terials Research Laboratory (MRL) at Case Western Reserve University through the MRL Program of NSF under Grant No. DMR 78-24150.

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Effect of Concentration on the Fluorescence Spectra and Lifetimes of Pyrene in Polystyrene Films[†]

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Received November 28, 1979

ABSTRACT: The emission spectra and lifetimes of pyrene-doped polystyrene films are investigated as a function of pyrene concentration. The excimer fluorescence observed in these films is shown to result from the formation of pyrene molecular pairs which satisfy the geometrical requirements for excimer formation. The predominant photophysical process leading to electronic excitation of these molecular pairs is shown to be dipole–dipole resonance transfer from pyrene monomers serving as energy donors. It is found that little or no energy migration between pyrene monomers occurs in these films.

Recently, the results of an investigation concerning the migration and transfer of singlet excitation in molecularly doped polymers were reported.[1] It was determined that the migration of the excitation among the system of like energy donors occurred by a series of random walk steps with each step occurring by dipole–dipole resonance transfer in the very weak coupling limit (Förster transfer).[2] These conclusions were based on measurements of the concentration dependence of the donor fluorescence lifetime in the presence of known concentrations of two types of fluorescence quenchers. An important distinction between those results and others concerning the migration and transfer in doped polymer films was the absence of self-quenching due to the formation of dimer or higher aggregate states which can serve as energy traps.[3] The occurrence of fluorescence self-quenching, which in certain cases is signaled by the presence of new emission such as excimer fluorescence, complicates interpretation of results since the concentration of the species responsible for the new emission is unknown.

The diffusion-limited formation of excited-state dimers in solution, resulting from the interaction of a ground-state molecule and an electronically excited molecule, was first observed by Förster and Kasper for the case of pyrene.[4] These excited-state dimers were subsequently termed excimers, and the pyrene molecule has long served as the prototype for a great number of investigations concerning excimers and excimer emission as observed for a variety of compounds both in fluid solution and in the solid state.[5] The observation of excimer emission from molecular crystals of a variety of compounds, again exemplified by pyrene, has been suggested as a diagnostic tool for determining the crystal structure since the translational freedom which allows the two molecules to achieve the proper orientation for excimer formation in solution is, of course, absent in the solid state and the two molecules

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[†] Presented in part at the Symposium on Photo- and Radiation Chemistry in Polymer Science, Joint ACS/JCS Honolulu Meeting, Honolulu, HI, Apr 1-6, 1979.

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must be properly preoriented.[6] The pyrene molecule has also been observed to yield concentration-dependent excimer fluorescence in rigid low-temperature matrices[7] and has been attributed, at least by one group of investigators, to the formation of microcrystallites.[8] Avis and Porter investigated the effect of concentration on the absorption and fluorescence of pyrene in solid solutions of poly(methyl methacrylate) and, on the basis of their measurements, concluded that the strongly concentration-dependent excimer to monomer fluorescence ratio was not the result of microcrystallite formation but rather from pairs of pyrene molecules close to the excimer conformation.[9] Here the results of an investigation concerning the effect of concentration on the fluorescence spectra and lifetimes of pyrene-doped polystyrene films are reported. As in the case of pyrene-doped poly(methyl methacrylate) films, the results are not consistent with formation of microcrystallites; however, in certain other respects, the conclusions arrived at here regarding the concentration dependence of the emission spectra of these films differ somewhat from those of Avis and Porter.[9]

Experimental Section

Materials. Pyrene (Princeton Organics, Prinz Quality), perylene (Aldrich Chemical Co., puriss. grade), polystyrene (Pressure Chemical Co., special polystyrene standard), benzene (Burdick and Jackson Laboratories, Inc., distilled-in-glass grade), and toluene (Burdick and Jackson Laboratories, Inc., distilled-in-glass grade) were used as received.

Film Preparation. Quantities of pyrene ranging from about 1 to 20 mg, along with typically 50–100 mg of polystyrene, were weighed out on a microbalance and placed in small glass vials. The solids were then dissolved in either benzene or toluene. Films were cast by placing a small quantitiy of the pyrene–polystyrene solution onto carefully cleaned $^1/_8$ in. × 1.25 in. fused-quartz disks. The solvent was evaporated by placing the disk on top of a small platform situated on top of a hot plate and covered by a large beaker. The temperature was adjusted to allow for slow evaporation of solvent in a fairly uniform temperature environment. The films appeared visually to be quite uniform in thickness and had excellent optical quality. Film thickness was varied by simply changing the volume of benzene or toluene used to dissolve the solids. The experimental results were shown to be independent of film thickness. For those experiments which utilized perylene as an energy acceptor, the pyrene–polystyrene solid mixture was dissolved in a known volume of a perylene–toluene solution of known concentration. The concentration of pyrene in each film was calculated from eq 1, where W_p is the weight of pyrene, MW

$$C = W_p/(\mathrm{MW})V \qquad (1)$$

the molecular weight of pyrene, and V the total volume of the pyrene plus polystyrene. The total volume V was determined from eq 2, where W_{ps} is the weight of polystyrene, ρ_p and ρ_{ps} are

$$V = \frac{W_p}{\rho_p} + \frac{W_{ps}}{\rho_{ps}} \simeq \frac{W_p + W_{ps}}{\rho_{ps}} \qquad (2)$$

the densities of pyrene and polystyrene, respectively, and the approximation is made that the densities of the pyrene and polystyrene are equal (1.04 g/cm^3).

Steady-State Fluorescence Measurements. Excitation for the steady-state fluorescence measurements was provided by a 250-W Hg–Xe source dispersed through a Jarrell-Ash 0.25-m monochromator. The emission, which was viewed at 90° to the exciting light, was focused onto the entrance slit of a McPherson 0.33-m monochromator and detected with an RCA 1P-28 photomultiplier tube mounted on the exit slit. The output of the photomultiplier tube was measured with a Keithley 610B electrometer and the emission spectra were recorded on a Mosley Model 7000AM X-Y recorder.

Fluorescence Decay Time Measurements. Transient fluorescence measurements were made on a time-correlated single-photon-counting system assembled with electronics from Ortec, Inc. The nanosecond light pulser, operating at 10 kV in air at 1 atm, yielded at the electrode separation used here a pulse repetition frequency of approximately 20 kHz and a pulse width of about 2-ns fwhm. The films were excited with the strong 337-nm nitrogen emission line which was isolated with a narrow-band interference filter (Ditric Optics, Inc.). The emission was viewed at right angles to the excitation with narrow-band interference filters to isolate particular regions of the emission band. Detection was with an RCA 8850 photomultiplier tube operated at 2.2 kV. Data was accumulated and stored on an Ortec Model 6220 pulse-height analyzer.

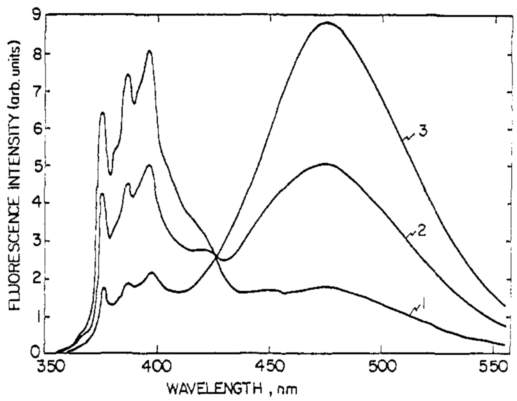

Figure 1. Typical emission spectra of pyrene-doped polystyrene films: (1) 3.84 × 10^{-4} mol/cm^3; (2) 6.58 × 10^{-4} mol/cm^3; (3) 9.35 × 10^{-4} mol/cm^3. The films were excited at 313 nm.

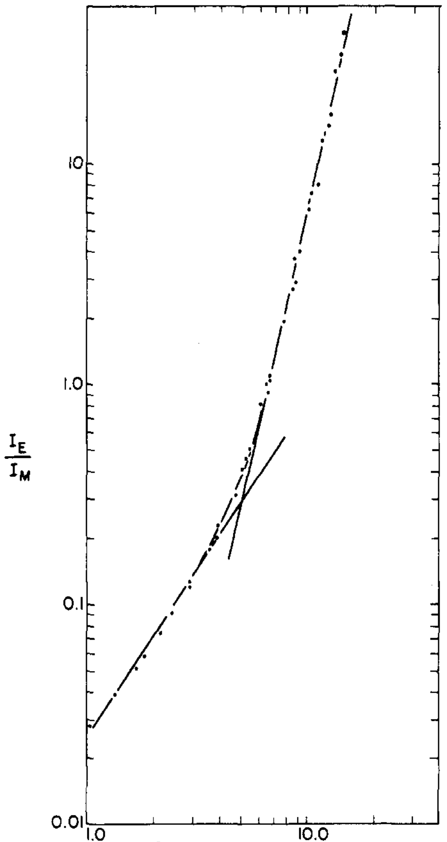

Figure 2. Ratio of the excimer to monomer fluorescence intensities in pyrene-doped polystyrene films as a function of pyrene concentration.

Results and Discussion

Typical emission spectra of pyrene-doped polystyrene films excited at 313 nm are shown in Figure 1. The ratio of the excimer fluorescence to monomer fluorescence intensity is seen to be strongly dependent on the pyrene

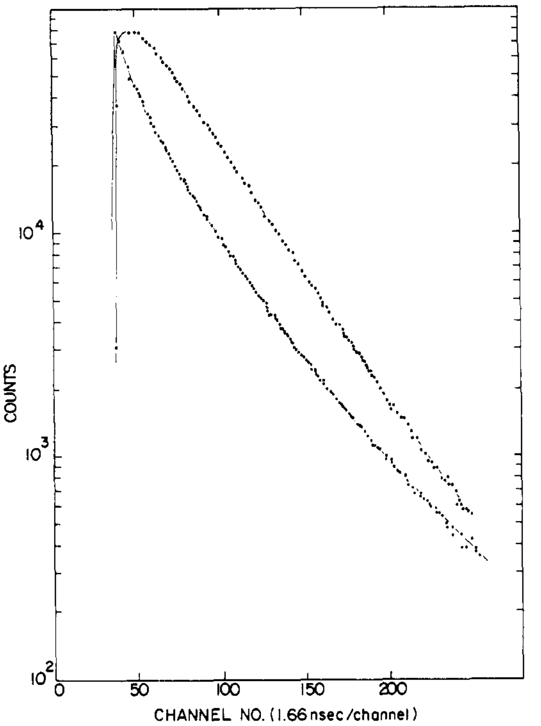

Figure 3. Typical emission response curves of a pyrene-doped polystyrene film. The pyrene concentration is 8.9×10^{-4} mol/cm^3. The upper curve is the excimer response curve and the lower curve is the monomer response curve.

concentration. Figure 2 is a log–log plot of this ratio for a large number of films as a function of the pyrene concentration. The ratio of the excimer fluorescence intensity, I_E, to the intensity of the monomer fluorescence, I_M, is here taken to be the ratio of intensities measured at the peak of the excimer fluorescence band (~472 nm) and the monomer fluorescence at 395 nm, wavelengths which correspond to pure excimer fluorescence and monomer fluorescence, respectively. This plot shows evidence for the existence of two rather distinct concentration regions, one at low concentrations where I_E/I_M is proportional to the ~1.5 power of the pyrene concentration and a second at high concentrations where I_E/I_M is proportional to the ~4.3 power of the pyrene concentration.

In addition to measurement of the emission spectrum of each film, from which the I_E/I_M ratio was determined, fluorescence decays were also measured at two different wavelengths for a majority of these films. Emission response curves were determined at 380 nm, corresponding to pure monomer fluorescence, and at 480 nm, where the emission is pure excimer fluorescence. Typical fluorescence response curves are shown in Figure 3. These particular curves were obtained on a film containing 8.9×10^{-4} mol/cm^3 of pyrene. The decay of the monomer fluorescence is seen to be nonexponenetial as is the excimer fluorescence with the latter response curve exhibiting a rise to maximum intensity delayed in time from that of the monomer fluorescence.

The fluorescence response curves, like the I_E/I_M ratios, are strongly dependent on the pyrene concentration. Qualitatively, the behavior of the response curves is as follows. At low pyrene concentration, where the contribution of excimer fluorescence to the total emission spectrum is very small, the monomer fluorescence decay becomes nearly exponential and in the limit, where no excimer fluorescence is observed, attains a lifetime of 275 ns with a pure single exponential decay. As the pyrene concentration increases, the monomer fluorescence response curve exhibits increasing departure from exponential decay and the time required to decay to e^{-1} of its initial value becomes increasingly less. Figure 4 shows a plot of the e^{-1} lifetimes of the pyrene monomer fluorescence as a function of the pyrene concentration.

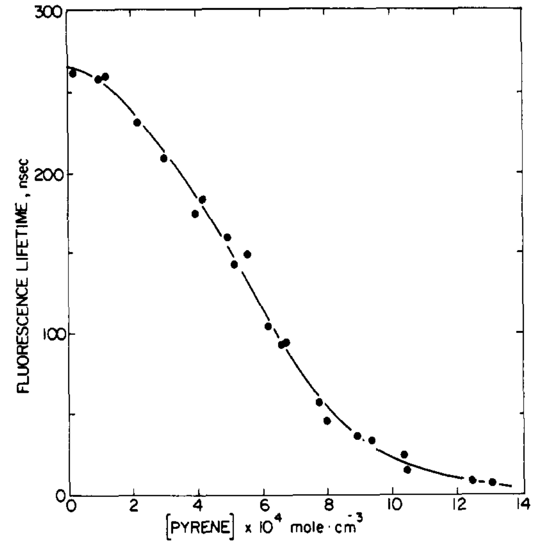

Figure 4. Pyrene monomer fluorescence lifetimes (e^{-1}) as a function of pyrene concentration in pyrene-doped polystyrene films.

The excimer fluorescence response curves are more complex and no attempt was made to analyze them in a quantitative fashion. A number of conclusions regarding the photophysics of these systems can be arrived at, however, simply from the more qualitative aspects of these response curves. First, and perhaps most important, is the rise and decay behavior of the excimer fluorescence. From this, the possibility that the increasing amount of excimer fluorescence arises from the formation of microcrystallites can be eliminated since this type of kinetic behavior is not observed in the pyrene crystal excimer fluorescence response curve. Furthermore, the decay portion of the excimer fluorescence response curve was very similar to the decay of the monomer fluorescence over the range of pyrene concentrations where the monomer decay time was greater than the limiting lifetime of the pyrene excimer observed at high concentrations. For example, at the pyrene concentration where the monomer decay was nearly exponential with a lifetime of 220 ns, the excimer decay was also 220 ns. On the other hand, the excimer decay was observed to approach a limiting value of approximately 45 ns at high pyrene concentrations where the monomer e^{-1} lifetime is continuously decreasing and which finally attains a value of about 10 ns at the highest pyrene concentration used here.

The above findings are suggestive of a process in which the excitation initially localized on a pyrene monomer is transferred via a nonradiative transition to sites in the film where two or more pyrene molecules are paired or aggregated and satisfy the configurational requirements necessary for excimer formation without any large-scale changes in relative orientation. This prompted a more detailed analysis of the pyrene monomer fluorescence decay curves.

For very dilute pyrene-doped polystyrene films in which excimer fluorescence is absent, the pyrene monomer fluorescence decay is strictly exponential and the time dependence is given by eq 3, where I^0 is the fluorescence intensity at time zero and τ_0 is the fluorescence lifetime.

$$I_0(t) = I^0 \exp(-t/\tau_0) \tag{3}$$

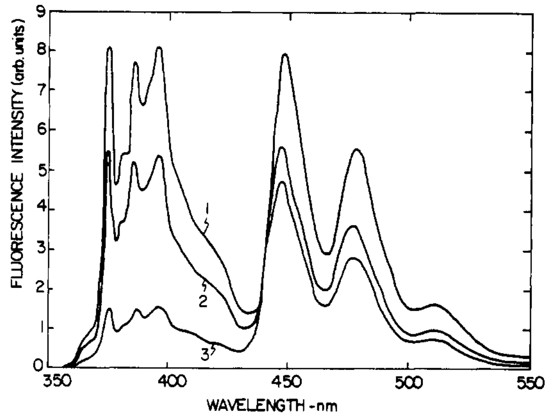

Figure 5. Typical emission spectra of 4.8 × 10^{-7} mol/cm^3 pyrene–polystyrene films containing various concentrations of perylene: (1) 8.22 × 10^{-7} mol/cm^3; (2) 2.06 × 10^{-6} mol/cm^3; (3) 1.03 × 10^{-5} mol/cm^3.

In the case of rigid solutions containing randomly dispersed energy donors and acceptors where the energy is transferred to the acceptor via the dipole–dipole resonance-transfer mechanism, the energy donor fluorescence decays in a nonexponential manner according to the relation given in eq 4,[10] where τ_0 is the donor fluorescence

$$I(t) = I^0 \exp[t/\tau_0 - 2(C/C_0)(t/\tau_0)^{1/2}] \qquad (4)$$

lifetime in the absence of acceptor, C is the concentration of acceptor, and C_0 is a critical acceptor concentration which is defined as that concentration where the rate constant for energy transfer from the donor is equal to the sum of rate constants for all other models of deactivation of the excited donor. Dividing $I(t)$ by $I_0(t)$ yields the expression given in eq 5 and, thus, eq 6 follows.

$$I(t)/I_0(t) = \exp[-2(C/C_0)(t/\tau_0)^{1/2}] \qquad (5)$$

$$\ln\,[I(t)/I_0(t)] = -2(C/C_0)(t/\tau_0)^{1/2} \qquad (6)$$

An example of such a rigid solution in which the donor and acceptor satisfy the criteria for Förster dipole–dipole resonance transfer is that of polystyrene films doped with pyrene as donor and perylene as acceptor. Typical steady-state fluorescence spectra of polystyrene films, each containing the same low concentration of pyrene and various concentrations of perylene, are shown in Figure 5. Clearly, the yield of pyrene fluorescence decreases in the presence of increasing amounts of perylene. Measurements were also made of the pyrene monomer fluorescence decays in the presence of various perylene concentrations. These decay curves were nonexponential and the results of an analysis, according to eq 6, are shown in Figure 6. From the slopes of these plots, it is possible to determine a value of the critical concentration, C_0, since the concentration of acceptor, C, and the lifetime, τ_0, of the donor in the absence of acceptor are known quantities. The critical distance for energy transfer from excited pyrene to ground-state perylene, that is the distance at which the rate constant for energy transfer is equal to the sum of rate constants for all other modes of deactivation of the pyrene lowest lying excited state, is then calculated from expression 7, where N is Avogadro's number and C_0

$$R_0 = (3/4\pi N C_0)^{1/3} \qquad (7)$$

is the critical concentration in terms of mol/cm^3. This yielded a critical distance of 35.2 ± 0.4 Å for the pyrene–perylene system, a value in excellent agreement with that reported by Mataga et al.[11]

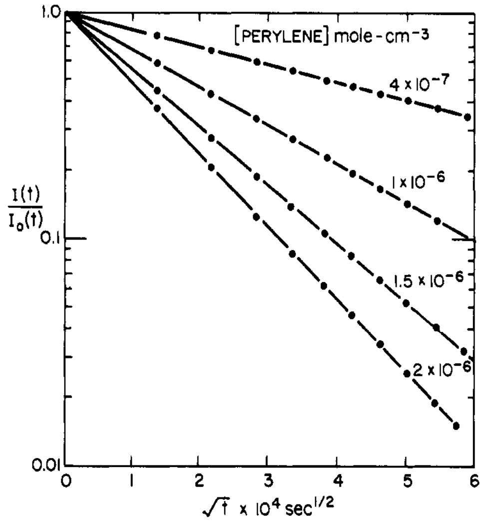

Figure 6. Results of analyzing the pyrene monomer fluorescence response curves for dilute pyrene–polystyrene films containing perylene according to eq 6.

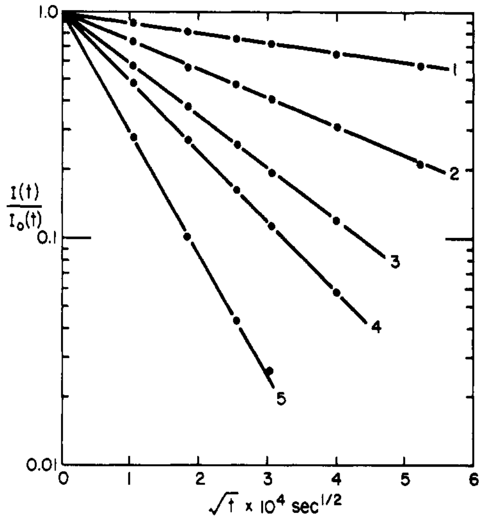

Figure 7. Results of analyzing pyrene monomer fluorescence response curves for pyrene-doped polystyrene films according to eq 6: (1) 4 × 10^{-4} mol/cm^3; (2) 6.76 × 10^{-4} mol/cm^3; (3) 7.78 × 10^{-4} mol/cm^3; (4) 9.35 × 10^{-4} mol/cm^3; (5) 1.04 × 10^{-3} mol/cm^3.

The pyrene monomer fluorescence decay curves for the heavily doped pyrene–polystyrene films were then similarly analyzed according to eq 6. Plots of log $I(t)/I_0(t)$ vs. $t^{1/2}$ obtained at five different concentrations of pyrene are shown in Figure 7. The agreement between experiment and eq 6 strongly suggests that the concentration dependence of the pyrene monomer fluorescence decay is the result of an increasing concentration of energy acceptors, and, as in the case of pyrene–perylene donor–acceptor pairs, energy is transferred to these acceptors via a single-step dipole–dipole resonance-transfer process. Here, however, contrary to the example with perylene as an acceptor a critical concentration, C_0, or critical distance, R_0, cannot be determined since the concentration of acceptors is unknown. Some insight into the nature of the energy acceptors in the pyrene–polystyrene films is obtained from values of the ratio C/C_0 as a function of donor concentration. A log–log plot of C/C_0 values, as determined from the data of Figure 7 vs. the pyrene concentration, is shown in Figure 8. There it is seen that in the low-concentration region C/C_0 values appear to approach a quadratic dependence on the pyrene concentration, whereas in the higher concentration region this dependence

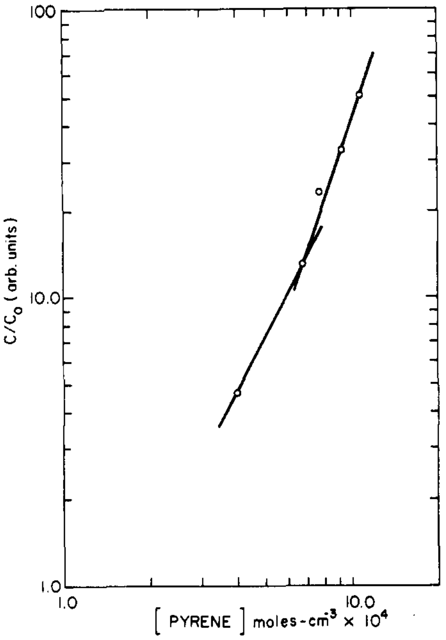

Figure 8. C/C_0 ratios of pyrene-doped polystyrene films as a function of pyrene concentration.

is significantly greater. Next, quenching factors were determined from the data of Figure 4 and plotted against the pyrene concentration. These are shown in Figure 9 when the log of the quenching factor, Q, defined as the ratio $(\tau_0 - \tau)/\tau$, where τ_0 is the pyrene fluorescence lifetime for the most dilute solution and τ is the e^{-1} lifetime for all other concentrations, is plotted vs. the pyrene concentration. The quadratic dependence of the quenching factor on the pyrene concentration in the low-concentration region where $Q \cong 1$ is clearly evident and at high concentrations where $Q \cong 1$, it is seen that Q is proportional to approximately the fourth power of the pyrene concentration. This behavior seems to constitute rather convincing evidence that the quenching sites or energy acceptors are pairs of pyrene molecules properly oriented to satisfy the conditions for excimer formation. In the case of single-step long-range transfer by dipole–dipole resonance, it can be shown that the donor fluorescence quantum efficiency is linear in acceptor concentration at concentrations where $C \ll C_0$ (i.e., small Q) and quadratic in acceptor concentration when $C \gg C_0$ (i.e., large Q).[12] Hence, the change from quadratic to approximately fourth-power dependence observed in the pyrene–polystyrene films indicates that the majority of the acceptors are, in fact, formed from two pyrene molecules. The deviation from strict fourth-power dependence in the high-concentration region could very well be due to the formation of pyrene trimers, tetramers, and other higher aggregates.

To this extent, the conclusions arrived at here are in agreement with the proposal of Avis and Porter that the excimer fluorescence observed in rigid plastic solutions is due to pairs of molecules formed by ground-state interaction.[9] The results are not consistent, however, with an interpretation in which excimer-forming pairs and monomer species act independently and that excimer fluorescence originates from light absorbed by pairs of molecules which differ slightly in their absorption spectrum. On the basis of the experimental results presented here, it appears that the dominant process leading to the concentration-dependent emission properties of the pyrene-doped polystyrene films is the formation of increasing concentration of energy acceptors with increasing pyrene concentration. The majority of these energy acceptors are pairs of pyrene molecules or dimers which, due to ground-state interaction, have an absorption spectrum sufficiently red-shifted to give spectral overlap with the pyrene monomer fluorescence which exceeds the overlap between the pyrene monomer fluorescence and absorption bands. This increased spectral overlap in essence implies a greater density of acceptor states which are isoenergetic with the pyrene monomer fluorescence than there are pyrene monomer states which could lead to energy migration within the donor system. Furthermore, it is probable that the transition moment linking the ground state and the lowest lying excited state of the dimer is greater than that of the symmetry-forbidden ($^1L_b \leftarrow {}^1A$), lowest lying transition of the pyrene monomer based on the limiting lifetime of ~45 ns observed for the excimer fluorescence at very high concentration. Effective spectral overalp between the energy donor emission band and the acceptor absorption band and a sufficiently allowed energy acceptor transition are both conditions which are important for dipole–dipole resonance transfer.[2] The monomer fluorescence response curves provide additional evidence of a process in which the excitation, initially localized on a pyrene monomer site, is transferred to the acceptors by the dipole–dipole resonance-transfer mechanism in the very weak coupling limit (Förster mechanism). These response curves, when analyzed according to eq 6, showed good agreement between experiment and the predictions of this equation which indicates that the rate of energy transfer from donor to acceptor depends on the inverse sixth power of the donor–acceptor separation. Energy migration within the pyrene monomer donor subsystem does not appear to be an important process in these films.

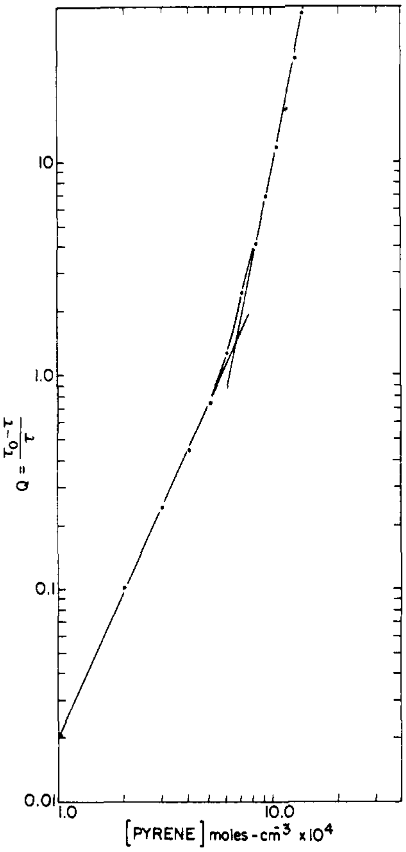

Figure 9. Quenching factors for pyrene-doped polystyrene films as a function of pyrene concentration.

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Infrared Studies of Hydrogen Bonding in Ethylene–Methacrylic Acid Copolymers and Ionomers

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ABSTRACT: The temperature dependencies of hydrogen-bond formation between carboxylic acid groups in two ethylene–methacrylic acid copolymers and a partially neutralized sodium salt have been investigated by infrared spectroscopy. The concentrations of hydrogen-bonded acid groups were determined by using absorbances at 1700 and 1750 cm^{-1} assigned to the dimer and monomer carbonyl stretching vibrations, respectively. Thermodynamic parameters were calculated by using carbonyl peak absorbances as well as integrated absorbances, both methods giving a heat of dissociation of 12 kcal mol^{-1}. Thus each hydrogen bond has a strength of about 6 kcal mol^{-1}. It is shown that the concentration of hydrogen-bonded dimers cannot be unambiguously determined by using only the 935-cm^{-1} absorbance assigned to the out-of-plane OH bend in a dimer. The carboxylic acid groups in the partially neutralized salt also establish a temperature-dependent equilibrium between bonded and nonbonded species with a heat of dissociation of 20 kcal mol^{-1}. The carboxyl asymmetric stretch of the salt consists of two overlapping peaks at 1565 and 1580 cm^{-1}. The relative absorbances of these bands are reversibly temperature dependent, suggesting that the salt groups exist in at least two kinds of environments.

Polar moieties attached as pendent groups along a polymer chain or directly incorporated into the backbone are known to interact with each other, thereby affecting the polymer's physical properties. For polymers containing carboxylic acids, amides, alcohols, amines, etc., the possibility of hydrogen bonding exists. Structural integrity, crystalline habits, and the location of the glass transition temperature can be influenced by the presence of hydrogen bonding.

Early investigations into the possibilities of realizing thermally reversible polymer gels were focused on carboxylic acid containing rubbers[1,2] and styrene–methacrylic acid copolymers.[3] It was found that incorporation of acid comonomer generally increases modulus and viscosity but does not produce a mechanically stable network. Efforts were then directed at elucidating the behavior of the carboxylic acid monomer–dimer equilibrium, principally by using infrared techniques. Longworth and Morawetz[3] used the absorbances at 1750 and 1700 cm^{-1}, respectively, to determine the temperature dependence of the relative concentrations of free and hydrogen-bonded carbonyl for styrene–methacrylic acid copolymers. Dimerization constants were calculated at 110 °C to be 0.36 and 0.12 mol/L for a 4.6 and 10.6 mol % acid copolymer, and the heat of dimerization was found to be 8–10 kcal/mol. They also reported that when the copolymers were cooled below T_g, a fraction of free carbonyl was "frozen in" and that this amount was independent of cooling rate. Fitzgerald and Nielsen[4] also investigated the temperature dependence of infrared spectra for styrene–methacrylic acid copolymers. Using the ratio of the absorbances at 1750 and 1700 cm^{-1}, they reported the energy difference between nonbonded and bonded forms as 3.61 kcal/mol.

In 1968 MacKnight and co-workers[5] published results of infrared studies on an ethylene–methacrylic acid copolymer containing 4.1 mol % acid comonomer. They investigated the temperature dependence of the relative intensities at 3540 and 1700 cm^{-1} assigned to the free hydroxyl stretch and the hydrogen-bonded carbonyl stretch, respectively. The extinction coefficient for the 3540-cm^{-1} band was determined indirectly by using the 1750-cm^{-1} band at the highest temperature and assuming the ratio of extinction coefficients (ϵ_{1750}:ϵ_{3540}) to be constant with temperature. The dimerization was found to be essentially complete at room temperature and the heat of dissociation of the dimers was reported to be 11.6 kcal/mol, in excellent agreement with literature values for low molecular weight carboxylic acids. Subsequently, Otocka and Kwei[6] criticized the use of the 1700- and 1750-cm^{-1} carboxyl absorbances to determine thermodynamic parameters. Owing to the high-pressure polymerization process utilized in preparing the ethylene–carboxylic acid copolymers, carbonyl groups are present as oxidation products. A curve analyzer revealed an additional peak at 1735 cm^{-1} in the IR spectra which can interfere with the analysis if the 1700- and 1750-cm^{-1} bands are used.

Otocka and Kwei selected the 935-cm^{-1} absorption to follow the temperature dependence of hydrogen bonding. This band is assigned to the out-of-plane OH bend in the dimer and is observed to decrease in intensity with increasing temperature in ethylene–acrylic acid copolymers. They assumed 100% dimerization at room temperature and found the ΔH for dimer formation to be −11.5 kcal/mol. The method using the 935-cm^{-1} band determines the

0024-9297/80/2213-0844$01.00/0