High Pressure Luminescence Probes in Polymers*

by

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Abstract

High pressure luminescence has proved to be a very powerful tool for characterizing crystalline solids and liquids. In this paper we treat two problems involving glassy polymers.

In the first problem we use the excited states of azulene and its derivatives to probe intermolecular interactions in PMMA and PS. In the second problem we study the change in emission intensity with pressure from two excimer states of polyvinylcarbazole as a pure polymer and in dilute solution in polystyrene (PS), polymethylmethacrylate (PMMA) and polyisobutylene (PIB). The relative emission from the two states depends strongly on the possibility for motion of polymer segments. The observations are related to the proximity to the glass transition.

High pressure has proved to be a very powerful tool for investigating electronic structure in general^{1-3/} and, in recent years, for investigating luminescence in particular.^{3-5/} Many of the luminescence studies have involved crystalline solids but in this paper we discuss two experiments where we probe the electronic structure and motional properties in glassy polymers at high pressure.

In our first example we use the excited states of azulene to probe electronic interactions in PS and PMMA at pressures where they are definitely glasses.

For localized excitations, the emission vs. internal conversion (thermal return to the ground state) problem can conveniently be described in terms of

a single configuration coordinate diagram. (See Fig. 1.) Along the vertical axis is plotted energy, while the horizontal axis is some normal mode of vibration of the system. Pressure couples to the volume, so that the configuration coordinate most affected in these experiments is the breathing mode of the system; it is an intermolecular coordinate, i.e., it involves the interaction of an atom or molecule with the environment. This point is discussed in detail elsewhere.^{2,6/}

Both optical absorption and emission occur vertically on such a diagram (the Franck-Condon principle) because they are rapid compared with atomic or molecular motions.

When the electron absorbs a quantum of light and moves to the upper electronic state it rapidly gives off vibrational energy (phonons) and reaches the bottom of the well. In this picture the fluorescence efficiency depends on the relative probability of emitting a photon or crossing thermally to the ground state at the intersection of the two electronic wells.

A quantitative calculation of the emission efficiency requires that one consider the barrier height in the presence of configuration interaction, the tunnelling probability, the probability of crossing to various excited vibrational levels of the ground state, and possibly anharmonicity. Appropriate relationships have been developed by Struck and Fonger.^{7/}

Here we use the diagram to predict some qualitative changes and compare them with experiment. From Fig. 1 we see that a shift to higher energy would lead to an increased barrier for the thermal process and thus to higher emission intensity, while a shift to lower energy would result in reduced intensity. Similarly, a decrease in relative displacement along the configuration coordinate ($\Delta_0 \rightarrow \Delta$) would decrease the probability of radiationless relaxation and increase emission intensity.

For organic molecules in particular, the direction and magnitude of shift will depend on the polarizability and/or dipole moment of the excited state relative to the ground state; if it is more polarizable, it exerts a greater attraction for the environment and a red shift (shift to lower energy) ensues. If it is less polarizable than the ground state one may expect a blue shift. These directions and magnitudes are modified by the polarizability of the environment.

We present a study of azulene and an azulene derivative - dicarboethoxy-chloroazulene (DCECA) in two solvents; polymethylmethacrylate (PMMA), and polystyrene (PS).^{8/} Azulene is an isomer of naphthalene with one five and one seven membered ring. For most molecules, no matter what the state to which an electron is excited, it returns thermally to the lowest excited state (S_1) before it emits, so information is obtained only about S_1 , the lowest excited state. Azulene emits from the second excited state (S_2) and some derivatives emit from both S_2 and S_1 . It is known that S_2 is significantly more polarizable than the ground state (S_0). For DCECA there is reason to believe that S_1 is less polarizable than S_0 . PMMA is a significantly less polarizable solvent than PS.

In Figures 2 and 3 we exhibit the shift of the emission peak and change in integrated intensity with pressure for the $S_2 \rightarrow S_0$ emission of azulene in PMMA and in PS. The peak shifts to lower energy with increasing pressure as would be expected from the above discussion. It shifts about twice as rapidly in PS as in PMMA, which is consistent with the greater polarizability of the former solvent. By 140 kilobars the efficiency in PMMA has dropped to ~2% of its initial value, while in PS at the same pressure the efficiency is less than 1% of the atmospheric value. Thus the shifts and intensity changes correlate with the discussion based on the configuration coordinate diagram. Substituted

azulenes give qualitatively similar results for the $S_2 \rightarrow S_0$ emission.

In Fig. 4 we show similar data for the $S_1 \rightarrow S_0$ emission of a substituted azulene in PMMA. For this material the S_1 state is less polarizable than the ground state. As one would predict, the peak shifts to higher energy with increasing pressure. At the same time the intensity increases by a factor of 40 in 130 kilobars. This too follows the prediction of our CC diagram. Finally, in Fig. 5 we exhibit data for the $S_1 \rightarrow S_0$ transition in the substituted azulene, in PS. Here there are more complicated interactions involving both a vertical and horizontal displacement of the potential wells. In the low pressure region the peak shifts to higher energy; it reaches a maximum near 80 kilobars, and then shifts to lower energy. Similarly, the intensity increases at low pressure, maximizes, and then decreases. This is a striking illustration of the relationship between emission energy and luminescent efficiency.

The second study involves the use of excimer emission of poly (N-vinylcarbazole) to probe the motion of polymer segments. The vast literature on this subject is reviewed in the original paper^{9/} and we refer only to a limited number of papers here.

When PVCA is cast into films by itself or in dilute solution with another polymer, it exhibits only excimer fluorescence centered at 430 nm at room temperature and atmospheric pressure.^{10,11,12-16/} The proposed mechanism by W. Klöppfer^{10/} is that of a hopping exciton model. The potential excimer forming sites are frozen in, and they act as traps of randomly moving excitons along the chain. This has been confirmed by later experiments involving different concentrations of a quenching molecule which acts as a competing trap.^{12-16/} The existence of yet a second kind of emission, with a shorter decay time than the excimer, was observed at 77 K by P. Johnson, *et al.*

Later observations of emission spectra and decay times pointed out the existence of a second intramolecular excimer in solution, and in film. This emission centered at 380 nm, is characterized as a shallow trap,^{15/} and a possible structure is given by G. Johnson,^{17/} and by A. Itaya, et al.^{18-19/}

In this study different films of PVCA in dilute solution with another polymer and a film of pure PVCA were subjected to pressures up to 40 kbars, and changes in the emission characteristics with pressure were observed and recorded. The existence of the second, high energy excimer was observed in all films at atmospheric pressure and room temperature. An increase in pressure produced an increase in intensity of the low energy excimer at the expense of high energy excimer intensity. The solvents used were polystyrene (PS), polymethylmethacrylate (PMMA), and polyisobutylene (PB). The PVCA was present in 0.2 wt.% concentration as a solute.

The measurements made include emission peak energies, intensities (area under the peak), and lifetimes. Here we are interested only in the ratio of the integrated intensity of excimer-2 to excimer-1. This ratio appears in Figures 6 and 7. The semilogarithmic plots show two regions where the data are reasonably linear. At low pressures there is a steeper slope for all four films, which changes to a less steep one as the pressure is raised above a certain point. The transition between regions is not sharp and occurs approximately at 2 kbars for pure PVCA, 4 kbars for PVCA in PS, 6 kbars for PVCA in PMMA, and 14 kbars for PVCA in PIB. The two slopes indicate the existence of two mechanisms; one controlling at the "low" pressure region and the other at the "high" pressure region.

It is clear that two distinct mechanisms of excimer interaction are involved. One is evident at high pressures, and the other is present only at low pressures. The pressure at which the transition from one to the other occurs is solvent dependent. An explanation of the emission behavior of PVCA can be provided, using the kinetic scheme of Figure 8 with some appropriate simplifications and assumptions. The nomenclature is an extension to that used by Birks,^{20/} and the mechanism is similar to that described by G. Johnson.^{17/} The rate constants k_{FM} and k_{IM} are those for radiative and nonradiative deactivation of the excited monomer respectively, with k_{FD_1} , k_{FD_2} and k_{IK_1} , k_{ID_2} having the corresponding meaning for the two excimers. D_1 and D_2 represent the excimers responsible for the 380 nm and 430 nm bands respectively. The star (*) represents an excited singlet state; unlike Johnson's nomenclature, D_1 and D_2 refer to ground state potential excimer sites and not the excited complexes. $k_{D_1D_2}$ and $k_{D_2D_1}$ are the association and dissociation rates of D_1 to D_2 , with k_{D_1M} , k_{MD_1} and k_{D_2M} , k_{MD_2} representing the same quantities between the monomer and the two excimers. The mechanism, represented by the last four rate constants, involves main chain conformational changes and/or side group motion to achieve the geometrical requirements necessary for excimer formation during the lifetime of excitation. $k_{E^fD_1}$ and $k_{E^fD_2}$ correspond to singlet exciton migration to preformed sites along the polymer chain, which satisfy the requirements for excimer formation prior to excitation; k_E represents the rate of energy transfer of singlet excitons and f_{D_1} , f_{D_2} are the concentrations of preformed excimer sites. This mechanism applies to both solutions and solid films of PVCA, but some of the rate constants become insignificant in films, depending on the temperature and pressure. One can assume that in polymer film k_{D_1M} , k_{MD_1} , k_{D_2M} and k_{MD_2} are negligibly small compared with the other k 's. This is a safe assumption, since

no monomer emission is observed from PVCA in any host polymer at any pressure. These rate constants also require a large rotation of the polymer backbone to occur, which is unlikely in our case. Under these limitations we obtain for Johnson's Eq. (6):

$$\frac{I_{D_2}}{I_{D_1}} = \frac{k_{FD_2}}{k_{FD_1}} \frac{k_{D_2D_1} (f_{D_2} + f_{D_1}) + k_{D_1} f_{D_2}}{k_{D_1D_2} (f_{D_2} + f_{D_1}) + k_{D_2} f_{D_1}} \quad (1).$$

In our case, f_{D_2} and f_{D_1} include the probability of capture of an exciton by a D_2 or D_1 site; they are therefore effective concentrations. In order to simplify equation (1), one can consider the following limiting cases:

(a) $k_{D_1D_2} \ll k_{D_2}$, $k_{D_2D_1} \ll k_{D_1}$ (i.e. no rotations are allowed to any appreciable extent), and equation (1) becomes

$$\frac{I_{D_2}}{I_{D_1}} = \frac{k_{FD_2} \tau_2 f_{D_2}}{k_{FD_1} \tau_1 f_{D_1}}, \quad (2)$$

where $\tau_1 = 1/k_{D_1}$, $\tau_2 = 1/k_{D_2}$.

If the ratio of radiative rates and the ratio of lifetimes is not varying, I_{D_2}/I_{D_1} depends only on the change of the relative probability of capture of an exciton by a D_2 or D_1 site.

(b) $k_{D_1D_2} \gg k_{D_2}$, $k_{D_2D_1} \gg k_{D_1}$ (i.e. a rearrangement between D_1 and D_2 is allowed, and proceeds efficiently). In this case equation (1) becomes

$$\frac{I_{D_2}}{I_{D_1}} = \frac{k_{FD_2} k_{D_2D_1}}{k_{FD_1} k_{D_1D_2}}. \quad (3)$$

If the ratio of the radiative rates is not changing, I_{D_2}/I_{D_1} depends on the rotational equilibrium constant between D_1 and D_2 .

Any intermediate cases, where one of $k_{D_2 D_1}$ is negligible relative to the other, cannot occur in a plastic medium, because it would deplete the respective population and resulting emission from one of the sites; this follows because there is no other way of forming or depleting sites.

In order to distinguish between mechanisms, it is useful to know the glass transition temperatures (T_g) of the different polymer films, and these are shown in Table I. On a molecular scale, the glass transition temperature is the temperature above which the polymer has acquired sufficient thermal energy for rotational motion, or considerable torsional oscillation, to occur about the majority of bonds in the main chain. Below this temperature, this form of motion takes place infrequently and the majority of inchain groups have fixed conformations. Some transitions can still occur at $T < T_g$; Boyer^{21/} has classified those and proposed that they be called $T_{g.g}$.

If such a transition is taking place between D_2 and D_1 at atmospheric pressure, one would eventually expect it to stop at some higher pressure, which should corollate inversely with T_g . In other words, the higher T_g , the lower the pressure, at room temperature, that the transition between D_2 and D_1 should stop. This, in fact, is observed with our data if we assume that the $D_2 \leftrightarrow D_1$ transition is the controlling factor at low pressures. From Figure 6 it is evident that the pressures at which the change in slope occurs have the following order:

$$P(\text{PVCA in PIB}) > P(\text{PVCA in PMMA}) > P(\text{PVCA in PS}) > P(\text{PCVA film}).$$

Also from Table I:

$$T_g(\text{PIB}) < T_g(\text{PMMA}) < T_g(\text{PS}) < T_g(\text{PVCA}).$$

This correlation leads one to conclude that mechanism (b) dominates at

low pressures, and only mechanism (a) is present at high pressures. We can now examine each pressure region separately.

(a) At the high pressure region, τ_2/τ_1 is approximately constant (see original paper).^{9/} The radiative rates (k_{FD_i}) are also constant with pressure. One can then take the logarithm of both sides of equation (2) to get

$$\ln \frac{I_{D_2}}{I_{D_1}} = \text{Constant} + \ln \frac{f_{D_2}}{f_{D_1}} \quad (4)$$

The number of preformed excimer sites cannot be changing, since all pathways of forming or destroying them do not exist at high pressures. What must be changing is the relative probability of capture. At equilibrium, this can be represented by a constant k_c , which is related to known thermodynamic quantities by

$$k_c \propto e^{-(\Delta G_c/RT)}, \quad (5)$$

and

$$\frac{\partial \ln(k_c)}{\partial P} = \frac{\partial \ln(I_{D_2}/I_{D_1})}{\partial P} = - \frac{\Delta V_c}{RT}, \quad (6)$$

where ΔG_c is the change of the Gibbs Free Energy for the above process. The volume extracted from this treatment is a thermodynamic equilibrium quantity, and represents the difference in volume of the system between the $D_1 \rightarrow D_1^*$ and $D_2 \rightarrow D_2^*$ transitions. This process can be expected to extend to the low pressure region also, but its contribution is small relative to process (b) (see Figure 7), and to a first approximation it can be subtracted out.

(b) In the low pressure region k_{FD_2}/k_{FD_1} is also approximately constant, and taking the logarithm of both sides of equation (4) gives

$$\ln \frac{I_{D_2}}{I_{D_1}} \approx \text{Constant} + \ln \frac{k_{D_2 D_1}}{k_{D_1 D_2}} \quad (7)$$

A change in the relative intensities is then only dependent on the change of the equilibrium distribution of the two sites. Similarly

$$\frac{k_{D_2 D_1}}{k_{D_1 D_2}} \propto e^{-(\Delta G_{12}/RT)} \quad (8)$$

and

$$\frac{\partial \ln(k_{D_2 D_1}/k_{D_1 D_2})}{\partial P} = \frac{\partial \ln(I_{D_2}/I_{D_1})}{\partial P} = - \frac{\Delta V_{12}}{RT} \quad (9)$$

ΔV_{12} represents the change in volume of the system for $D_1^* \rightarrow D_2^*$.

One can extract these volumes from the slopes of the different lines in Figures 6 and 7. The effect of the slope at high pressures is subtracted from that at low pressures and ΔV 's can be calculated according to

$$\Delta V = - (\text{slope}) \cdot \frac{RT}{1000} \quad (10)$$

where $T = 295^\circ K$,

and $R = 83.14 \text{ (cm}^3 \text{ bar/mole}^\circ K)$.

The approximate molar volume (V_{mol}) can also be calculated from the density (1.059 g/cm^3), and the molecular weight (193.2 g/mole) of the monomer;

$V_{\text{mol}} = 182.4 \text{ cm}^3/\text{mole}$. ΔV 's and ΔV 's/ V_{mol} of PVCA in all polymer films are given in Table II.

The first observation one can make is that there is a net reduction of the system volume for both processes. ΔV_{12} , which represents the process of $D_1^* \rightarrow D_2^*$, is at its largest only 3% of total molar volume, which indicates

that a very small rearrangement is necessary for the process. This confirms that the initial assumption that some movement in the polymer films is possible at low pressures. A second observation is that the change in volume for the two processes is solvent dependent. The order of decreasing T_g is followed by the decreasing ΔV 's, which implies that the less rigid solvents can rearrange with less volume change.

The observations of the total intensity variation with pressure presented in the original paper^{9/} also confirm the assumptions made about the nature of the controlling mechanisms. Emission of the D_2 excimer is more efficient ($\tau_2 > \tau_1$), and any shift of the equilibrium distribution towards D_2 can be expected to increase the total intensity. The extent and pressure range where the increase occurs, follows the same order as that of the existence of mechanism (b). The largest increase in intensity is observed for PVCA in PIB, for which equilibrium between D_1 and D_2 is affected by pressure over the largest range. The smallest increase in intensity is observed for the PVCA film, for which mechanism (b) is in effect over the shortest range of pressure. The eventual decrease in intensity can be attributed to an increase of the non-radiative rate (k_{1D}) with pressure. This is due to the fact that radiationless transitions to the ground state increase as the separation of the two states decreases. From the above argument one would expect the order of quenching by internal conversion to be:

$$Q_{\text{OPVCA film}} > Q_{\text{(PVCA in PS)}} > Q_{\text{(PVCA in PMMA)}} > Q_{\text{(PVCA in PIB)}} ,$$

and this is experimentally observed.

Table I.

Glass Transition Temperatures of Polymer Films

Polymer	$T_g(^{\circ}\text{K})$
PVCA	423
	481
	498
PS	373
PMMA (isotactic)	318
	328
PIB	200

Table II.

 ΔV 's of PVCA in All Host Polymers

Polymer	ΔV_c (cm ³ /mole)	$\Delta V_c/V_{mol}$	ΔV_{12} (cm ³ /mole)	$\Delta V_{12}/V_{mol}$
PVCA film	-2.0	0.011	-5.1	0.028
PVCA in PS	-1.6	0.009	-5.0	0.027
PVCA in PMMA	-1.1	0.006	-3.9	0.021
PVCA in PIB	-0.9	0.005	-2.1	0.012

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8