ENERGY TRANSFER, EXCIMER, AND EXCIPLEX EMISSION AS PROBES FOR POLYMER MISCIBILITY

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Abstract - General mechanisms for energy transfer between chromophores, energy migration in polymers, and formation of excimers and exciplexes are briefly reviewed. Fluorescence emission arising from any one of these phenomena may be utilised to study polymer-polymer interactions at the molecular level. A number of examples are presented to illustrate the complementary nature of results derived from the various processes, and the degree of additional information which may be provided for the investigation of polymer miscibility (compatibility) in films.

INTRODUCTION

In recent years there has been a growing interest in amorphous polymer blends because of the ease with which material properties may be influenced by purely physical means (Ref. 1 & 2). It appears that the morphology of a polymer blend on a distance scale of approximately 10nm is important in determining mechanical properties, but there are very few ways in which interactions between particular segments on different polymer chains may be studied. A clearer understanding of polymer-polymer interactions at the molecular level would have enormous importance in predicting and controlling miscibility (compatibility), and hence morphology, in polymer blends.

The intrinsic sensitivity of fluorescence emission techniques offers a possibility for studying what will necessarily be relatively low concentrations of paired, or otherwise interacting species, in a typical polymer blend. Pioneering work in this area was reported by Morawetz and his collaborators (Ref. 3 - 5) who utilised the phenomena of non-radiative energy transfer between chromophores located on different polymer chains. Frank and collaborators (Ref. 6 & 7) have reported related studies in which excimer forming sites on a guest macromolecule were utilised to determine the extent of mixing of guest and host macromolecules. In our own studies (Ref. 8), the phenomenon of exciplex interactions has been shown to afford similar information although the interacting molecular units are not so common, or so simple, as those used by the other groups. Nevertheless the three methods should be regarded as entirely complementary and generally revealing of new levels of molecular interactions in polymer blends. Before outlining the results of these independent studies, it is necessary to explain fully the nature and origins of the three fluorescence emission processes employed.

NON-RADIATIVE ENERGY TRANSFER

In this introduction, we shall be concerned with electronic energy transfer processes (Ref. 9), by which we mean the overall events that may be identified as occurring as shown

\[ D^* + A \rightarrow D + A^* \]

where D represents a donor molecule, A represents an acceptor molecule and the asterisk represents electronic excitation. Conceptually, it is supposed that at some initial time electronic excitation may be unambiguously associated with D and at some later time electronic excitation is unambiguously associated with A. The actual molecular dynamics of a real system will depend not only on the interactions between molecules but also the molecular
and excitation mechanics which are possible for the system. By this is meant the mobility or immobility of groups or electronic excitation within a molecule and the intermolecular mobility or immobility of molecules and electronic excitation. Knowledge of the rate of energy transfer and the rate of decay of $D^*$ allows evaluation of the efficiency of energy transfer. The rates and efficiencies in turn, are determined by both features of molecular structure and the available molecular mechanics.

The transfer of energy from $D^*$ to $A$ may occur radiatively via the following sequence:

$$
D^* \rightarrow D + h\nu_D \quad \text{emission}
$$

$$
A + h\nu_D \rightarrow A^* \quad \text{reabsorption}
$$

In this case, the donor serves as a "molecular lamp" capable of irradiating light into its environment. If a photon, $h\nu_D$, happens to be absorbed by $A$, then a net transfer of the type $D^* \rightarrow A^*$ will have been effected. The radiative mechanism of energy transfer has been termed "trivial" because of the simplicity of the physical processes involved. However, the process may be significant in systems where the donor possesses a high quantum yield of emission which overlaps a region of strong acceptor absorption. Apparently related, though mechanistically distinct, processes are known as radiationless electronic energy transfers arising from either Coulombic interactions between the electrons and nuclei of one molecular system and the electrons and nuclei of another molecular system, or: Exchange interactions between the overlapping electron clouds of two molecular systems. The electron exchange mechanism is relatively short range in nature (collisional contact) and is primarily responsible for the many examples of transfer of triplet donor excitation energy to a ground state singlet acceptor molecule. It has not found a role so far in the study of polymer miscibility and hence will not be discussed further. In contrast, the Wigner Spin Rules permit singlet-singlet energy transfer which may readily occur via the Coulombic (dipole-dipole) mechanism and has found application in studies of the luminescence of polymer films.

In the Coulombic interaction we view the electron cloud of $D^*$ as oscillating back and forth along the molecular frame. To a nearby acceptor, $D^*$ appears to be an oscillating electric dipole. The electronic interactions between $D^*$ and $A$ may, in fact, be treated in precisely the same fashion as the interaction of a light wave and $A$. The reason for this is that the electric field of a light wave may be approximated as an oscillating electric dipole. As a result of this analogy we expect that if electronic energy transfer occurs via Coulombic interactions between $D^*$ and $A$, the following situations will obtain:

1. Electronic energy transfer will be possible through space, since the electronic interactions do not require direct overlap of electron clouds.

2. The rate of energy transfer will depend on the magnitude of the electric oscillations of $D^*$ and the absorption coefficient of the transition $A \rightarrow A^*$.

The broad spectra of polyatomic molecules in condensed phases guarantees sufficient coincidence between $D^*$ and $A$ transitions if the absorption spectrum of $A$ overlaps the emission spectrum of $D^*$. Indeed, the number of possible simultaneous isoenenergetics which deactivate $D^*$ and excite $A$ may be deduced from knowledge of the electronic emission spectrum corresponding to the $D^* \rightarrow D$ transition and the absorption spectrum corresponding to the $A \rightarrow A^*$ transitions.

Efficiency ($E$) of energy transfer between $D^*$ and $A$ by the Coulombic mechanism may be expressed by a relationship originally proposed by Förster (Ref. 10), and is frequently referred to as Förster-type energy transfer:

$$
E = \frac{R_0^6}{R_0^6 + r^6}; \quad R_0^6 = (8.8 \times 10^{-25}) J n^{-4} \alpha_0^2 r_D^6
$$

where $r = \text{distance between energy donor and acceptor}$

$R_0 = \text{characteristic distance at which half of the excitation energy is transferred}$
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\[ J = \text{overlap integral between the emission spectrum of the} \]
\[ \text{donor and the absorption spectrum of the acceptor} \]
\[ n = \text{refractive index of the medium} \]
\[ \kappa^2 = \text{function of the mutual orientation of donor and acceptor} \]
\[ \text{transition moments} \]
\[ \phi_D^0 = \text{fluorescence quantum yield of the donor in the absence} \]
\[ \text{of the acceptor.} \]

In favourable cases, \( R_0 \) may be as large as 4nm with values of 1-2nm to be expected for a range of typical aromatic chromophores (Ref. 9).

**ENERGY TRANSFER PROCESSES IN POLYMERS AND EXCIPER FORMATION**

A basic assumption made in the interpretation of energy transfer processes in polymers is that concepts developed for energy transfer between low molecular weight chromophores in solution are valid for chromophores inbedded in polymer systems. A major new feature is the inhibition of molecular diffusion and molecular structure. A second distinctive feature of macromolecules such as polymers is the occurrence of sequential structural units containing chromophores which are attached to the backbone or main chain of a polymer. If the pattern of sequential bonding is repetitive and orderly, domains of the polymer may exist which are ordered in nature and this may be favourable to certain types of energy transfer processes.

Ignoring, for the moment, inter-macromolecular events, excitation energy imparted to any segment of the polymer backbone (by direct excitation or by energy transfer) may migrate along the chain by a succession of Förster-type energy transfer steps. In this case it is assumed that the emission and absorption spectra of all units are identical e.g.

\[ \text{hv} \]
\[ \text{M - M - M - M - M* etc} \]

Energy migration along the polymer chain may continue until a suitable trapping process is encountered. A particularly important trap for singlet state excitation energy in polymer is called an excimer. If an excited donor molecule \( D^* \) comes into the proximity of a ground state molecule \( D \), the formation of an excimer is possible. An excimer is an electronically excited species of the type \( D-D\). Several important characteristics of excimers are:

1. Excimer formation requires close approach of \( D^* \) and \( D \) and usually requires specific structural interactions;
2. Excimer formation is detectable by excimer emission, which is usually distinct from that of \( D^* \) (Figure 1). Excimers are therefore, excited states of dimeric units which are repulsive in their ground states.

As indicated in Figure 2 excimer sites may be formed by suitable orientations of nearest neighbour groups in a polymer, or by pairing of relatively remote groups in any given macromolecule. For entangled polymer chains such as would be encountered in blends, there will also be the possibility of inter-macromolecular site-site interactions with formations of emitting excimers. Likewise, although not referred to specifically and notwithstanding energy migration processes within one polymer coil, energy transfer between suitably located donor and acceptor units may occur both intra-macromolecularly and inter-macromolecularly.

**EXCIPLEX INTERACTIONS**

An exciplex (Ref. 9 & 11) is formed by interaction of one excited molecule with another molecule in its ground state. In contrast to the usual donor-acceptor complexes, the two components are thought to interact repulsively.
Fig. 1. Schematic energy surfaces showing excimer formation and emission. The emission to the non-quantised ground state is structureless.

Fig. 2. Schematic description of excimer formation by energy migration between nearest neighbours along a polymer backbone and by intramolecular interactions between non-nearest neighbours (Ref. 9).
when both are in ground states. Binding in the exciplex arises mainly from charge transfer between the two units, much as is envisaged for the excited states of charge transfer complexes, and it is customary to denote exciplex formation as a donor-acceptor interaction. It should be noted however that exciplexes involve collisional interaction between a locally excited component and a ground-state component and, since most molecules in their excited states are simultaneously better donors and acceptors than in their ground states, the range of molecules participating in exciplex formation will be much greater than for ground-state charge transfer. It contrast to the previous cases where energy transfer was involved, exciplex phenomena involve electron transfer and the commonly employed use of D and A imply electron donor and electron acceptor capability respectively. Clearly molecules will be the better electron donors or acceptors according to the relative values of their ionisation potentials and electron affinities and exciplex emission may be represented as follows:

\[
\begin{align*}
D & \xrightarrow{hv} D^* \\
\rightarrow(D^+A^-) & \xrightarrow{hv} D + A \\
\text{exciplex}
\end{align*}
\]

Exciplex interaction may involve components that are independently bonded to a particular molecular framework but nevertheless interact in a through-space manner and, since exciplex formation is a special form of excited state quenching, luminescence studies afford a highly convenient experimental probe for molecular interactions in such systems, especially where the exciplex is itself a luminescing species. Exciplexes are often referred to as heteroexcimers by analogy with the well established tendency of aromatic molecules to form excimers - by collisional interaction of a ground-state molecule with a corresponding excited-state molecule. An important distinction between exciplexes and excimers is that the former exhibit substantial polar character with little or no geometric requirements for stabilisation; in contrast excimer formation appears to demand substantial eclipsing of the molecular framework involved and there is no resultant dipole moment.

POLYMER MISCIBILITY AS STUDIED BY NON-RADIATIVE ENERGY TRANSFER

It is well established that the negligible entropy of mixing of two polymeric species helps to ensure that most polymer pairs form incompatible mixtures (Ref. 1 & 2). Miscibility arises only when the enthalpy of mixing is favourable (i.e. negative or even zero). Morawetz and Avrami (Ref. 3) first reported an extremely elegant method of studying mixtures of polymers utilising the general principles of non-radiative energy transfer between chromophores located on different polymer molecules. Poly(methylmethacrylate) forms incompatible mixtures with copolymers of methylmethacrylate (MMA) and n-butylmethacrylate (BMA) when the BMA content reaches about 40 mol%. Incorporation of energy donor and acceptor 'labels' was easily achieved by free radical copolymerisation.

\[
\begin{align*}
\text{NMA} & \quad \text{AMA} \\
\text{CHOCOC=CH}_2 & \quad \text{CHOCOC=CH}_2 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

The naphthyl methacrylate (NMA) and the anthracene methacrylate (AMA) were copolymerised with MMA and mixtures of MMA and BMA respectively. Incorporation of the energy donor (naphthalene) and acceptor (anthracene) units was restricted to between 1.2 and 1.4 mol%. Fluorescence emission spectra of films cast from mixed polymer solutions gave varying ratios of donor to
acceptor emission \((\frac{I_D}{I_A})\) with \(I_D\) measured at 336nm and \(I_A\) at 408nm. Values of \(\frac{I_D}{I_A}\) increased steadily from about 0.1, for a polymer blend consisting of pMMA and p(MMA-co-10% BMA), to an essentially constant value of approximately 0.5 for polymer blends consisting of pMMA and p(MMA-co-BMA), in which BMA content increased beyond 40 mol%.

Evidently the fluorescence technique reflects a decrease in energy transfer efficiency with decreasing compatibility as the BMA content increases. It is also clear that the technique permits characterisation of the decreasing interpenetration of the polymeric components, rather than the simple compatible or incompatible classifications derived from other techniques, such as determination of glass transition temperatures.

Later work by Morawetz and his group (Ref. 4 & 5) has involved other donor units (e.g. carbazole) and polymer pairs studied include poly(styrene)-poly(2,6-dimethyl-1,4-phenylene ether) which is generally regarded as a fully miscible system. The original papers should be consulted for the experimental details and insight provided. Much wider utilisation of the Morawetz technique can now be anticipated as a result of the stimulus provided by these initial reports.

EXCIMER FLUORESCENCE AS A PROBE FOR POLYMER MISCIBILITY

As noted in the introductory section, experimental work in this area has been conducted largely by Frank and his collaborators (Ref. 6 & 7). The most important system reported as a guest (excimer forming) polymer is poly(2-vinylnaphthalene) (P2VN).

An excimer is an excited molecular complex which is formed between two identical aromatic rings, one of which is in a singlet electronically excited state, e.g. two suitably orientated naphthalene units in P2VN. Three nominal types of excimer forming sites may be envisaged for aromatic vinyl polymers such as P2VN involving:

(a) Intermolecular interaction between naphthalene rings on different polymer chains, important in films of homopolymer and in regions of aggregation (phase separation) in blends.

(b) Intramolecular interaction between naphthalene rings on non-adjacent chain segments; this may be regarded as a special case of (a) above.

(c) Intramolecular interaction between naphthalene units on adjacent chain segments.

Experimentally the population of suitable excimer forming sites is proportional to the ratio of excimer emission intensity \((I_E)\) to the emission from isolated naphthalene units \((I_N)\). For P2VN naphthalene emission is highly structured and may be measured conveniently at 340nm whereas the naphthalene excimer emission is broad and structureless and centred around 400nm.

In the work of Frank and collaborators (Ref. 6 & 7), the excimer probe (P2VN) is dispersed (0.2 wt%) in the host polymer. Typically in a series of methacrylate host polymers, values of \(\frac{I_E}{I_N}\) varied from about 0.4 for polyisopropylmethacrylate) and poly(sec-butylmethacrylate), to a value of 3.5 for poly(phenylmethacrylate). It is highly significant that a plot of
$I_E/I_N$ versus differences in solubility parameter (methacrylate-P2VN) gave a symmetric curve with a well defined minimum at zero difference in solubility parameter. Clearly the excimer probe is sensitive to the host matrix. Whereas nearest neighbour intramolecular excimer formation would not be expected to be greatly influenced by the nature of the host matrix, both long range intramacromolecular and any intermacromolecular excimer formation will be markedly influence by polymer coil expansion and intermolecular entanglements. In a good host medium there will be extensive interpenetration of guest and host chains causing the local concentration of aromatic rings to fall. In addition, expansion of the chain will reduce the likelihood of chain back bending. Both effects lead to a reduction in the values of $I_E/I_N$ and hence cause the minimum in the plot of emission intensity ratios versus differences in solubility parameters. One possible complication would be differential degrees of mixing of high and low molecular weights P2VN with the various poly(alkylmethacrylates).

In a later paper Semerak and Frank (Ref. 7) showed clearly that P2VN becomes progressively less miscible with monodisperse polystyrene as the host molecular weight increased up to a limiting value. Increases in the ratio $I_E/I_N'$ indicative of decreasing miscibility, consistently preceded visible signs of phase separation. These observations, like those of Morawetz reported earlier, are extremely significant and again point to the simplicity and sensitivity of the fluorescence technique for studies of polymer miscibility.

**EXCIPEX EMISSION AS A PROBE FOR POLYMER MISCIBILITY**

We have already noted that exciplexes are similar in nature to the photochemically excited states of charge transfer complexes but do not require ground state association for their formation. In fact much published work relating to exciplex interactions utilises molecules which in their ground state could, at best, only be described as extremely weak donors or acceptors. Exciplex intermediates probably occur in very many excited state quenching processes but are not easily detected except when the exciplex emits light (usually fluorescence) at longer wavelength than the emission of either donor or acceptor partner. Exciplex emission is therefore, a valuable probe for charge transfer processes in excited states and should be subject to the same kinds of polymer chain effects described for charge transfer excited states.

It has been known for almost a decade that the fluorescence emission of carbazole derivatives, including poly(9-vinylcarbazole) (PV$_{CZ}$) is quenched by many weak electron acceptors such as dimethylterephthalate (Ref. 12 & 13). In many cases the quenching is accompanied by the appearance of a typical, structureless fluorescence emission at wavelengths longer than those of monomeric carbazole fluorescence. A diagrammatic representation of competing quenching and emission processes for the carbazole-terephthalate system is given below. ($\nu > \nu' > \nu''$).

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  \[ \text{carbazole} \quad \text{tereph.} \]
  \[ \text{int.conversion} \quad \text{quenching} \]
  \[ \text{carbazole} \rightarrow (\text{carbazole}, \text{tereph}) \]
  \[ \text{carbazole emission} \rightarrow \text{carbazole + tereph.} \]
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Recent studies by Williams and collaborators (Ref. 14) have established, by flash photolytic techniques, that the transient absorption spectra of exciplexes from PV$_{CZ}$ and other carbazoles with dimethyl terephthalate are identical with the cation radical of the carbazole and the anion radical of the terephthalate.
Tazuke and his collaborators (Ref. 15 & 16) have shown that carbazole and terephthalate units may be incorporated into essentially oligomeric polyesters by suitable step growth reactions. These materials exhibited the usual exciplex emission at wavelengths longer than the emission edge of the carbazole chromophore and the total fluorescence spectra consist of mixtures of both carbazole and exciplex emissions.

In our own work we have synthesised copolymers of a variety of carbazole containing monomers with the terephthalate containing 2-(4-methoxycarbonyl-benzoyloxy)ethyl methacrylate. Emission from copolymers of N-vinylcarbazole with the terephthalate-containing methacrylate are interesting but difficult to interpret because of the influence of excimer forming sites in the PVC2 sequences. For simplicity of interpretation we synthesised copolymers of the carbazole-containing methacrylate (CARB) (Ref. 17) with methylmethacrylate (MMA) and with the terephthalate containing methacrylate (TEREPH) (Ref. 18).

All copolymers of CARB and TEREHP exhibit both carbazole and exciplex emission in dilute solution which is concentration independent and must, therefore, be intra-polymeric in origin. In contrast the same copolymers exhibit only exciplex emission in solvent cast films, implying a substantial inter-polymeric exciplex interaction with efficient energy migration between carbazole units prior to population of trap (exciplex) sites. Varying compositions of the copolymer have the effect of changing the ratio of carbazole to exciplex emission in dilute solutions of the various macromolecules but, in all cases, emission from films arises almost exclusively from the exciplex traps. Typical fluorescence emission spectra for one copolymer in solution and in film are given in Figure 3. It is interesting that the solution spectra suggest the occurrence of more than one type of exciplex emission. However the spectra, as recorded, are not corrected for wavelength sensitivity in the detector system and this point needs further clarification.

Observations of strong exciplex emission from copolymer films as indicated in Figure 3 prompted synthesis of copolymers having donor (carbazole) and acceptor (terephthalate) units for analysis as blends, along the lines pioneered by Morawetz (Ref. 3 - 5). However, in contrast to the energy transfer technique, observation of exciplex emission requires rather higher molar concentrations of donor and acceptor units. It is not possible therefore to assume any degree of compatibility, or otherwise, based on the data from more traditional techniques for the common polymers.

Several series of copolymers have been synthesised and fluorescence emissions spectra recorded for films cast from solutions of mixtures of copolymers. Some instability in fluorescence emission was observed, especially for the methacrylate series of copolymers, but reasonably consistent data may be obtained by essentially instantaneous recording of the exciplex emission intensity (I_E) at 420-450nm and monomeric carbazole emission (I_C) at 365nm.

In all cases excitation was at 330nm, a wavelength at which only the carbazole unit absorbs. Representative emission spectra for three types of polymer blends are given in Figure 4 and Figure 5 shows how the ratio I_E/I_C varies with blend composition.

As in the cases of energy transfer and excimer techniques, the data in Figure 5 show the sensitivity of luminescence probes in studying variation in
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interpenetration of polymer molecules. Apparently, for the compositions indicated, the butylacrylate-co-tereph polymer is completely compatible with the MMA-co-CARB polymer. Interestingly when the carbazole and the terephthalate are both incorporated at relatively low loadings in BMA, no exciplex emission can be detected for blend compositions having more than a 3:1 ratio of either copolymer. It remains to make measurements of compatibility by more usual techniques for the same blends of copolymers before any detailed interpretation can be attempted.

CONCLUSION

Three different fluorescence emission techniques may be used to probe for polymer-polymer interactions at a molecular level. Naturally, since cast polymer films are employed, there are likely to be variations in data as a result of the non-equilibrium nature of the blends. Similarly variation in molecular weight distribution between polymer components will have important effects on any data obtained. Nevertheless the fluorescence methods afford
highly convenient ways of studying inter-polymer penetration at levels much below those where phase separation would be expected.

The energy transfer technique has the advantage of requiring only very low molar concentrations (1%) of chromophores so that the data obtained may relate to the bulk polymer to which the labels are attached. However, energy transfer may occur over relatively long distances. In contrast, the exciplex emission technique requires contact between donor and acceptor units and is thus highly complementary to the energy transfer method. Unfortunately exciplex emission intensities are relatively low and hence rather large molar concentrations (5—15%) of electron donor and acceptor chromophores are required.

Excimer emission studies are perhaps the most sensitive to changes in polymer interpenetration but must necessarily be limited to a very narrow range of blend components.

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