

EMISSION SPECTROSCOPY AND ELECTRONIC ENERGY MIGRATION AND TRANSFER IN POLYMERS

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ABSTRACT

Emission spectroscopy is used to identify excited states in aromatic organic polymers and to follow the depletion processes of these states. Energy migration and transfer processes within individual polymer molecules and through bulk polymer samples can be separated and assessed through an examination of concentration effects on the emission spectra. In aromatic polymers such as polystyrene, singlet migration and excimer formation is highly efficient in properly oriented individual polymer molecules; in the bulk polymer, excimer formation competes with other singlet trapping modes. Triplet energy migrates not only within polymer chains but also across chains in the bulk polymer. In the bulk polymer this energy can be trapped by non-polymer impurities, giving impurity phosphorescence, or by chain impurities or defects, generating delayed exciplex fluorescence as well as delayed fluorescence different from that observed in dilute solutions. From these results, it can be inferred that the photochemistry of a polymer may often reflect the photochemistry of a trap or defect.

INTRODUCTION

Chemical changes induced by light in organic polymer systems may be divided into two broad categories: those resulting from the absorption of light by the polymer itself and those taking place as a consequence of light absorption by molecules other than those of the polymer. In the latter category would be included polymer reactions that occur because a photosensitizer has been added to the system, chemical attacks on polymers by photoexcited molecules, or reactions of polymers with free radicals formed by a photodissociation of some constituent of the system. In this paper, polymer photochemistry will be considered primarily in terms of the events occurring after the polymer itself absorbs light energy prior to the primary photochemical event. Our concern, then, will be with the excited states thus produced and with the manner in which these excited states relieve themselves of their excess energy. In addition to photodissociation, which would constitute the primary *photochemical* process of the polymer molecule, there are many radiative and non-radiative routes of excited state depletion. Each of these depletion processes takes place at the expense of the sum of the remaining processes; it is therefore important in the ultimate control of the photochemistry to understand the nature of the excited states in polymers

and, as will be seen, the physical locus of these states within the individual polymer molecule or within the solid polymer.

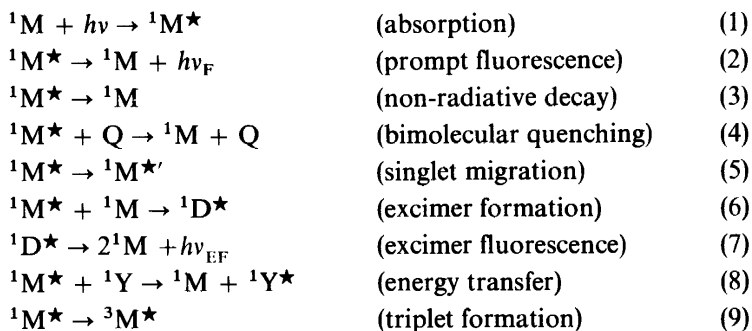
The radiative processes of interest are suitably observed by emission spectroscopic methods. These photophysical processes and the methodology involved have been extensively reviewed both generally¹⁻³ and in a polymer context⁴. Aromatic polymers such as polystyrene (PS), poly(1-vinylnaphthalene) (P1VN), and poly(2-vinylnaphthalene) (P2VN), and copolymers of 1-vinylnaphthalene and styrene (P1VN/S) or methyl methacrylate (P1VN/MMA) are suitable subjects for investigation, since their emissions occur in easily accessible spectral regions. The spectroscopic properties of the phenyl and naphthyl chromophores are quite well known, and small molecule model compounds are readily available. In the present work, the properties of these chromophores will be considered within the context of several polymer environments: (1) isolated in a non-interacting environment; (2) on polymer chains in which interaction with an adjacent chromophore on the same chain is possible; (3) on polymer chains in which interaction between chains is possible; and (4) in environments in which a relatively few polymer chains contain defects or bound impurities or in which an impurity not part of any polymer chain is present. The fourth environment is probably the most important, for it represents the condition most commonly encountered in practical polymer systems.

To some extent, the phenomena occurring in these environments can be separated by the degree of separation of chromophores and of the chains upon which they are situated. Solutions of a given polymer in an 'inert' solvent such as poly(methyl methacrylate) (PMMA) or in a low-temperature glassy matrix exemplified by 1:1 tetrahydrofuran/diethyl ether (T/E) allow changes in the separation of individual polymer chains. With sufficiently dilute solutions, phenomena within individual chains can be observed, and the effect of small quantities of impurities can often be neglected. In concentrated solutions or in the neat polymers, both intrachain and interchain effects would be expected, and the influence of impurities would be maximized. Chromophore concentrations can be varied in another way through incorporation into copolymers, the second constituent of which may be interacting or non-interacting with the chromophores of interest. As long as an emitting chromophore is present, each polymer or copolymer system will yield emission spectra that are, in various aspects, concentration-dependent or concentration-independent, and information concerning the point or points of interaction of the excited species can be adduced. The excited species themselves can be separated and identified through a time-resolution of the spectra and through an analysis of the decay of the bands. Events kinetically dependent upon the initially formed singlet excited states will be much shorter-lived than those depending upon the relatively long-lived triplet states. A single non-interacting excited state will decay exponentially. The dependence of an emission upon the intensity of the exciting light can be used to separate monophotonic from biphotonic processes.

Each of these tools of the emission spectroscopist is available to the polymer chemist. In this paper, their application to specific polymer systems will be reviewed with the objective of identifying the true 'chemical' reactant in subsequent photochemical transformations of the polymer.

SINGLET PRODUCTION AND DEPLETION

Absorption of a photon by an aromatic polymer produces first a chromophore in an excited singlet state. Subsequent events involving these singlets have been considered and reviewed⁴ by many authors and will not be dealt with in detail here. The most important of these processes in polymers are:



The superscripts 1 and 3 here denote the singlet and triplet states, respectively, of an individual chromophore such as a phenyl group in PS; the star indicates the lowest excited state.

Prompt and excimer fluorescence are the major short-lived (lifetimes are usually less than 10^{-6} sec) emissions observed in the spectra of aromatic polymers. Prompt fluorescence will be seen where the opportunity for interaction between the excited singlet and another chromophore is restricted,

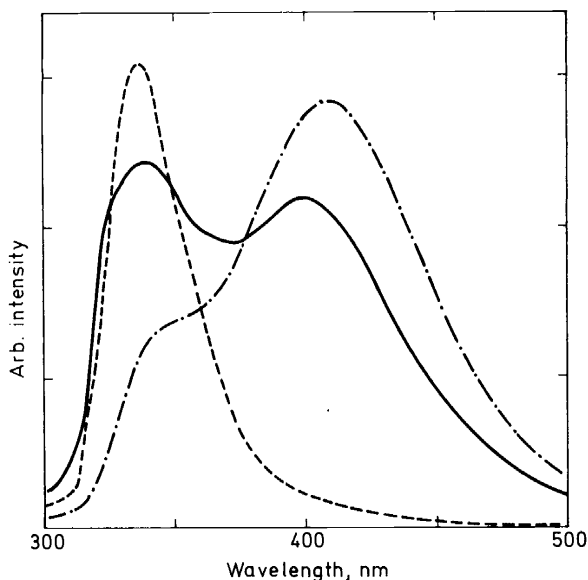


Figure 1. Prompt emission spectra of 10^{-6} M (1VN) solutions in T/E at 25° : ----- 1% 1VN P1VN/MMA; ——— 62% 1VN P1VN/MMA; -·-·-·- P1VN; λ_{ex} 260 nm. (In this and the other figures, absolute intensities are not comparable.)

as in a P1VN/MMA copolymer containing a small proportion of incorporated 1VN, as shown in *Figure 1*. The spectrum of the one per cent copolymer is almost identical to that of a solution of a model compound, 1-ethylnaphthalene. As the proportion of 1VN in the copolymer increases, the prompt fluorescence intensity decreases and there is observed a new structureless emission, shifted about 6000 cm^{-1} to lower energies. This is excimer fluorescence, due to processes 6 and 7. The excimer is not observable in the absorption spectrum because its ground state is dissociated. Prompt emission from dilute solutions of the homopolymer itself at room temperature is almost entirely that from the excimer⁵. Similar emission has been observed from other vinylaromatic polymers. Studies with model compounds indicate that the excimer forms as a result of interaction (process 6) between adjacent chromophores on a polymer chain in which the chromophores are separated by a three carbon atom segment⁶. The interaction, based on analogy with aromatic hydrocarbons, involves a nearly face-to-face conformation of the two rings. In certain cases, notably poly(acenaphthylene)⁷, the formation of the excimer must take place intramolecularly between rings far removed from each other on the chains; the interaction probably occurs through the close approach of chromophores on adjacent turns of the polymer coil.

Intramolecular excimer formation in polymers is, of course, temperature-dependent. Activation energies for this type of excimer formation are somewhat less than those for the corresponding two-unit model compounds and much less than for the corresponding aromatic hydrocarbon. In a fluid solution, polymer segmental motion must allow many conformations favourable to excimer formation. The nearly 100 per cent efficiency of excimer formation at room temperature in solutions of polymers such as PS indicates rapid intramolecular migration of singlet energy to sites favourable to excimer formation, and these act as energy traps. As the temperature is lowered, segmental motion is reduced, and fewer excimer sites are available. The conformations leading to excimer formation can, in effect, be frozen in place. The temperatures at which rigidization occurs fixes the excimer sites then existing, and below that temperature the excimer spectrum is largely independent of temperature⁷. Thus, dilute solutions of PS or P1VN in T/E show no excimer fluorescence at 77°K ⁵; at the temperature of glass formation, about 110°K , excimer fluorescence is also not observed. These same polymers as neat films or as dilute solutions in poly(methyl methacrylate), both formed as solids at room temperature, have essentially an unchanging excimer spectrum as the temperature is reduced to 77°K even though the quantum yield for prompt fluorescence does increase through this range⁷.

One additional process involving excited singlets has been observed with small molecules but has thus far not been reported for polymers. This process is termed 'exciplex' formation; it is analogous to excimer formation but results from interaction between molecules of different species. Like the excimer, its ground state is dissociated.

At the temperatures at which solid vinylaromatic polymers are used in practice, it is clear that the excimer state is a most important singlet excited state, and it must exert a profound effect on the singlet photochemistry of the polymer. Nonetheless, the sites for excimer formation must be viewed as simply one kind of energy trap in competition with other traps (process 8)

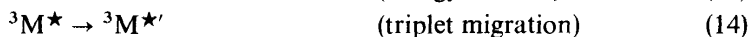
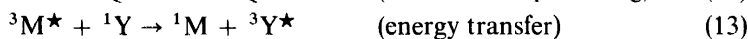
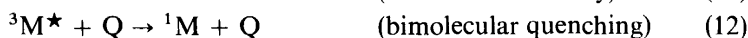
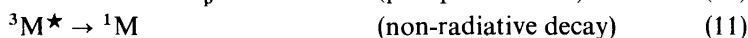
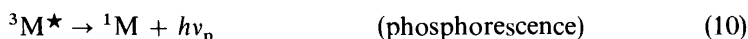
as shown by Klöpffer⁸ with poly(*N*-vinylcarbazole). In dilute solutions, there is little opportunity for singlet energy migration (process 5) from chain to chain, and thus traps other than excimer sites may be unimportant unless they appear on almost every chain⁷. In the neat polymer film, however, such interchain migration is possible even during the very short singlet lifetime. If a suitable trap is present in sufficient concentration, it is also probable that singlet energy transfer from the excimer to the second trap will occur.

The degree to which excimer formation takes place also affects the triplet quantum yield, since the excited singlet population is correspondingly reduced⁷. Thus, not only the photochemistry based on the excited singlet state, but also that based on the long-lived triplet state, is strongly influenced as well. Again, the importance of the excimers in polymer photoreactions is emphasized.

TRIPLET PRODUCTION AND DEPLETION

Triplet production in aromatic molecules by direct absorption of light is spin-forbidden and therefore of low efficiency. It may be an important process where intense light sources such as a flash or a laser are used. Most triplets in the polymers under consideration will be formed through process 9, intersystem crossing, or through energy transfer from some other constituent in the system. Triplet lifetimes are quite long (10^{-5} sec up to 100 sec) relative to singlet lifetimes (typically 10^{-9} to 10^{-6} sec), and thus the potential for photochemical reaction through the excited triplet state may be much higher than from the excited singlet state. Of perhaps greater importance where energy migration is possible, the longer triplet lifetimes allow greater migration distances than for the excited singlet. A wider variety of interactions involving triplets can therefore take place: additional excited states are formed, and each generates its own emission.

Among the more important monophotonic processes involving triplets are :

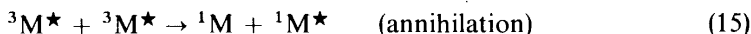


Of these, only processes 10 and 13 yield discrete spectra, the first as a natural property of the chromophores themselves and the second resulting from the presence of a triplet energy acceptor, which in turn emits its own phosphorescence. The energy transfer process can take place by any of several mechanisms (see, for example, ref. 2), but in aromatic hydrocarbons one of the most common is that which can occur by electron exchange within distances of 10 to 20 Å. A contact energy transfer process, diffusion-controlled in solutions of small molecules, is also frequently observed. In aromatic polymers, the counterpart of the contact transfer process is seen in dilute solutions of copolymers such as P1VN/S containing a small proportion of 1VN, in which most of the energy is absorbed in the long S-segments and

emitted as phosphorescence from the short 1VN-segments after migration (probably, but not certainly, by process 14) through the chain of phenyl groups followed by a highly efficient transfer (process 13) to the naphthyl group as a triplet acceptor⁹. The equivalent transfer process is not observed in the equivalent mixture of homopolymers.

These emission spectra are examples of *delayed* emissions, so-called because they can be observed at a point in time much removed from that at which the *prompt* emissions (fluorescence, excimer fluorescence) have decayed to negligible intensities. The difference derives from the long lifetime of the triplet state. These spectra are easily obtained by employing a rotating shutter in the spectrometer; this allows the observation of the emission after the exciting light has been cut off and at the same time eliminates short-lived emission and scattered light. A concomitant disadvantage, process 12, is also a result of the long triplet lifetime. Triplets (and therefore phosphorescence) are frequently readily quenched by oxygen, for example, and therefore phosphorescence is rarely observed in aerated fluid solutions; other impurities may also effectively quench phosphorescence in fluid solution. As a result, most delayed emission spectra are obtained at low temperature (typically that of liquid nitrogen) in rigid media. Phosphorescence from polymers such as PS or P1VN can be seen in dilute solutions in T/E glasses at 77°K, for example, or in films consisting of solutions in PMMA, although it is difficult to obtain PMMA free of interfering acceptor emission¹⁰.

Other triplet processes are of great significance in the analysis of the delayed emission spectra of aromatic polymers. The most important of these processes is that of triplet-triplet annihilation, process 15, which results in the formation of an excited singlet and a ground-state singlet:



The excited singlet can fluoresce just like one formed by direct excitation, but the observed lifetime of the emission will depend on the square of the triplet concentration; it is therefore called *delayed fluorescence* (a second type of delayed fluorescence results from the absorption of a second photon by the triplet, exciting it to an upper level, ${}^3M^{**}$, from which it crosses back to the ${}^1M^*$). In addition, the formation of an excited singlet state chromophore and a ground state singlet during triplet annihilation presents a potential for excimer formation. The resulting emission is termed *delayed excimer fluorescence*, and it, too, will depend on the square of the triplet concentration. *Delayed exciplex fluorescence* has also been observed in a single report¹⁰ in polymers.

Polymer systems derived from 1- and 2-vinylnaphthalene and from styrene provide a suitable series of prototype materials with which to follow the fate of triplet energy by means of delayed emission spectra. It is of particular interest to contrast the results obtained from dilute solutions with those from concentrated solutions or films of the neat polymers.

Dilute ($10^{-3}M$ or less in chromophore concentrations) solutions of PS, P1VN, or P2VN in T/E glasses at 77°K produce the phosphorescence spectra expected from the respective chromophores. Relative to the appropriate model compounds, the phosphorescence spectra of the homopolymers are somewhat less intense, shifted slightly to longer wavelengths, and the

phosphorescence lifetimes are somewhat shorter. The vinylnaphthalene homopolymers also generate a delayed fluorescence that has been shown¹¹ to result from triplet-triplet annihilation due to migrating triplets within individual polymer chains. The absence of an analogous delayed fluorescence from dilute PS solutions may be the consequence of a low quantum yield for the emission. Intramolecular energy migration does occur in PS, however,

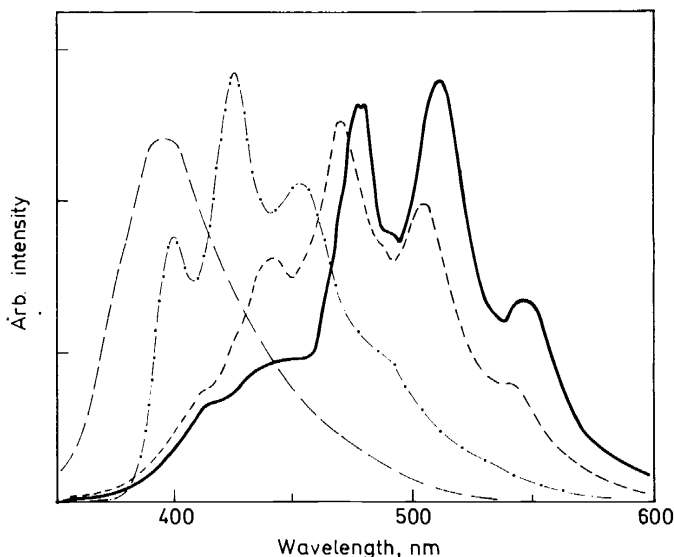


Figure 2. Delayed emission spectra of PS films at 77°K: — sodium naphthalene initiation; - - - phenyl lithium initiation; - · - · thermal initiation; - - - 10^{-3} M solutions in T/E; λ_{ex} 260 nm.

as demonstrated by the delayed emission spectra of a series of P1VN/S copolymers, from which only the emission from the 1VN-segments was observed even though a major proportion of the incident light was absorbed by the S-segments⁹. If the 1VN-segments in these copolymers are sufficiently long, delayed fluorescence is also observed. An analysis of the decay of these emissions suggests that the phosphorescence originates near the ends of the 1VN segments, while the delayed fluorescence results mostly from the annihilation of freely migrating triplets in the copolymers. In the P1VN homopolymer, this annihilation appears to take place at a variety of energy traps or defects present in most of the polymer chains¹².

It might be expected that the delayed emission spectrum of a solid film of a polymer would be similar to that of a dilute solution of the same polymer with any emissions due to interchain interaction superimposed on the intrachain spectra. In practice, this is not so. Rather, the spectrum of impurities is commonly seen. For example, Figure 2 compares the spectra of films of three samples of PS initiated by various means with the spectrum of dilute solutions of the same samples. The latter spectrum is that of typical PS

phosphorescence from non-interacting chains, and it is similar to the phosphorescence from a dilute solution of toluene. The spectrum of the sodium naphthalene-initiated PS film closely approaches that of naphthalene; the other two film spectra are unidentified, but they are clearly also not spectra expected from PS itself.

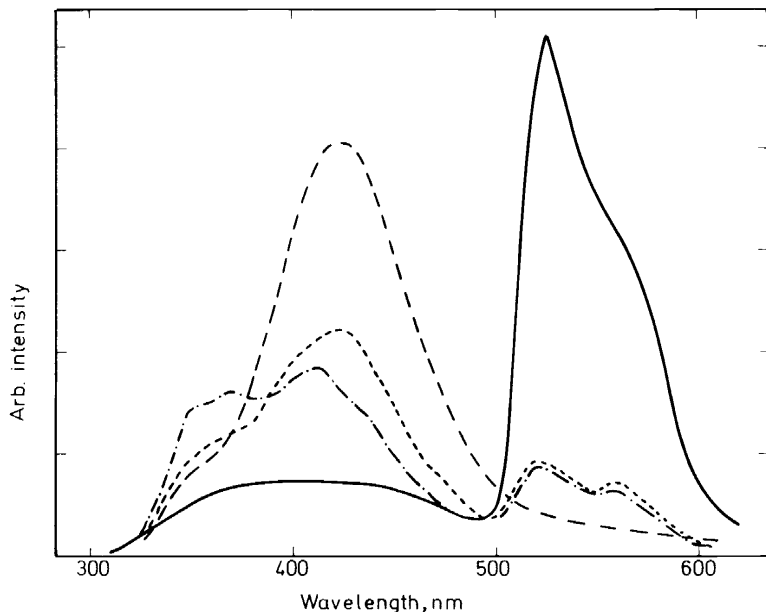


Figure 3. Delayed emission spectra of P1VN films at 77°K: — P1VN-III; - - - P1VN-IV; ····· P1VN-VII; - · - · P1VN-X; VII was initiated by benzoyl peroxide, the others by azodiisobutyronitrile; λ_{ex} 290 nm.

Sample history similarly influences the results with P1VN and P2VN. Since impurities could not be detected in the absorption spectra, and the excitation spectra are those of the polymers, it is evident that energy transfer and migration processes are involved. A general investigation of triplet depletion routes in solid films of these polymers and in the P1VN/S series was therefore undertaken¹⁰. The observed delayed emissions fall qualitatively into three spectral regions: (a) 325–375 nm, identified with delayed fluorescence; (b) 375–450 nm, identified with delayed exciplex fluorescence; and (c) > 450 nm identified with phosphorescence.

In Figure 3, the delayed emission spectra of four films from various samples of amorphous P1VN are given. The spectrum of a P2VN sample prepared by azodiisobutyronitrile initiation is similar to that of P1VN-X. Methanol extraction of the P1VN-III sample left a polymer whose spectrum also is similar to P1VN-X. Analogous results are obtained with P1VN/S

copolymers. For example, in *Figure 4* is given a 'spectral history' of a copolymer containing 34 per cent 1VN-derived units. The original polymer film gave a delayed emission spectrum much like that of a P1VN-III film; reprecipitation gave a polymer whose film spectrum resembles that of P1VN-X. This material on standing in air developed a spectrum containing

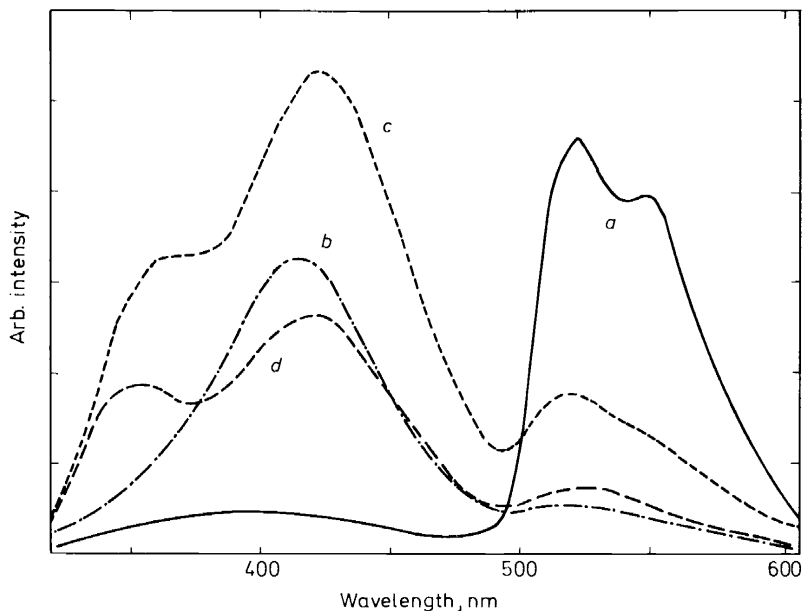


Figure 4. Delayed emission spectra of 34% 1VN P1VN/S films at 77°K: (a) purified polymer after two years storage in air and darkness; (b) polymer of (a) after two reprecipitations; (c) polymer of (b) after standing two months; (d) polymer of (c) after further reprecipitation; λ_{ex} 230–290 nm.

delayed emission in the 350 nm region; further purification did not eliminate the source of this emission. From these results, it is concluded that the phosphorescence in the 450–600 nm region of these spectra originates in an extractable impurity; once this impurity is removed, the major delayed emission occurs in the 375–450 nm region, with a smaller peak near 355 nm.

The spectra were also followed as a function of polymer concentration. Three such spectra are shown in *Figure 5* for P1VN-IV, which emphasizes the point that the spectral bands observed in the neat film are not associated with entities in every chain. Not only are the spectral profiles different, but the phosphorescence in the 450–600 nm region decays exponentially with a lifetime of 2.0 sec for the 10^{-3} M solution, but for the film, the phosphorescence decays non-exponentially with a lifetime of less than 0.2 sec. The same kind of change in spectral profiles and phosphorescence lifetimes were observed through the series of P1VN/S copolymer films; the P1VN/S films containing

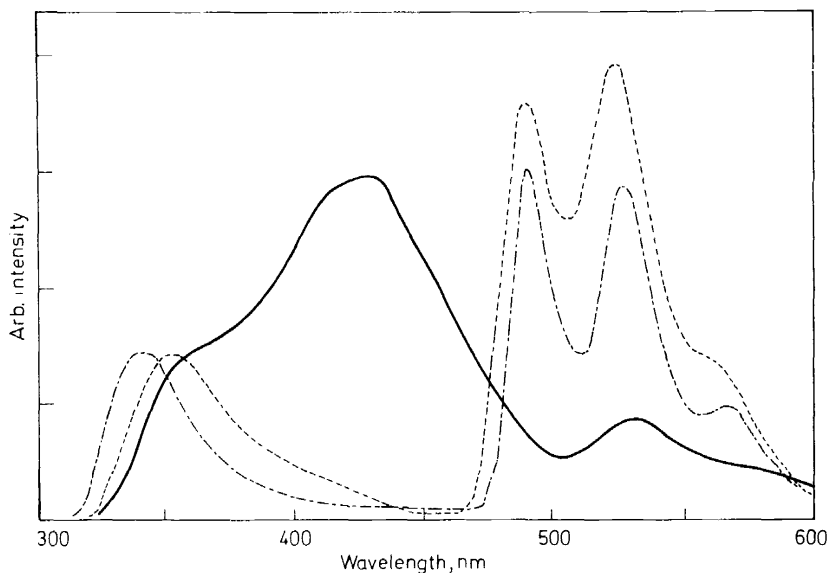


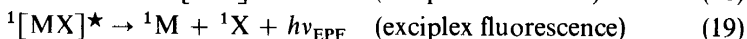
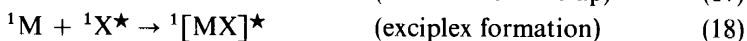
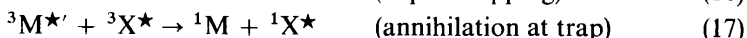
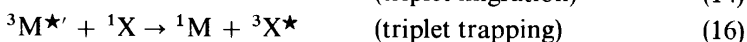
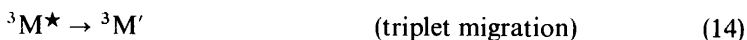
Figure 5. Delayed emission spectra of P1VN-IV at 77°K: ——— neat film; - - - - 0.32M (1VN) in T/E; - · - · - 10^{-3} M (1VN) in T/E; λ_{ex} 290 nm.

less than 8 mole per cent 1VN gave spectra similar to that of a dilute solution of P1VN but without the 340 nm emission. Emission intensity measurements as a function of incident light intensity showed that while at any concentration the phosphorescence in the 450–600 nm region is monophotonic, the delayed emissions in the 325–375 nm and 375–450 nm regions are biphotonic and therefore likely to result from triplet–triplet annihilation.

Spectra obtained from 1-ethylnaphthalene as a function of concentration in T/E gave similar results, except that no delayed emission appeared in the 375–425 nm region. As the concentration increased from 0.5 to 1.0M, both the phosphorescence intensity and lifetime abruptly dropped, the profile of the phosphorescence changed as it did with P1VN, and delayed fluorescence was observed at 340 nm. In part, these results may originate with the formation of microcrystallites in the more concentrated solutions^{13, 14}. However, the observation of a new phosphorescence at just the concentrations where the average intermolecular distance (15 Å at 1M) makes triplet migration and transfer possible by an exchange mechanism suggests that such processes are indeed operating and that in concentrated solutions, the emission originates with an impurity. In the polymer and copolymer films, microcrystallites are not likely to be present, and the results are qualitatively similar to those with 1-ethylnaphthalene. Indeed, in the P1VN/S series, the changeover from a naphthalenic phosphorescence to the unknown short-lived phosphorescence occurs between the 8 and the 22 mole per cent 1VN copolymers, for which the calculated statistical distances between maximally dispersed 1VN units in the films are 15 Å and 10 Å, respectively.

The neat polymer films thus appear to contain two kinds of triplet-trapping entities, and both are present at very low concentrations. The first is extractable and therefore is not associated with any polymer chain. Triplet migration (process 14) along and across chains followed by transfer by an electron exchange mechanism results in trapping at the impurity, which in turn emits the short-lived phosphorescence observed in the 500–550 nm region. In addition, some annihilation (process 15) also occurs at the impurity, yielding impurity delayed fluorescence at about 355 nm. The spectral properties of the impurity are suggestive of a naphthalenic carbonyl compound.

Removal of the extrachain traps allows triplet trapping at sites associated with a few polymer chains. These may be chain impurities or simply some kind of a physical defect in a few chains; an analogy may be drawn to the defects induced by pressure in a naphthalene crystal, which leads to broad delayed excimer fluorescence in the 375–450 nm region¹⁵. In the polymer chain, the close packing of chromophores allows facile interaction between a trap excited state and an adjacent chain chromophore; the equivalent interaction would be far less likely in neat 1-ethylnaphthalene. The biphotonic delayed emission in the 375–450 nm region observed in the polymer spectra is somewhat displaced to longer wavelengths from the prompt excimer fluorescence, and therefore the emission is identified with delayed exciplex fluorescence occurring as a result of the following sequence of processes:



where ${}^3M^*$ represents a migrating triplet and X is a chain trap. Accompanying this emission is delayed fluorescence from ${}^1X^*$.

With dilution, the interchain processes cannot occur because of large chain separations, and therefore the spectra observed in the polymer films are not seen in the solutions. The spectra of the latter are those generated from the average polymer chain and little transfer to impurities in very low concentrations can take place.

To the extent that the photochemistry of P1VN and similar aromatic polymers is a triplet process, it is clear that impurities, either separate from the polymer or as parts of a few chains, may be a controlling factor in solid polymers. As long as the absorbed energy localizes at a trap, further reactions are likely to be those of the trap rather than the polymer itself. The implications to such polymer photoreactions as degradation are clear: the impurity traps may act as stabilizers or they may be the locus of degradation. Indeed, a pure polymer might be less stable than an impure one. A high degree of plasticization with a photo-inert material might serve to separate chains sufficiently that trapping phenomena may be reduced. All of these factors should be considered in the molecular design of polymer systems.

SUMMARY

Emission spectroscopy has been used with aromatic polymers to identify the more important excited states and some of the processes by which they are depleted. The excited singlet state generally undergoes migration and either eventual intramolecular conversion to the excimer state or trapping. The excimer state formation reaction is temperature-dependent in fluid solution, but in a rigid glass or solid polymer the excimer sites are frozen in. Triplet state formation in polymers is in competition with excimer formation. In solid aromatic polymers in which migration can occur, triplet depletion is largely controlled by the presence of extraneous trapping impurities; in their absence, triplets are trapped by impurities in a few chains. Dilute solutions of the same polymers show the excited state formation and depletion processes of the average polymer chain, and impurities in low concentration are relatively unimportant.

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