30) Cotton, J. P.; Nierlich, M.; Boue, F.; Daoud, M.; Farnoux, B.; Jannink, G.; Duplessix, R.; Picot, C. *J. Chem. Phys.* **1976**, *65*, 1101.
(31) Okono, K.; Wada, E.; Kunita, K.; Himatsu, H.; Fukuro, H. *J. Phys., Lett.* **1979**, *40*, L171.
(32) Schaefer, D. W.; Lin, J. S. *Macromolecules* **1983**, *16*, 1017.
(33) Okono, K.; Wada, E.; Kunita, K.; Fukuro, H. *J. Appl. Crystallogr.* **1978**, *11*, 134.
(34) Geissler, E.; Hecht, A. M.; Dupplessix, R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 225.
(35) Candau, S.; Bastide, J.; Delsanti, M. *Adv. Polym. Sci.* **1982**, *44*, 30.
(36) Nystrom, B.; Roots, J. *J. Macromol. Sci., Rev. Macromol. Chem.* **1980**, *C19*, 35.
(37) Nystrom, B.; Roots, J. *Prog. Polym. Sci.* **1982**, *8*, 333.
(38) Vaughan, J. M. In "Static and Dynamic Properties of the Polymeric Solid State"; Pethrick, R. A., Richards, R. W., Eds.; Reidel: Dordrecht, 1982.
(39) Nossal, R. In "Scattering Techniques Applied to Supramolecular and Non-equilibrium Systems"; Chen, S.-H., Chu, B., Nossal, R., Eds.; Plenum: New York, 1981.
(40) Parkinson, W. W.; Keyser, In "The Radiation Chemistry of Macromolecules"; Dole, M., Ed.; Academic Press: New York, 1973; Vol II.
(41) Weiss, P.; Herz, J.; Hild, G.; Rempp, P. *Makromol. Chem.* **1970**, *135*, 249.
(42) Davidson, N. S. Ph. D. Thesis, University of Strathclyde, Glasgow, UK, 1984.
(43) Kostorz, G. In *Treatise Mater. Sci. Technol.* **1979**, *15*.
(44) Farnoux, B.; Jannink, G. In "Scattering Techniques Applied to Supramolecular and Non-equilibrium Systems"; Chen, S.-H., Chu, B., Nossal, R., Eds.; Plenum: New York, 1981.
(45) Kuhn, W. *Kolloid Z.* **1939**, *87*, 3.
(46) Davidson, N. S.; Geissler, E.; Richards, R. W., submitted to *Polymer*.
(47) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(48) Patterson, G. D.; Jarry, J. P.; Lindsey, C. P. *Macromolecules* **1980**, *13*, 668.
(49) Daoud, M.; Jannink, G. *J. Phys., Lett.* **1980**, *41*, 217.
(50) King, J. S.; Boyer, W.; Wignall, G. D.; Ullman, R. *Macromolecules* **1985**, *18*, 709.
(51) Muthukumar, M.; Edwards, S. F. *Polymer* **1982**, *23*, 345.

Intermolecular Correlation Functions from Förster Energy-Transfer Experiments

Glenn H. Fredrickson

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received April 26, 1985*

ABSTRACT: Fluorescence experiments that probe the transfer of electronic excitations between donor and trap chromophores are investigated as a means of studying intermolecular correlations in macromolecules. Expression for the observables in such experiments are derived, and specific applications are discussed. The theory may allow fluorescence experiments to be used to study the correlation hole in polymer melts and in bulk samples, spatial correlations in the dilute–semidilute regime of solutions, the structure of block copolymers, segment distributions away from surfaces or interfaces, and the time evolution of density fluctuations in spinodally decomposing mixtures. A variety of other applications are possible.

I. Introduction

Illumination of a chromophore or dye molecule with a source of radiation can lead to the absorption of photons and the creation of a singlet electronic excited state. When an ensemble of such chromophores in a condensed medium at room temperature is illuminated, the resulting excited states or *excitations* are effectively localized on the individual chromophores. These excitations can decay through the familiar process of fluorescence but can also be transferred nonradiatively to nearby unexcited chromophores. This latter process is referred to as electronic excitation transport (EET).[1] An expression for the rate at which an excitation is transferred from an excited chromophore (the donor) to an unexcited chromophore (the acceptor) a distance r away was first derived by Förster.[2] If the energy of the excited acceptor molecules

0024-9297/86/2219-0441$01.50/0

is significantly lower than that of the excited donors, then EET is an irreversible process and the acceptors are referred to as traps. In this case the expression derived by Förster for the rate of donor to trap transfer is

$$w(r) = (1/\tau)[R_0^{\mathrm{DT}}/r]^6 \tag{1.1}$$

where τ is the observed lifetime of the donor excitation and R_0^{DT} is the Förster radius of the donor–trap chromophore pair. The Förster radius has been measured for a number of chromophore pairs in solution[3] and can be obtained in a variety of ways through spectroscopic measurements.[1,3,4] Typical values of R_0^{DT} vary between 10 and 50 Å.

Because the rate of EET depends strongly on the distance of separation between donors and acceptors and EET is a process that competes with donor fluorescence, the donor fluorescence intensity (or the trap fluorescence intensity in the case of fluorescent traps) will be very sensitive to trap concentration. For this reason EET can be used as a local probe of the structure of polymers that contain fluorescent labels. In a number of experimental and theoretical studies, we[5-7] and several other workers[8-12] demonstrated how fluorescence experiments could be used to probe intramolecular correlations and the size of macromolecules. By attaching chromophore labels at multiple sites on a polymer chain, it is possible to probe the characteristic ratio of linear chains,[5] the mean squared end-to-end distance or radius of gyration of macromolecules,[6,8-12] and intramolecular segment correlation functions.[7] Ediger, Domingue, and Fayer[13] also demonstrated how EET between labels on different chains could be used to study the size of micelles. At a more qualitative level, fluorescence experiments have been used to study polymer blend compatibility.[33]

Except for the last two experimental studies, the works discussed above were primarily concerned with the elucidation of *intramolecular* polymer structure. In the present paper, we demonstrate how simple trapping experiments can be used to study *intermolecular* correlation functions. Such experiments are often easier to perform than fluorescence depolarization studies and offer information similar to that obtained through X-ray or neutron scattering experiments. The trapping experiments, in contrast to conventional scattering experiments, can be performed in the laboratory by using relatively inexpensive optical equipment. As with scattering techniques, the primary concern when using EET as a structural probe is whether the introduction of labels significantly perturbs the polymeric system under study. We assume in the following that donor and trap chromophores can be selected for a given system, such that their introduction at sufficiently low concentration will not measurably influence the structure of the material. The energy-transfer technique also requires an optically transparent host material, so our analysis will be restricted to such systems.

A variety of applications exist for the experiment and theory proposed in this paper. The correlation hole in linear, branched, or star polymers can be studied, as well as various correlations in block copolymers, such as joint–joint correlation functions. The technique could also be used to analyze the distribution of segment density away from a surface or interface and possibly to study the time evolution of density fluctuations in a phase-separating system. A detailed study of the dilute–semidilute regime in polymer solutions may also be possible. In the next section we discuss the trap fluorescence experiment in detail and present the connection between the fluorescence observable and a many-body transport problem. A simple, yet accurate, approximate solution to the many-body problem that relates the fluorescence observable to the pair correlation function of the chromophore labels in the material is given. Section III contains a discussion of how the fluorescence technique can be used to extract structural information of the type discussed above. A detailed treatment of the correlation hole is presented as an example of the use of the theory to interpret fluorescence experiments. Finally, in section IV we discuss some of the practical aspects of choosing an appropriate donor–trap chromophore pair for a given application and summarize our results.

II. Trapping Experiment and Connection with the Many-Body Problem

In a trapping experiment, one can obtain information about the distribution of distances between donor and trap labels by monitoring the rate of EET through fluorescence measurements. The initial step in the experiment is to label the polymer of interest with donor and trap chromophores. Since we are primarily interested in intermolecular correlations, it is most convenient if each labeled polymer molecule contains only a single chromophore. The placement of the labels on the polymer may be dictated by convenience in the synthetic procedure and by the particular correlation function to be probed. After preparation, the labeled molecules are dispersed in the medium of interest, which may be a solvent or a bulk sample of the unlabeled material.

For the experiments proposed here, the donor concentration should be very small so that energy transfer between donor chromophores can be neglected in comparison with that between donors and traps. It is convenient to define two dimensionless concentrations of donor and trap labels[14]

$$C_{\mathrm{D}} = (4/3)\pi(R_0^{\mathrm{DD}})^3\rho_{\mathrm{D}} \tag{2.1}$$

$$C_{\mathrm{T}} = (4/3)\ \pi(R_0^{\mathrm{DT}})^3\rho_{\mathrm{T}} \tag{2.2}$$

In these equations, ρ_{D} and ρ_{T} are the respective number densities of donor and trap labels in the host material and R_0^{DD} is the Förster radius for donor–donor EET. An approximate criterion for the neglect of donor–donor energy migration is to require[5,14]

$$C_{\mathrm{D}} \ll C_{\mathrm{T}} \tag{2.3}$$

Thus, the labeled samples should be prepared such that chains containing donors are scarce and eq 2.3 is satisfied.

The fluorescence experiment is performed by exciting the labeled sample with a pulse of radiation at a wavelength where donor absorption is significant but trap absorption is negligible. Thus, at time 0+ only donor chromophores are excited. At later times the donor excitations decay through fluorescence or through energy transfer to trap chromophores. As a result, the donor fluorescence intensity decays with time, and measurements of its decay provide information about the distribution of molecules that contain traps relative to molecules labeled with donors.

Consider a system of volume V that contains N polymer molecules, each labeled with a trap and a single molecule labeled with a donor. (Only a single donor need be considered because we assume donor–donor transport can be neglected.) Because the various decay processes are independent, $H(t)$, the probability that the donor is excited at time $t > 0$, given that it was excited at $t = 0$, can be written

$$H(t) = e^{-t/\tau}\int \mathrm{d}\mathbf{R}\ P(\mathbf{R})\prod_{i=1}^{N} \exp[-w(r_i)t] \tag{2.4}$$

where **R** represents the set of positions of the traps relative to the donor, $(r_1, r_2, ..., r_N)$, and $P(\mathbf{R})$ is the normalized probability distribution function for these positions. The rate of EET from the donor to the ith trap, $w(r_i)$, is assumed to obey the Förster expression, eq 1.1. *The experimental donor fluorescence intensity is directly proportional to $H(t)$.*

The difficulty in applying eq 2.4 to fluoresence measurements is that the experimental situation corresponds to the thermodynamic limit ($N \rightarrow \infty$, $V \rightarrow \infty$, $\rho_T = N/V$ constant). Hence, we cannot perform the integration for most choices of $P(\mathbf{R})$. However, it is tractable for the special case of uncorrelated trap positions, $P(\mathbf{R}) = 1/V^N$. For this case the integrand factors into a product of terms, one for each trap molecule, and the integrals can be easily performed. The result is[15]

$$G_0(t) \equiv e^{t/\tau}H(t) = \exp\left(-\left[\pi C_T{}^2 \frac{t}{\tau}\right]^{1/2}\right) \tag{2.5}$$

For the more general situation where there are correlations among the positions of the donors and traps, the integrand does not factor and we are faced with solving a many-body problem to evaluate the integral. Such problems are difficult and in most instances cannot be solved exactly, but the reward of obtaining an accurate approximate solution is that fluorescence experiments can be used to probe intermolecular correlations. Indeed, the extent to which the fluorescence intensity deviates from eq 2.5 is a measure of such correlations.

In the Appendix we discuss various techniques for obtaining an approximation to $G_0(t)$ in the presence of correlations among chromophore positions. The accuracy of low-order approximations based on these techniques is analyzed, and the results are used to identify a simple, yet accurate, expression for $G_0(t)$ that depends only on the pair correlation function of chromophore labels. In a homogeneous, isotropic medium, the general expression for this approximation is

$$G_0(t) = \exp\left\{-\rho_T \int \mathrm{d}\mathbf{r}\ g(r)(1 - \exp[-w(r)t])\right\} \tag{2.6}$$

where $w(r)$ is given by eq 1.1 and $\rho_T g(\mathbf{r})$ represents the density of trap labels at position $\mathbf{r}$ relative to the donor position. For the special case of chains labeled at one end, $g(\mathbf{r}) = g(r)$ is the *radial distribution function* of chain ends.[26]

It is convenient to introduce the *pair correlation function*,[27] $h(\mathbf{r})$, defined by

$$\rho_T g(\mathbf{r}) = \rho_T[1 + h(\mathbf{r})] + V^{-1} = \rho + \rho_T h(\mathbf{r}) \tag{2.7}$$

where $\rho = V^{-1} + \rho_T$ is the total number density of chromophores and hence chains. The pair correlation function satisfies the normalization condition

$$\rho_T \int \mathrm{d}\mathbf{r}\ h(\mathbf{r}) = -1 \tag{2.8}$$

When eq 2.7 is substituted into eq 2.6, we obtain the following result for the normalized donor fluorescence intensity:

$$H(t) = e^{-t/\tau}G_0(t) = \exp\left\{-\frac{t}{\tau} - \left[\frac{\pi C^2 t}{\tau}\right]^{1/2} - \rho_T \int \mathrm{d}\mathbf{r}\ h(\mathbf{r})(1 - \exp[-w(r)t])\right\} \tag{2.9}$$

with

$$C = (4/3)\pi(R_0{}^{\mathrm{DT}})^3 \rho \tag{2.10}$$

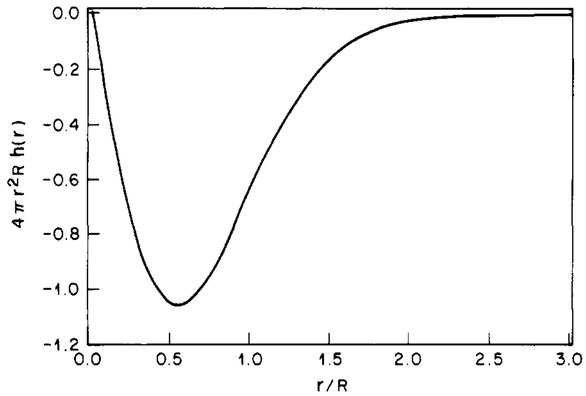

Figure 1. Pair correlation function in the random-phase approximation for a melt of end-labeled chains.

Because τ and C are known optical and material properties, donor fluorescence intensity measurements provide time-dependent estimates of $Q(t)$, where

$$Q(t) = -\rho_T \int \mathrm{d}\mathbf{r}\ h(\mathbf{r})(1 - \exp[-w(r)t]) \tag{2.11}$$

Equation 2.11 can be written as a Laplace transform, with $h(\mathbf{r})$ obtained by inverting the transform.[10] This is a difficult procedure, however, unless the fluorescence data is free of scatter. A better way to study intermolecular correlations is to assume a functional form for $h(\mathbf{r})$, integrate eq 2.11, and compare with $Q(t)$ from experiment. In the next section we discuss this approach for the study of the correlation hole[26,28] in melts and bulk polymers. Other applications of eq 2.9–2.11 are discussed.

III. Application to the Study of Intermolecular Correlations

A. Analysis of the Correlation Hole. The correlation hole in polymer melts or in the bulk can be studied by X-ray or neutron scattering.[26,28] However, it can also be studied in the laboratory by performing a fluorescence experiment of the type discussed in section II. For this purpose we consider a collection of polymer molecules, each labeled at one end with a donor or a trap. A small concentration of chains that contain a donor are mixed with trap-labeled chains. The composition of the mixture should be chosen such that the dimensionless concentrations of labels satisfy $C_D \ll C_T$. Fluorescence experiments can then be performed to extract $h(\mathbf{r})$ and elucidate the nature of the correlation hole.

In order to apply eq 2.9, it is necessary that τ and $R_0{}^{\mathrm{DT}}$ be determined. The lifetime of the donor excitation can be measured through transient fluorescence experiments on a sample that contains a low concentration of donor-labeled chains mixed into a host material of chains without labels.[12] The Förster radius, $R_0{}^{\mathrm{DT}}$, can be obtained from absorption and emission spectra of unlabeled material in which a small concentration of donor- or trap-labeled chains have been placed.[1-4]

de Gennes[28] has developed a random-phase approximation (RPA) for the Fourier transform of $h(\mathbf{r})$ that is appropriate for a melt of Gaussian chains labeled at one end. The expression can be written

$$\rho_T h(\mathbf{q}) = \rho_T \int \mathrm{d}\mathbf{r}\ e^{i\mathbf{q}\cdot\mathbf{r}} h(\mathbf{r}) = \frac{[1 - e^{-x}]^2}{2[1 - x - e^{-x}]} \tag{3.1}$$

where $x = q^2R^2/6$ and R^2 is the mean squared end-to-end distance of a molecule. Equation 3.1 can be numerically inverted to obtain $h(\mathbf{r}) = h(r)$. In Figure 1 we have plotted $4\pi r^2 Rh(r)$ vs. r/R. The "correlation hole", which has an area of -1, is seen to extend out to $r \approx 2R$.

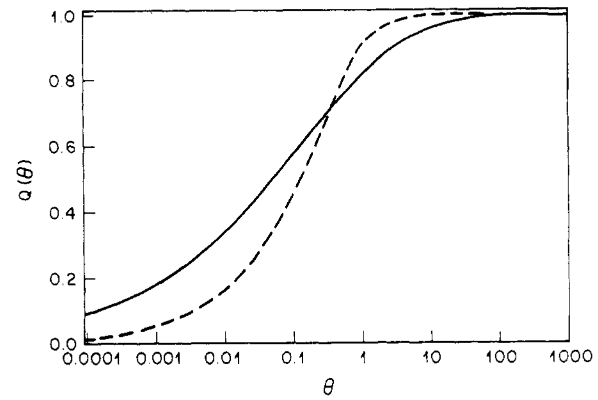

Figure 2. Q vs. $\theta = (R_0^{\mathrm{DT}}/R)^6 t/\tau$ for the RPA correlation hole and the "hard sphere" hole: solid curve, RPA result for end-labeled chains; dashed curve, eq 3.4 for the "hard sphere" hole.

The above numerical results for $h(r)$ can be used to calculate $Q(t)$ from eq 2.11. We find that Q can be expressed as a universal function of the dimensionless variable $\theta = (R_0^{\mathrm{DT}}/R)^6 t/\tau$. $Q(\theta)$ is plotted as the solid curve in Figure 2. Note that the donor fluorescence intensity is given by

$$H(t) = \exp\left\{-t/\tau - \left[\frac{\pi C^2 t}{\tau}\right]^{1/2} + Q(\theta)\right\} \tag{3.2}$$

Experimentally, one can only measure $H(t)$ accurate for at most two decades in time about $t = \tau$. It is also important to note that C can be interpreted as the average number of chromophores (and hence chains) in a sphere of radius R_0^{DT}. Since R is usually the same order of magnitude as R_0^{DT}, it is apparent from Figure 2 that all three terms on the right-hand side of eq 3.2 could contribute for the times of interest. As a result, there should be no difficulty designing an experiment that will allow $Q(\theta)$ to be resolved from donor fluorescence decays.

The utility of Figure 2 should be emphasized. If τ and R_0^{DT} have been previously determined, a measurement of $H(t)$ *at a single time* is sufficient to obtain an estimate of R from the figure. Thus, in addition to facilitating the study of intermolecular correlations, trapping experiments can be used to measure the end-to-end distance of chains in the bulk.

To test the sensitivity of the fluorescence experiment to the shape of the correlation hole, we have calculated $Q(\theta)$ for a "hard sphere" hole of radius R

$$\rho_{\mathrm{T}} h(\mathbf{r}) = -\left[\frac{4}{3}\pi R^3\right]^{-1}, \qquad r < R$$

$$\rho_{\mathrm{T}} h(\mathbf{r}) = 0, \qquad r \geq R \tag{3.3}$$

Note that $\rho_{\mathrm{T}} h(\mathbf{r})$ is properly normalized. With the Förster rate, the integral in eq 2.11 can be performed analytically. We obtain

$$Q_{\mathrm{HS}}(\theta) = 1 - \exp(-\theta) + (\pi\theta)^{1/2} \operatorname{erfc}(\theta^{1/2}) \tag{3.4}$$

Equation 3.4 is plotted as the dashed curve in Figure 2. $Q(\theta)$ calculated from the "hard sphere" $h(\mathbf{r})$ is seen to change significantly faster than the RPA result over the times of experimental interest. Hence, the proposed fluorescence experiments should at least be sensitive to the gross shape of the correlation hole.

In the following sections we discuss a variety of other applications of the theory described in section II. A detailed feasibility study of the proposed experiments is not given, but instead experiments are suggested that we believe are likely to be successful and yield useful information. In general, the feasibility of a particular experiment will depend on the type of system and molecular weight, as well as on the fluorescent labels employed. In some circumstances, the use of labels with a small Förster radius will restrict experiments to the study of low molecular weight chains. References 4, 12, and 13 are careful experimental investigations of EET in liquids and polymers and should be quite helpful in designing experiments of the type considered here. Furthermore, these references provide concrete evidence that related experiments can be performed.

B. Analysis of Correlations in Solution. Trap fluorescence experiments may prove useful for structural studies of polymer solutions at concentrations near the overlap concentration, c^*. By labeling chains in the manner described for the study of the correlation hole, EET experiments could allow one to monitor the degree of coil interpenetration as the polymer concentration is varied across c^*. It may be possible to see a gradual transition in which $Q(t)$ behaves according to eq 3.4 in dilute solution but crosses over to a time dependence appropriate for interpenetrated chains in a good solvent as the concentration is increased above the critical concentration. One would expect to see a dramatic increase in the rate of EET when the screening length, ξ, becomes comparable with R_0^{DT}.

C. Application to Block Copolymer Studies. There are a variety of possible applications of EET experiments to the study of block copolymer structure. Liebler[29] has derived an RPA expression for the pair correlation function of homogeneous diblock melts that can be used in conjunction with fluorescence experiments to probe the correlation hole. The results of such experiments could be compared with the neutron scattering study of Bates.[30] Fluorescence experiments on molecules that are labeled at the joint or at random locations within a block might also be useful for testing current theories of diblock structure in ordered phases.[29,31]

D. Application to the Kinetics of Phase Separation. Another possible application of trap fluorescence experiments would be to study the structural evolution of a polymeric system undergoing a first- or second-order phase transition. As an example, one could work with the PS–PVME system, which has lower critical solution temperature. A convenient way to study such a system would be to prepare labeled PS chains that contain a naphthalene end group and PS chains that contain an anthracene end label. It is unlikely that such labels would cause the thermodynamic properties of the tagged material to be much different from that of pure PS. Aggregation caused by specific interactions of the labels is also not expected. The system to be studied would consist of a mixture of PS–A, a very low concentration of PS–N, and PVME molecules. The naphthalene end groups would serve as energy donors and the anthracene groups as energy acceptors or traps.

In the homogeneous, one-phase state, trap fluorescence measurements probe the equilibrium pair correlation function of PS chain ends in such a system. As the temperature is raised, the fluorescence intensity changes in response to changes in $h(\mathbf{r})$. (It is important to note that R_0^{DT} and τ may be temperature-dependent.) If the system is quenched into the unstable, two-phase region, the fluorescence intensity will evolve as the system begins to undergo spinodal decomposition. Because the time scale for the evolution of $h(\mathbf{r})$ is so much slower than the rate of EET, the theory presented in this paper can be used with $h(\mathbf{r})$ replaced by its instantaneous value. Time-dependent fluorescence measurements under such conditions, however, are difficult because data collection by single-photon-counting techniques may require averaging over times comparable to structural relaxation times in the material. Thus, it is desirable to perform a photostationary state fluorescence experiment in which the ratio of trap to donor fluorescence intensities (I_T/I_D) is monitored under continuous excitation.[1] This ratio of fluorescence intensities is conveniently related to the integral of $H(t)$,[32] $\delta = \int_0^\infty dt\, H(t)$

$$\frac{I_T}{I_D} = \frac{q_{FT}}{q_{FD}}\left[\frac{\tau}{\delta} - 1\right] \tag{3.5}$$

where q_{FT} and q_{FD} are the respective quantum efficiencies of the trap and donor chromophores. Thus, the structure of the spinodally decomposing system can be monitored under continuous excitation where the fluorescence observable is related to $h(\mathbf{r})$ via eq 2.9 and 3.5. Linearized theories for the behavior of $h(\mathbf{r})$ at short times can be compared with the observed fluorescence results.

E. Other Applications. Other applications of the energy-transfer technique are possible. For instance, it might be possible to attach chromophores to a cross-linking agent that could be incorporated into an elastomeric network. Trapping experiments could then provide information about the concentration and distribution of cross-link junctions. If donor labels could be attached to a surface whose polymer adsorption properties are of interest, the fluorescence technique might be used to probe segment densities away from the surface. This experiment could be performed by allowing trap-labeled polymer molecules to be adsorbed on the surface (containing previously attached donors). By monitoring the donor to trap EET, the distribution function of trap and hence segment density near the surface could be analyzed.

IV. Discussion and Conclusions

In the present paper a theory was developed that should allow donor fluorescence measurements to be used for the study of intermolecular correlations. Previously theories were concerned primarily with the study of intramolecular correlations. The most important result of the present work is eq 2.9, which related the pair correlation function of chromophore labels to the fluorescence intensity. It was demonstrated how this relationship can be used to probe the correlation hole in bulk polymers and melts. Other applications, such as structural studies of polymer solutions and block copolymers, were discussed. A study of the kinetics of phase separation may also be possible with the technique.

It is important that an appropriate donor–trap chromophore pair be chosen for a given application. Ideally, one would like select a pair with a large R_0^{DT}, because this facilitates the study of large molecules. However, those labels with the largest Förster radii are often bulky and may have very short lifetimes. Such labels could significantly perturb their environment and thus bias the structural information obtained from fluorescence measurements. The disadvantage of donor chromophores with a short lifetime is that very high-resolution excitation and detection equipment is then required. One must also be careful that specific interactions among the labels or between labels and units of the polymer will not cause aggregation, phase separation, or significant perturbation of the material structure. Thus, labels must be chosen with care. This author is optimistic, however, that suitable fluorescent tags can be chosen for a given application.

Throughout this paper we have assumed that the orientation-averaged Förster rate described by eq 1.1 is appropriate for the systems under consideration. Other transfer rates can be easily incorporated into the present formalism if it is believed that such rates accurately describe the mechanism of energy transfer. Our results can also be extended in a straightforward manner to the orientation-dependent Förster rate if the labels have limited or no local mobility on the time scale of τ. This extension has been described in detail in previous publications.[4-7,12,13,32]

Table I
EET among Randomly Distributed Donors

scheme	A_3	% error
exact	0.8056	
I	1.2337	+53.1
II	0.6169	−23.4
III	0.7854	−2.5
IV	0.1686	−79.1

Table II
EET to Traps on an Ideal Chain

scheme	B_3	% error
exact	4.3605	
I	5.9079	+35.5
II	1.9693	−54.8
III	3.3442	−23.3
IV	−0.5945	−113.6

Acknowledgment. The author thanks M. D. Ediger, R. F. Loring, and E. Helfand for many useful discussions.

Appendix: Analysis of the Many-Body Problem

A. Approximation Schemes. There are several different approaches that have been developed for the analysis of many-body energy-transfer problems. The formalism is applicable to related transport problems in disordered media,[16] but only the EET problem is considered here. Haan and Zwanzig[17,18] formulated an elegant theoretical framework to describe the migration of excitations among randomly distributed donor chromophores. They found a scaling relationship between concentration and time and showed on the basis of physical and mathematical arguments that the Laplace transform of $G_0(t)$

$$\hat{G}_0(\epsilon) = \int_0^\infty dt\, e^{-\epsilon t} G_0(t) \tag{A.1}$$

can be written in the form

$$\hat{G}_0(\epsilon) = \frac{1}{\epsilon + K(1/\epsilon)} \tag{A.2}$$

The quantity, $K(1/\epsilon)$, which is often referred to as a self-energy or memory function in the many-body literature, can be defined through its series expansion in chromophore concentration. Gochanour, Andersen, and Fayer[19] (GAF) subsequently showed that it is possible to renormalize the self-energy such that eq A.2 can be written

$$\hat{G}_0(\epsilon) = \frac{1}{\epsilon + \tilde{K}[\hat{G}_0(\epsilon)]} \tag{A.3}$$

Thus, $\tilde{K}$ depends on ϵ only through its explicit dependence on $\hat{G}_0(\epsilon)$. Both eq A.2 and A.3 are exact results. Although they were originally derived for EET among randomly distributed donors, the equations have also been extended to the more general case of donors and traps[14] and to include correlations among donor and trap positions.[5] Recently, Nieuwoudt and Mukamel[20,21] presented two additional equations for $G_0(t)$

$$G_0(t) = \exp\left\{-\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} \frac{d\epsilon}{\epsilon^2} \exp(\epsilon t) F(1/\epsilon)\right\} \tag{A.4}$$

and

$$G_0(t) = \exp\left\{-\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}\frac{d\epsilon}{\epsilon^2}\exp(\epsilon t)\tilde{F}[\hat{G}_0(\epsilon)]\right\} \qquad (A.5)$$

Equation A.4 is an exact relation between $G_0(t)$ and a memory function $F(1/\epsilon)$. As before, $F(1/\epsilon)$ can be defined through its expansion in powers of chromophore concentration. Equation A.5 was obtained by Nieuwoudt and Mukamel by *proposing* that $F(1/\epsilon)$ can be renormalized in the same manner as $K(1/\epsilon)$, i.e., $\tilde{F}[\hat{G}_0(\epsilon)] = F(1/\epsilon)$. This was not proven, however.

Equations A.2–A.5 provide four independent methods for obtaining successive approximations to $G_0(t)$. By approximating the respective memory functions with a truncated expansion in powers of chromophore concentration, the four equations yield approximate expressions for $G_0(t)$. As more and more terms in the expansions are retained, these approximate expressions presumably converge to the exact $G_0(t)$. The rates of convergence, however, may differ greatly. Thus, to obtain an accurate approximation for $G_0(t)$ from a low-order truncation of a memory function expansion, it is necessary to investigate these rates of convergence. To distinguish the various approximation schemes, we label approximations based on eq A.2–A.5 with Roman numerals I, II, III, and IV, respectively. Scheme I was adopted by Haan,[18] Ediger and Fayer,[11–13] and the present author[5] for a variety of EET problems. Scheme II was used by GAF,[19] Loring, Andersen, and Fayer,[14] and for polymer-related problems in ref 5 and 6. Scheme III was considered by several workers[5,22–23] and was recently employed to interpret fluorescence depolarization experiments in polymers.[7] In previous studies approximations based on schemes I and III were referred to as Pâde and cumulant approximants, respectively. Scheme IV was developed and studied by Nieuwoudt and Mukamel.[21]

In order to assess the rates of convergence of the various schemes, we compare the lowest order approximations in which the respective memory functions are approximated by truncating their expansions at first order in chromophore concentration, C. For two problems of interest the $O(C^2)$ predictions of the four approximations are compared with the exact $O(C^2)$ results. In both cases it is found that scheme III is superior at this level of approximation. The results are summarized in Tables I and II.

B. EET among Uncorrelated Donors. The first problem we consider is Förster EET (described by eq 1.1 with R_0^{DT} replaced by R_0^{DD}) among randomly distributed donor chromophores. In this case $G_0(t)\exp(-t/\tau)$ represents the probability that the initially excited donor is still excited at time t. $G_0(t)$ has the following exact density expansion:[18]

$$G_0(t) = 1 + A_2[C_D{}^2t/\tau]^{1/2} + A_3[C_D{}^2t/\tau] + ... \qquad (A.6)$$

where $A_2 = -(\pi/2)^{1/2}$, $A_3 = 0.80555$, and C_D was defined in eq 2.1. In all four schemes, approximation of the memory function by its expansion to $O(C_D)$ results in an approximation for $G_0(t)$ that correctly reproduces the coefficient, A_2. However, the predictions for A_3 from the various approximations are quite different. These predictions are shown in Table I and are compared with the exact value of A_3 given above. It is clear that for EET among randomly distributed donors, scheme III, the cumulant approximant, is far superior to the other methods at leading order.

C. Direct Trapping on an Ideal Chain. The second problem of interest is more closely related to the trapping experiment discussed in section II. We consider a linear, Gaussian polymer chain in the limit that its length approaches infinity. One donor chromophore and an average of q_T trap chromophores per Kuhn segment are placed at random along the contour of the chain. The rate of EET between the donor and traps is assumed to obey eq 1.1. The present problem is a special case of the EET problems considered in ref 5. Because there is no donor–donor transfer, $\exp(-t/\tau)G_0(t)$, the probability that the donor is excited at time t is described by eq 2.4. Hence, the various schemes for approximating $G_0(t)$ correspond to techniques for approximating the integral in eq 2.4.

The density expansion appropriate for the present problem is[5]

$$G_0(t) = 1 + B_2[\bar{C}_T{}^3t/\tau]^{1/3} + B_3[\bar{C}_T{}^3t/\tau]^{2/3} + ... \qquad (A.7)$$

where $B_2 = -4(3^{1/2})/\Gamma(1/3)$, $B_3 = 4.3605$, and

$$\bar{C}_T = \pi q_T(R_0{}^{DT}/a)^2 \qquad (A.8)$$

with a the Kuhn segment length. When the four approximation schemes are applied[24] at first order in $\bar{C}_T$, predictions for B_3 are obtained. These predictions are summarized in Table II. From the table it is clear that scheme III is again superior to the other three methods at this level of approximation. It is interesting that scheme IV does such a poor job of estimating both A_3 and B_3. This may suggest that the renormalization of $F(1/\epsilon)$ proposed by Nieuwoudt and Mukamel is not correct or at least is not useful at low order for application to energy-transfer problems.

We note that the calculation of B_2 requires knowledge of the two-chromophore correlation function, while calculation of B_3 requires knowledge of both two- and three-chromophore correlation functions.[5] For an ideal chain, all such functions are known. At lowest order in $\bar{C}_T$ the various schemes approximate correlation functions of order three and higher in terms of the two-chromophore correlation function. The cumulant approximant, scheme III, appears to do the best job of mimicking the true structure of the material, based only on knowledge of the pair correlation function.

D. General Expression for the Cumulant Approximant. We now turn back to the problem of evaluating eq 2.4 for the case of arbitrary correlations among the positions of the traps and donor. Because the ideal experimental situation corresponds to a very small label concentration,[25] we expect that approximations based on the expansion of memory functions to leading order in concentration will be adequate. The cumulant approximant, which was shown to be superior to the other three schemes for two relevant EET problems, was also demonstrated to be accurate for the problem of donor–donor energy migration on an ideal chain.[7] Thus, we expect that it will provide an accurate approximation to $G_0(t)$ for more general situations of correlations among chromophores. In homogeneous, isotropic materials the cumulant approximant is obtained by inserting the leading term in the density expansion of $F(1/\epsilon)$ into the right-hand side of eq A.4. For the trapping problem discussed in section II, this procedure leads directly to eq 2.6.

References and Notes

(1) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970.
(2) Förster, Th. *Ann. Phys.* (*Leipzig*) **1948**, *2*, 55.
(3) Berlman, I. B. "Energy Transfer Parameters of Aromatic Compounds"; Academic Press: New York, 1973.
(4) Miller, R. J. D.; Pierre, M.; Fayer, M. D. *J. Chem. Phys.* **1983**, *78*, 5183.
(5) (a) Fredrickson, G. H.; Andersen, H. C.; Frank, C. W. *Macromolecules* **1983**, *16*, 1456. (b) *Macromolecules* **1984**, *17*, 54. (c) *Macromolecules* **1984**, *17*, 1496.

(6) Fredrickson, G. H.; Andersen, H. C.; Frank, C. W. *J. Chem. Phys.* **1983**, *79*, 3572.
(7) Fredrickson, G. H.; Andersen, H. C.; Frank, C. W. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 591.
(8) Katchalski-Katzir, E.; Haas, E.; Steinberg, I. Z. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 44.
(9) Stryer, L. *Annu. Rev. Biochem.* **1978**, *47*, 819.
(10) Ohmine, I.; Silbey, R.; Deutch, J. M. *Macromolecules* **1977**, *10*, 862.
(11) Ediger, M. D.; Fayer, M. D. *Macromolecules*, **1983**, *16*, 1893.
(12) Ediger, M. D.; Domingue, R. P.; Peterson, K. A.; Fayer, M. D. *Macromolecules* **1985**, *18*, 1182.
(13) Ediger, M. D.; Domingue, R. P.; Fayer, M. D. *J. Chem. Phys.* **1984**, *80*, 1246.
(14) Loring, R. F.; Andersen, H. C.; Fayer, M. D. *J. Chem. Phys.* **1982**, *76*, 2015.
(15) Förster, Th. Z. Naturforsch. A *Astrophys., Phys. Phys. Chem.* **1949**, *4*, 321.
(16) *J. Stat. Phys.* **1983**, *30* (2), a collection of papers presented at the Symposium on Random Walks, Gaithersburg, MD, June 1982.
(17) Haan, S. W.; Zwanzig, R. *J. Chem. Phys.* **1978**, *68*, 1879.
(18) Haan, S. W. Ph.D. Thesis, University of Maryland, College Park, MD, 1977.
(19) Gochanour, C. R.; Andersen, H. C.; Fayer, M. D. *J. Chem. Phys.* **1979**, *70*, 4254.
(20) Mukamel, S. *J. Stat. Phys.* **1983**, *30*, 179.
(21) Nieuwoudt, J.; Mukamel, S. *Phys. Rev. B: Condens. Matter* **1984**, *30*, 4426.
(22) Ching, W. Y.; Huber, D. L.; Barnett, B. *Phys. Rev. B: Condens. Matter* **1978**, *17*, 5025.
(23) Godzik, K.; Jortner, J. *J. Chem. Phys.* **1980**, *72*, 4471.
(24) In applying scheme II to this problem we used the modification of eq 3.3 derived in ref 5 and 14. In scheme IV, $\exp(B_2[\bar{C}_T^{\,3}t/\tau]^{1/3})$ was not factored out of $G_0(t)$ as in ref 21 because it is not an exact result in any limit of the present problem.
(25) The motivation of working at a low chromophore concentration was discussed in section I.
(26) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(27) Hansen, J. P.; McDonald, I. R. "Theory of Simple Liquids"; Academic Press: New York, 1976.
(28) de Gennes, P. G. *J. Phys.* (*Les Ulis, Fr.*) **1970**, *31*, 235.
(29) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(30) Bates, F. S. *Macromolecules* **1985**, *18*, 525.
(31) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1976**, *9*, 879; **1978**, *11*, 960; **1980**, *13*, 994.
(32) Fredrickson, G. H.; Frank, C. W. *Macromolecules* **1983**, *16*, 1198.
(33) Amrani, F.; Hung, J. M.; Morawetz, H. *Macromolecules* **1980**, *13*, 649.

Computer-Assisted Resolution of Phosphorescence Spectra from Solid Films of Poly(*N*-vinylcarbazole)

Richard D. Burkhart* and Ishmael Dawood

Department of Chemistry, University of Nevada, Reno, Nevada 89557.

Received September 6, 1985

ABSTRACT: Triplet emission spectra were recorded for solid film samples of poly(*N*-vinylcarbazole) prepared by free radical polymerization at temperatures ranging from 2 to 160 °C. The low-temperature polymerizations were initiated photochemically. The phosphorescence spectra could be resolved by computer methods into three overlapping Gaussian components exhibiting peak maxima at 477 (±3), 507 (±3), and 542 nm (±3 nm). Inconsistent results were obtained from attempted two-component fits and it is concluded that there are at least three emitting triplet excimeric species present. The 477-nm band is believed to be associated with the half-eclipsed excimer while that at 507 nm is assigned to the normal sandwich excimer. The 542-nm band is thought to be due to an extended excimer consisting of three properly oriented chromophore groups. Relative oscillator strengths of these three emissions were determined for all polymer samples. Certain regularities in these values were found, depending upon polymerization conditions and mode of sample treatment.

Introduction

Poly(*N*-vinylcarbazole) (PVCA) when subjected to photoexcitation produces a rich array of photophysical phenomena, including photoconductivity, fluorescence, excimer fluorescence, phosphorescence, delayed fluorescence, excimer phosphorescence, and delayed excimer fluorescence. The latter four emissions originate from the triplet state of PVCA and are the primary focus of the present work.

In point of fact, the scope of the present study can be even more narrowly defined since it is only pure solid films of PVCA that will be considered here. It has been pointed out in earlier work[1] that the triplet luminescence of PVCA is entirely excimeric in character when it is solid films that are being photoexcited. On the other hand, no emission due to triplet excimers has been reported from frozen solutions of PVCA. Thus, a restriction to triplet luminescence from solid films is de facto a restriction to triplet excimer emission.

The modes of polymerization and sample preparation studied in this work are associated with effects that are essentially thermal in character. These may be characterized as (a) effects of polymerization temperature and (b) effects of thermal treatment of sample films. We should hasten to remark, at this point, that the polymerization temperature can indeed influence many characteristics of the resulting polymer, not the least of which is average molecular weight. The influence of average molecular weight on the triplet emission spectra of PVCA and other polymers has already been thoroughly explored by others,[2,3] however, and, apart from recognizing its influence on relative emission intensities of delayed fluorescence and phosphorescence, it is not of primary interest here.

A concern over the effects that polymerization temperature may have upon triplet luminescence characteristics of PVCA is prompted by two earlier observations. It had been noted by Houben and co-workers[4] that PVCA prepared by cationic polymerization at −78 °C emitted a relatively larger proportion of its excimer fluorescence at a wavelength corresponding to the sandwich type of excimer rather than the higher energy half-eclipsed excimer. This latter excimeric species incidentally has been shown to arise from a half-overlapped orientation of carbazolyl