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 concentra-
tions 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 collabor-
ators (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 informa-
tion 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

$$D^* + A \longrightarrow D + A^*$$

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 associat-
ed 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:

$$D^* \longrightarrow D + h\nu_D \qquad\qquad \text{emission}$$

$$A + h\nu_D \longrightarrow A^* \qquad\qquad \text{reabsorption}$$
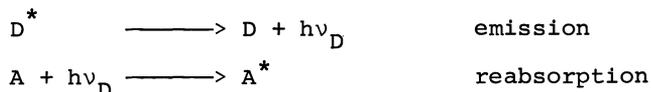
In this case, the donor serves as a "molecular lamp" capable of irradiating
light into its environment. If a photon, $h\nu_D$, happens to be absorbed by A,

then a net transfer of the type $D^* \longrightarrow A^*$ 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 inter-
action 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 $A \longrightarrow A^*$.

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 isoenergetics which deactivate D^* and excite A may be deduced
from knowledge of the electronic emission spectrum corresponding to the
$D^* \longrightarrow D$ transition and the absorption spectrum corresponding to the $A \longrightarrow A^*$
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:

$$E = R_o^6 /R_o^6 + r^6); \quad R_o^6 = (8.8 \times 10^{25}) \, J \, n^{-4} \, \kappa^2 \, \phi_D^o$$

where   r = distance between energy donor and acceptor

     R_o = characteristic distance at which half of the excitation
         energy is transferred

J = overlap integral between the emission spectrum of the
       donor and the absorption spectrum of the acceptor

n = refractive index of the medium

κ^2 = function of the mutual orientation of donor and acceptor
       transition moments

ϕ_D^O = fluorescence quantum yield of the donor in the absence
       of the acceptor.

In favourable cases, R_O 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 EXCIMER 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.

hν

L___→M — M — M — M — M* etc
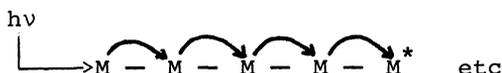
Energy migration along the polymer chain may continue until a suitable
trapping process is encountered. A particularly important trap for singlet
state excitation energy in polymer is called an excimer. If an excited donor
molecule D^* comes into the proximity of a ground state molecule D, the
formation 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-macromolecul-
arly 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
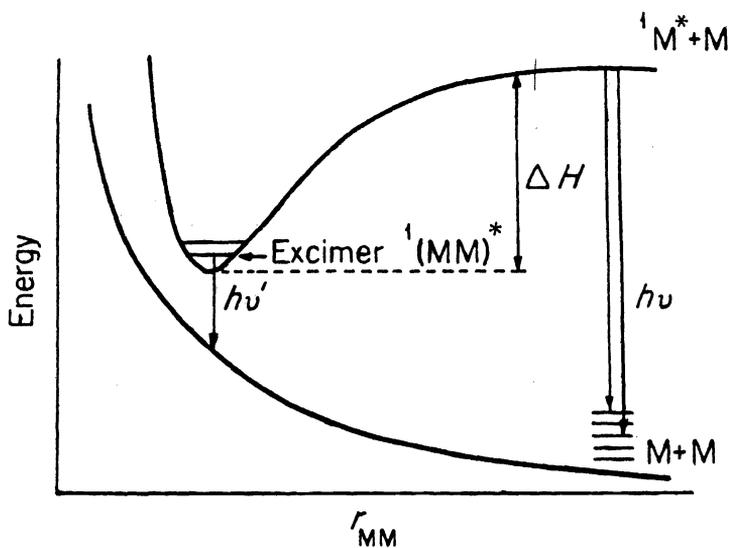
Fig. 1.   Schematic energy surfaces showing excimer formation
          and emission.   The emission to the non-quantised
          ground state is structureless.
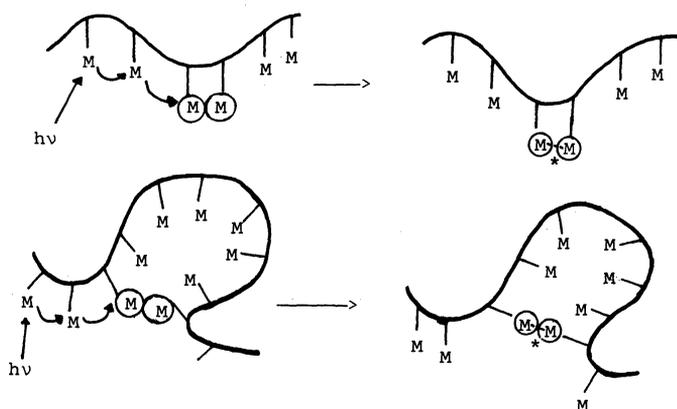
Fig. 2.   Schematic description of excimer formation by energy
          migration between nearest neighbours along a polymer
          backbone and by intramolecular interactions between
          non-nearest neighbours (Ref.9).

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 com-
ponent 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 very 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 implys 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:

$$D \xrightarrow{h\nu_D} D^* \underline{\quad A \quad}$$

$$\xrightarrow{\quad} (D^+A^-)^* \xrightarrow{h\nu'} D + A$$
$$\text{exciplex}$$

$$A \xrightarrow{h\nu_A} A^* \underline{\quad D \quad}$$
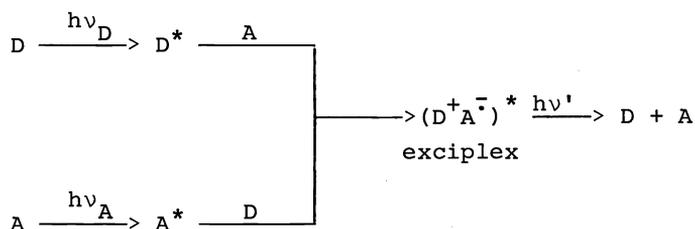
Exciplex interaction may involve components that are independently bonded to
a particular molecular framework but nevertheless interact in a through-
space manner and, since exciplex formation is a special form of excited state
quenching, luminescence studies afford a highly convenient experimental probe
for molecular interactions in such systems, especially where the exciplex is
itself a luminescing species. Exciplexes are often referred to as hetero-
excimers 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.

NMA
$CHOCOC=CH_2$ CH_3 CH_3

AMA
$CHOCOC=CH_2$ CH_3 CH_3
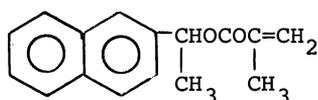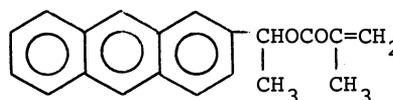
The naphthyl methacrylate (NMA) and the anthracene methacrylate (AMA) were
copolymerised with MMA and mixtures of MMA and BMA respectively. Incorpora-
tion of the energy donor (naphthalene) and acceptor (anthracene) units was
restricted to between 1.2 and 1.4 mol%. Fluorescence emission spectra of
films cast from mixed polymer solutions gave varying ratios of donor to

acceptor emission ($^I D/I_A$) with I_D measured at 336nm and I_A at 408nm.
Values of $^I D/I_A$ 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 compat-
ible 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-vinylnapthalene) (P2VN).
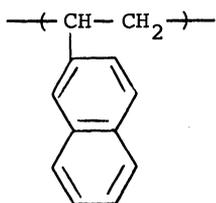
P2VN

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 proportion-
al 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 I_E/I_N varied from about 0.4 for poly-
isopropylmethacrylate) 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 liklihood 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.

EXCIPLEX EMISSION AS A PROBE FOR POLYMER MISCIBILITY

We have already noted that exciplexes are similar in nature to the photo-chemically 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) (PVC$_z$) 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 diagramatic representation of competing quenching and emission processes for the carbazole-terephthalate system is given below.   ($h\nu > h\nu' > h\nu''$).

```
                 carbazole                      carbazole + tereph.
                     ↑                                  ↑
                     | int.conversion                   | quenching
                     |                                  |
carbazole ──hν──> (carbazole)* ──terephthalate──> (carbazole, tereph)*
                     |                                  |
           carbazole | -hν'                    -hν'' | exciplex
           emission  |                                 | emission
                     ↓                                  ↓
                 carbazole                      carbazole + tereph.
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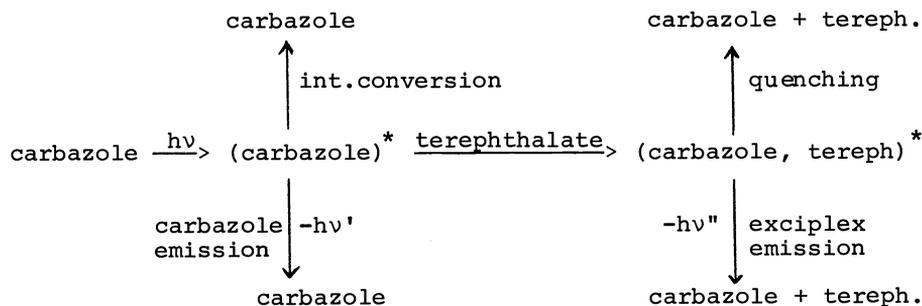
Recent studies by Williams and collaborators (Ref. 14) have established, by flash photolytic techniques, that the transient absorption spectra of exciplexes from PVC$_z$ and other carbazoles with dimethyl terephthalate are identical with the cation radical of the carbazole and the anion radical of the terephthalate.

Tazuke and his collaborators (Ref. 15 & 16) have shown that carbazole and
terephthalate units may be incorporated into essentially oligomeric poly-
esters 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 PVC_Z
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 TEREPH exhibit both carbazole and exciplex
emission in dilute solution which is concentration independent and must,

$$CH_2=CCOOCH_3 \quad (CH_3)$$

MMA

CARB: carbazole $N-CH_2CH_2OCOC(CH_3)=CH_2$

TEREPH: $COOCH_3$; $COOCH_2CH_2OCOC(CH_3)=CH_2$

$$CH_2=CHCOOBu^n$$

BA
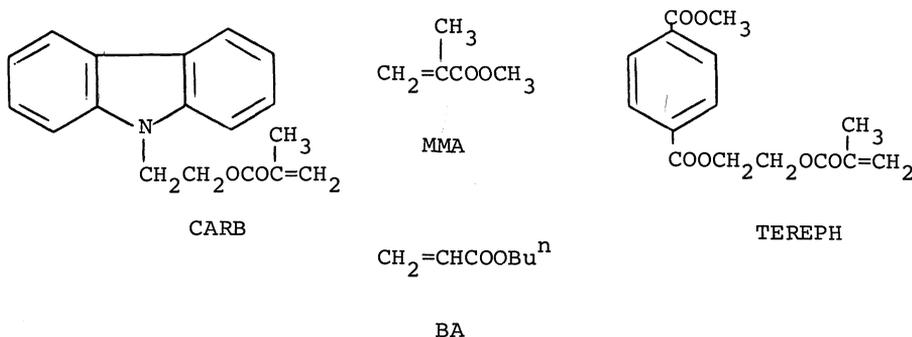
therefore, be _intra-polymeric_ in origin. In contrast the same copolymers
exhibit only exciplex emission in solvent cast films, implying a substantial
inter-polymeric exciplex interaction with efficient energy migration between
carbazole units prior to population of trap (exciplex) sites. Varying
compositions of the copolymer have the effect of changing the ratio of
carbazole to exciplex emission in dilute solutions of the various macro-
molecules 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
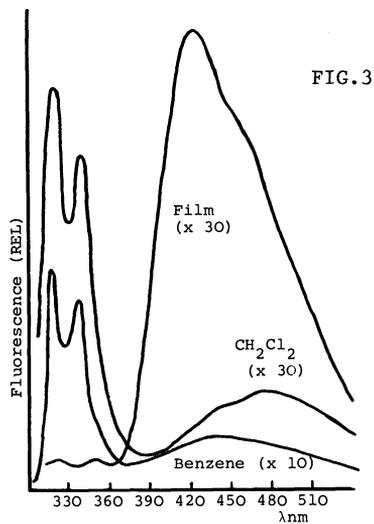
Fig.3. Exciplex Emission Spectra of Copolymer Carb (21%)-co-Tereph (79%) 10^{-4}M [Carb].
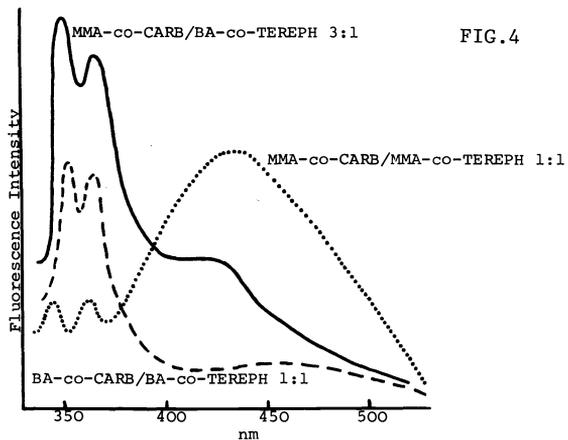
Fig.4. Emission Spectra of Cast Polymer Films.
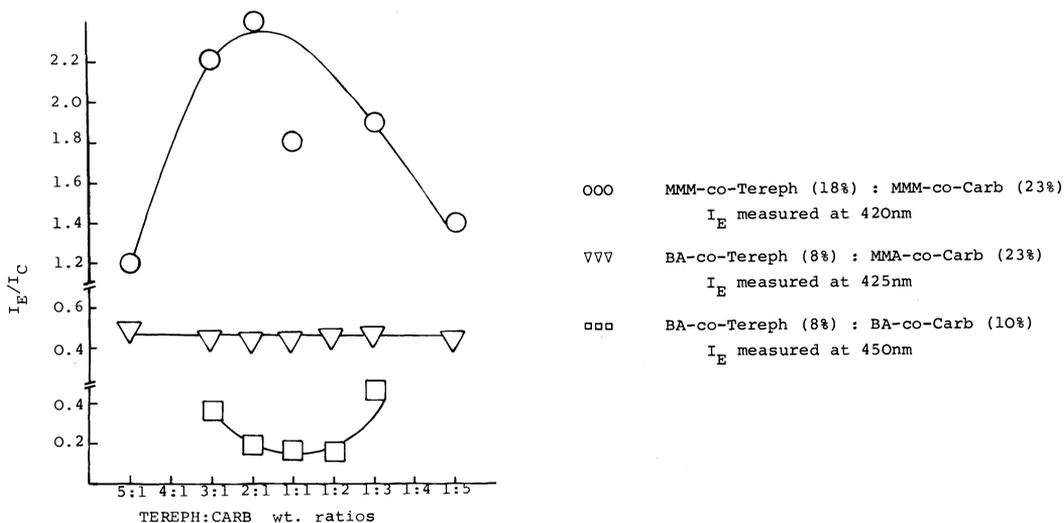
Fig.5. Exciplex/Carbazole Emission Ratios as a Function of Blend Composition

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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