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Triplet Processes
in
Polymer Matrices

A Thesis

presented for the degree of

DOCTOR OF PHILOSOPHY

in the Faculty of Science of the

University of St. Andrews

by

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September 1982

United College of St. Salvator
and St. Leonard, St. Andrews.

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by me, and that it has not been submitted in any previous application for a Higher Degree.

This thesis describes results of research carried out at the Department of Chemistry, United College of St.Salvator and St.Leonard, University of St.Andrews, under the supervision of Dr. J.R.MacCallum since the 1st October, 1979.

Kenneth T. Moran.

CERTIFICATE

I hereby certify that Kenneth Thomas Moran has spent twelve terms of research under my supervision, has fulfilled the conditions of Ordinance No. 12 and Resolution of the University Court 1967, No. 1, and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Dr. J.R.MacCallum.

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SUMMARY

The phosphorescence decay of a selection of aromatic compounds, spanning a wide range of spectral properties, was studied as a function of polymer host environment. The influence of the polymer matrix on the decay characteristics was considered in terms of the exponential life-time of the additive, establishing differences between aliphatic and aromatic polymers. Furthermore, there was a distinct correlation between the observed behaviour and the value of ΔE_{D-A} , the triplet energy level difference between additive (donor) and polymer (acceptor). The results were interpreted by invoking a thermally assisted triplet-triplet electronic energy transfer mechanism to be operative between donor and acceptor. Increased efficiency of transfer was associated with those donors possessing a high triplet energy level relative to that of the polymer.

The mode of phosphorescence decay was found to be both matrix specific and temperature dependent. Temperature dependent deviation from single exponential decay was only observed for high energy triplet donors and attributed to a bimolecular interaction occurring as a consequence of triplet-triplet electronic energy transfer to and triplet migration in the polymer host. Non-exponential decay data was analysed in terms of a mechanism containing triplet-triplet annihilation steps, yielding composite uni- and bimolecular rate constants k_1 and k_2 . The applicability of the proposed mechanism was assessed by comparing the predicted and experimental activation energies derived from k_1 and on the nature of the decay curves.

The temperature dependence of donor phosphorescence was studied

from 77 K to 298 K in a range of polymers. The k_1 and k_2 Arrhenius plots of the high energy triplet donors exhibited irregularities, allowing the acquisition of temperature transitions, some of which correlated with reported polymer structural relaxations. However, the temperature studies highlighted certain anomalies, so undermining the suitability of the temperature dependence of phosphorescence life-time to unequivocally identify polymer relaxations.

Electronic energy transfer experiments using the donor/acceptor systems benzophenone/ferrocene and anthrone/ferrocene were carried out in various polymer films at 77 K. Donor phosphorescence intensity decay data for different acceptors concentrations was analysed by both dipole-dipole and exchange energy transfer mechanisms, producing R_0 parameters for each system. Comparison of R_0 values led to the conclusion that polymer matrices, especially polystyrene, could influence electronic energy transfer mechanisms between randomly dispersed donor/acceptor combinations.

To Russell

General Introduction

GENERAL INTRODUCTION

The transfer and migration of electronic energy as photophysical processes have been extensively studied in organic crystals [1], biological systems [2] and in organic polymers [3]. The latter topic constitutes the substance of this thesis, developed principally from photophysical considerations. Besides offering a challenging problem in chemical physics, due to the unique structural properties of polymers, energy transfer has practical consequences in the photodegradation and photostabilization of commercial polymers [4,5].

In recent years the use of luminescence measurements for the study of a great diversity of phenomena occurring in synthetic and natural polymers has become widespread. Electronic energy transfer between chromophores attached to a polymer chain has been invoked to explain several facets of polymer photophysics, including excimer formation [6], unexpectedly efficient quenching by small molecules [7,8] and energy transfer to chemically bound traps [9].

The ability to render stability to synthetic polymers by the addition of dopants is in many instances the result of energy transfer processes and a detailed understanding of such events is of vital importance in photostabilization [10]. Polymers which do not absorb wavelengths > 290 nm should be resistant to sunlight, but polyethylene and poly(vinylchloride), neither possessing chromophores in their repeat unit, are both very sensitive to such electromagnetic radiation [11], suggesting the presence of absorbing impurities introduced during synthesis, high temperature processing, or storage [12], further implicating the involvement of energy transfer events in polymer photodegradation. The two most important species in

this respect are carbonyls [13,14] and hydroperoxides [15,16]. Once a bond has been broken at any point in the polymer molecule, overt degradation has begun, but if the energy of the photon, absorbed by either the polymer or impurity, can be dissipated non-radiatively before dissociation occurs, inhibition to photodegradation will have been effected [17]. Hence, to combat the problems of photodegradation and to enhance the efficiency of photostabilization, necessitates a comprehensive knowledge of the photophysical processes which occur between the point of photon absorption and bond dissociation.

The aim of the present study overlaps both with the fundamental interest and the practical technological importance of polymer photophysics. Particular emphasis has been focussed on the problem of whether or not certain polymers are capable of accepting electronic energy at the triplet level and so establishing their suitability for use in luminescence studies requiring inert support media. The approach involved performing classical energy transfer experiments between a given donor/acceptor pair randomly dispersed in a polymer host. The photochemical interest stems from investigations into the phosphorescence behaviour of the chosen molecules, aromatic hydrocarbons and aromatic ketones, as a function of temperature and polymer host environment.

Within the present context, concerted research into triplet state photophysics reflects the importance of the triplet state in photochemistry and introduces the photochemical overtones of the study. A number of condensed aromatic hydrocarbons have found application as triplet quenchers[18], triplet energy acceptors [19] and have been utilized as stabilizers [20]. Studying the phosphorescence of ketones in polymers is of particular importance as

both aliphatic and aromatic ketones play a prominent role in polymer photooxidation [21]. Their specific interaction with hydroperoxides in this respect has been the subject of numerous investigations [22,23,24]. Much of the recent work on the quenching of excited carbonyl chromophores by energy transfer to uv stabilizers has been summarized in reference [25].

Investigations of this nature require specific luminescence instrumentation and during the course of the present study a computer controlled phosphorimeter was constructed, employing a nitrogen laser excitation source and capable of signal averaging sub-millisecond decay events.

Experimental

CHAPTER ONE

1.1 MATERIALS

The chemical materials used throughout this study were all of commercial origin and were purified and handled by standard techniques [26].

1.1.1 Solutes

The solid solutes anthrone (B.D.H.), carbazole (B.D.H.), ferrocene (B.D.H.), benzophenone (Fisons), benzil (Fisons) and phenanthrene (Fisons) were all repeatedly recrystallized from either freshly distilled hexane or ethanol. The solutes triphenylene (Koch-Light) and naphthalene-d-8 (Sigma) were used as received. The subsequent purity of the carbonyl solutes and ferrocene was checked by thin layer chromatography.

Liquid acetophenone (B.D.H.) was repeatedly distilled under reduced pressure, discarding all but the middle fraction of the distillate.

1.1.2 Solvents

All solvents were dried and distilled prior to use. Dichloromethane was dried over calcium chloride. Tetrahydrofuran was refluxed over lithium aluminium hydride and passed through an alumina column.

1.1.3 Commercial Homopolymers

Commercial homopolymers poly(methylmethacrylate) (RAPRA), polystyrene (RAPRA) and poly(vinylacetate) (B.D.H.) were purified by dropwise precipitation into a large excess of methanol. The polymer was then pumped dry at the water pump and the procedure repeated at least three times. The polymer was finally dried and stored in a vacuum oven for one week. Poly(vinylchloride) (B.P. Chemicals) was purified in a similar fashion; dissolution being from tetrahydrofuran.

1.1.4 Preparation of Homopolymers

The preparation of poly(ethylmethacrylate) and poly(n-butylmethacrylate) was carried out by free radical polymerization at 60^o C in deoxygenated benzene solution using azobisisobutyronitrile (0.1 mol %) as initiator. In each case the monomer (B.D.H.) was freed from inhibitor by successive washings with a 10 % w/v solution of sodium hydroxide and dried over anhydrous sodium sulphate. The monomer was then filtered and distilled under reduced pressure immediately prior to use. Polymer conversions were kept low, typically < 20 % and the resulting homopolymer was purified by the method outlined.

1.1.5 Preparation of Copolymers

A range of styrene/methylmethacrylate copolymers was prepared by free radical polymerization in deoxygenated benzene solution at 60° C. The compound azobisisobutyronitrile served as the source of initiating radicals and copolymer conversions were purposely kept within 10-15 %.

Styrene (Aldrich Chemical Company) was freed from inhibitor by successive washings with a 10 % w/v solution of sodium hydroxide, washed with distilled water, dried over anhydrous calcium chloride and finally distilled under reduced pressure immediately before use. The monomer methylmethacrylate (B.D.H.) was freed from inhibitor following the same procedure, the drying agent being anhydrous sodium sulphate.

The required volumes of monomers, weight of initiator and volume of benzene were transferred to the reaction vessel which was then attached to a vacuum line. The reaction mixture was thoroughly degassed by several freeze/pump/thaw cycles before being immersed in a water bath held at 60° C. The range of monomer feed mixtures is outlined in Table 1.1. After the reaction time had elapsed, the mixture was added dropwise to a large excess of methanol in order to precipitate the copolymer. The copolymer was then filtered and dried, dissolved in dichloromethane and precipitated from methanol; the procedure was repeated at least three times to ensure the complete removal of unreacted monomer. The copolymers were finally dried in a vacuum oven for one week.

The copolymers were analysed by proton n.m.r. spectroscopy to determine their % composition, the spectra being consistent with those

reported for random styrene-methylmethacrylate copolymers [27]. The composition of each copolymer is also given in Table 1.1.

1.2 POLYMER CHARACTERIZATION

This short section gives an indication of polymer purity and an estimation of polymer molecular weights.

1.2.1 Ultra-Violet Spectroscopy

Ultra-violet spectra of the polymers used during the present study were obtained using a Unicam SP 800 spectrometer. The spectra acquired for polystyrene, poly(methylmethacrylate) and poly(vinylacetate) agreed with those published in the literature [28], confirming each, together with the other polymers used, not to absorb in the region > 280 nm. Polymer transparency in such a region indicates the absence of absorbing impurities and allows selective excitation of guest molecules that absorb at wavelengths > 300 nm.

1.2.2 Polymer Molecular Weights

The molar mass distribution and associated molar mass averages quoted in this study were obtained using gel permeation chromatography; the service was provided by the Polymer Supply and Characterization Centre (RAPRA). Gel permeation chromatography separates polymer samples into fractions according to their size by means of a sieving action. This is achieved using a non-ionic stationary phase of spheres, often crosslinked beads of polystyrene, whose pore size distribution can be controlled.

A polymer is characterized best by a molar mass distribution and the associated molar mass averages, rather than by a single molar mass [29]. The common polymer mass averages are defined as follows, where N_i is the number of molecules of species i of molar mass M_i ,

$$\langle M \rangle_n = \frac{\sum N_i M_i}{\sum N_i}$$

$$\langle M \rangle_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$\langle M \rangle_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

where M_n is the number average molar mass, M_w the weight average molar mass and M_z a higher mass average. The breadth and distribution can often be gauged by establishing the heterogeneity index (M_w/M_n). Table 1.2 lists the relevant data for the homopolymers and the data in Table 1.3 pertains to the copolymers.

The following polymer abbreviations were used :

PVAc Poly(vinylacetate)

Psty Polystyrene

PMMA Poly(methylmethacrylate)

PEMA Poly(ethylmethacrylate)

PnBMA Poly(n-butylmethacrylate)

TABLE 1.1

COPOLYMER	STYRENE	METHYL- METHACRYLATE	STYRENE	METHYL- METHACRYLATE
NO	ml	ml	%	%
1	3	27	17.0	83.0
2	9	21	51.0	49.0
3	21	9	60.5	39.5
4	27	3	87.0	13.0

TABLE 1.2

POLYMER	Mn	Mw	Mz	Mn/Mw
	$\times 10^5$	$\times 10^5$	$\times 10^5$	
PVAC	0.94	5.17	14.01	5.48
Psty.	1.19	3.06	5.60	2.56
PMMA	0.34	0.94	1.62	2.73
PEMA	2.46	4.98	12.80	2.02
PnBMA	0.25	1.01	2.02	4.01

TABLE 1.3

COPOLYMER	Mn	Mw	Mz	Mw/Mn
NO	$\times 10^5$	$\times 10^5$	$\times 10^5$	
1	1.24	2.65	4.07	2.14
2	0.69	1.48	2.23	2.15
3	0.65	1.28	1.90	2.00
4	0.60	1.28	1.93	2.14

1.3 EMISSION SPECTROSCOPY

An emission spectrum is a plot of emission intensity, at a fixed absorption intensity, as a function of frequency or wavelength of emitted light. However, most reported spectra are not true emission spectra but are presented as uncorrected spectra because of certain instrumental problems, principally the varying wavelength response of the photomultiplier [30].

1.3.1 The Emission Spectrometer

The Perkin-Elmer Hitachi MPF-2A spectrofluorimeter is constructed for the measurement of both excitation and emission spectra. It has the additional facility for the detection of spectra at reduced temperatures and can be adapted with the relevant accessories to measure the polarization of the emitted luminescence.

The principles behind the operation of the spectrometer can be simply outlined as follows. The excitation source employed is a 150 Watt xenon lamp connected to a requisite power supply, generating an intense optical output. The spectral breadth of the output consists of numerous lines covering the wavelength range from 280 nm into the infra-red region. Consequently, the light emitted from the lamp must be passed through a monochromator from which emerges a beam of reduced spectral range depending on the excitation slits. The excitation slits can be set to give a band pass of 1-40 nm, thus allowing a degree of selective excitation. This beam is then imaged by means of a quartz lens onto the sample contained within a special

light tight compartment. Sample luminescence is subsequently focussed onto emission slits of a similar band pass potential before dispersion in the emission monochromator. The emergent light strikes the detecting photomultiplier producing an electrical signal which is amplified and ultimately recorded on chart paper.

In practice, the acquisition of spectra is carried out automatically, with the excitation monochromator set at the desired wavelength and the emission monochromator slowly scanned over the spectral region of interest. All the emission spectra reported were not corrected for the wavelength response of the photomultiplier.

1.4 PHOSPHORESCENCE LIFE-TIME APPARATUS

During the present study phosphorescence life-times were measured over a wide time scale, ranging from milliseconds to seconds and utilizing three different types of apparatus. Although there are certain design features common to each, and the principles behind their use was similar, each instrument was particularly suited to measuring life-times over a specific time scale.

For measuring long phosphorescence decay events, typically 2-20 s, use was made of the emission spectrometer described previously, fitted with standard accessories and denoted as Apparatus A.

A large section of the work to be reported involved the measurement of millisecond life-times using an instrument constructed from commercial and custom built components. The experimental layout of this apparatus was devised and assembled by Dr. T.M. Shepherd of

this department, and will be referred to as Apparatus B. The apparatus was under the operational control of a Nascom 1 microcomputer.

The third set of instrumentation used in this study, referred to as Apparatus C, was particularly versatile, employing a pulsed nitrogen laser as excitation source and involving detection equipment capable of recording fast transients in the sub-millisecond domain to slow decaying phosphorescence in the seconds region. This apparatus was acquired late into the present study and a great deal of effort was invested in making it operational.

1.4.1 Signal Averaging

When signals are large there is little difficulty with noise, however, in many situations the signal is comparable to or less than the noise and so special techniques have to be instituted to extract the true signal. One technique developed to improve the signal to noise ratio (SNR) is signal averaging and is applicable to measuring spectra or the decay of transients [31]. This facility was offered by both Apparatus B and C described in the following sections.

This method requires that the spectrum or transient decay should be repeatable and that there be some synchronizing trigger to which the signal is accurately related in time. The signal must be stored so that it may be averaged with subsequent scans and such an operation can be performed using a multi-channel averager or microcomputer. The former method was employed in Apparatus B whereas the latter alternative performed the task in Apparatus C. If noise is random, then it is expected that it will eventually average to zero while the

signal tends to its true value. It can be shown that the signal to noise ratio improves as the square root of the number of scans.

1.4.2 Apparatus A : Continuous Excitation

Life-time determinations in the 3-20 s time region were routinely carried out using the MPF-2A spectrometer in which the voltage output of the photomultiplier was transferred using a Solartron data transfer unit to a Facit 4070 paper tape punch. The decay of phosphorescence could be monitored with a constant sampling rate of 0.3 s or 1.0 s; the selected speed was also recorded on the paper tape. The time constant of the amplifier, approximately 0.3 s, had no appreciable effect on long time decay curves, but imposed a lower detection limit of 3 s.

The excitation source was a 150 Watt xenon lamp, allowing continuous sample excitation. After establishing a steady state concentration of triplet species, the excitation shutter was closed whilst simultaneously switching on the data transfer unit to sample the voltage decay at the predetermined interval. The voltage decay was generally followed until three or four first order life-times had elapsed. The resulting intensity data were analysed by the method of least-squares where the time base was considered error free, producing a first order phosphorescence life-time. The calculation was executed by a computer programmed in Fortran.

1.4.3 Apparatus B : Flash Lamp Excitation

The use of Apparatus B allowed the signal averaged decay of transients to be accurately measured over sweep times ranging from 5 to 50 ms. The excitation source consisted of an E.G. and G. FX-31 flash tube having a wide spectral range. The power supply for the flash tube was custom built, capable of supplying 200-800 V and was generally operated at 500 V. The spectral range was reduced by the intervention of a black glass filter of band pass 300-900 nm, and was focussed by means of a quartz lens onto the sample holder held within a clear Dewar flask. Right-angled viewing was used, in which the resultant sample emission was focussed onto the entrance slits of a Hilger and Watts prism monochromator. The band width and centre wavelength of the emission striking the EMI 9526 photomultiplier was controlled by varying the slit widths and prism settings of the monochromator.

The photomultiplier voltage was controlled by a Brandenburg high sensitivity power supply. The photomultiplier was in turn linked to a Data Laboratories DL 201 signal averager responsible for capturing and storing the transient. By use of an interface the stored data held within the memory of the signal averager was transferred to the memory of a Nascom 1 microcomputer, thereby enabling immediate kinetic analysis to be performed. The output data, listed on the printer, was in the form of logarithmic intensity readings as a function of time together with a first order life-time and correlation coefficient. This data could then be transferred to the university mainframe computer for further kinetic analysis. The decay curve was viewed on

an X-Y oscilloscope during the averaging process.

The technique of signal averaging requires accurate synchronization between the initiation of the excitation flash and the instrument responsible for monitoring the decay profile. Such a function was performed by the signal averager which initiated the recording cycle by pulsing the flash tube at set time intervals then scanning the decay for the selected sweep time. Pulse rates occurred at an interval of typically 0.5 s, thus enabling the transients sufficient time to decay before further excitation. The number of averages was pre-selected and generally chosen to be 64 or 128. In all cases a background reading, obtained with the flash tube inoperative, was subtracted from the final averaged decay profile before any kinetic analysis was performed in order to eliminate errors due to the A/D converter not being accurately zeroed. The photomultiplier voltage was varied to give a satisfactory display on the oscilloscope screen. The Delay Before switch on the signal averager, that is, the time interval between the excitation flash and the start of the recording cycle was adjusted to eliminate any interference from the excitation flash. Consequently, the results presented in the ms region acquired using Apparatus B do not start from time $t=0$ s, but generally at time at least 5% later.

1.4.4 Apparatus C : Pulsed Laser Excitation

The principal components of this apparatus were a nitrogen laser excitation source and a transient recorder for data acquisition, the range of which allowed decay events of 0.1 ms to 8 s to be studied. The versatility of the equipment was further enhanced by interfacing the transient recorder to a microcomputer, thereby enabling the entire data acquisition cycle and subsequent manipulation to be under computer control. The essential elements and basic design features are similar to those of Apparatus B, but additional advantages were introduced. The individual components of the apparatus, the interface, the synchronisation of events, and the controlling program will now be described.

1.4.4.1 Individual Components

The individual components constituting Apparatus C are outlined schematically in figure 1.1.

Excitation Source

The excitation source used was a Lambda Physik K 600 pulsed nitrogen laser emitting monochromatic radiation at 337.1 nm which is based on an electronic transition in the triplet manifold of molecular nitrogen following excitation by a very fast high voltage discharge.

The reproducibility of the output power of the laser pulse, a highly desirable characteristic important in minimizing noise levels,

is mainly dependent on the following factors; the working voltage, the gas pressure, and the pulse repetition rate. An optimization was carried out using the the data provided by the manufacturers, establishing an operational balance between these factors and reducing the problem of power instability. The vacuum pump supplied serves to maintain a constant flow of nitrogen gas in the laser head at a pressure between 40 and 200 Torr, which is sufficient to allow operation within the repetition frequency range 50-100 Hz. At lower pulse rates, relevant to the present study, reduction in the gas flow was achieved by adjusting the flow regulation valve.

When using lasers in spectroscopic studies spurious electromagnetic interference emanating from the laser can cause problems with neighbouring electrical equipment, however extreme care had been taken by the manufacturers in the construction of the laser to eliminate this possibility. To this end, the sides of the laser housing were either soldered together or spot welded at close intervals and the connecting coaxial cables were additionally protected by metal hoses.

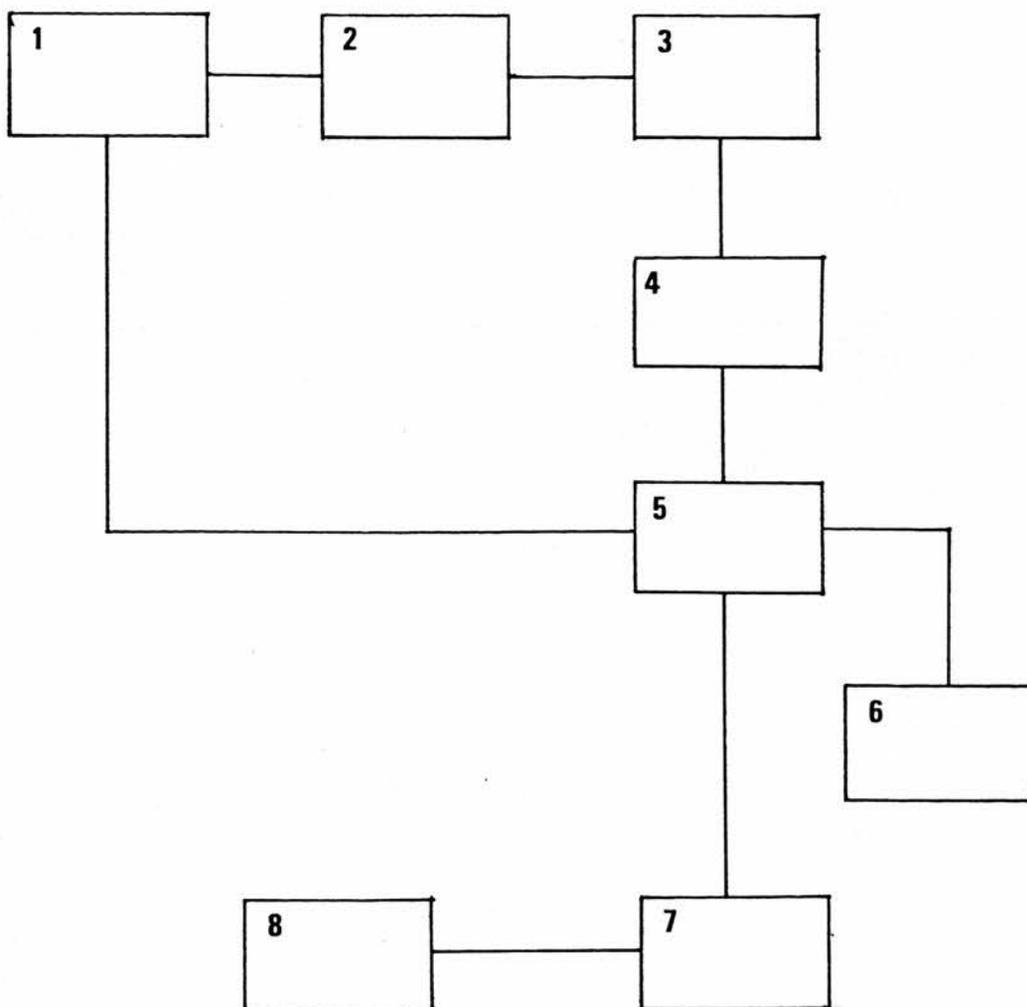
Some of the laser specifications are outlined in Table 1.4. The magnitude of the laser light pulse may be described in terms of the number of photons it contains, which in the present case, using the data in Table 1.4, can be shown to equal approximately 10^{12} photons/pulse. This number is proportional to the total energy of the pulse and varies inversely with wavelength for a given energy content. The instantaneous peak power, typically measured in Watts, is given by the pulse energy divided by its characteristic duration.

An operational factor of importance is the pulse repetition frequency which normally must be low enough that full relaxation of

the sample can occur between pulses, otherwise the build up of metastable states or species will interfere with the intended measurement or lead to mis-interpretation. At the other extreme, excessively low repetition rates can make optical alignment, signal optimization and data collection tedious and difficult.

The use of lasers in excited state photochemistry has become increasingly popular [32] and reference [33] further illustrates the complexity and diversity of laser application in photophysical studies.

Figure 1.1



1. Nitrogen Laser
2. Sample Compartment
3. Monochromator
4. Photomultiplier
5. Transient Recorder
6. Oscilloscope
7. Apple Microcomputer
8. Printer

TABLE 1.4

SPECIFICATION	UNITS
PULSE DURATION	4 - 5 ns
REPETITION RATE	200 - 2 Hz
ENERGY PER PULSE MAX.	2 mJ
AVERAGE PULSE POWER MAX.	225 mW
AMPLITUDE STABILITY	2 ± 5 %

Data Acquisition

The Datalab DL 920 transient recorder was used to monitor the experimental luminescence decay signal. The transient recorder is a digital instrument designed to capture single shot or repetitious events and present them for display on an oscilloscope. The additional feature of a general interface card provides for a convenient data link to a microcomputer. During the recording cycle each sample of signal is converted into a digital number and stored in a memory of 4096 words. The sampling rate or data acquisition interval is defined by the sweep time divided by 4096; the sweep time being the time period over which the recording cycle takes place and the current model offers an extensive sweep range varying in increments from 0.2 ms to 8.0 s.

The transient recorder presents a selection of operational modes and was routinely operated in the delayed mode. This mode enables a prescribed portion of the decay curve to be ignored and is used when a suitable trigger occurs before the signal is recorded. The trigger is usually derived from an external source and was taken to be the laser excitation pulse. The commencement of the recording sweep may therefore be delayed from the trigger by setting the increment variable delay control; giving the means of obtaining the maximum number of sample points over the region of interest. The data reported using this apparatus appears in chapter three, and unless stated otherwise, was derived from decay curves in which the first 1% of any sweep time was disregarded. This was a precaution introduced to eliminate the effects of spurious factors interfering with the

decay process, such as scattered light, emission from the sample holder, or any time constants encountered in either the photomultiplier or additional smoothing circuits.

Sample Compartment and Temperature Accessory

The sample compartment was essentially a rectangular metallic box with detachable lid, the geometry of which was such that sample emission was viewed at 90° to the direction of excitation. The inside of the box was sprayed with mat black paint in order to minimize light reflection. A cylindrical light tunnel was used to provide the link between the exit outlet of the laser head and a variable iris/shutter system attached to the inside wall of the sample compartment. Thus, provision was made for varying the dimensions of the excitation beam and for cutting it off completely from the sample.

The excitation beam passing through the iris would then strike the sample holder held in a glass Dewar vessel by means of a tufnol adaptor. Two additional holes were drilled in the adaptor into which a ground glass joint, used to secure one end of an evacuated condenser forming part of the temperature variation accessory, and a temperature probe were fitted. The temperature probe, in the form of a flexible patch sensor, consisted of a platinum wire grid mounted within a sandwich of glass-filled P.T.F.E. insulation, and was connected to a platinum resistance thermometer of operational range -210° C to $+800^{\circ}$ C. The probe was positioned adjacent to the sample holder, but out of the path of the laser beam. The sample holder itself was angled at 45° to the incident laser excitation.

The optical arrangements consisted of two lenses located between

the outer face of the sample Dewar and the entrance slits to the monochromator, positioned at 90° to the direction of excitation. One was responsible for collecting the sample emission and the other for focussing it onto the monochromator slits.

A second Dewar vessel was stationed directly behind the sample Dewar, the function of which was to provide the source of cool nitrogen gas from a reservoir of liquid nitrogen for temperature variation. The Dewar lid was fitted with a corresponding ground glass socket into which the other end of the condenser was placed, the latter providing a bridge between the Dewars and a heating element wired to a variable transformer. When switched on, the heating element caused the reservoir of liquid nitrogen to boil, sending cold gas up through the condenser and onto the sample holder. In this manner, controlled temperature variation from 77 K to room temperature could be readily achieved.

Miscellaneous

The cathode type of the photomultiplier, EMI 9557 QB, was bialkali, chosen to give maximum quantum efficiency over the wavelength range of interest and was fitted with a fused silica window to extend its spectral coverage from 200 to 600 nm.

The device used for isolating a particular spectral region for analysis was a high quality grating monochromator functional over the range 150 to 900 nm. The entrance and exit slits were routinely set at 5 mm and 20 nm respectively.

A Telequipment D1010 oscilloscope with time base capacity $0.2 \mu\text{s}/\text{div}$ to $0.2 \text{ s}/\text{div}$ was used to obtain a visual display of the

decaying transient.

Additional equipment included an Apple II microcomputer with a 56 K memory storage facility linked to an Anadex printer.

1.4.4.2 The Interface

Gate Microsystems Ltd. were contracted to design and write a software interface which would allow the Datalab DL 920 transient recorder to be compatible with the Apple II Plus microcomputer. The transient recorder contains the standard TTL binary digital output interface whereas the microcomputer is fitted with the CCS 7720 parallel interface. Having established compatibility, a controlling computer program could then be written which would dictate the functions of the transient recorder and perform any required numerical analysis on the experimental data. The controlling program was written by the present author and will be briefly outlined in a following section.

The interface and driver routines were written in 8080 Assembler and T6502 Assembler respectively, and were held in the Fortran library "FORLIB.REL" contained on the same disk as the controlling program. These routines were accessed by specific call statements in the controlling program and were responsible for working the transient recorder in the operational sequence PRIME, ARM, TRIGGER and XFER, the first being called only once while the last three are called, in that order, for each sample or run.

The statement,

```
CALL TRANRC(OPTION,ARRAY(1))
```

is used for accessing the recorder and the variable "OPTION" should contain 1, 2, 3, or 4. The correct sequence is,

```
PRIME=1
```

then in a do loop for N runs

```
ARM=2
```

```
TRIGGER=3
```

```
XFER=4
```

The variable option on return will contain zero if the call was successful, otherwise it will contain an error code. The options PRIME and ARM are responsible for setting up the recorder prior to action, the option TRIGGER initiates the recorder to capture the incoming signal and the option XFER, transfers the digitized waveform from the recorder memory to that of the microcomputer.

1.4.4.3 The Synchronization of Events

The technique of signal averaging requires accurate synchronization between the onset of the excitation flash and the instrument(s) responsible for capturing the transient decay. For Apparatus C this meant synchronizing the laser, transient recorder and Apple microcomputer to act in a strictly defined sequence.

The laser requires a positive pulse of 1-2 μ s duration and amplitude 5-50 V to fire whereas the transient recorder will trigger into the sweep mode with almost any type of pulse, + or -, depending on the front panel control settings. The Apple microcomputer is capable of producing a TTL type pulse nominally from + 5 V to 0 V and the original intention was to use this pulse to trigger the transient recorder which in turn was modified to fire the laser, thus synchronizing the sequence of events to the internal functions of the computer. However, such an approach proved to be impossible because of the inability of the laser to fire reliably at slow pulse rates. Slow pulse rates were necessary to accommodate long lived phosphorescence, transfer of the captured decay data and subsequent numerical computation time.

The problem was overcome by operating the laser at a reliable speed of approximately 10 Hz from its internal time base generator. The trigger pulse from the microcomputer to the transient recorder was used to initiate a timing circuit (delay monostable) which would hold an electrical gate open for 150 ms. During this delay period the timing circuit via a logical OR gate sent back a pulse to the microcomputer to indicate that the transient recorder had accepted the

trigger pulse and was in the sweep mode, even though the recorder was still awaiting the correct trigger pulse. Sometime during the 150 ms time period the laser flashes, producing a synchronizing pulse which is used to genuinely trigger the transient recorder into the sweep mode and also resets the delay timer ready for the next pulse from the microcomputer.

Hence, the synchronizing logic circuit required the laser to run freely at 10 Hz, giving sufficient time for the transient recorder/Apple microcomputer handshake and data manipulation to be completed, before allowing another incoming laser pulse to start a new recording cycle.

1.4.4.4 The Controlling Program

The operational format of the software interface was incorporated into a master computer program, written in Microsoft Fortran 80, thereby allowing not only the functions of the transient recorder to be under direct computer control but providing the basis for efficient on line data processing. The basic outline of the controlling program LASER7.FOR, a listing of which appears in Appendix I, will now be introduced in which emphasis will be given to the running details.

The program was designed in such a way so as to enable any operator unfamiliar with computers to perform the experiment to acquire emission intensity decay data. With this aim in mind, the program was composed in the form of a collection of numbered options, each specific for a particular task. The options appear in an "Options Table", the contents of which are displayed on the VDU screen on first running the program and are subsequently echoed after

executing the previously selected option. Each option is called by typing in the corresponding option number when prompted by the computer. Initially, the option sequence 1-4 must be followed, thereafter the options can be called as the operator desires. On initiating an option where there is an element of choice, the subsequent actions are determined by a question/answer routine between the computer and operator. The options will now be briefly described in turn.

The function of option number 1 is to define the sweep time over which the decay signal is to be monitored and to calculate the elements of the time array corresponding to each captured data point. This is achieved by typing in the sweep time in seconds and the percentage delay required. The computer program has a 1 % default percentage delay setting.

Option 2 is designed for the input of convenient experimental details such as, a chemical description of the sample, the temperature, the emission wavelength of interest and any other miscellaneous details.

The function of option 3 is rather important and must always be executed prior to obtaining legitimate decay data via option 4. This option should be initiated under the exact conditions used to obtain decay data but with the iris/shutter device closed to excitation. Under such conditions the transient recorder should display a straight base line on the oscilloscope screen, an averaged value of which is calculated by the microcomputer. This background reading is stored and used in option 5 where it is subtracted from each legitimate data point before any kinetic analysis is performed in order to eliminate errors due to the analogue to digital converter not being accurately

zeroed. If, however, the background reading is found to be greater than 10, the computer instructs the operator to adjust the offset dial on the transient recorder until the condition is satisfied. Ideally, the offset should be in a position such that the background reading is in the range 1-3.

Option 4 is entirely responsible for acquiring the transient decay data and on calling this option the operator is prompted for the number of averages required, the maximum allowed being 127; the number dictated by the memory storage capacity of the microcomputer.

Option 5 is concerned with correcting the data for the background contribution and for determining subsequent numerical presentation. After completion of the background correction, the computer prompts the operator for further information regarding numerical processing. The data can either be analysed in terms of the numbers obtained directly from the transient recorder or can be artificially correlated. This latter alternative is convenient for comparing decay curves where each curve is standardized to an initial intensity value; the subsequent differences in intensity being exactly the same as the uncorrelated data.

Option 6 performs a least squares linear regression on the decay data, calculating a first order life-time, correlation coefficient and the corresponding best straight line data. On entering this option, the computer prompts for the number of channels over which the calculation is to be performed. Due to computer memory restrictions, a maximum of 1000 equally spaced time points or channels, covering the entire sweep time, are available for analysis. The life-time, correlation coefficient, and experimental details are then echoed on the VDU screen.

Option 7 operates the Anadex printer to provide a hard copy of the calculated results. On entering this option, the life-time, correlation coefficient and experimental details are automatically printed out. The operator is then prompted to determine whether or not the intensity/time numbers are also to be printed out, and on receiving an affirmative reply, the computer prompts for the data output increment governing the number of data points to be printed.

Initiation of option 8 terminates the program and is used to end the experiment.

1.5 Experimental Procedures

The following sections outline the methods by which the polymer films were prepared and doped and the procedures involved prior to determining a life-time measurement.

1.5.1 Preparation of Doped Polymer Films

Phosphorescence life-times have been reported for many molecules containing n,π and π,π chromophores in various polymers. The method chosen to dope the polymer is of importance and could conceivably influence the decay process. In recent years a number of different procedures have appeared in the literature but some have proved to be quite unsatisfactory.

Often a weighed amount of phosphorescent material is dissolved in a known volume of monomer to which an initiator has been added and the system is then polymerized under vacuum. Considering the sensitivity of luminescence measurements to environment and the ease with which

organic molecules can quench triplet states, such a procedure is not recommended. Clearly, the main disadvantages of such a preparation are, incomplete polymerization leaving residual monomer and the presence of persistent radical species. The importance of residual monomer in influencing the phosphorescence of aromatic compounds in poly(methylmethacrylate) has been demonstrated [34]. Indeed, samples prepared in this way were shown to contain radicals. The situation is further complicated if the dopant concerned reacts with radicals formed during polymerization, leading to the possibility of it becoming chemically bonded to the polymer.

Another reported procedure involves placing a thin polymer film in a desiccator containing the dopant and leaving it there until the dopant has penetrated the film. This method is also unsatisfactory, as permeation is never completely homogeneous, often leaving an aggregation of molecules on or near the surface of the film.

Hence, an alternative procedure was chosen which involved embedding the phosphorescent molecule into a film made from pre-polymerized polymer and thereby reducing the possibility of spurious interference. This method allowed a polymer film of a desired thickness to be doped with a phosphorescent probe of specified concentration. Knowing the density of each polymer, a stipulated weight could be dissolved in a certain volume of solvent containing a controlled amount of additive. The resultant solution was then thoroughly mixed and filtered before a specific volume was carefully pipetted onto a clean, dry glass disc of known diameter. A glass dish was placed over the disc to allow slow solvent evaporation, ensuring the formation of optically clear films. This film casting procedure was always carried out in a dark room. After a few hours the glass

dish was removed and the polymer film peeled off the disc. The film was then secured onto a cardboard sheet to prevent it buckling and pumped out over night in a vacuum oven. This latter procedure would facilitate the complete removal of the casting solvent, which in most cases was dichloromethane.

The diameter of each film was 4.0 cm, thus enabling at least three 1 cm sections to be cut from it and so allowing the life-time to be checked for different sections of the same film. This is a major advantage over the first procedure described, as in that case the polymerization conditions could never completely guarantee a reproducible environment for the additive.

1.5.2 Life-Time Determination

Phosphorescence has been shown to be sensitive to triplet quenchers, particularly oxygen [35,36], and so prior to use each polymer film was pumped out under high vacuum for at least two hours using the standard combination of rotary oil and mercury diffusion pumps, and held under vacuum for the experimental duration. Liquid nitrogen traps were placed at either side of the diffusion pump to condense mercury vapour and another stationed immediately in front of the sample holder port on the vacuum line.

In the case of Apparatus A, the above conditions were conveniently satisfied by designing a sample holder, linked to the vacuum line, which neatly penetrated the sample compartment of the emission spectrometer, thus allowing life-time data to be recorded under conditions of high vacuum. The glass stem of the sample holder was held secure by a positioning device screwed into the compartment

lid directly above the luminescence cavity. This enabled the sample holder to be moved horizontally, vertically or to be rotated in relation to the path of the excitation beam. The quartz face of the sample holder was positioned at 45° to the incident beam such that back viewing was attained. Provision was also made for the inclusion of a quartz Dewar in the sample compartment. When recording life-time data or spectra at 77 K the Dewar flask could be filled from outside the compartment via a filter funnel attachment bored through lid of the spectrometer.

A mutually compatible sample holder for use with Apparatus B and Apparatus C could also be attached to the above vacuum line. Before recording a measurement, the film within the sample holder was pumped out under vacuum for two hours and then placed in the sample compartment Dewar. When readings were required at 77 K, the sample holder was allowed to equilibrate in liquid nitrogen for thirty minutes.

In all cases the film sample holder consisted of a modified 1 mm absorption cell made from high quality far uv quartz glass (Thermal Syndicate Ltd.).

Phosphorescence

in

Polymer Hosts

CHAPTER TWO

2.1 ORGANIC LUMINESCENCE

Organic photoluminescence is consequent upon absorption of a photon by organic molecules and is understood in terms of radiative and non-radiative events which deactivate the excited states produced. Radiative transitions involve dissipation of energy by photon emission whereas non-radiative transitions are processes in which light is transformed into heat.

The following sections briefly introduce some topics and concepts fundamental to an understanding of organic photoluminescence.

2.1.1 Definition of Multiplicity

The orbital properties of an electron in an electronic state can be discussed in terms of specific quantum numbers [37] and in particular, the spin motion of the electron is characterized by the spin quantum number s shown to equal $+$ or $- 1/2$. The total spin quantum number, S , is given by the vector sum of s for all the individual electrons.

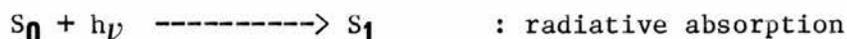
The term $2S+1$ is introduced to define the spin multiplicity of an electronic state, specifically referring to the spin degeneracy of that state and allows differentiation between the two commonly encountered electronic states of an organic molecule in which the spins are either paired ($S=0$) or parallel ($S=1$). In accordance with the definition of spin multiplicity, the former state is referred to

as a singlet whilst the latter is known as a triplet.

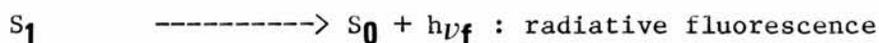
2.1.2 Fluorescence

Fluorescence is defined as a radiative transition occurring between states of the same spin multiplicity, the most common example of which is the $S_1 \rightarrow S_0$ transition [38]. The sequence of photophysical events leading to fluorescence are depicted in Figure 2.1.

Initial absorption of light by the ground state, S_0 , raises the molecule in energy terms into the vibrational level of a specific excited singlet state S_n within the singlet manifold; the value of n determined by the wavelength of the absorbed radiation.



The excited state singlet molecule non-radiatively distributes its excess vibrational energy as thermal energy to the surrounding medium, a process occurring in typically 10^{-12} s, resulting in an excited singlet state in its zeroth vibrational level [38]. The molecule then undergoes a further rapid non-radiative transition, referred to as internal conversion, to a vibronic level of the S_1 excited state, which then also vibrationally deactivates to yield the zeroth vibrational level of that state from which fluorescence occurs [38].

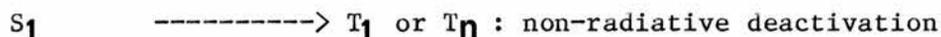


Most radiative transitions occur in accordance with Kasha's rule, which states, " the emitting electronic level of a given multiplicity is the lowest excited level of that multiplicity" [39]. Azulene [40] and fluorescence emission from ovalene [41] in poly(methylmethacrylate) provide interesting exceptions.

Non-radiative transitions compete with fluorescence in determining the fate of the S_1 state. In addition to emitting a photon, the S_1 state can undergo non-radiative deactivation returning to a vibronic level of the ground state.

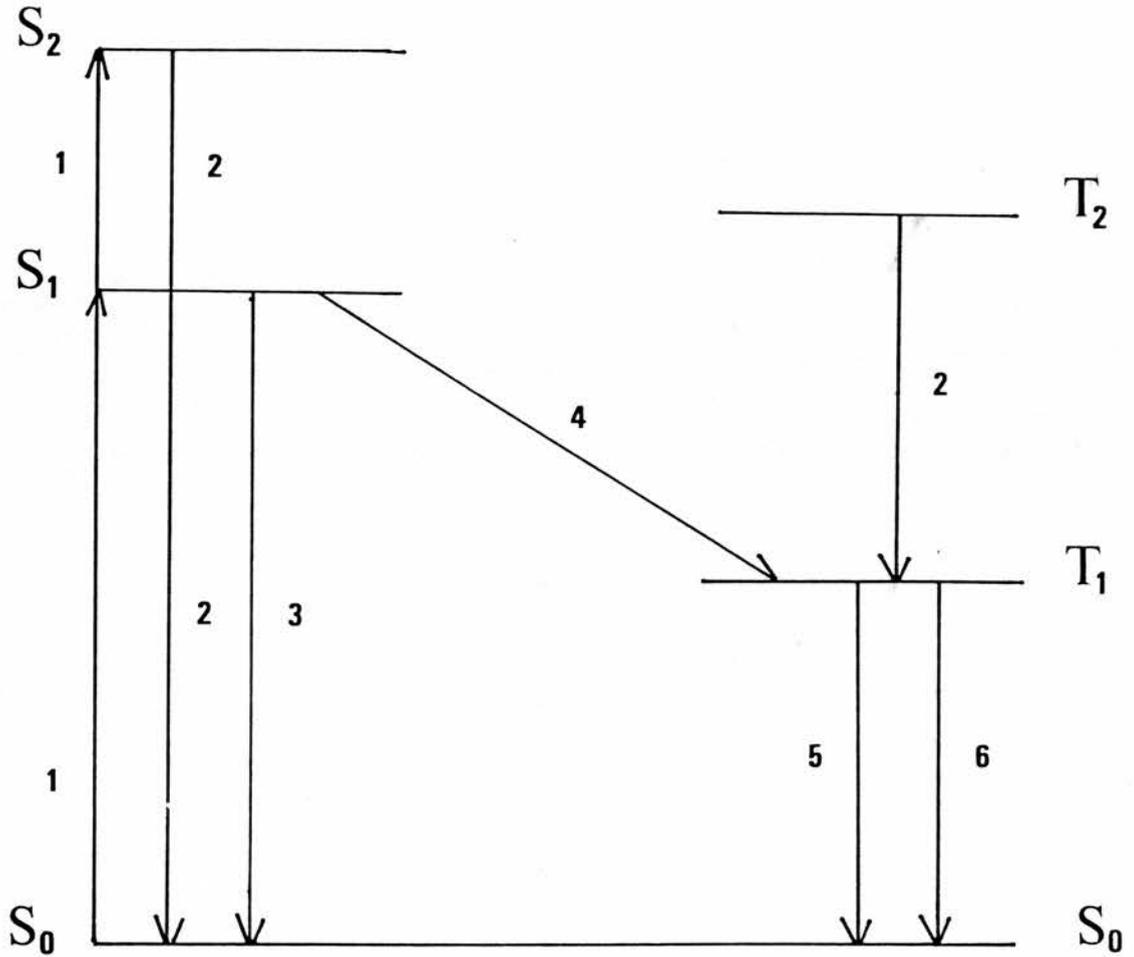


The S_1 state is also susceptible to a different type of non-radiative deactivation route leading to the formation of an excited triplet species. This transition, known as intersystem crossing, can occur from the zero point vibrational level or thermally populated levels of S_1 [42].



The duration or life-time of singlet state emission is typically 10^{-8} - 10^{-9} s. Hence, excited singlet states are deactivated by a range of competitive processes, the balance of which determines the magnitude and relative importance of the characteristic fluorescence parameters such as life-time and quantum yields.

Figure 2.1

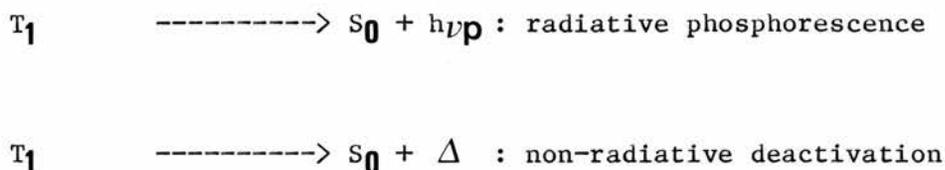


1. Absorption (Ia)
2. Internal Conversion (kGM)
3. Fluorescence (kFM)
4. Intersystem Crossing (kTM)
5. Intersystem Crossing (kGT)
6. Phosphorescence (kPT)

2.1.3 Phosphorescence

Phosphorescence is defined as radiative emission of a photon occurring between states of different spin multiplicity, the most common example being the $T_1 \rightarrow S_0$ transition [43]. The series of events culminating in phosphorescence from the lowest excited triplet state are also shown in Figure 2.1.

Due to the small probability associated with the direct electronic absorption $S_0 \rightarrow T_1$ [44], the triplet state is not nominally accessible by direct optical excitation but is generally populated via the non-radiative mechanism of intersystem crossing operating on an excited singlet state. The efficiency of this complex mechanism is dependent upon the nature of the excited species concerned and for some states on the chemical environment [45]. Once formed, the excited triplet state is also subject to competing radiative and non-radiative deactivation paths.



In accordance with Hund's rule [46] the energy of the singlet state is greater than that of the corresponding triplet state, that is, S_n is of higher energy than T_n .

2.1.4 Spin Selection Rules

Electronic transitions are subject to multiplicity selection rules forbidding transitions involving a change in the total electron spin quantum number [47]. Hence, radiative fluorescence is spin allowed whereas radiative phosphorescence is spin forbidden. The fact that the latter is observed indicates some relaxation of the selection rule, and this is due to the intersystem crossing mechanism of spin-orbit coupling which introduces a small admixture of singlet character into triplet states and a small admixture of triplet character into singlet states.

M.A.El-Sayed [48,49] has demonstrated that spin-orbit coupling between singlet and triplet σ, σ^* states of the same or different configurations is forbidden to the first order, but that spin-orbit coupling between σ, σ^* and π, π^* states is allowed.

2.1.5 Definition of Life-Time and Rate Parameters

The probability of a unimolecular process is independent of time and it is expressed as a first order rate parameter k_x , measured in s^{-1} . If an excited molecular species decays by a unimolecular process with a rate constant k_x , the rate of decay can be written as,

$$-\frac{d[A^*]}{dt} = k_x [A^*] \quad \dots 2.1$$

Integration yields,

$$[A^*] = [A_0^*] \exp(-k_x t) \quad \dots 2.2$$

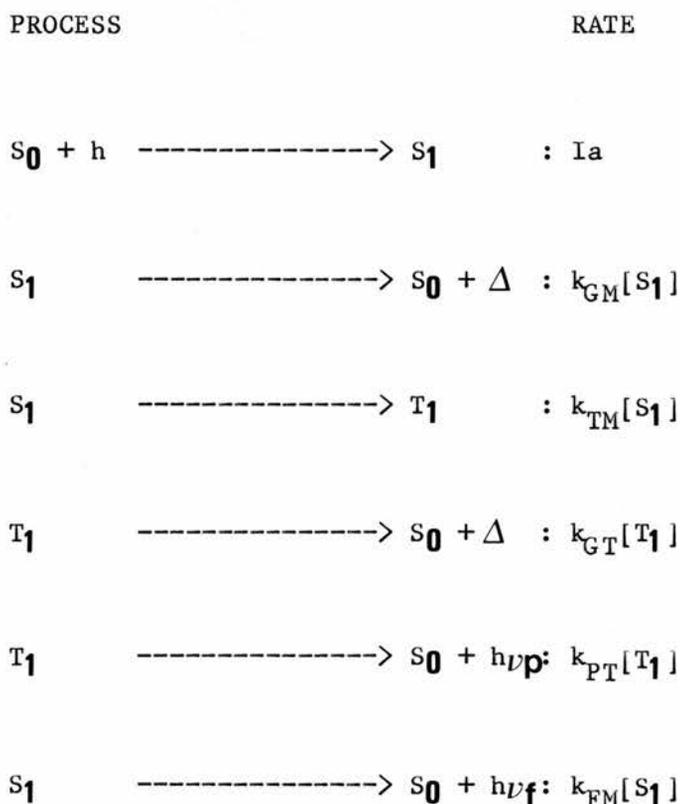
And in the form of a linear plot,

$$\ln[A^*] = \ln[A_0^*] - k_x t \quad \dots 2.3$$

Hence, the value of k_x can be obtained from the resulting straight line and the mode of decay is termed exponential. Often in luminescence studies such a plot is non-linear and under such circumstances the mode of decay is termed non-exponential.

Having established this terminology, it is necessary to consider the events following photon absorption in more depth, with particular reference to phosphorescence. In the following discussion, the

notation of J.B.Birk's [50] will be employed to describe the relevant rate parameters. In the absence of irreversible photochemical reactions and a specific bimolecular quenching, the photophysical scheme outlined defines the important deactivation paths of a molecule raised to its lowest excited singlet state S_1 .



The steady state analysis, applicable to conditions of constant illumination, leads to the following expressions for excited singlet and triplet concentration

$$I_a = (k_{TM} + k_{FM} + k_{GM}) [S_1]$$

$$[T_1] (k_{PT} + k_{GT}) = k_{TM} [S_1]$$

By definition [50] the total rate parameter k_x is the sum of all the unimolecular processes, other than dissociative, operating on an excited state. This leads to the definition of an emission life-time τ , which is equal to the inverse sum of all the rate processes that deactivate the excited state. Hence,

$$\tau = 1 / \sum_{i=0}^n (k_i) \quad \dots 2.4$$

On applying this criteria to the photophysical scheme outlined, a simple expression is derived for the phosphorescence or triplet life-time.

$$\tau_T = 1 / (k_{PT} + k_{GT}) = 1 / k_T \quad \dots 2.5$$

In electronic spectroscopy the luminescence emission intensity is used to follow the course of the decay and if the system is thought to obey the above scheme, it can be deduced from equation 2.3 that a plot of $\ln(\text{Phos. Int.})$ against time ought to be linear with gradient $-k_T$. Before continuing, it is necessary to clarify a point of potential confusion. Radiative life-times, τ^0 , are the life-times that would be observed in the absence of all other non-radiative deactivation processes by which the molecule could return to the ground state.

The development and interpretation of radiative and non-radiative transition theories are discussed in detail in references [51,52,53,54]. The definition of quantum yields provides another method of quantifying photophysical and photochemical events.

Definitions of triplet quantum yield, Φ_{TM} , phosphorescence quantum efficiency, q_{pT} and phosphorescence quantum yield, Φ_{PT} , are given in reference [55].

2.2 Excited State Interactions

In order to understand how excited state species behave in certain environments and how this behaviour can help elucidate photophysical properties pertaining to the solvent or environment, it is necessary to be aware of both unimolecular and bimolecular processes in which excited states can become involved. The following section briefly introduces a few such processes involving triplet states and their occurrence in polymer media.

2.2.1 Delayed Fluorescence

Delayed fluorescence, in which the emission decays more slowly than normal fluorescence from the same molecule, can arise by several mechanisms, of which the most closely investigated are thermally activated delayed fluorescence and triplet-triplet annihilation [56].

2.2.1.1 E-Type Delayed Fluorescence

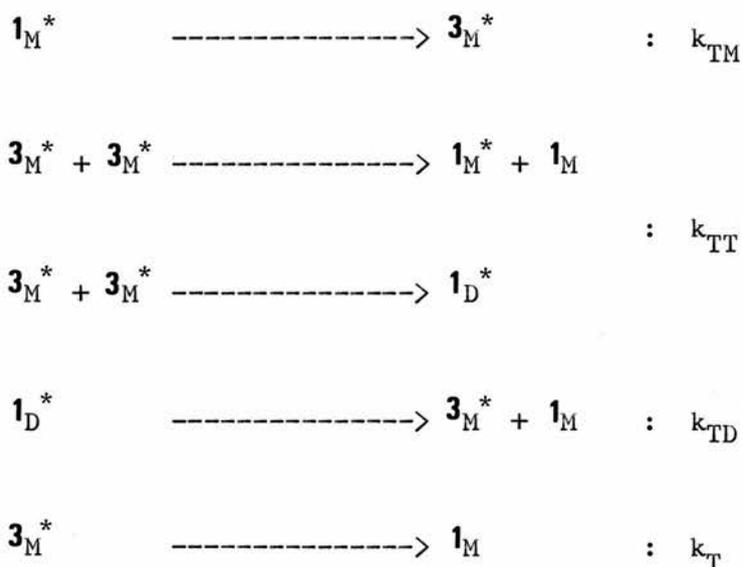
E-type delayed fluorescence, unimolecular in origin, and first observed in Eosin [57], involves fluorescence emission from S_1 after the excitation has resided temporarily in the triplet manifold [58]. This effect has been observed in both liquid and solid phases [30]. The process consists of thermal activation from the zero point vibrational level of T_1 through an energy ΔE_{S-T} , that is, the $S_1 - T_1$ energy gap [59]. The ratio of the intensities of delayed fluorescence (I_{DF}) and phosphorescence (I_P) decreases exponentially with the singlet-triplet splitting and with the reciprocal of the absolute temperature.

$$I_{DF}/I_P \propto \exp -(E_S - E_T)/RT \quad \dots 2.6$$

Hence, this emission is not predicted to occur appreciably at low temperatures and for molecules possessing large values of ΔE_{S-T} , such as aromatic hydrocarbons [59].

2.2.1.2 P-Type Delayed Fluorescence

This type of emission was first observed for pyrene [60] and has its origin in a bimolecular interaction between triplet excited states, termed triplet-triplet annihilation, resulting in the formation of the excited singlet state species responsible for the delayed fluorescence [61]. The following kinetic scheme has been proposed by J.B.Birks [62], where M and D represent monomer and excimer species respectively.



Under conditions of flash excitation J.B.Birks [62] derived the following equation for the rate of $\mathbf{3}_M^*$ formation,

$$\frac{d[\mathbf{3}_M^*]}{dt} = k_{TM}[\mathbf{1}_M^*] + k_{TD}[\mathbf{1}_D^*] - k_T[\mathbf{3}_M^*] - k_{TT}[\mathbf{3}_M^*]^2 \quad \dots 2.7$$

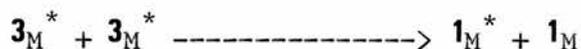
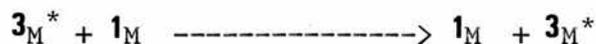
If repopulation of the triplet state is ignored and $k_{TM}[\mathbf{1}_M^*]$ and

$k_{TD} [1D^*]$ are neglected in comparison with the other terms [63,67], equation 2.7 reduces to

$$\frac{d[{}^3M^*]}{dt} = -k_T[{}^3M^*] - k_{TT}[{}^3M^*]^2 \quad \dots 2.8$$

The mode of fluorescence decay can now be discussed in terms of k_T and k_{TT} . If $k_T \gg k_{TT}[{}^3M^*]$, experimentally corresponding to low excitation intensity, then the emitted delayed fluorescence is expected to decay exponentially. However, if the experimental conditions are such that $k_T \ll k_{TT}[{}^3M^*]$, then delayed fluorescence intensities have a common non-exponential bimolecular decay. Both such limiting cases have been observed experimentally [64]. There are numerous confirmed examples of P-type delayed fluorescence in rigid solutions at 77 K [65,66] and similar observations have been reported in studies utilizing poly(methylmethacrylate) as a rigid matrix [67] and for certain polymers containing aromatic or heterocyclic moieties in monomer repeat units [68,69,70].

A mechanism for triplet-triplet annihilation in the solid state, shown below, has been proposed by A.N.Naqvi [71] who suggested the involvement of ${}^3M^*$ energy migration, leading to an electron exchange interaction.



Hence, the link between P-type delayed fluorescence in rigid solution

and triplet energy migration involving interaction between adjacent triplet excited and singlet ground state monomer units along a polymer chain is particularly relevant.

2.3 MOLECULES UNDER INVESTIGATION

The triplet spectral characteristics of the molecules used in the present study are listed in Table 2.1. The photophysical properties of benzophenone have been well documented in an extensive range of host media [72,73,74,75,76], reflecting the active interest shown in the luminescence properties of n, π^* triplet states [77,78,79,80,81]. The data correlated in Table 2.2 illustrates the magnitude and variation in the reported phosphorescence life-times of some aromatic ketones in a selection of hydrocarbon/alcohol glasses at 77 K.

In contrast to the short phosphorescence life-times of aromatic ketones, aromatic hydrocarbons possessing π, π^* triplet states are generally associated with long phosphorescence life-times. For example, the triplet decay of naphthalene-d-8 and triphenylene have been shown to be exponential in hydrocarbon glasses at 77 K, with life-times of 22 s [82] and 16 s [83] respectively.

TABLE 2.1

MOLECULE	T_1	E_T kJ mol ⁻¹	ΔE_{S-T} kJ mol ⁻¹	ϕ_{TM}	ϕ_{PT}
ACETOPHENONE	$n\pi^*$	308	21	1.0	0.62
ANTHRONE	$n\pi^*$	300	22	1.0	<1.0
CARBAZOLE	$n\pi^*$	294	59	<1.0	<1.0
BENZOPHENONE	$n\pi^*$	290	21	1.0	0.74
TRIPHENYLENE	$\pi\pi^*$	285	84	0.9	0.50
PHENANTHRENE	$\pi\pi^*$	260	86	0.80	0.13
NAPHTHALENE-d-8	$\pi\pi^*$	254	126	0.38	0.10
BENZIL	$n\pi^*$	213	24	0.92	<1.0

TABLE 2.2

MOLECULE	MATRIX/GLASS	τ_T MS	Ref
ANTHRONE	ether/ethanol	1.7	78
ACETOPHENONE	E.P.A.	8.0	124
ACETOPHENONE	ether/ethanol	2.8	222
BENZOPHENONE	E.P.A.	5.8	117
BENZOPHENONE	ether/toluene	3.9	93
BENZOPHENONE	ether/ethanol	4.7	132
BENZOPHENONE	heptane	5.2	80

2.4 POLYMER SUPPORT MATRICES UNDER INVESTIGATION

The use of polymers as inert host matrices or solvents to study the phosphorescence of organic molecules has become increasingly popular [67,84,85] and can be rationalized in terms of certain advantages that plastics offer over the more traditional inert solvents used in such studies. For instance, boric acid glasses are difficult to obtain free of impurities and glucose glasses are sensitive to moisture [86]. The most commonly used solvents, the hydrocarbon/alcohol glasses, are severely restricted by the temperature range they can accommodate. These reasons have made poly(methylmethacrylate), which remains a solid glass up to 100° C, very popular as an inert support matrix and coupled with its ease of preparation, optical clarity and the fact that it can be machined to desired shapes or used as thin films, makes its use even more attractive.

Many plastics are available but they may not all be suitable for a given study, being restricted by solubility, absorption spectrum or other physical properties. A necessary feature of a support matrix is that it should be inert, that is, not directly interfere with the decay processes and its absorption spectrum should not prohibit the selective excitation of a wide class of molecules. Unavoidably, the solvent, whether polymer or glass, will play a role in the decay process to the extent of accepting vibrational energy from molecules as they undergo internal conversion and vibrational deactivation. However, it is only when the matrix is directly capable of accepting electronic energy or if it contains a heavy atom, that it exercises a

significant perturbation over the characteristic decay processes of the guest molecule, and thereby raising the question of its validity for use as an inert support host.

Polymers such as poly(1-vinylnaphthalene) and poly(vinylcarbazole) would not fall into the class of commonly considered inert matrices; the former possessing an accessibly low triplet energy level and the latter displaying an absorption spectrum that would make selective guest excitation difficult to achieve. Similarly, poly(vinylchloride), although not possessing a readily accessible triplet level or prohibitive absorption spectrum, could not be considered inert due to the presence of the heavy atom chlorine. Such considerations have led to the use of poly(methylmethacrylate), poly(vinylacetate) and even polystyrene as support hosts in photophysical studies.

The triplet behaviour of organic molecules studied in poly(methylmethacrylate) have been explained without seriously considering the involvement of the polymer triplet energy level [84]. However, evidence from a variety of sources [87,88,89] has prompted the suggestion that the triplet level of poly(methylmethacrylate) could conceivably become involved in guest triplet decay mechanisms, thus raising doubt concerning the applicability of allegedly inert polymers as host matrices. The conditions required for electronic energy transfer to occur, one form of non-radiative matrix involvement, are outlined in detail in Chapter Four. However, at the present juncture, it is necessary to emphasize the importance of the energy levels of the participants in the transfer. Electronic energy transfer involving triplet states is most favoured when the energy difference between the donor and acceptor states is large, resulting

in exothermic transfer. Reports have also appeared invoking the possibility of endothermic electronic energy transfer in polymer systems [88,89].

Table 2.3 lists the triplet energy levels of some commonly considered inert polymers together with a selection of polymers that have been shown to display photophysical processes at the triplet level. When a molecule does not exhibit spectral luminescence it is difficult to obtain reliable estimates of its excited state energy levels and to overcome this problem indirect experimental methods have to be applied [87,91]. Such is the case for the quoted polymeric ester triplet energy levels in Table 2.3. When the polymer displays luminescence emission, the task of locating the position of excited states is simpler and assignment more dependable.

TABLE 2.3

POLYMER	E_T kJ mol ⁻¹	Ref
POLY(METHYLMETHACRYLATE)	297	87
POLY(VINYLCETATE)	290	190
POLY(VINYLCARBAZOLE)	300	190
POLYSTYRENE	286	190
POLY(1-VINYLNAPHTHALENE)	220	240
POLY(VINYLBENZOPHENONE)	281	233
POLY(PHENYLVINYLBENZOPHENONE)	290	233

2.5 FACTORS INFLUENCING PHOSPHORESCENCE DECAY

The various problems inherent in understanding the phosphorescent emission of a triplet excited state molecule make it necessary to clearly define all the perturbations whether intrinsic or extrinsic, intramolecular or intermolecular, which could conceivably interfere with the decay mechanism. These extraneous perturbations can be conveniently introduced and discussed in terms of the following factors, the heavy atom effect, non-heavy atom solvents and temperature.

2.5.1 The Heavy Atom Effect

The heavy atom effect is most pronounced when the parent structure possesses weak intersystem crossing; a situation typified by most aromatic hydrocarbons containing only π, π^* excited states. A classical example of the internal heavy atom effect is exhibited by naphthalene and its halo-derivatives [92], in which successive substitution of halogen atoms for a hydrogen atom leads to a decrease in Φ_{FM} and an accompanying increase k_{GT} and k_T , resulting in a reduction in the phosphorescence life-time.

In contrast, similar effects in molecules containing the carbonyl group are not so important due to their intrinsically strong spin-orbit coupling resulting in an efficient intersystem crossing mechanism [93]. Recent reports indicate that the situation might not be as simple as first thought [94]. The results of a comprehensive study by N.Hirota et al. [95,96,97] conform to the generally accepted

view that the triplet decay characteristics of n, π^* states are not significantly altered by the presence of external heavy atoms [98,99]. However, in their concluding remarks, these authors felt it necessary to qualify the previously accepted rule that the absence of a heavy atom effect can be used as a diagnostic in differentiating between π, π^* and n, π^* triplet excited states.

There are numerous examples in the literature confirming the enhancement of the $S \rightarrow T$ process brought about by external agents such as oxygen [100], xenon [101] and organic halides [102].

2.5.2 Non-Heavy Atom Solvents

A brief review of reported phosphorescence life-times of a selection of molecules clearly illustrates that they may vary drastically in solid solutions even in the absence of heavy atoms [103]. For example, the phosphorescence life-time of benzene at -190°C has been reported as follows: 7 s in E.P.A [104], 5 s in dioxane [104], 3.3 s in ethanol [105], 0.95 s in water [105] and 0.6 s in the heavy atom solvent carbon tetrachloride [105]. The difference in the low temperature life-time of naphthalene-d-8 in durene and in an E.P.A. glass, 16.5 s and 22 s respectively, indicates that the triplet decay processes are altered by the environment [82].

Consideration of Table 2.2 shows how the life-time of benzophenone is dependent on the solvent. Although no definite conclusions can be drawn from this evidence alone, it is interesting to note that when toluene forms part of the glass the life-time is reduced, whereas alcoholic glasses are associated with slightly larger life-times. It has been stated that the life-time and phosphorescence

spectra of aromatic carbonyl and related compounds are dependent upon the nature of the environment [95,106,107,108,109].

2.5.3 The Effect of Temperature on Triplet Decay

The influence of temperature plays an important role in determining the observed luminescence behaviour of a molecule, for the intrinsic decay features of the excited state may have a specific temperature dependence irrespective of additional thermally induced processes and it is important to be aware of and to distinguish between such instances. In this context, except for benzene and its alkyl derivatives, the triplet life-time of aromatic hydrocarbons in dilute rigid solution is considered to be temperature independent [110]. Moreover, from a theoretical view point [110,51,52] the radiationless rate parameters appearing in the luminescence life-time expressions are thought to depend largely on intramolecular vibrational perturbations characteristic of the molecule under investigation. In addition, theory predicts that there will be no marked temperature effect on the radiationless transition probability between the lowest triplet and the ground state singlet [111].

The situation is further complicated by numerous reports appearing in the literature concerning the temperature dependence of both $\pi\pi^*$ and n,π^* triplet excited states [87,112,113,114] and each confirms the observation that the phosphorescence life-time decreases with increasing temperature. The limiting factor on the high temperature studies is often the phosphorescence quantum efficiency of the sample [67]. Hence, the relationship between luminescence

parameters and temperature is not simple and often the experimentally observed temperature dependence is greater than that predicted by theory, which implicates the involvement of thermally induced external quenching mechanisms [115].

Although the effects of temperature on phosphorescence life-time are discussed in the current chapter, the topic is considered in more detail in Chapter Three.

2.6 THE SIGNIFICANCE OF EXPONENTIAL AND NON-EXPONENTIAL DECAYS

In the course of the present chapter the occurrence of non-exponential triplet decays will be associated with a possible bimolecular interaction involving the polymer host matrix. Consequently, it is necessary to introduce other proposed explanations for the observation of non-exponentiality.

It has been established that a luminescence decay process described by equation 2.3 can be considered as unimolecular and the mode of decay termed exponential. Departures from exponentiality, usually most apparent at the initial part of the decay curve, can be considered as evidence for the occurrence of some bimolecular process or interaction operating on the excited state [67], but this need not always be so. A number of causes for non-exponentiality have been proposed, ranging from experimental faults such as sample impurities or instrumental inconsistencies to specific photophysical phenomena.

F.E.El-Sayed et al. [67] reviewed the literature for reported cases of triplet decay non-exponentiality, finding it to be rationalized in terms of, quenching by impurities [116,117], oxygen molecules [112], the aggregation of solute molecules [118] and in the

case of polymer solvents, to pseudo-first order quenching processes occurring in regions of relatively low viscosity [84].

These examples involve interactions between the molecule under investigation and external agents. However, in addition to the excited state interactions outlined in section 2.2, there have been suggestions that the molecule could interact with the electronic energy levels of the matrix or solvent [119,120]. The distinction between exponential and non-exponential decays and their use as a diagnostic in implicating a specific process is further complicated by acknowledging that certain molecules, irrespective of the solvent or temperature, always exhibit non-exponential decays [121,122,123]. A classical example is the aromatic ketone acetophenone, in which a vibronic interaction between neighbouring n, π^* and π, π^* triplet states is thought to be responsible for the non-exponentiality [124].

Electronic energy transfer, discussed in detail in Chapter Four, provides another explanation for the observation of non-exponentiality, easily demonstrated by classical energy transfer experiments [125,126]. In the absence of an energy acceptor, the luminescence decay of the donor is exponential, but deviates from exponentiality in the presence of an acceptor. Hence, the bimolecular process of electronic energy transfer is also associated with non-exponential donor decays, but does not follow the decay function of a bimolecular event.

2.7 EMISSION SPECTROSCOPY

Spectral information obtained from the absorption and emission properties of organic molecules can establish the nature of the emitting state and highlight the influence of the environment on that state [127]. Indeed, it is widely recognised that solvents can affect the energies of n,π^* and π,π^* triplet states of aromatic ketones [94,128] resulting in significant spectral shifts and that solvent polarity can have pronounced effects on the photochemistry and photophysics of these ketones [129,130,131]. Consequently, it was necessary to investigate the effect of polymer environment on the phosphorescence spectra of the molecules used in the present study.

2.7.1 n,π^* and π,π^* Phosphorescence in Polymers

The phosphorescence spectra of aromatic carbonyl compounds generally show a vibrational pattern characteristic of the C=O stretch in the ground state and such a pattern is consistent for emission from an n,π^* triplet state if the transition is localized on the carbonyl group [132]. In contrast, the phosphorescence spectra of aromatic molecules possessing a π,π^* triplet state exhibit a pattern of C=C vibrations indicative of the aromatic ring in S_0 . This difference is confirmed in figures 2.2 and 2.3, depicting the phosphorescence of benzophenone and naphthalene-d-8 in poly(methylmethacrylate) at 77 K. Hence, molecules display characteristic phosphorescence spectra when studied in polymer support matrices.

The direction and magnitude of a spectral shift will depend on

the polarizability and/or the dipole moment of the excited state relative to the ground state and on the polarizability of the medium [133]. If the excited state is more polarizable than the ground state, it exerts a greater attraction for the environment and a red shift to lower energy ensues; the converse results in a blue shift. Polystyrene is more polarizable than poly(methylmethacrylate) and is therefore predicted to interact with excited states to a greater extent. However, comparison of Figure 2.2 with Figure 2.4 shows the phosphorescence spectra of benzophenone to be identical in poly(methylmethacrylate) and polystyrene; indicating that differences in polymer polarizability do not discernibly alter the energy levels of triplet states.

2.7.2 Aromatic Ketone Fluorescence : Comment

During the course of the present study it was necessary to propose the occurrence of triplet-triplet annihilation in order to explain the triplet decay behaviour of aromatic ketones at certain temperatures. A direct consequence of such an interaction is the emission of P-type delayed fluorescence. However, the experimental detection of such an emission presents a formidable task and, considering its mechanistic importance, deserves to be commented upon.

Many aromatic aldehydes and ketones possess large rates of intersystem crossing ($k_{TM} = 10^{10} - 10^{11} \text{ s}^{-1}$) [80,134], resulting in correspondingly low quantum yields for prompt fluorescence ($< 10^{-4}$) [135], making such an emission difficult to observe. However, recent advances in the technique of time resolved

spectroscopy enabled M.W.Wolf et al. [136,137] to investigate aromatic carbonyl systems in which they successfully time resolved prompt fluorescence from the total emission and to identify E-type and P-type delayed fluorescence in solution at room temperature. While these results have been questioned by some [138], they have been confirmed by others [139]. This work [136,137] established the prompt fluorescence of the aromatic carbonyls considered, including benzophenone, to consist of a broad, structureless band which severely overlapped the phosphorescence band; a factor relevant to the present study. From the emission spectra presented, the prompt fluorescence component of benzophenone first appears at approximately 380 nm. Earlier work by P.F.Jones and R.Calloway [140] had placed the location of benzophenone delayed fluorescence in the region 385-475 nm in various polymer matrices at 300 K.

Figure 2.5 compares the effect of temperature on the appearance and location of the phosphorescence emission of benzophenone in the polymer poly(methylmethacrylate). It is clearly evident that the distinct structured resolution observed at 77 K diminishes at room temperature as a consequence of temperature broadening. In addition, emission at ambient temperatures starts to occur at lower wavelengths. However, bearing in mind the difficulties in the detection of aromatic carbonyl fluorescence, prompt or delayed, the ambient spectra shown fall short of conclusive evidence confirming delayed fluorescence, but would appear to be consistent with previous reports [140].

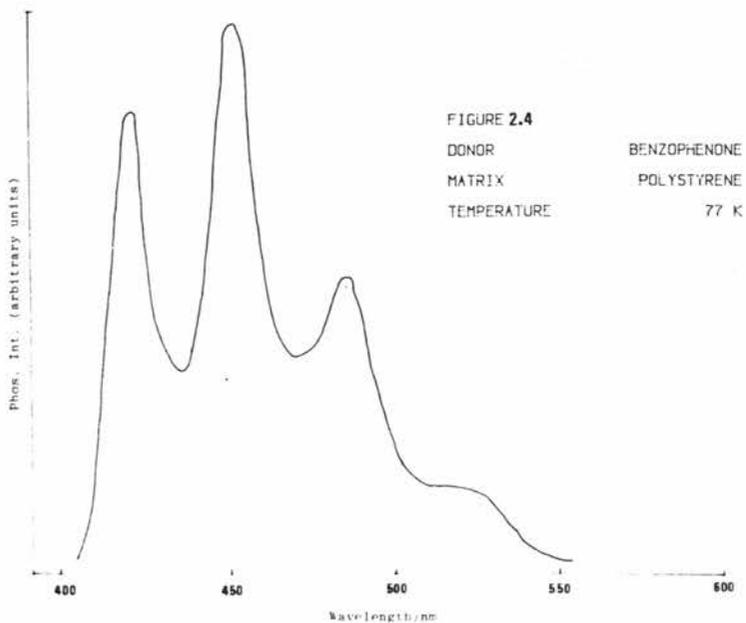
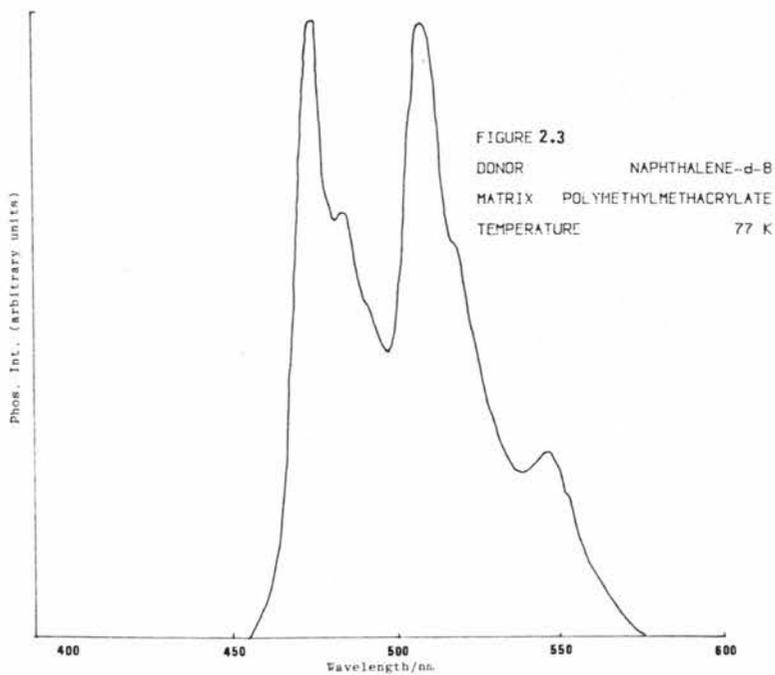
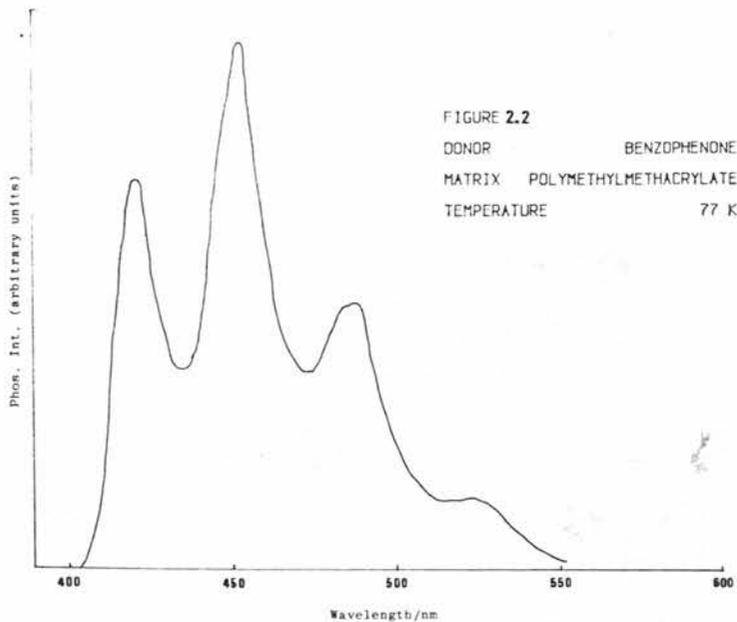
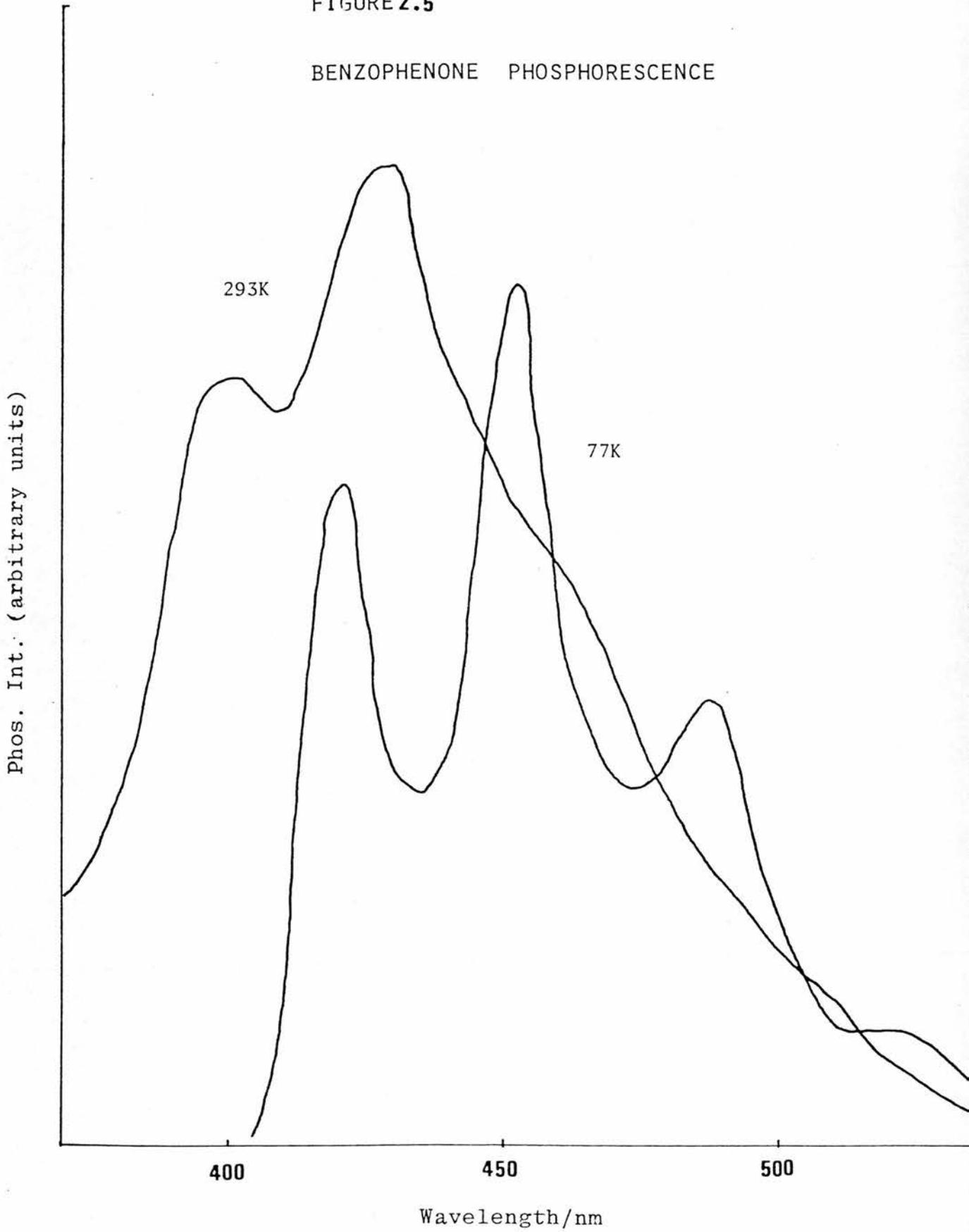


FIGURE 2.5

BENZOPHENONE PHOSPHORESCENCE



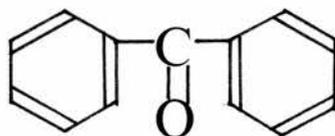
2.8 PHOSPHORESCENCE DECAY IN HOMOPOLYMERS

This section presents phosphorescence life-time data for the systems investigated. Each set of decay data was analysed in terms of a standard least squares fitting routine; the calculation performed by a computer programmed in Fortran. The quoted life-times represent the average of a number of runs carried out on different strips of the same polymer film and strips taken from different films. The quoted error covers any slight emission wavelength dependence and realistically estimates the reliability of the apparatus.

When using Apparatus B, a compromise between the desire to reduce the signal to noise ratio to a minimum whilst exposing the thin polymer film to short durations of exciting light, led to the signal averager being set for 64 scans, resulting in a noise reduction factor of 8. For each molecule the life-time was observed to be independent of concentration within the range 10^{-2} - 10^{-3} M. The aromatic hydrocarbons and aromatic carbonyls were investigated using Apparatus A and B respectively.

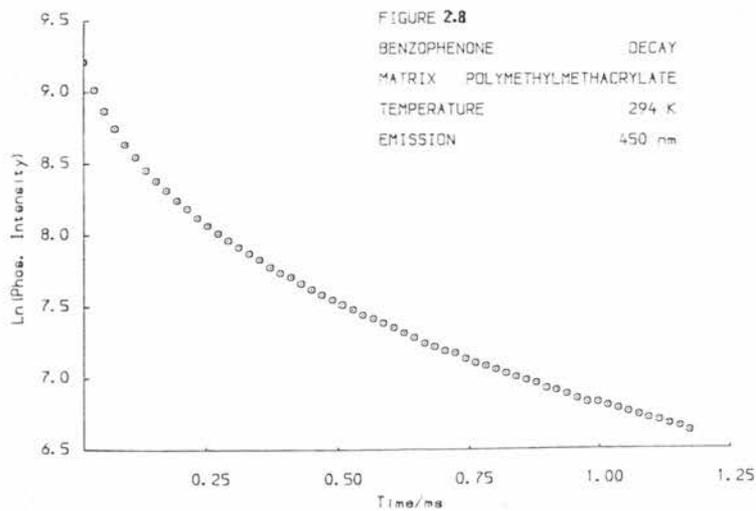
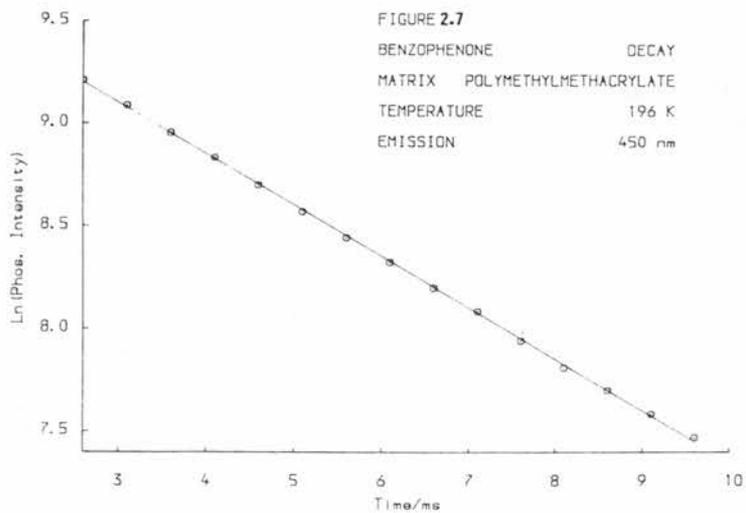
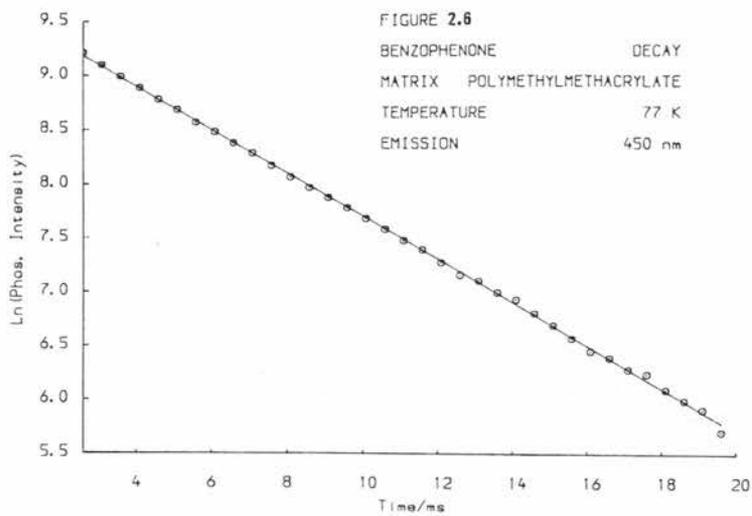
2.8.1 Decay of Benzophenone

The decay of benzophenone triplet emission was followed on the phosphorescence peak located at 450 ± 20 nm. In all the polymers studied decay at 77 K was always found to be strictly exponential over a sweep time of 20 ms. On raising the temperature to 196 K decays in the aliphatic polymers remained sufficiently exponential for equation 2.3 to apply, but a distinct departure from exponential behaviour was observed for the host matrix polystyrene. At this temperature the sweep time was reduced to 10 ms. Decay at room temperature was markedly non-exponential in all the polymers studied and so at such temperatures first order life-times could not be obtained.



Benzophenone

A representative sample of first order decay plots are shown in Figures 2.6-2.11 and the life-time data is shown in Tables 2.4-2.5.



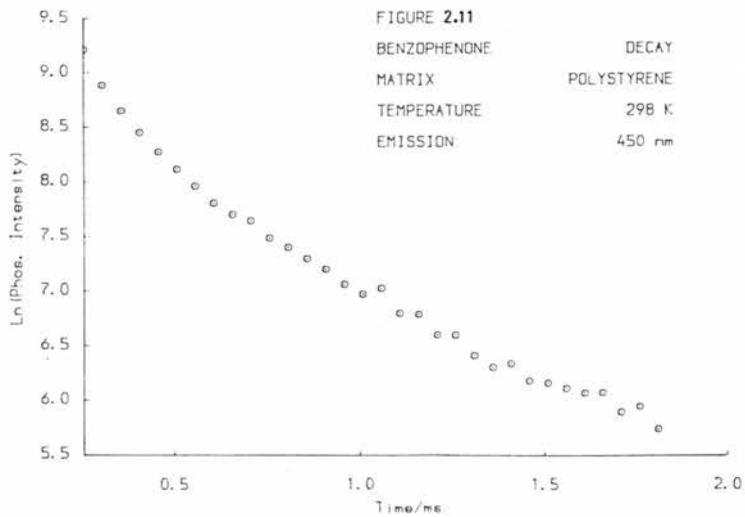
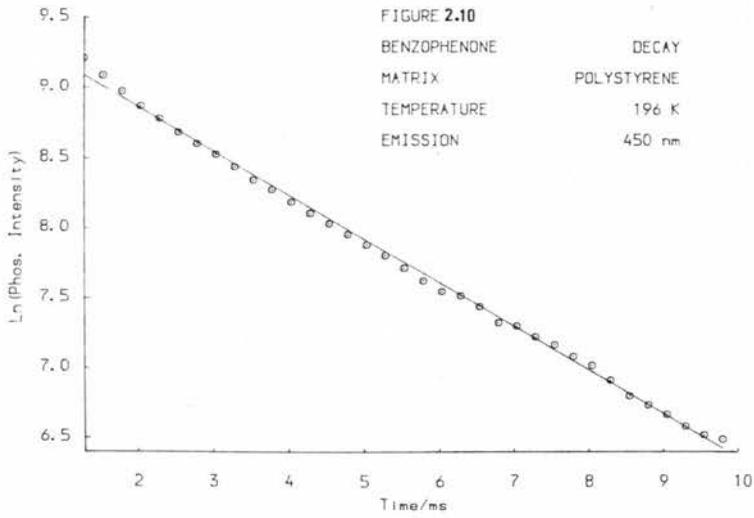
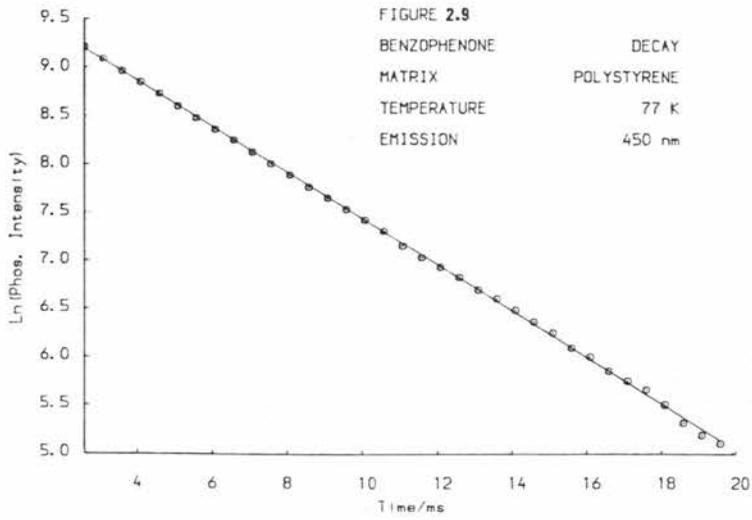


TABLE 2.4

DONOR BENZOPHENONE

POLYMER	τ_T ± 0.15 ns	TEMPERATURE 77K	
		k_T s^{-1}	DECAY MODE
POLY(METHYLMETHACRYLATE)	4.88	205	exp.
POLY(ETHYLMETHACRYLATE)	4.90	204	exp.
POLY(n-BUTYLMETHACRYLATE)	4.82	207	exp.
POLY(VINYLACETATE)	4.78	209	exp.
POLY(VINYLBUTYRAL)	4.95	202	exp.
POLYSTYRENE	4.25	235	exp.
POLY(VINYLCHLORIDE)	4.70	213	exp.

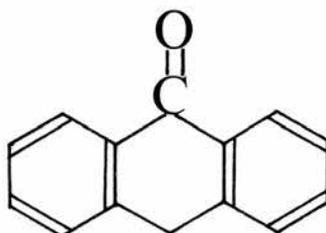
TABLE 2.5

DONOR BENZOPHENONE

POLYMER	τ_T ± 0.15 ns	TEMPERATURE 196K	
		k_T s^{-1}	DECAY MODE
POLY(METHYLMETHACRYLATE)	4.0	250	exp.
POLY(VINYLACETATE)	4.0	250	exp.
POLYSTYRENE	—	—	n. exp.

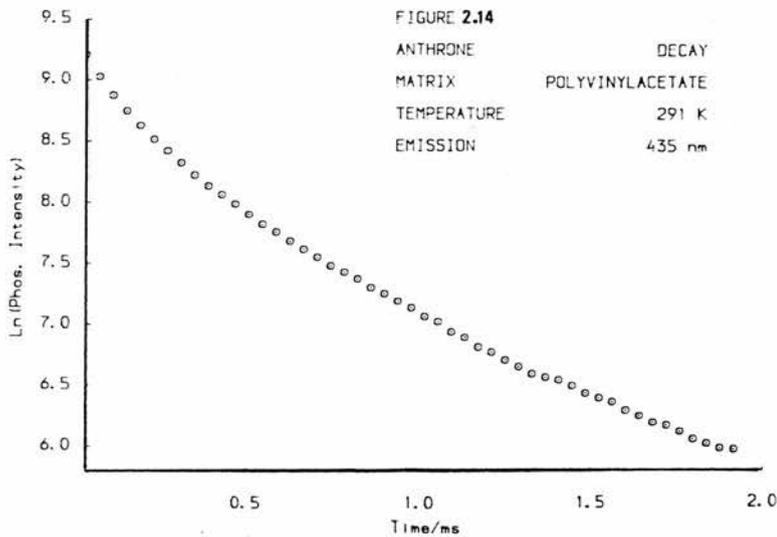
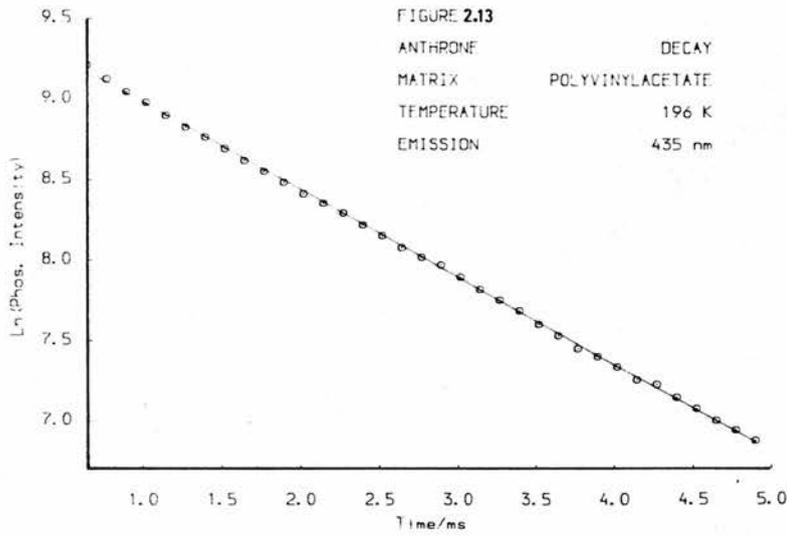
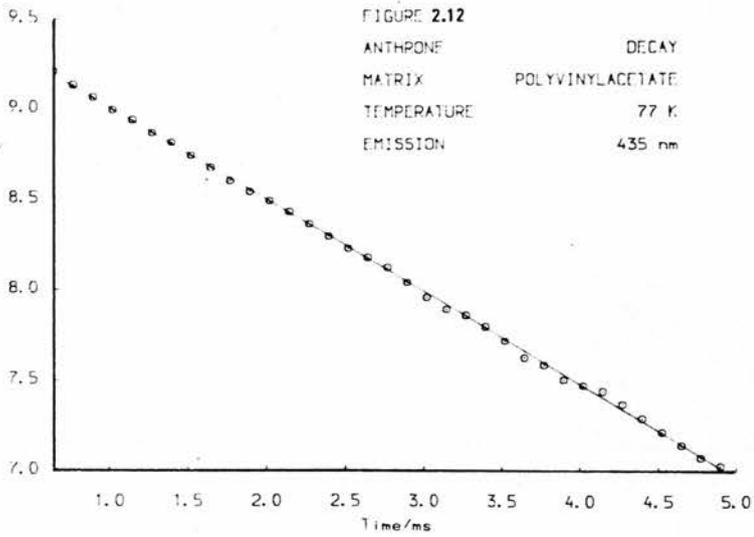
2.8.2 Decay of Anthrone

The depletion of the anthrone triplet state was followed on the phosphorescence maximum occurring at $435 \text{ nm} \pm 20 \text{ nm}$. In the range of polymers studied, decay of anthrone at 77 K was always consistently exponential over a sweep time of 5 ms, corresponding to decay over nearly three first order life-times. Decays measured at 196 K were still exponential in the aliphatic matrices, but non-exponential in polystyrene. However, at room temperature decay was significantly non-exponential in all the polymers used.



Anthrone

Examples of first order decay plots are shown in Figures 2.12-2.17 and the relevant life-time data is correlated in Tables 2.6-2.7.



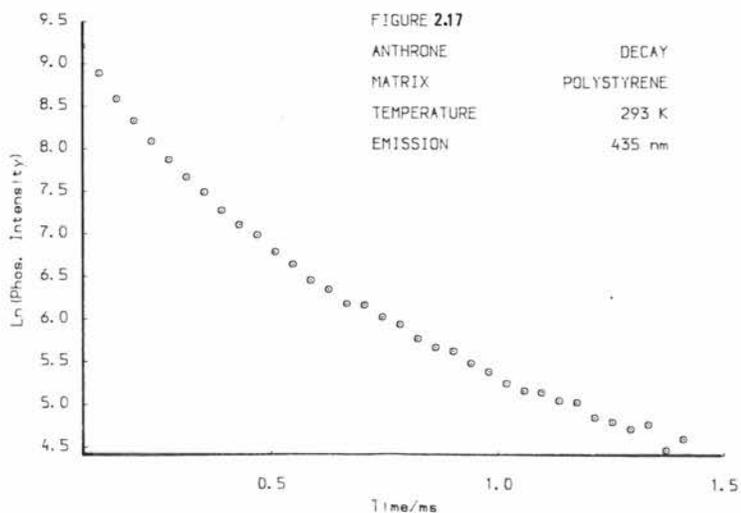
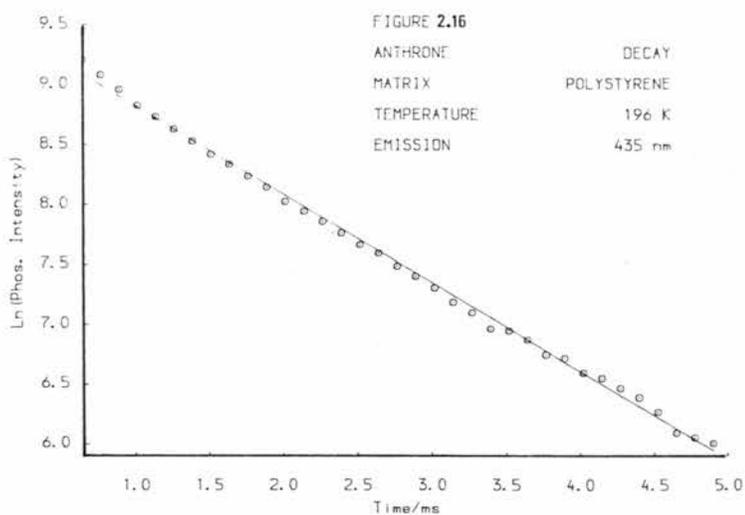
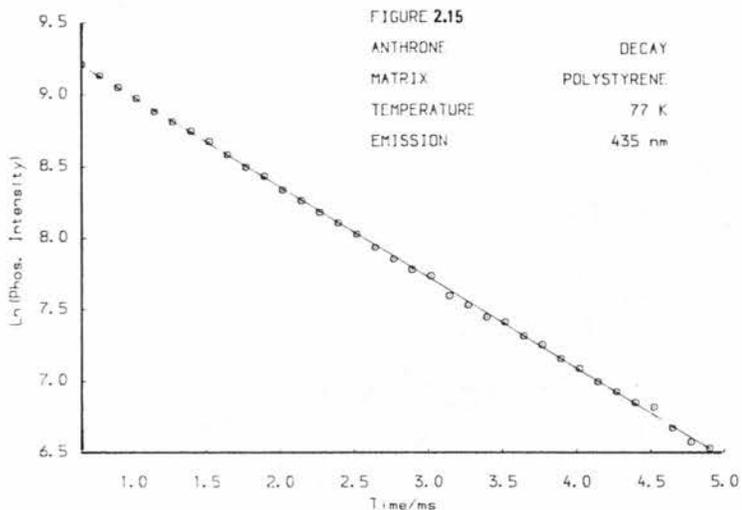


TABLE 2.6
DONOR ANTHRONE

POLYMER	τ_T ± 0.10 ms	TEMPERATURE 77K	
		k_T s^{-1}	DECAY MODE
POLY(METHYLMETHACRYLATE)	1.93	518	exp.
POLY(ETHYLMETHACRYLATE)	1.87	535	exp.
POLY(n-BUTYLMETHACRYLATE)	1.80	555	exp.
POLY(VINYLACETATE)	1.93	518	exp.
POLY(VINYLBUTYRAL)	1.94	515	exp.
POLYSTYRENE	1.60	625	exp.
POLY(VINYLCHLORIDE)	1.78	562	exp.

TABLE 2.7
DONOR ANTHRONE

POLYMER	τ_T ± 0.10 ms	TEMPERATURE 196K	
		k_T s^{-1}	DECAY MODE
POLY(METHYLMETHACRYLATE)	1.75	571	exp.
POLY(VINYLACETATE)	1.80	555	exp.
POLYSTYRENE	—	—	n. exp.

2.8.3 Decay of Benzil

The phosphorescence behaviour of benzil appeared to be more complicated in that decays measured at 77 K were not perfectly exponential and the phosphorescence life-time exhibited a wavelength dependence. However, first order life-times in accordance with equation 2.3 were estimated for decay in the aliphatic polymers, but not in polystyrene where departure from linearity was too severe. The decay of benzil at 196 K was even more non-exponential, consistent with the other aromatic carbonyl compounds.



Benzil

The experimental life-time data are shown in Table 2.8.

TABLE 2.8
DONOR BENZIL

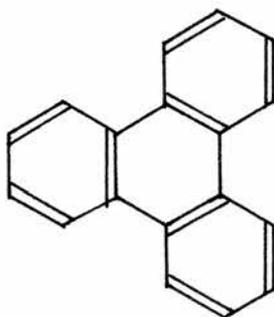
POLYMER	τ_T ± 0.15 ms	TEMPERATURE 77K	
		k_T s^{-1}	DECAY MODE
POLY(METHYLMETHACRYLATE)	5.48	182	exp.
POLY(VINYLCETATE)	5.46	183	exp.
POLYSTYRENE	—	—	n. exp.

TABLE 2.9
DONOR TRIPHENYLENE

POLYMER	τ_T ± 1.0	TEMPERATURE 77K	
		k_T s^{-1}	DECAY MODE
POLY(METHYLMETHACRYLATE)	16.0	0.063	exp.
POLY(VINYLBUTYRAL)	15.5	0.065	exp.
POLYSTYRENE	11.0	0.091	exp.

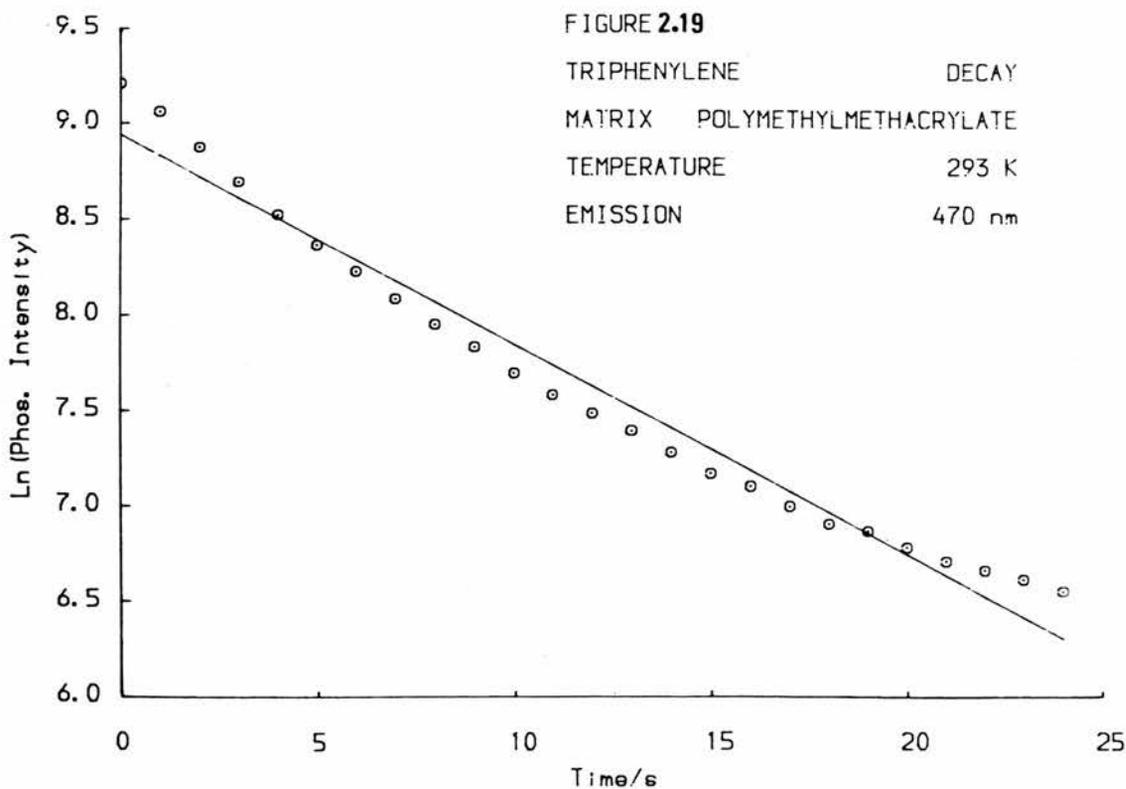
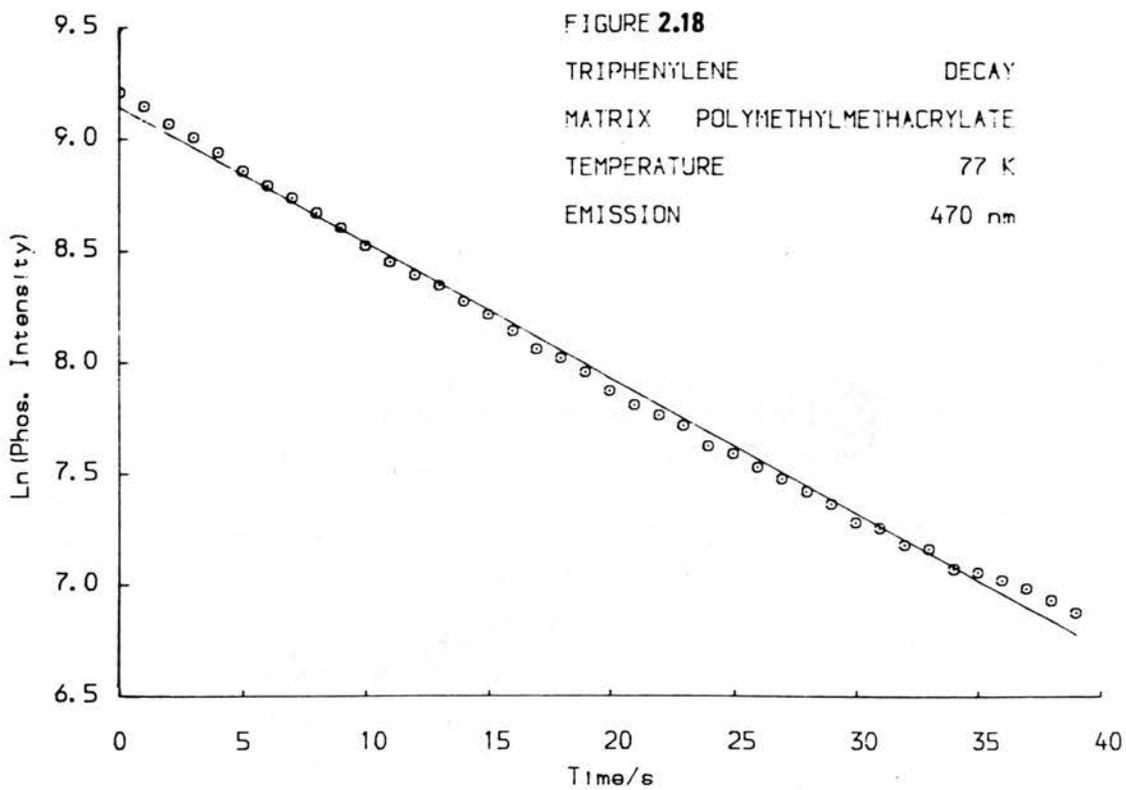
2.8.4 Decay of Triphenylene

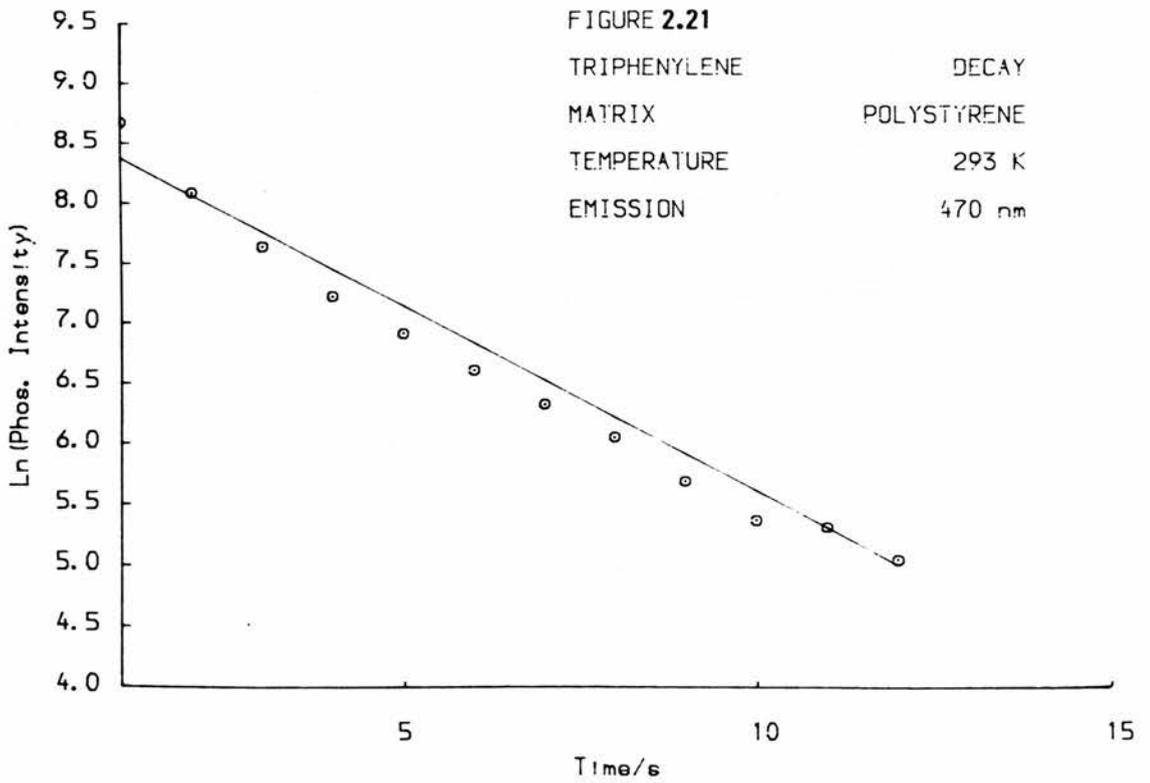
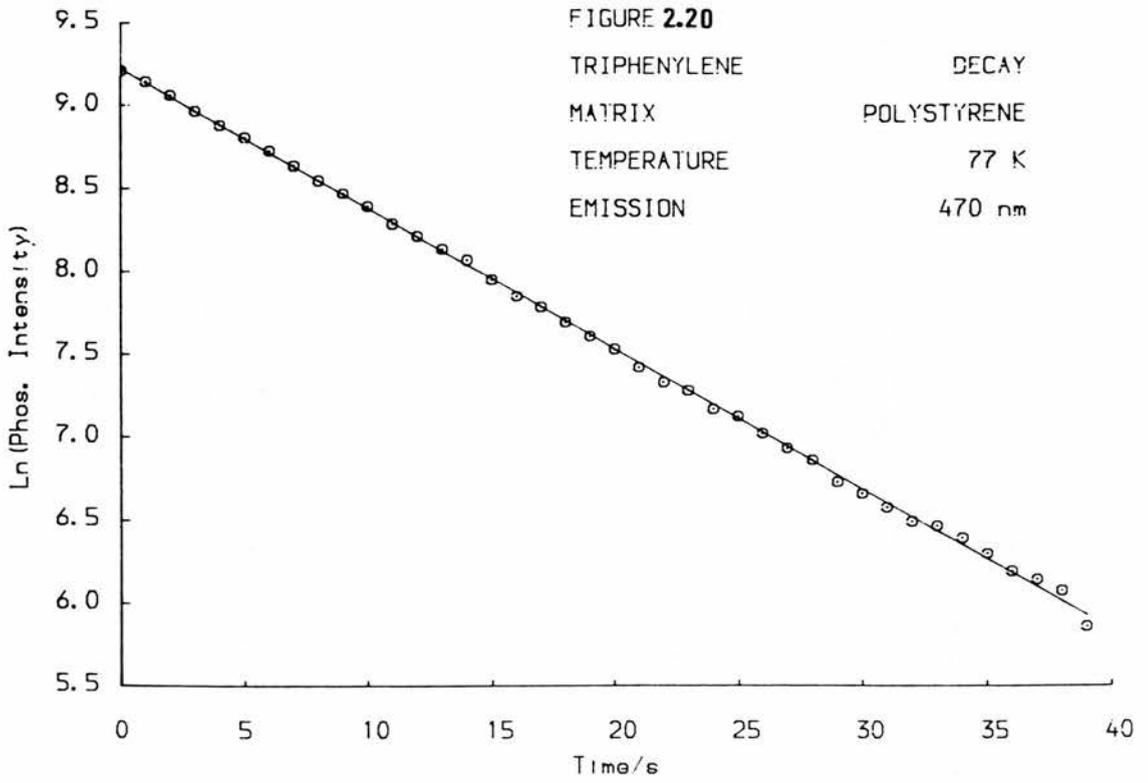
The decay of triphenylene phosphorescence was followed at wavelengths between 460-510 nm, with excitation occurring in the range 290-310 nm. The life-time was found to be independent of both these variables within the quoted experimental error. Decay at 77 K was found to be exponential over approximately three first order life-times in all the polymers considered. However, departures from linearity were observed at room temperature, particularly in polystyrene.



Triphenylene

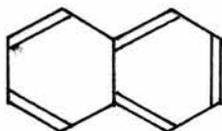
Examples of first order decays are shown in Figures 2.18-2.21 and the associated life-time data outlined in Table 2.9.





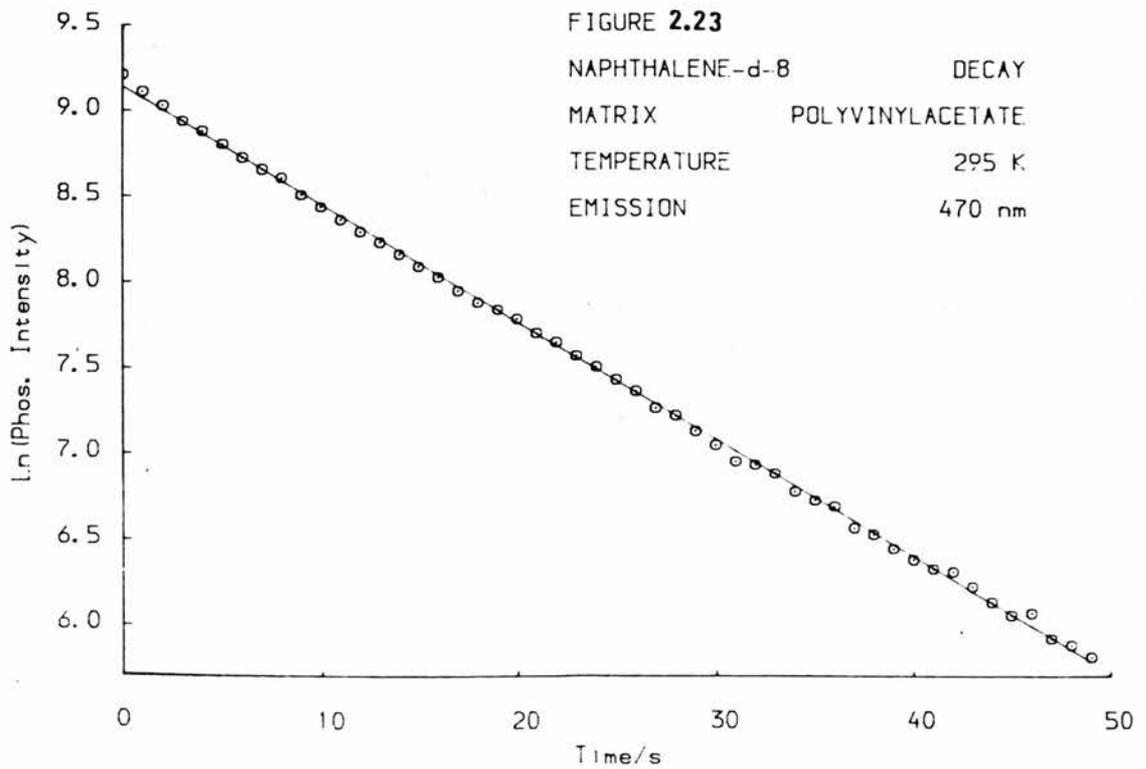
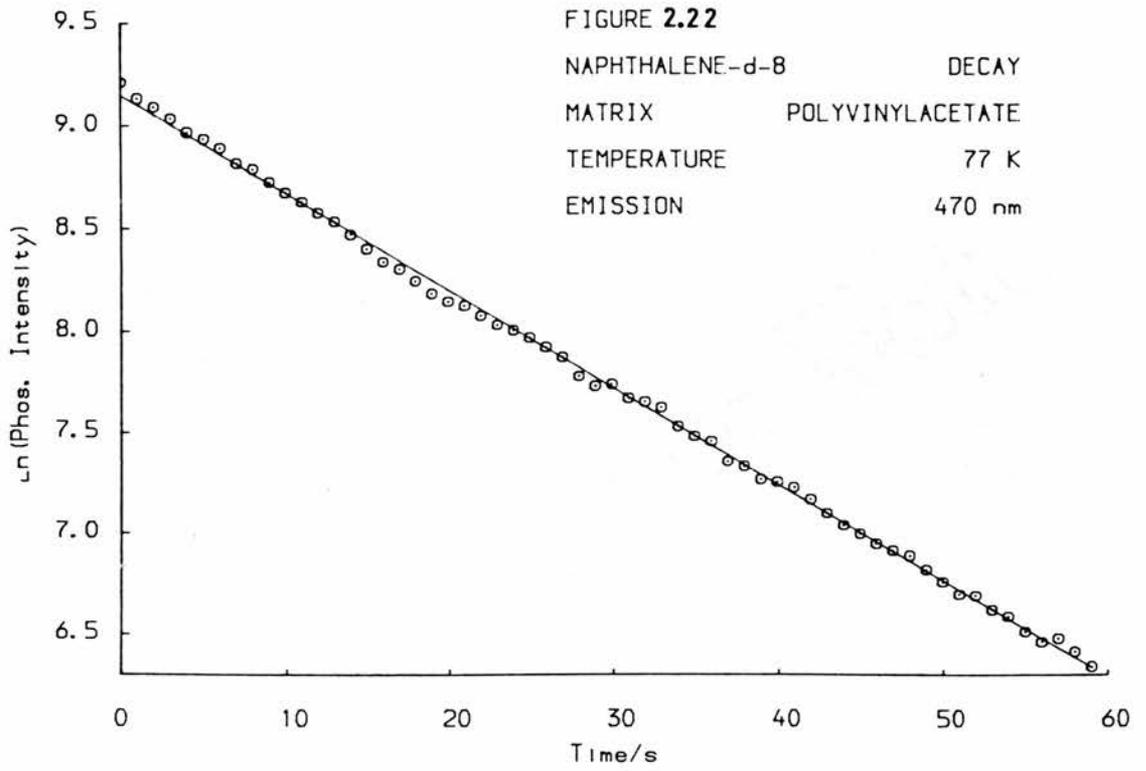
2.8.5 Decay of Naphthalene-d-8

The triplet decay of naphthalene-d-8 was followed on the phosphorescence peak located at approximately 470 nm and the life-time was found to be independent of excitation wavelength within the quoted error. The decay at 77 K was shown to be exponential in all the polymers studied. In addition, the room temperature decay in the aliphatic polymers was still exponential but non-exponential in polystyrene.



Naphthalene-d-8

A typical selection of first order decay plots are shown in Figures 2.22-2.25 and the relevant life-time data is listed in Tables 2.10-2.11.



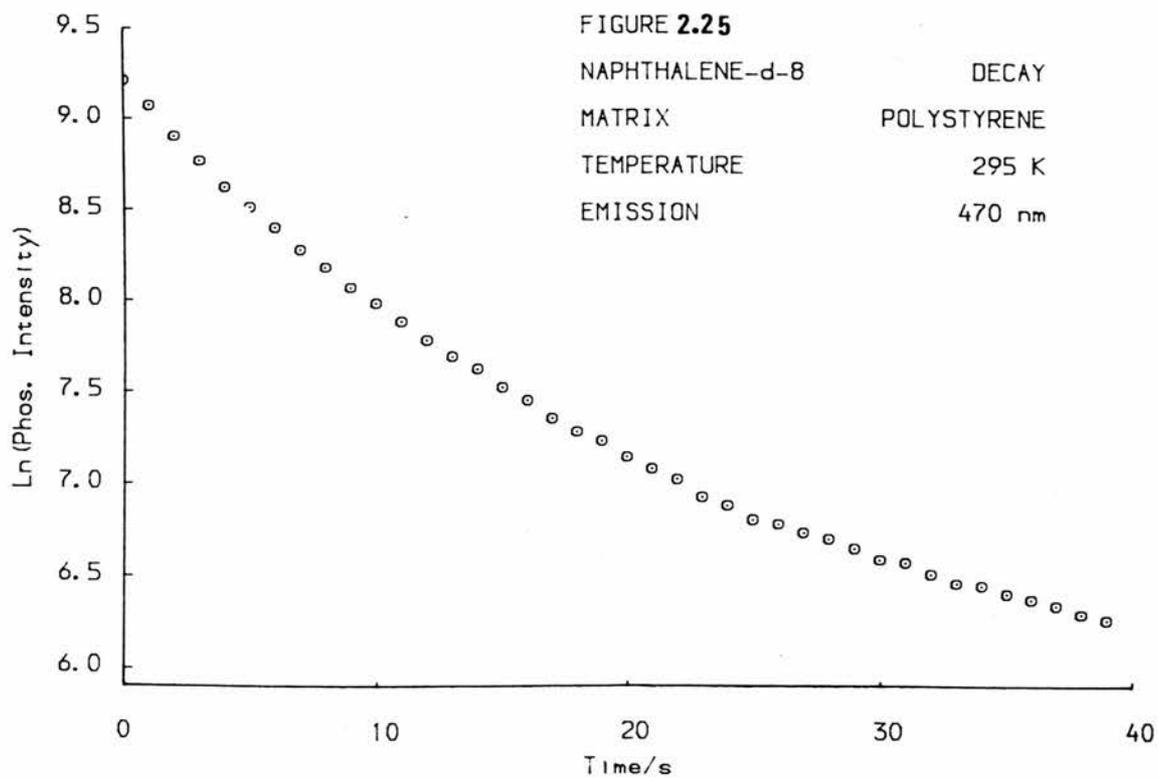
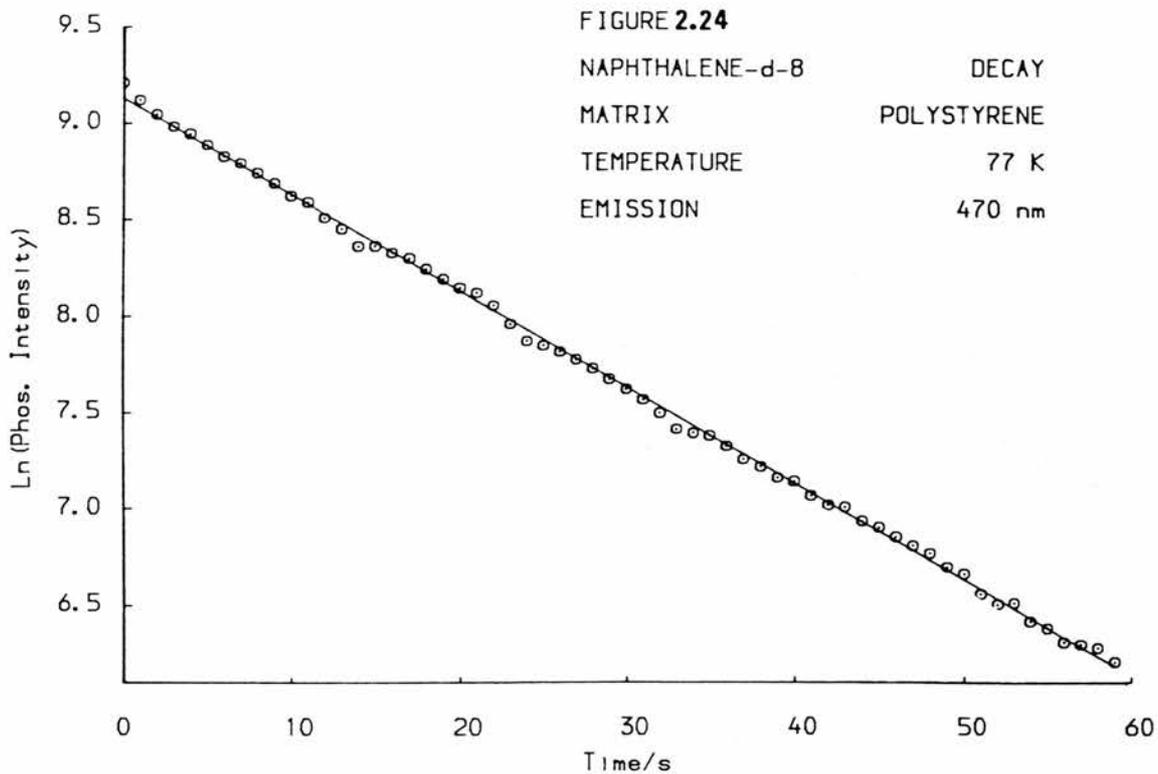


TABLE 2.10
DONOR NAPHTHALENE-d-8

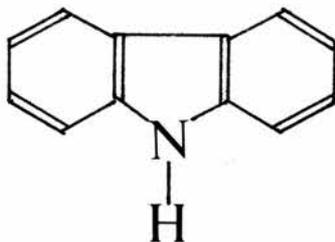
POLYMER	TEMPERATURE 77K		
	τ_T $\pm 1.0s$	k_T s^{-1}	DECAY MODE
POLY(METHYLMETHACRYLATE)	18.5	0.054	exp.
POLY(ETHYLMETHACRYLATE)	20.3	0.049	exp.
POLY(n-BUTYLMETHACRYLATE)	18.0	0.055	exp.
POLY(VINYLACETATE)	21.2	0.047	exp.
POLY(VINYLBUTYRAL)	17.5	0.057	exp.
POLYSTYRENE	8.4	0.119	exp.
POLY(VINYLCHLORIDE)	19.0	0.053	exp.

TABLE 2.11
DONOR NAPHTHALENE-d-8

POLYMER	TEMPERATURE 295K		
	τ_T $\pm 1.0s$	k_T s^{-1}	DECAY MODE
POLY(METHYLMETHACRYLATE)	12.1	0.083	exp.
POLY(VINYLACETATE)	14.0	0.071	exp.
POLYSTYRENE	—	—	n. exp.

2.8.6 Decay of Carbazole

The decay of carbazole phosphorescence was measured on emission peaks located at 410 nm and 440 nm, with the excitation monochromator set at either 300 nm or 337 nm and under such conditions the life-time was constant within the quoted error. Decay at 77 K was found to be exponential over approximately four first order life-times in both polymers studied and remained so at 193 K but with a shorter life-time.



Carbazole

Typical first order decay plots are shown in Figures 2.26-2.27 and the life-time data is correlated in Tables 2.12-2.13.

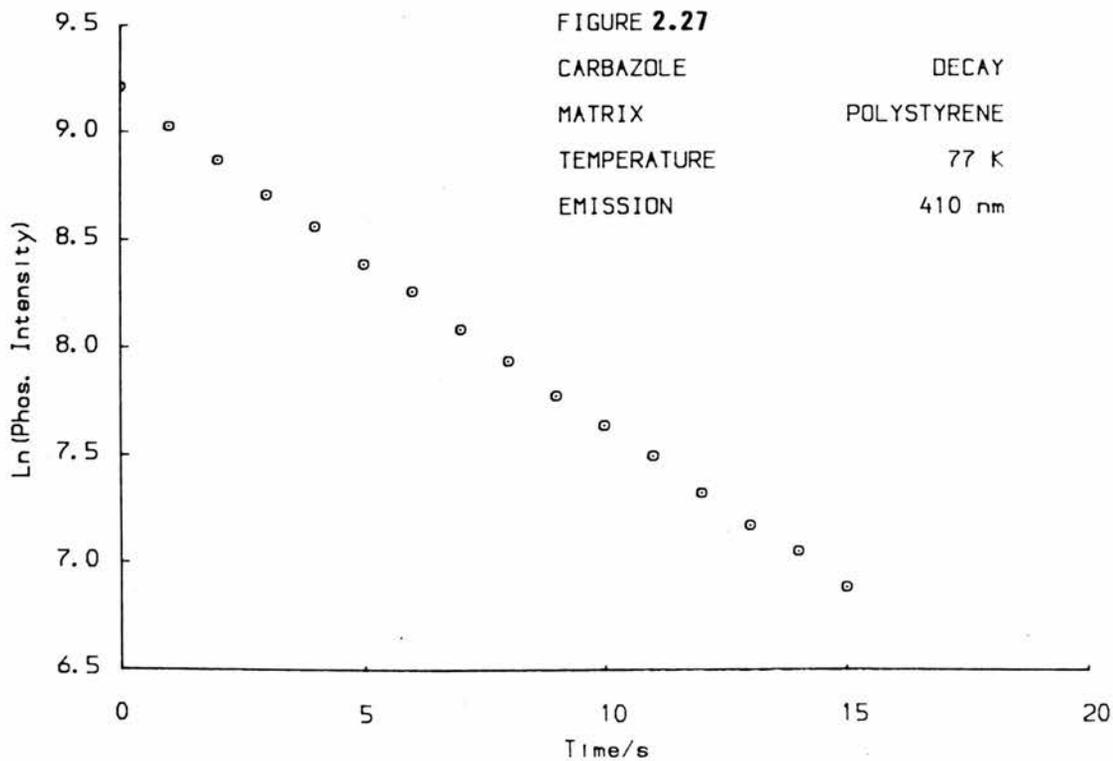
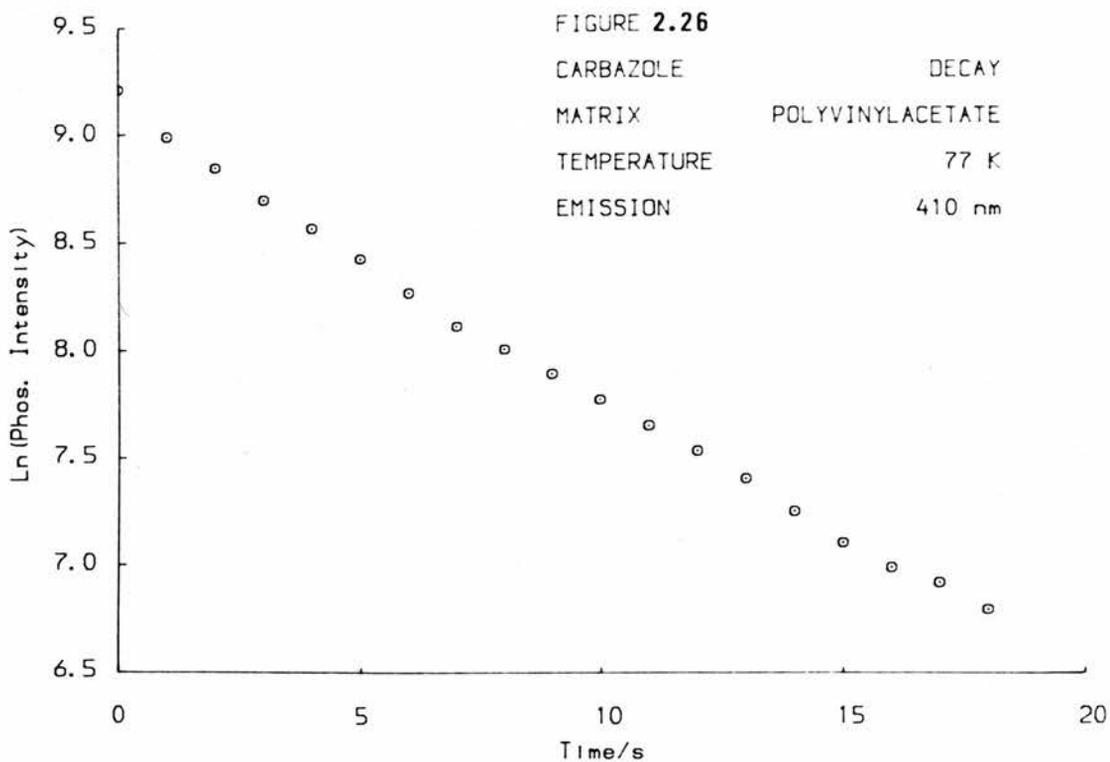


TABLE 2.12
DONOR CARBAZOLE

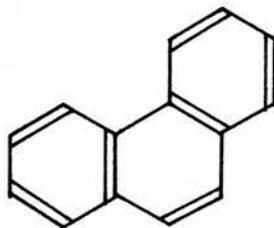
POLYMER	τ_T $\pm 0.5s$	TEMPERATURE 77K	
		k_T s^{-1}	DECAY MODE
POLY(VINYLAETATE)	8.80	0.114	exp.
POLYSTYRENE	6.65	0.150	exp.

TABLE 2.13
DONOR CARBAZOLE

POLYMER	τ_T $\pm 0.5s$	TEMPERATURE 193K	
		k_T s^{-1}	DECAY MODE
POLY(VINYLAETATE)	7.90	0.127	exp.
POLYSTYRENE	5.80	0.172	exp.

2.8.7 Decay of Phenanthrene

The phosphorescence decay of phenanthrene was studied at 470-500 nm and found to be exponential over the temperature range 77-298 K in both polystyrene and poly(vinylacetate). The decay was measured using the excitation source and optics of Apparatus C coupled to data transfer unit of Apparatus A.



Phenanthrene

Decay plots are illustrated in Figures 2.28-2.29 and the life-time data appears in Tables 2.14-2.15.

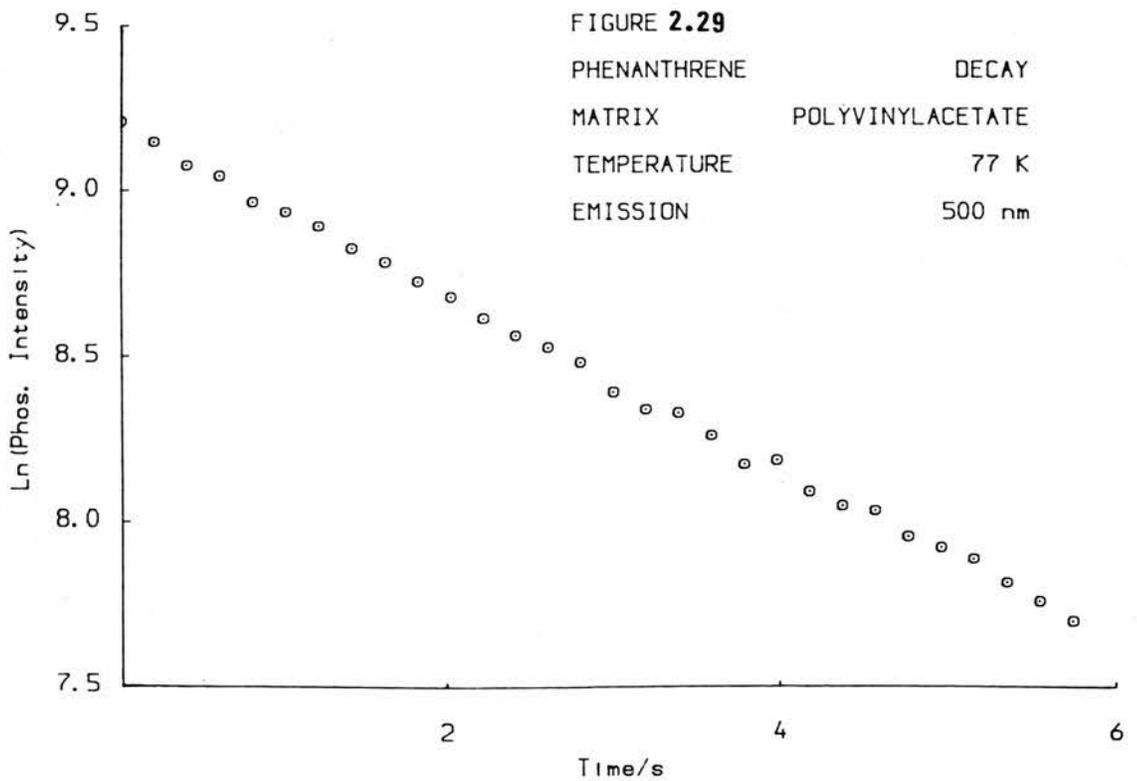
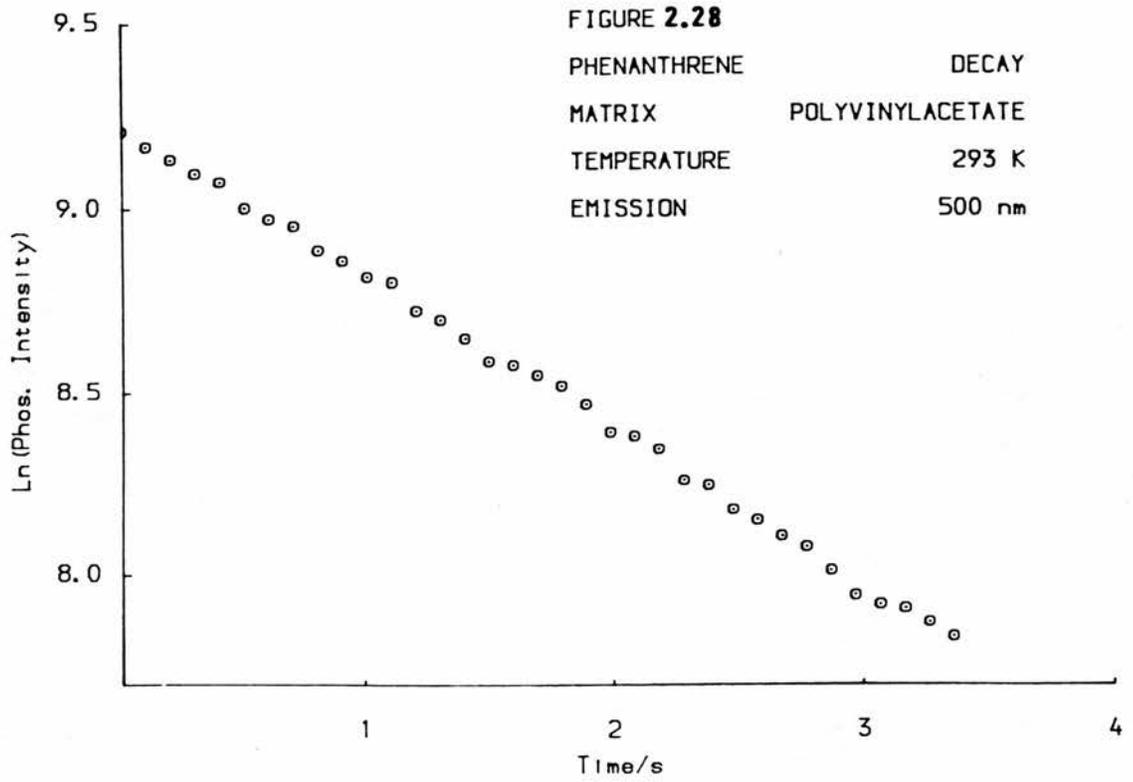


TABLE 2.14
DONOR PHENANTHRENE

POLYMER	τ_T $\pm 0.3s$	k_T s^{-1}	TEMPERATURE 77K
			DECAY MODE
POLY(VINYLAETATE)	3.83	0.261	exp.
POLYSTYRENE	3.40	0.294	exp.

TABLE 2.15
DONOR PHENANTHRENE

POLYMER	τ_T $\pm 0.3s$	k_T s^{-1}	TEMPERATURE 293K
			DECAY MODE
POLY(VINYLAETATE)	2.54	0.394	exp.
POLYSTYRENE	2.38	0.420	exp.

2.9 PHOSPHORESCENCE DECAYS IN COPOLYMERS

The results presented in this section concern the triplet decay of benzophenone and anthrone in a series of styrene-methylmethacrylate copolymers.

2.9.1 Decay of Benzophenone at 77 K

The phosphorescence decay of benzophenone was measured over three first order life-times and found to be exponential in all the copolymers. The life-time data is listed in Table 2.16 and each represents the average of at least four different runs. On raising the temperature to 196 K the decays departed from exponential behaviour. Figure 2.30 shows the relationship between k_T and X_S , the mole fraction of styrene in the copolymer.

2.9.2 Decay of Anthrone at 77 K

Consistent with the results previously reported at 77 K for the constituent homopolymers, the phosphorescence decay of anthrone was found to be exponential over three life-times in each of the copolymers. Life-times are outlined in Table 2.17. Deviations from exponentiality were observed at 196 K. Figure 2.31 illustrates the linear relationship between k_T and X_S , the mole fraction of styrene in the copolymer.

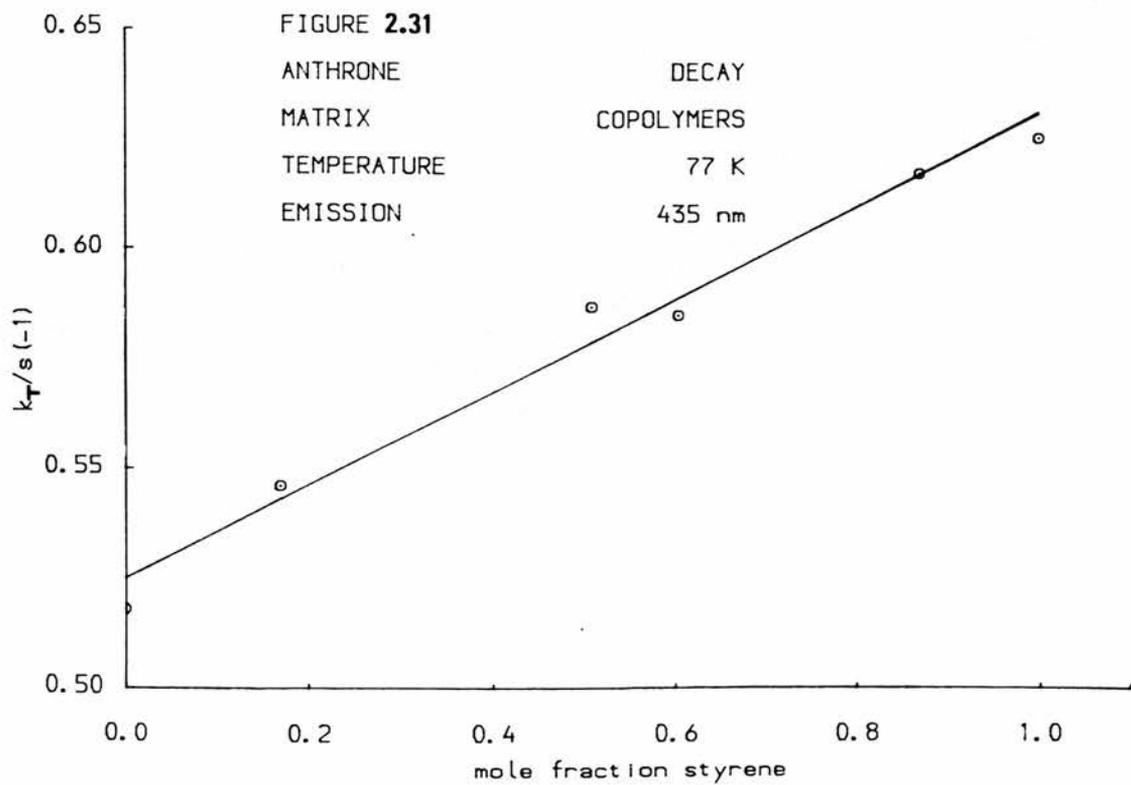
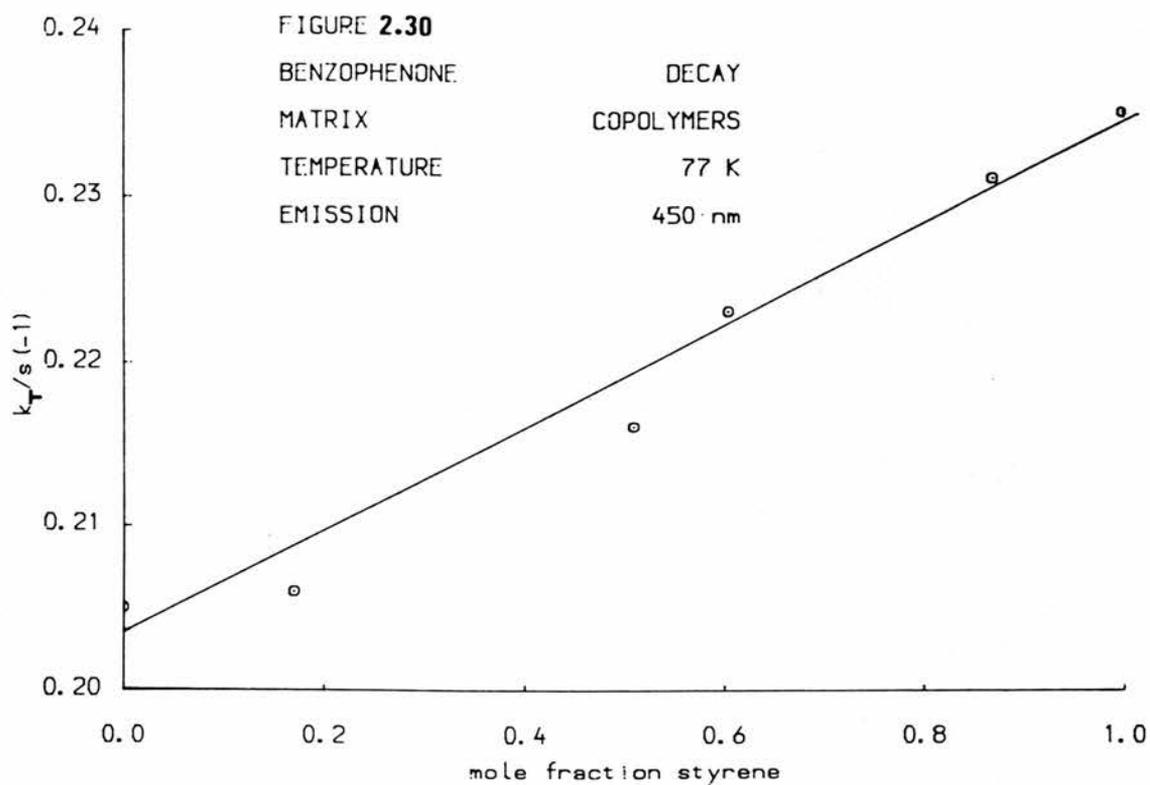


TABLE 2.16
DONOR BENZOPHENONE

COPOLYMER	% STYRENE	% METHYL- METHACRYLATE	TEMPERATURE 77K	
			τ_T ± 0.10 ms	k_T s^{-1}
1	17	83	4.85	0.206
2	51	49	4.63	0.216
3	60.5	39.5	4.49	0.223
4	87	13	4.32	0.231

TABLE 2.17
DONOR ANTHRONE

COPOLYMER	% STYRENE	% METHYL- METHACRYLATE	TEMPERATURE 77K	
			τ_T ± 0.10 ms	k_T s^{-1}
1	17	83	1.83	0.546
2	51	49	1.70	0.588
3	60.5	39.5	1.71	0.585
4	87	13	1.62	0.617

2.10 DISCUSSION OF RESULTS

The experimental results will now be discussed in detail and from consideration of the preceding sections, it is evident that a variety of physical factors can operate competitively on excited triplet states. For this reason, results were gathered at three conveniently accessible temperatures in order to examine the influence of matrix on the decay at that temperature and not principally to study the effect of temperature. The effect of varying the temperature will be investigated separately in Chapter Three.

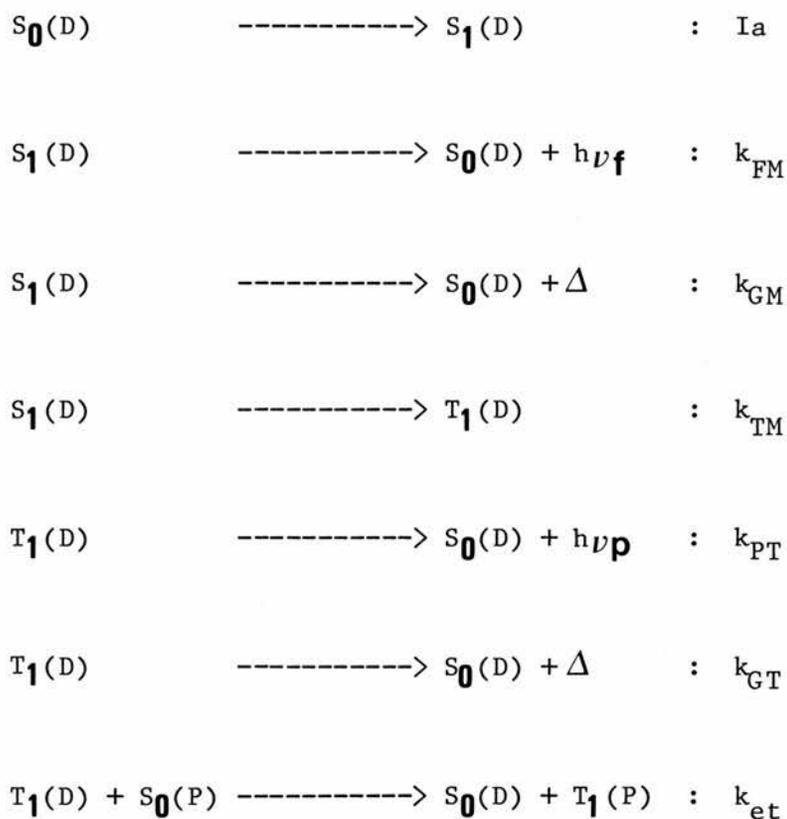
Hence, at any given temperature the results will be initially analysed in terms of the properties of the matrix and the dopant molecule. To aid understanding in this respect, the molecules were classified into groups of high and low energy triplet donors; the distinction is relative to the triplet energy level difference between the donor and polymer, denoted by ΔE_{D-A} .

2.10.1 High Energy Triplet Donors

Consultation of Table 2.1 places the short phosphorescence life-time donors anthrone and benzophenone and the long phosphorescence life-time donors triphenylene and carbazole into this category.

2.10.1.1 Low Temperature Results

The following discussion will attempt to explain why the triplet life-time of a donor molecule is matrix dependent and rationalize the observation of exponential decays. The kinetic scheme outlined below will be used to introduce the concept of electronic energy transfer between the triplet donor and the triplet level of the polymer host. The initial approach is based on that adopted by S.P.McGlynn et al. [87].



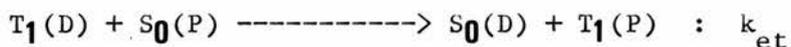
The symbols D and P denote the donor molecule and the polymer repeat unit respectively and the relevant rate parameter is indicated after each equation. In accordance with the reasoning behind equation 2.4,

the phosphorescence life-time of the donor molecule in the above scheme is given by,

$$\tau_T = 1/(k_{PT} + k_{GT} + k_{et}[S_0(P)]) \quad \dots 2.9$$

If it is assumed that $[S_0(P)]$ is essentially constant and independent of time, then exponential decays would be expected analogous to equation 2.3. Indeed, apart from the exceptions outlined, exponential decays were observed at 77 K from which first order life-times were obtained. The problem now arises of explaining the variation in the magnitude of τ_T within the series of polymers investigated. Assuming the effects already discussed to be negligible (Section 2.7.1), then for a given donor molecule at 77 K the only difference between each system is the triplet energy level of the polymers. See Table 2.3.

The significance of the energy level difference between the donor and acceptor in energy transfer studies has received comment and from this view point triplet-triplet energy transfer would be expected to occur to polystyrene with a greater efficiency in comparison with transfer to the aliphatic matrices. The critical step is,



It is proposed that an increased efficiency of energy transfer to polystyrene would be accompanied by an increased value of k_{et} , ultimately leading to a reduction in the overall triplet life-time for donors suspended in polystyrene. This fact is reflected in

Tables 2.4-2.15. Hence, the phosphorescence life-time of high energy triplet donors is sensitive to the nature of the polymer environment.

Comparison of Tables 2.1 and 2.3 indicates that energy transfer from anthrone and benzophenone to polystyrene would be exothermic whereas transfer from triphenylene is essentially isoenergetic. However, in the case of poly(methylmethacrylate), only transfer from anthrone would be exothermic; transfer from the other donors being slightly endothermic. Such a transfer condition would reduce the efficiency, but need not be entirely prohibitive and is given credence by other reported instances of endothermic energy transfer [88,90]. In the present situation energy transfer, whether exo- or endothermic, would have a limited efficiency and such a fact is important when considering the ultimate fate of the exciton. If only a small proportion of the triplet donors undergo transfer to the polymer, there is a reduced probability of further time dependent bimolecular interactions occurring between triplet excited states; a fact consistent with the observed exponential decays.

On increasing the temperature from 77 K to 196 K the decay of anthrone and benzophenone, whilst remaining exponential in the aliphatic polymers, becomes non-exponential in polystyrene. The onset of non-exponentiality is gradual and matrix dependent, occurring at temperatures approximately 15-20 K lower in polystyrene compared with the aliphatic polymers. Furthermore, in the aliphatic matrices the magnitude of τ_T at 196 K is reduced from that recorded at 77 K. Many authors have commented upon the temperature dependency of phosphorescence [82,87,112,141], but the evidence to date suggests that such a dependence cannot be represented by a simple function [142,143]. At a given temperature for the same donor, the

varying life-times and different decay observations must be attributable to the electronic properties of the polymer solvent and in particular, the triplet energy level.

The triplet decay behaviour of acetophenone has been demonstrated by many workers to be non-exponential irrespective of the temperature or the nature of the host solvent, making interpretation of the decay data difficult [124]. Consequently, its use as a probe in reflecting non-radiative interactions with the polymer host was severely restricted. However, the results obtained did conform to the general trend in that decay was faster in polystyrene.

2.10.1.2 Ambient Temperature Results

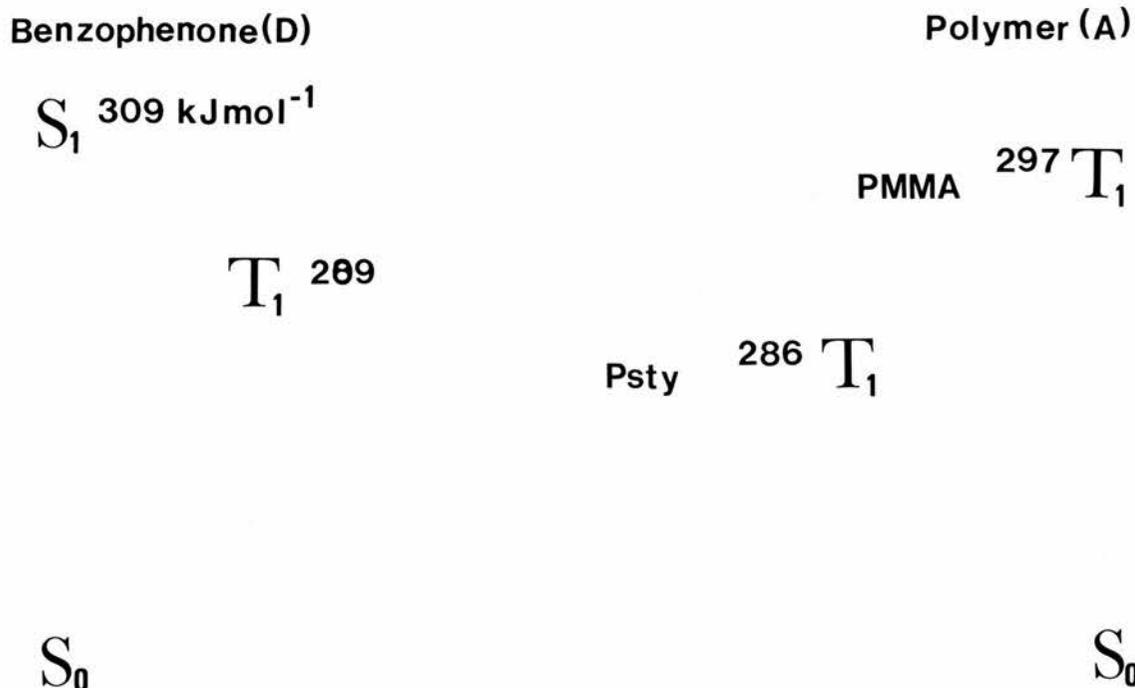
Consultation of the relevant decay curves for the high energy triplet donors at ambient temperature confirms them to be non-exponential in all the polymers, with concomitant reduction in both luminescence intensity and the time scale over which the decay could be observed. The departure from exponentiality was more pronounced for decays in polystyrene than for decays in the aliphatic polymers and life-times could no longer be obtained from equation 2.3.

Consider first the decay of the aromatic carbonyl compounds benzophenone and anthrone in polystyrene and poly(methylmethacrylate), taking the latter to represent the aliphatic polymers. Aromatic carbonyl compounds are associated with small energy gaps between their lowest excited singlet and triplet states [144] and as a consequence can undergo thermally activated delayed fluorescence [61,145]. Indeed, such an emission has been reported for benzophenone in both

solid solution [146] and polymer matrices [140]. The energy gap between the lowest n, π^* singlet and the lowest n, π^* triplet for benzophenone is reported to be 21 kJ mol^{-1} [144] and so for thermally activated fluorescence to occur such a gap must be overcome by a fraction of the triplet state benzophenone donors, the magnitude of which is given by the Boltzmann expression. At high temperatures an appreciable Boltzmann distribution among the vibrational levels is predicted [147,148] and since the rate of vibrational relaxation is rapid (10^{-13} s) compared with the rate of triplet decay (10^3 - 10^{-1} s) the distribution will always be in a state of thermal equilibrium. Thermally activated E-type delayed fluorescence has been reported for benzophenone in the polymer host poly(chlorotrifluoroethylene) [149]; a polymer not expected to possess an accessible triplet level between the lowest excited singlet and triplet levels of benzophenone.

Consider the implications of the above facts in terms of the present proposal of thermally activated energy transfer with reference to Figure 2.32.

Figure 2.32



The first point to note is that the lowest triplet level of poly(methylmethacrylate) lies between the S_1 and T_1 states of the donor benzophenone and the T_1 of polystyrene is lower than T_1 of the donor. At 298 K thermal activation of the donor vibrational levels has been shown to occur [140,146,149] and so when benzophenone is studied in either poly(methylmethacrylate) or polystyrene at such a temperature, triplet energy transfer to these polymers can offer an alternative or competitive non-radiative decay route to E-type delayed fluorescence. As more donor vibrational levels become populated on raising the temperature, the number of matching or resonant energy transfer modes between donor and polymer acceptor would also be expected to increase. A similar argument can be applied to the room temperature decays of triphenylene and carbazole in which thermally activated delayed fluorescence would not be expected to offer a viable competitive route to energy transfer to the polymer due to the prohibitively large singlet-triplet energy gap characteristic of these molecules [62].

However, the process of thermally activated energy transfer, on its own, cannot account for the observation of non-exponential decays. If the consequence of increased transfer efficiency is associated with the formation of more polymer triplet states, and if triplet energy migration along the polymer chains is possible, then additional time dependent triplet interactions could occur, in particular, triplet-triplet annihilation. The latter process, being bimolecular in origin, would then account for the observed non-exponential decay. Hence, in view of the present argument, more kinetic steps must be appended to the first order scheme already

outlined; the steps being, triplet energy migration along the polymer chain and annihilation between two triplet species, either polymer/polymer or polymer/donor. The annihilation between two donor triplets being less likely in a rigid polymer matrix under conditions of dilute concentration. The resulting delayed fluorescence would originate from either the donor or polymer excited singlet state.

2.10.2 Low Energy Triplet Donors

The probability of energy transfer occurring is dependent on a number of factors, an important one being the magnitude of ΔE_{D-A} , the energy difference between the donor and acceptor. It would seem reasonable to suppose, even when invoking the possibility of a thermally activated contribution to energy transfer, if the magnitude of ΔE_{D-A} was too large, the probability of transfer would diminish markedly.

Experimentally, the molecules naphthalene-d-8 and phenanthrene fall into the class of low energy triplet donors (See Table 2.1). It is evident from Table 2.10 that there is little difference in the phosphorescence life-time of naphthalene-d-8 measured in polystyrene, poly(methylmethacrylate) and poly(vinylacetate) at 77 K. This observation should be compared with the behaviour of triphenylene, Table 2.9, the life-time of which is appreciably reduced in polystyrene. Both these molecules possess π, π^* triplet states and have characteristically long triplet life-times but significantly different triplet energy levels. Consequently, it is proposed that energy transfer can occur from the high energy donors to the polymers, particularly polystyrene, but is unlikely to occur at 77 K from the

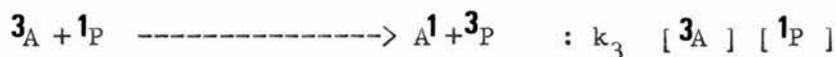
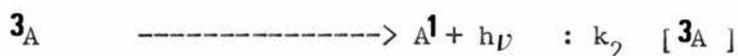
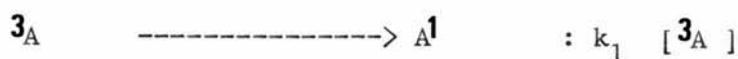
low energy donors due to the prohibitively large value of ΔE_{D-A} . Table 2.10 also shows that the phosphorescence decay of naphthalene-d-8 measured in poly(vinylchloride), whilst remaining exponential, yields a life-time markedly reduced from the value recorded in non-heavy solvents and such an observation is consistent with similar studies performed in glass solvents [92]. Hence, in polymers where energy transfer was not feasible, τ_T was independent of matrix at 77 K, but in the presence of a heavy atom the value was reduced significantly.

Corroborative evidence in favour of energy transfer occurring from specific donors is found by comparing the triplet decay of high and low energy donors at room temperature. In the case of naphthalene-d-8 Figure 2.23 shows that whilst decay in the aliphatic polymers remains exponential but with reduced life-time, deviations from pure exponentiality are observed for triphenylene as shown in Figure 2.19. However, Figures 2.21 and 2.25 show both molecules to decay non-exponentially in polystyrene. The observation of exponential naphthalene-d-8 decays in the aliphatic matrices can be explained by the large values of ΔE_{D-A} resulting in a low probability for transfer but the accompanied reduction in life-time is difficult to rationalize. However, a small extent of transfer may be sufficient to reduce the life-time by offering the triplet state an alternative decay route, but due to its inefficiency, subsequent bimolecular interactions are not important. This is essentially the same argument forwarded to explain the difference in donor life-time as a function of polymer solvent at 77 K. Alternatively, k_{GT} may well possess an intrinsic temperature dependence irrespective of environment or the possibility of competitive energy transfer events.

It is significant that the decay of triphenylene phosphorescence is non-exponential in the aliphatic polymers, consistent with its high triplet level, but that the decay of naphthalene-d-8 should be non-exponential in polystyrene is surprising considering its low triplet energy level. However, the decay of a similar donor, phenanthrene, was found to be exponential in polystyrene at room temperature, but these results do not preclude the possibility that the combination of temperature and the lower triplet level of polystyrene could provide conditions for energy transfer to occur.

2.10.3 Copolymer Results

Tables 2.16 and 2.17 show the phosphorescence life-times of benzophenone and anthrone to decrease in a series of styrene-methylmethacrylate copolymers as the styrene content increases. A.N.Jassim et al. [88] observed a similar trend when investigating the triplet life-time of triphenylene in such copolymers, proposing that the matrix quenches the triplet state of the additive; the styrene unit being more efficient than the methylmethacrylate unit. Based on the following mechanism, in which A and P represent the additive and polymer unit respectively, the authors [88] derived an expression predicting a linear relationship between k_T and X_S , the mole fraction of styrene in the copolymer.



Figures 2.30 and 2.31 illustrates such plots for benzophenone and anthrone, both of which are linear. Hence, the reduction in additive life-time is clearly related to the styrene content and is consistent with its lower lying triplet level which would enhance the efficiency of triplet additive deactivating energy transfer processes.

2.10.4 Polymer Physical Properties : Comment

Section 2.5 reviewed some of the perturbations to which phosphorescence is sensitive and in this respect, it would seem reasonable to suppose that polymer physical properties such as refractive index or polarity could conceivably influence the decay mechanism and so offer an alternative explanation to the results reported.

Equations exist linking the phosphorescence radiative rate constant k_{PT} , one component of the triplet life-time expression, with the refractive index of the solvent medium [150]. The influence of the refractive index is small for most molecules, but significant effects are predicted if the solvent medium promotes the mixing of those pairs of singlet and triplet states which are responsible for the transition moment of phosphorescence [151]. Solvents have been shown to affect the energies of S_1 n, π^* states of benzophenone [152,153]. However, in studies on substituted benzophenones, M.A.Winnik et al. [151] found the radiative rate constant to be solvent independent, suggesting that pairs of singlet and triplet states which mix by spin-orbit coupling are similarly solvent sensitive. In addition, they demonstrated the location of the 0,0 band of phosphorescence to be independent of solvent polarity; an observation in accord with the phosphorescence spectra shown in Figures 2.2 and 2.4.

This evidence, coupled with the fact that the refractive index of polystyrene and poly(methylmethacrylate) are nearly equal, 1.59 and 1.49 respectively [154], tends to minimize the importance of such

effects. Moreover, phosphorescence in polymer hosts has been shown to display a marked temperature dependence, whereas the refractive index of poly(methylmethacrylate) has been reported to vary by only 2 % from 77 K to 298 K [155]. Departures from first order kinetics were also observed requiring, in the absence of a dual emission mechanism, the introduction of bimolecular interactions to furnish a suitable explanation. Hence, it is suggested that physical polymer properties, such as those considered, could not offer a satisfactory explanation to rationalize the range of effects reported.

2.11 LITERATURE REVIEW

Numerous investigations have been performed on the phosphorescence of mixed crystal systems in which the triplet energy level of the guest (donor) is less than the triplet energy level of the host (acceptor) [156,157,158,159]. The temperature dependence of guest phosphorescence was explained in terms of a thermally activated triplet energy transfer step and S.P.McGlynn et al. [156] further qualified the applicability of the proposal by limiting its use to cases where the guest-host triplet energy level separation, ΔE_{D-A} , is less than 3000 cm^{-1} or 35 kJ mol^{-1} .

N.Hirota et al. [157] studied the phosphorescence behaviour of guest phenanthrene in host biphenyl over a wide temperature range. Within the context of the present study phenanthrene is considered to be a low energy triplet donor but in this example, where ΔE_{D-A} equals 19 kJ mol^{-1} , a value within S.P.McGlynn's limit, it qualifies as a high energy level donor. These authors [157] found the decay to be exponential at 77 K but to depart from exponentiality at elevated temperatures; behaviour entirely consistent with the present high energy donors studied in polymer media. Hence, in crystalline media thermally assisted triplet energy transfer from guest to host can occur, ultimately leading to additional bimolecular interactions. It appears [160] that guest-to-guest migration via the host T_1 exciton band usually occurs on a time scale shorter than guest triplet life-times. The migration process may also be temperature dependent. However, it seems that the temperature dependence is almost entirely confined to an initial T_1 guest \rightarrow T_1 host activation step.

Extending S.P.McGlynn's argument to phenanthrene triplet decay in poly(vinylacetate) and polystyrene at 293 K, where ΔE_{D-A} is 62 and 54 kJ mol⁻¹ respectively, exponential decays would be more likely and such is the case experimentally.

S.P.McGlynn et al. [156] commented that departures from exponentiality become less important as a function of time. By measuring τ_T as a function of temperature, the value of k_T extracted from the long time linear region of the decay plot, these authors obtained a value of ΔE_{therm} which they compared favourably with the triplet energy level difference ΔE_{D-A} , for the respective guest-host systems chrysene-phenanthrene and naphthalene-d-8-biphenyl, to conclude that the temperature dependence of τ_T is controlled by thermally activated intermolecular guest-host triplet energy transfer processes.

To further substantiate the importance of ΔE_{D-A} in such studies S.P.McGlynn et al. [156] performed similar experiments on guest pyrene in host biphenyl for which $\Delta E_{D-A} = 74$ kJ mol⁻¹, finding no significant change in τ_T over the temperature range studied. This result is in accord with the expectation of a low triplet energy donor system, where the life-time is predicted to be essentially temperature independent, corroborating the current results obtained for such systems in polymer media and forming the basis of S.P.McGlynn's thermal activation limit prediction. In addition, it provides evidence to suggest the absence of competitive unimolecular depletive processes. Furthermore, H.Sternlicht et al. [160] presented a theory describing triplet state energy transfer which considers the transfer via virtual triplet states of the host crystal and is dependent upon the separation of triplet host and guest energies and therefore on

temperature. In conclusion, there exists ample evidence in mixed crystal systems that the triplet level of the guest can be thermally activated to a vibrational level within its triplet manifold degenerate with the triplet energy level of the host to which transfer can occur [161].

It is now necessary to progress from doped crystals to systems in which polymers provide the host support matrix. The authors J.L.Kropp and W.R.Dawson [114] studied the radiationless deactivation of triplet coronene in poly(methylmethacrylate) as a function of temperature, deriving two activation energies, the largest being approximately 58 kJ mol^{-1} . This value is significantly greater than the $S_1 -- T_1$ energy gap of coronene, thus indicating that thermally activated delayed fluorescence may not be the only depletive T_1 process operating. Indeed, the authors proceeded to suggest that the temperature dependence of triplet decay may be due to thermal activation from triplet coronene to triplet polymer. The observed activation energy predicts the triplet level of poly(methylmethacrylate) to be located at 297 kJ mol^{-1} .

As a continuation from his studies in crystalline media, S.P.McGlynn et al. [87] studied the phosphorescence life-time of a number of aromatic hydrocarbons in poly(methylmethacrylate) as a function of temperature, finding in each case that the sum of the derived activation energy and the triplet level of the molecule concerned was equal to approximately 298 kJ mol^{-1} . They suggested that this value represented the lowest triplet level of the polymer and consequently concluded that an intermolecular energy transfer from the triplet level of the guest molecule to the triplet level of the polymer was occurring. This work also uncovered a second, smaller,

activation energy, which the authors proposed to be intramolecular in nature and associated with k_{GT} .

F.E.El-Sayed [162] carried out similar experiments to those performed by S.P.McGlynn et al. [87], finding the activation energies to be smaller and furthermore, observing them to be constant and independent of the solute. The authors rationalized the discrepancies between the results as being due to S.P.McGlynn's neglect of donor non-exponentiality at higher temperatures. F.E.El-Sayed [162] also used polystyrene as a host matrix and obtained lower activation energies; a fact consistent with the lower triplet level of polystyrene. Although not specifically proposing triplet energy transfer to either polymer, the authors did suggest that the observed behaviour is related to the nature of the matrix.

Results have also been presented on the phosphorescence behaviour of molecules with low triplet levels in polymer solvents, providing a situation similar to that reported by S.P.McGlynn et al. [156] for crystalline media. A.Beckett [111] measured the phosphorescence life-time of anthracene, possessing a triplet level at 176 kJ mol^{-1} , in poly(methylmethacrylate) and found the decay to exponential at both 77 K and 298 K with life-times of 48 ms and 25 ms respectively. In this example the value of the ΔE_{D-A} is 120 kJ mol^{-1} which far exceeds the limit suggested by the work in crystalline media over which thermally activated energy transfer can occur. This fact is consistent with the observation of exponential decay at 298 K. In an earlier study by W.H.Melhuish and R.Hardwick [163] whilst reporting exponential decay for triplet anthracene at both 80 K and 300 K, they obtained slightly shorter life-times. Although both sets of results indicate the impracticality

of thermal transfer from triplet anthracene to poly(methylmethacrylate), the different values of τ_T at 77 K and 298 K suggests that phosphorescence decay in polymeric hosts is not completely temperature independent. The results of N.Geactinov et al. [85] can be rationalized in a similar manner. These authors found the triplet decay of dibromoanthracene to be exponential in poly(vinylacetate) at room temperature and the magnitude of the life-time to be essentially matrix independent, in line with its low triplet energy level. In another study, R.E.Kellog et al. [164] measured the phosphorescence life-time of a range of aromatic hydrocarbons with low triplet levels in poly(methylmethacrylate) at 77 K and 298 K. Although not stating the mode of decay at 298 K, the small change observed in τ_T on progressing from 77 K indicates that thermally activated triplet processes are not important for such systems.

In comparison with the wealth of data concerning phosphorescence life-times in the region > 1.0 s, there have been fewer reported cases of phosphorescence work in the millisecond time domain carried out in polymer matrices. However, in one study M.A.West et al. [84] investigated the absorption and emission spectra and triplet decay of some aromatic and N-heterocyclic compounds in poly(methylmethacrylate). For most molecules the decays were shown to be non-exponential at 293 K, the exceptions being anthracene, acridine, 3,4 benzopyrene, phenanthridine and phenazine; the molecules with the lowest triplet energy levels of the group studied. This result is consistent with both the present study and S.P.McGlynn's thermal activation limit. The authors did not invoke the possibility of thermally assisted triplet energy transfer between the molecules

displaying non-exponentiality and the polymer host, but preferred to explain their results in terms of viscosity effects within the polymer. However, with regard to this latter point, their method of sample preparation is open to criticism, giving rise to the possibility of unreacted monomer interfering with additive decay.

The following references provide additional evidence implicating either an energy transfer process or an electronic quenching mechanism to be occurring between the polymer host and suspended additive. In a thorough study, performing classical energy transfer experiments between donors and acceptors dispersed in poly(methylmethacrylate) at 77 K, F.Wilkinson et al. [89] concluded that the polymer was providing a further weak transfer channel, most likely at the triplet level. A.N.Jassim et al. [88] proposed triplet energy transfer from triphenylene and coronene to a series of styrene-methylmethacrylate copolymers at 77 K. Other authors have suggested polymer involvement in triplet decay processes, although not specifically proposing energy transfer to be operative. R.E.Kellog et al. [82] reported the phosphorescence life-time of several aromatic hydrocarbons in poly(methylmethacrylate) as a function of temperature. They proposed that the reduction in τ_T could be associated with the phonon population of the polymer or due to some temperature dependent interaction.

Not all the papers appearing in the literature on this topic are in favour of thermally activated triplet processes occurring between additives and polymer hosts. For example, P.F.Jones and S.Siegel [112] studied the effect of temperature on τ_T using, amongst others, the aromatic hydrocarbons biphenyl and pyrene, spanning a donor triplet energy range of 201-275 kJ mol⁻¹ in

poly(methylmethacrylate). They found that of all the molecules studied, the largest temperature effects were observed for pyrene, the molecule with the lowest triplet level. In terms of the size of ΔE_{D-A} , biphenyl would have been expected to exhibit the most pronounced temperature effect. Consequently, this led the authors to conclude that non-radiative decay via thermal activation to the T_1 state of poly(methylmethacrylate) is not important for the solutes they studied. Hence, on the strength of the exceptional behaviour observed for pyrene, a molecule known for its complex photophysical properties, the authors excluded the possibility of biphenyl involvement in thermally activated processes; at point at variance with its ΔE_{D-A} value of 22 kJ mol^{-1} .

W.H.Melhuish [165] measured the life-time of benzophenone in poly(methylmethacrylate) at 77 K and 320K, reporting the decay to be exponential at both temperatures; a fact conflicting with the present case and other studies [120]. The authors H.W.Offen and D.E.Hein [166] examined the environmental effects of polystyrene and poly(methylmethacrylate) on the triplet life-time of triphenylene at 77 K, reporting the values to be 11.5 s and 16.0 s respectively. Although these values are in agreement with those presented in Table 2.9, the authors did not invoke energy transfer to explain the matrix dependence, but ascribed the lower value in polystyrene to dispersive forces.

Hence, there is conclusive evidence in the literature in support of thermally assisted triplet energy transfer in doped crystalline media in which the triplet level of the guest is less than that of the crystal host and considerable evidence suggesting that such is also the case for polymeric host media. Subsequent bimolecular

triplet-triplet interactions have been unequivocally identified in crystal hosts [158] but not as yet for the polymers used in the present study. Clearly, to further test the proposal of donor thermal activation as a precursor to additional bimolecular events, it would be advantageous to study the detailed temperature dependence of donor phosphorescence in a range of polymers. Such an investigation was carried out, the results of which appear in Chapter Three.

2.12 CONCLUSIONS

This chapter has provided experimental evidence demonstrating the triplet phosphorescence decays of molecules containing π, π^* and n, π^* excited states to be polymer matrix dependent. Furthermore, life-times were found to be shorter in the aromatic polymer polystyrene compared with the aliphatic polymers. The results indicated a definite correlation between the observed phosphorescence behaviour and ΔE_{D-A} , that is, the triplet energy difference between donor and polymer. Departures from unimolecular decay were shown to be temperature dependent.

The results were explained in terms of a triplet-triplet energy transfer mechanism from the donor to the polymer, the process being thermally assisted and ultimately leading to further bimolecular interactions.

Phosphorescence

as a

Function

of

Temperature

CHAPTER THREE

3.1 INTRODUCTION

The function of the work described in this chapter was to investigate the influence of temperature on the phosphorescence decay characteristics of high energy triplet donors dispersed in a range of polymers and to analyse the intensity decay data in terms of a mechanism involving bimolecular triplet-triplet annihilation steps. The rationale behind the choice of mechanism derives from the conclusions of the preceding chapter.

3.2 The Kinetic Scheme

The following kinetic analysis concerns uni- and bimolecular interactions operating on the lowest triplet state of the donor molecule. The unimolecular deactivation routes have been discussed and their cumulative effect considered in terms of a composite rate constant k_1 , given by,

$$k_1 = k_{PT} + k_{GT} + k_{et} [\text{So(P)}] \quad \dots 3.1$$

Under conditions of no donor quenching, the reciprocal sum of k_{PT} and k_{GT} represents the phosphorescence life-time. Equation 3.1 can be further complicated by acknowledging both k_{GT} and k_{et} to exhibit a temperature dependence. Separation of the radiationless decay rate coefficient k_{GT} into temperature-independent and temperature-dependent components and writing the latter and k_{et} in an Arrhenius form, results in,

$$k_{GT} = k_{GT}^{\circ} + k_{GT}'$$

$$k_{GT}' = k_{GT}^{\circ} + A \exp(-E_{GT}/RT)$$

$$k_{et} = B \exp(-\Delta E_{et}/RT)$$

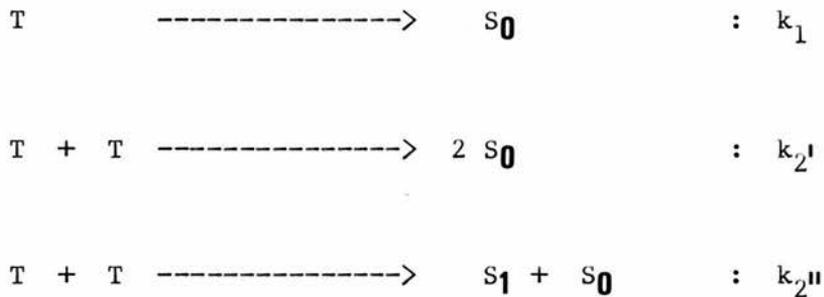
where k_{GT}° and k_{GT}' represent the temperature independent and temperature dependent components of k_{GT} and E_{GT} and ΔE_{et} represent the activation energies for non-radiative decay and energy transfer

respectively. Equation 3.1 can now be written as,

$$k_1 - k_0 = A \exp(-E_{GT}/RT) + B \exp(-\Delta E_{et}) \quad \dots 3.2$$

where $k_0 = k_{PT} + k_{GT}$. In such an analysis k_0 is derived from the reciprocal life-time measured at 77 K which is assumed to equal the value at absolute zero. Clearly, such a procedure is not entirely satisfactory [167,168] but is commonly adopted in the literature [169,170,171].

The expression for k_1 can now be incorporated into a mechanism in which uni- and bimolecular processes competitively deactivate the triplet state. The proposed mechanism is shown below; T denoting a triplet state species.



Bimolecular interaction can occur between donor and polymer triplet states, and if the simplifying conditions discussed in section 2.2.1.2 prevail [62,63], then,

$$-d[T]/dt = k_1[T] + k_2[T]^2 \quad \dots 3.3$$

the integration of which yields,

$$[T] = \left[\left(\frac{1}{[T_0]} + \frac{k_2}{k_1} \right) \exp k_1 t - k_2/k_1 \right]^{-1} \quad \dots 3.4$$

where $[T]$ and $[T_0]$ are the triplet state concentrations at times $t = t$ and $t = 0$ respectively and $k_2 = k_2' + k_2''$. This complex expression contains three experimental unknowns, namely, $[T_0]$, k_1 and k_2 . Hence, the experimental decay curves were analysed in terms of equation 3.4, the form of which is non-exponential, by means of an iterative curve fitting procedure, yielding fitted values of the three unknowns. Details of the curve fitting procedure are given in Chapter Four, section 4.3.2.

This approach allowed the rate parameter k_1 to be studied over an extensive temperature range by applying equations 3.1 and 3.4 to exponential and non-exponential intensity decay data respectively. Use of equation 3.2 then enabled estimates of the activation energy associated with k_1 to be established, and so providing a means of testing the proposal of thermally activated triplet-triplet energy transfer from donor to polymer, as the model predicts,

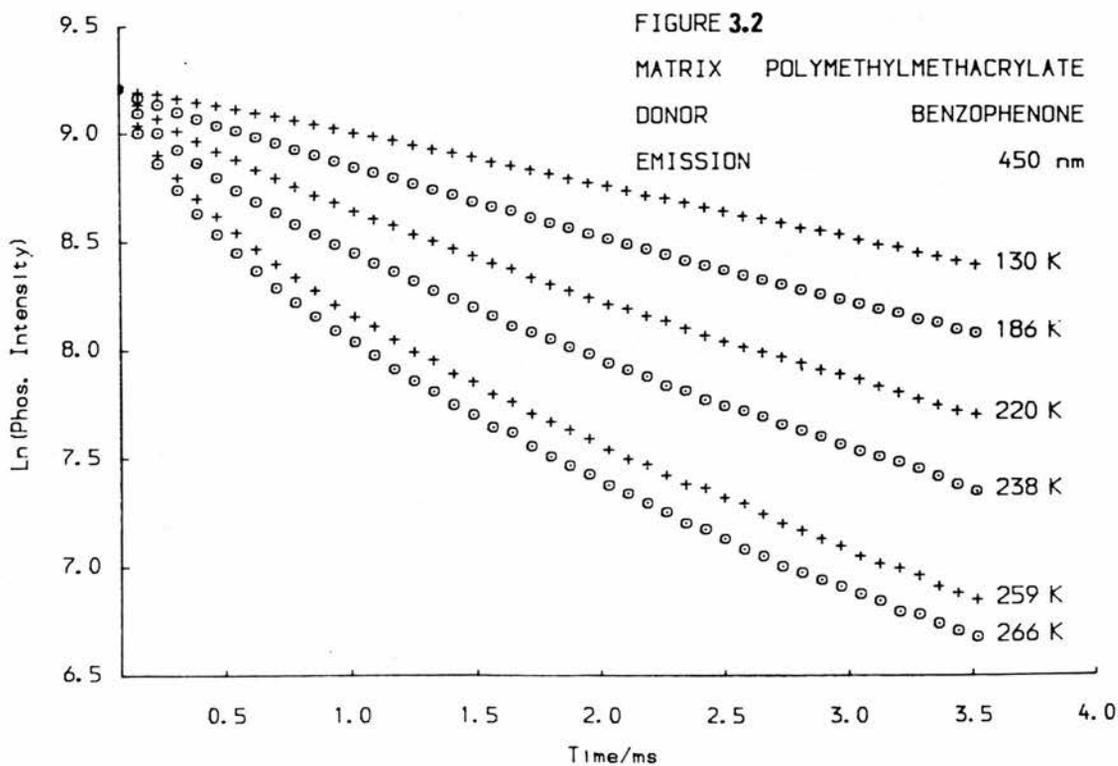
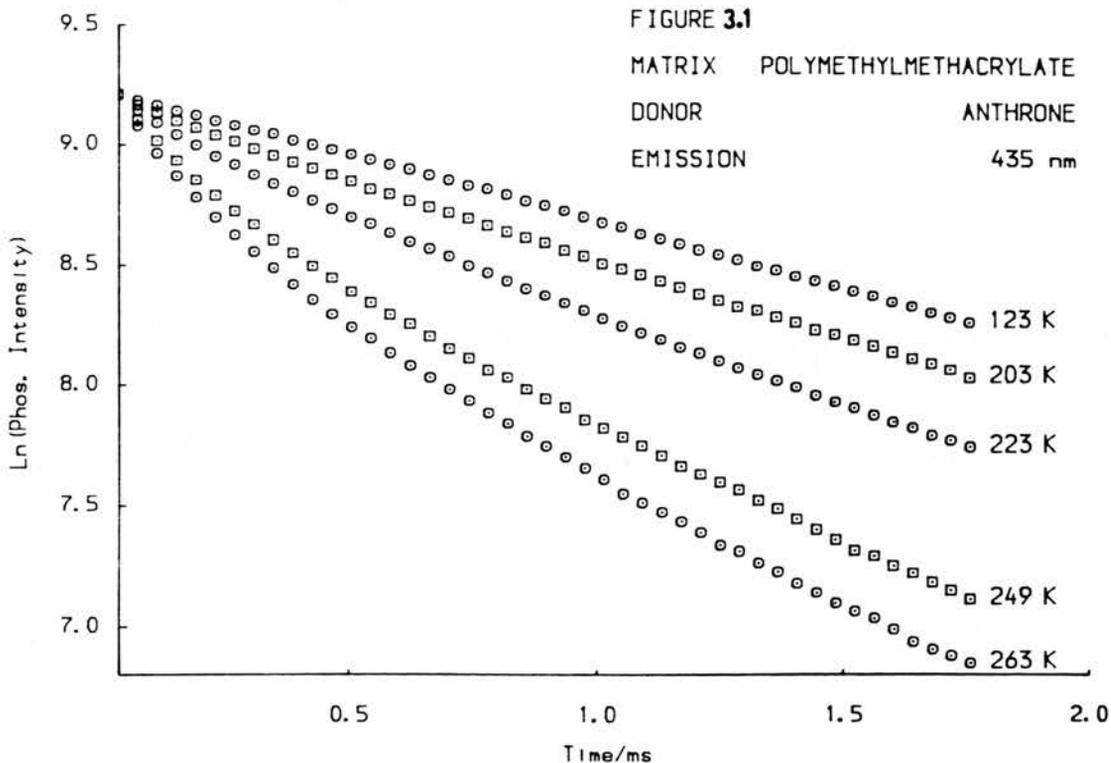
$$E_T (\text{Polymer}) = E_T (\text{Donor}) + \Delta E_{et} .$$

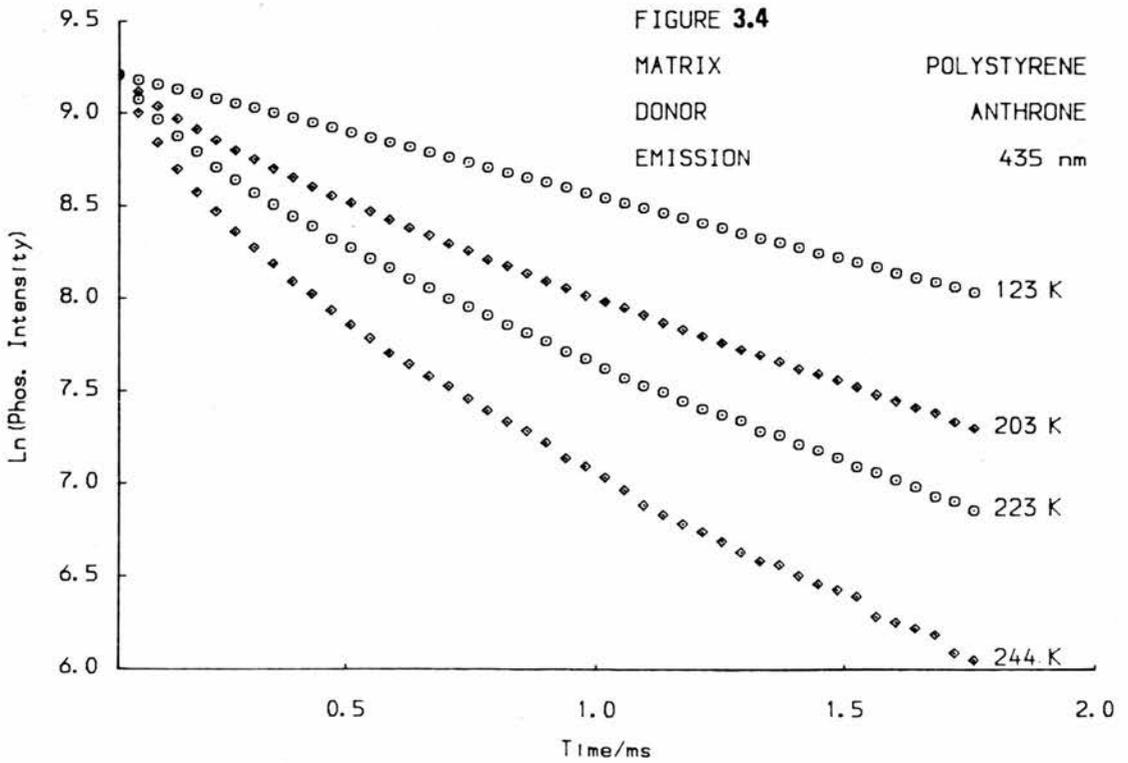
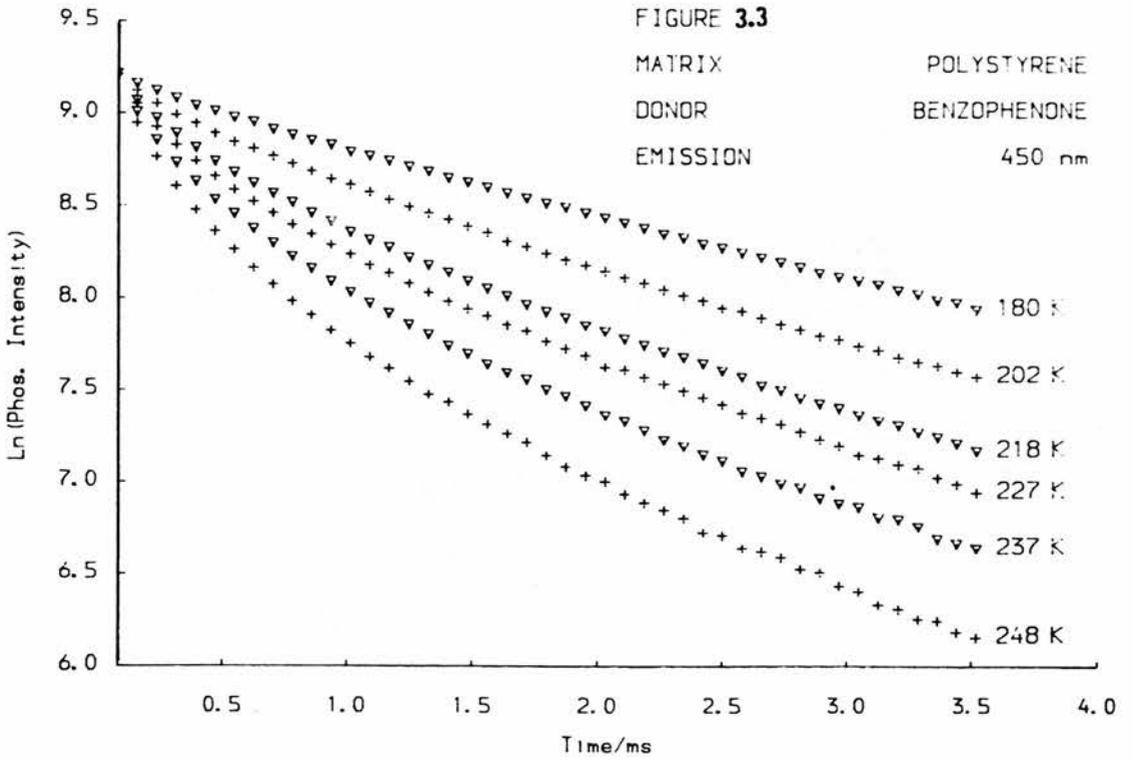
3.3 GENERAL OBSERVATIONS

The mode and life-time of the triplet state deactivation of the high energy donors were found to be temperature dependent in all the polymers studied. It is apparent from Figures 3.1-3.4, depicting first order decay plots as a function of temperature, that the onset and degree of non-exponentiality are both matrix and temperature dependent. In general terms, slowly raising the temperature from 77 K causes a slight reduction in the first order life-time, the decay remaining exponential. At a certain temperature the matrix specific onset of non-exponentiality occurs. Progressing further into the non-exponential temperature region, the intensity of phosphorescence emission was observed to decrease in the order,



In the context of the proposed mechanism, for anthrone and benzophenone, it is important to observe that the k_1 component of the decay curve remained essentially constant after the onset of non-exponentiality and only increased significantly at higher temperatures. However, the contribution of k_2 increased steadily from the onset of non-exponentiality. For carbazole, the collection of insufficient intensity data points over the initial part of the decay curve meant that estimates of k_2 could not be obtained using the fitting routine. However, values of k_1 were derived from the long time linear region of the decay plot and were found to increase with temperature from 77 K, at first gradually and then more rapidly.





3.4 PRESENTATION OF EXPERIMENTAL RESULTS

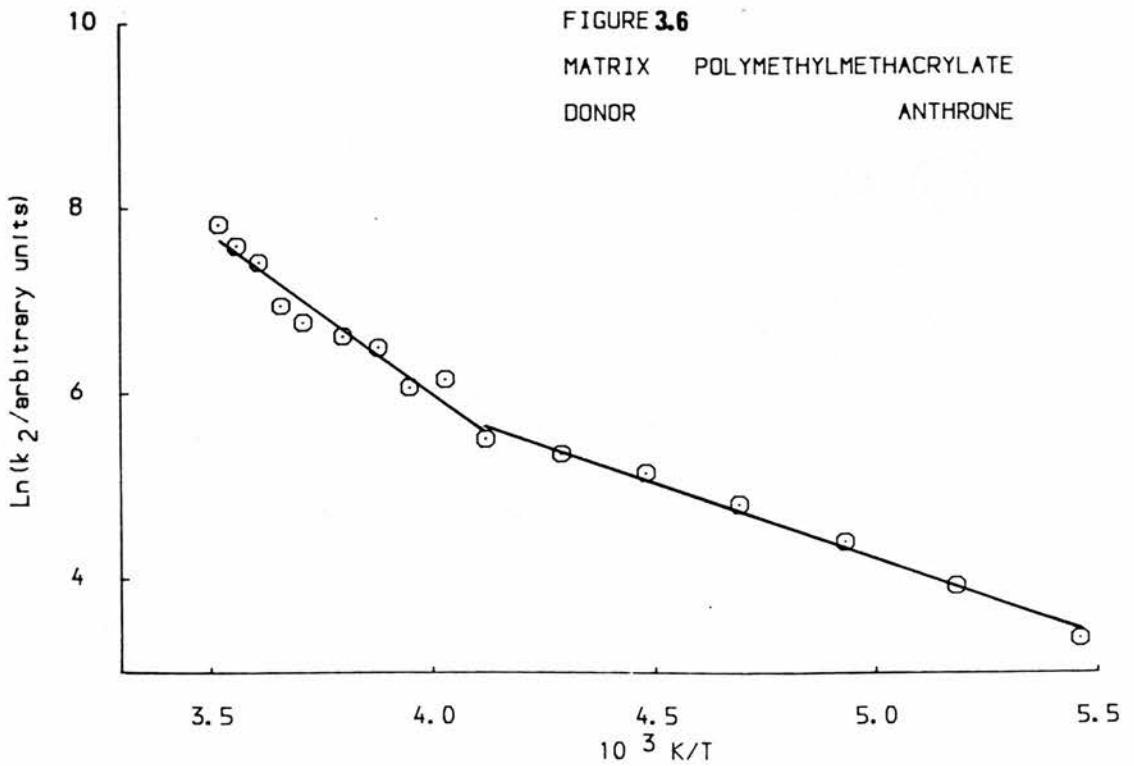
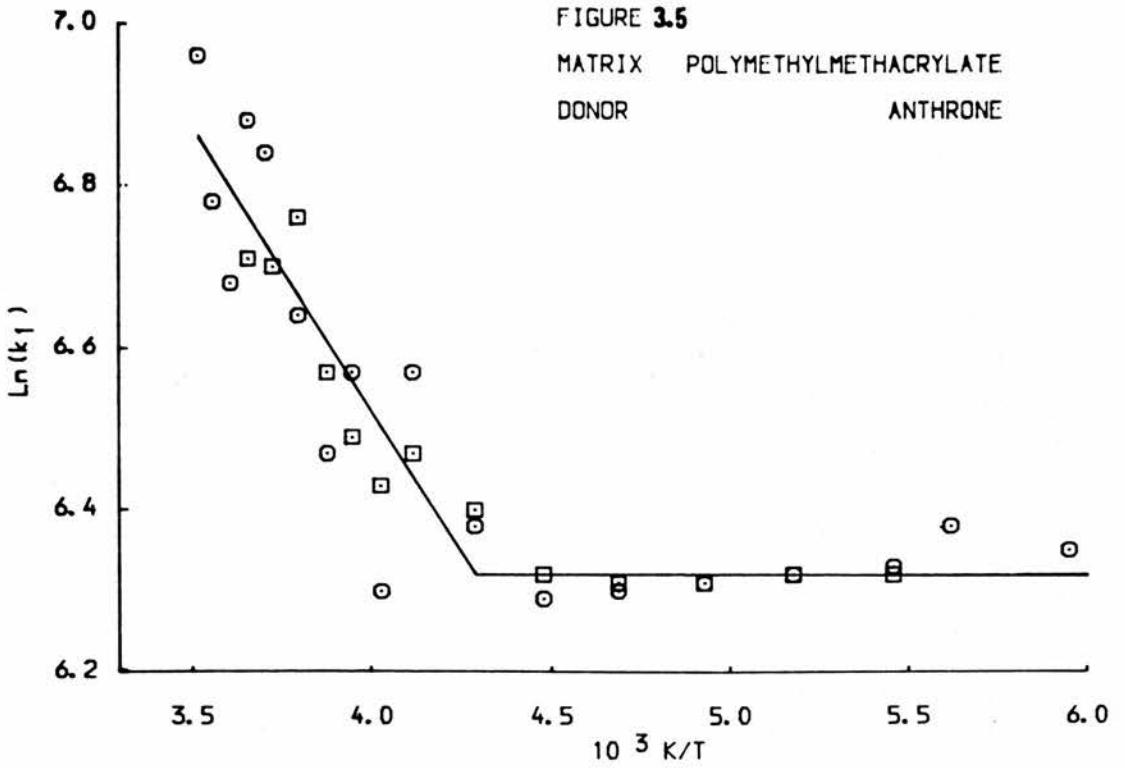
This section presents the results obtained for each donor/polymer system in terms of tables correlating temperature transitions, uncorrected Arrhenius plots and where relevant, corrected Arrhenius plots together with tables listing the activation energies associated with k_1 and k_2 .

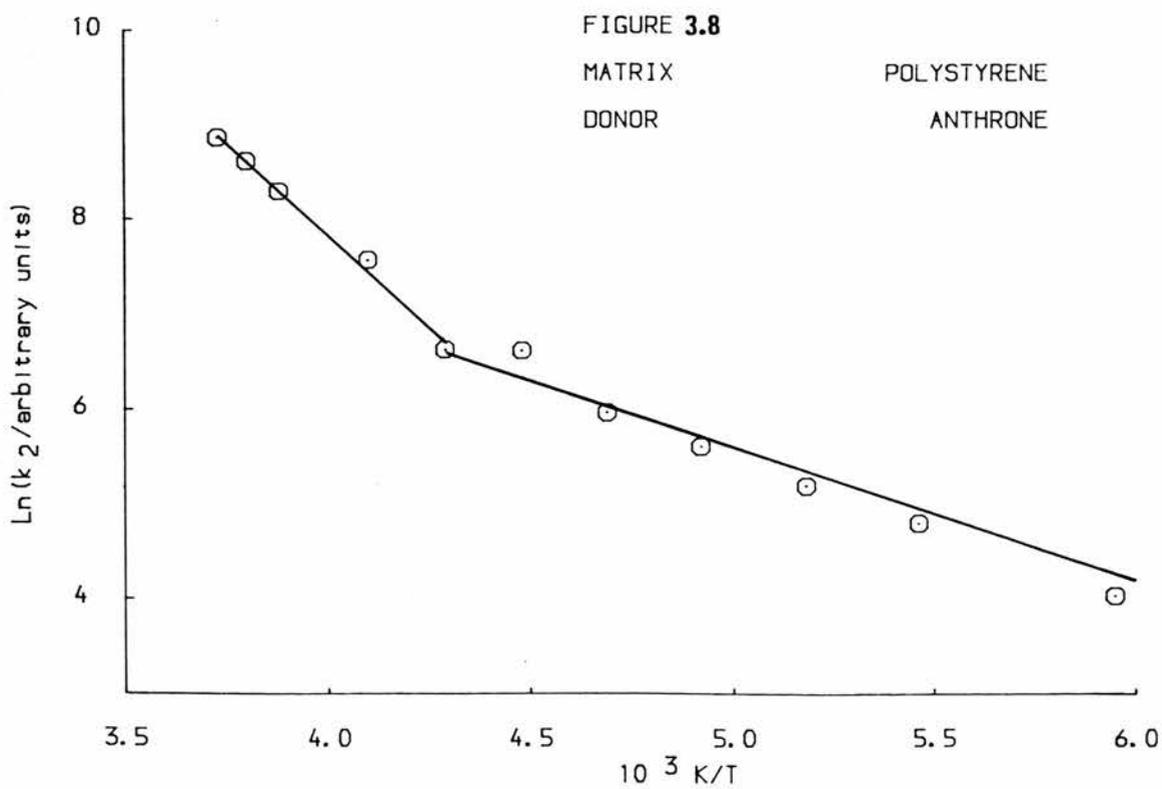
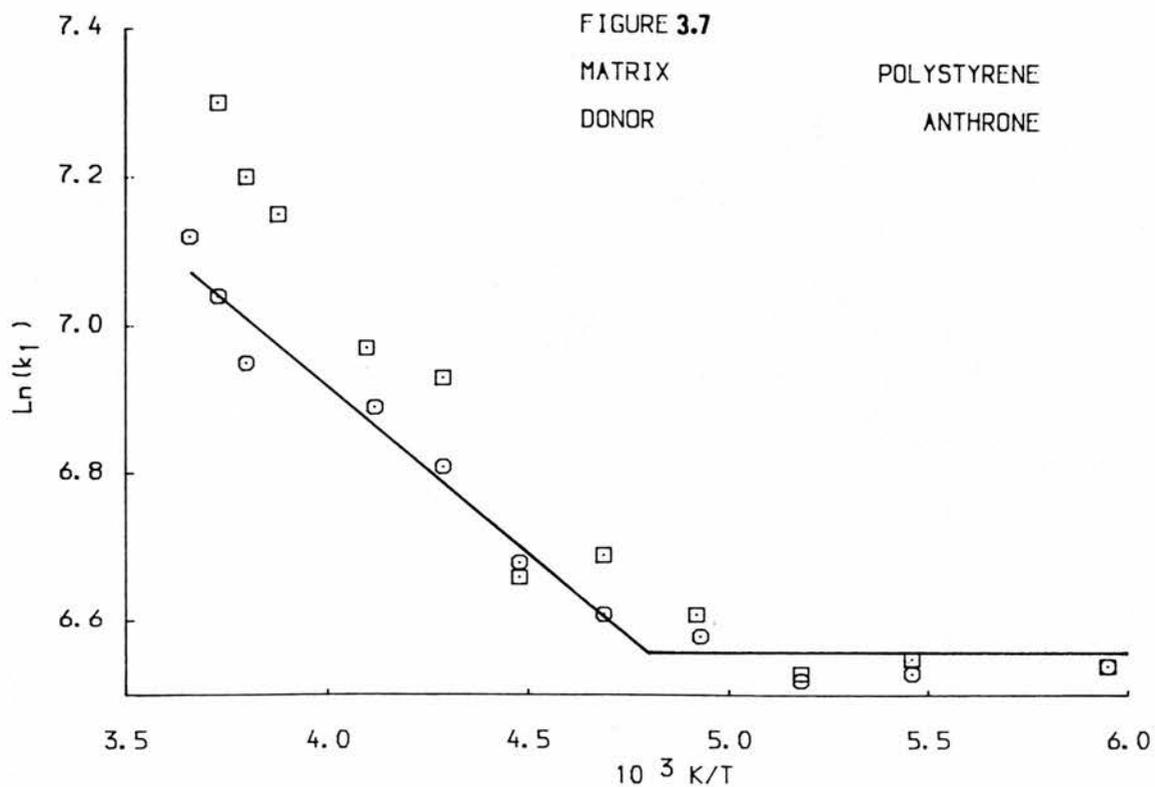
3.4.1 Donor : Anthrone

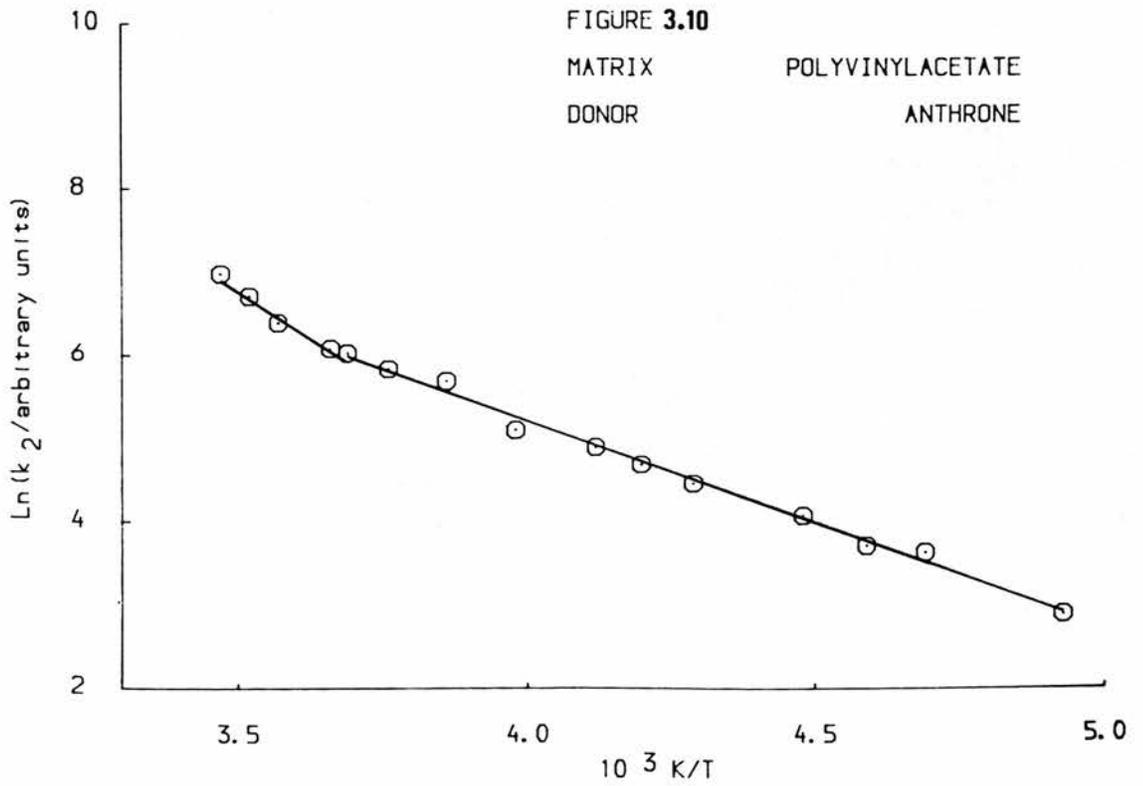
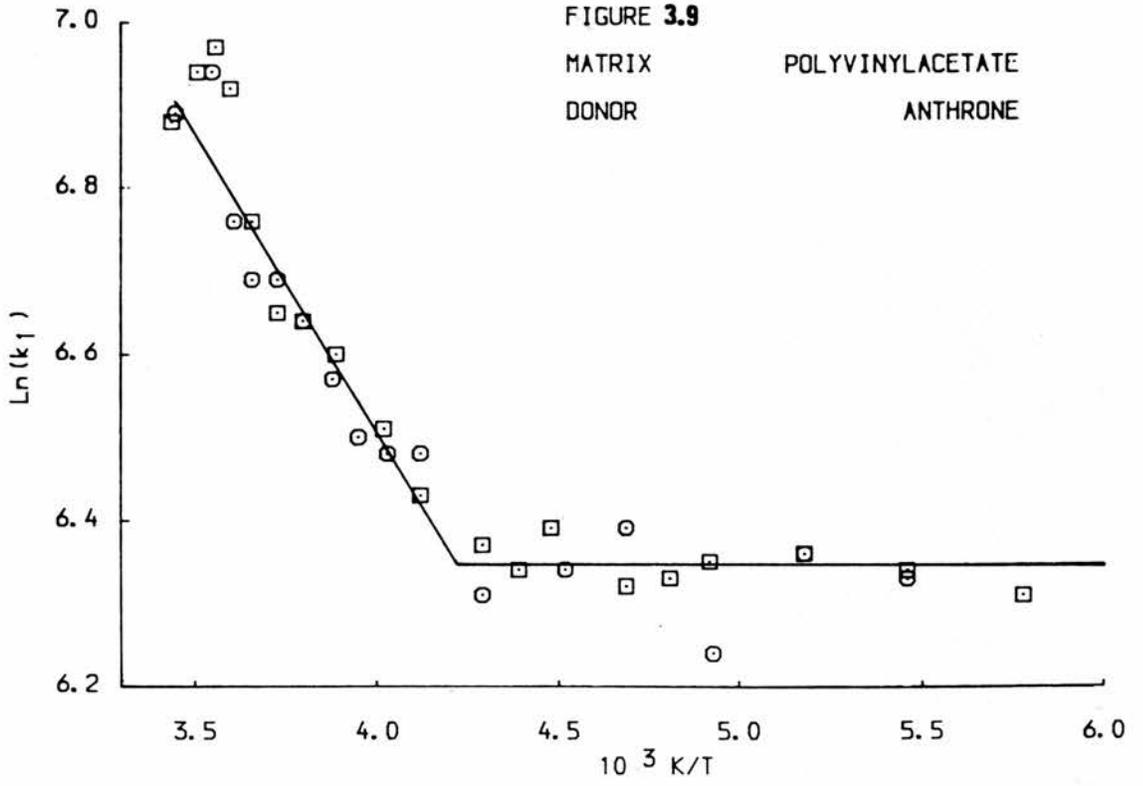
The rate constant k_1 was studied as a function of temperature and was found to remain essentially constant on progressing from 77 K through the onset of non-exponentiality to a specific transition temperature above which it was observed to increase. However, the value of k_1 taken from the last linear $\ln(\text{Phos. Int.})$ versus time plot was always greater than subsequent values of k_1 derived using equation 3.4 over a limited temperature period after the onset of non-exponentiality in which k_1 was expected to be constant from the figures shown and confirmed to be so by the fitting routine. This irregularity was observed for both anthrone and benzophenone in all the polymers and was attributed to the method of analysis.

Figures 3.5-3.10 show the uncorrected Arrhenius plots for k_1 and k_2 ; the values of each rate parameter was taken directly from the fitting routine, illustrating each to exhibit a discontinuity, thereby allowing the definition of two separate linear regions. The temperatures at which the discontinuities or transitions occurred for each polymer are correlated in Table 3.1, together with the

temperatures indicating the onset of non-exponentiality. The activation energies, $E_{a_1}(\Delta E_{et})$, for k_1 were obtained using equation 3.2, assuming the contribution of k_{GT} to be small, giving the corrected Arrhenius plots shown in Figures 3.11-3.12 and are listed in Table 3.2. The activation energies obtained from k_2 data, E_{a_2} , above and below the temperature transition, are also shown in Table 3.2.







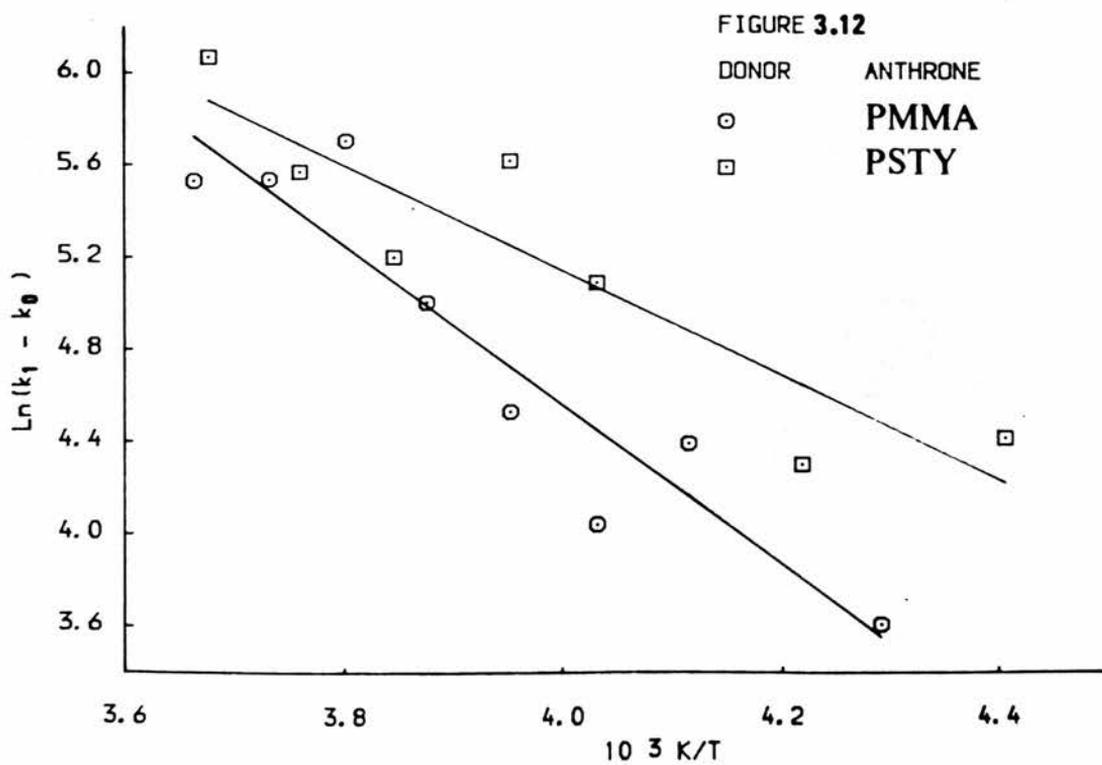
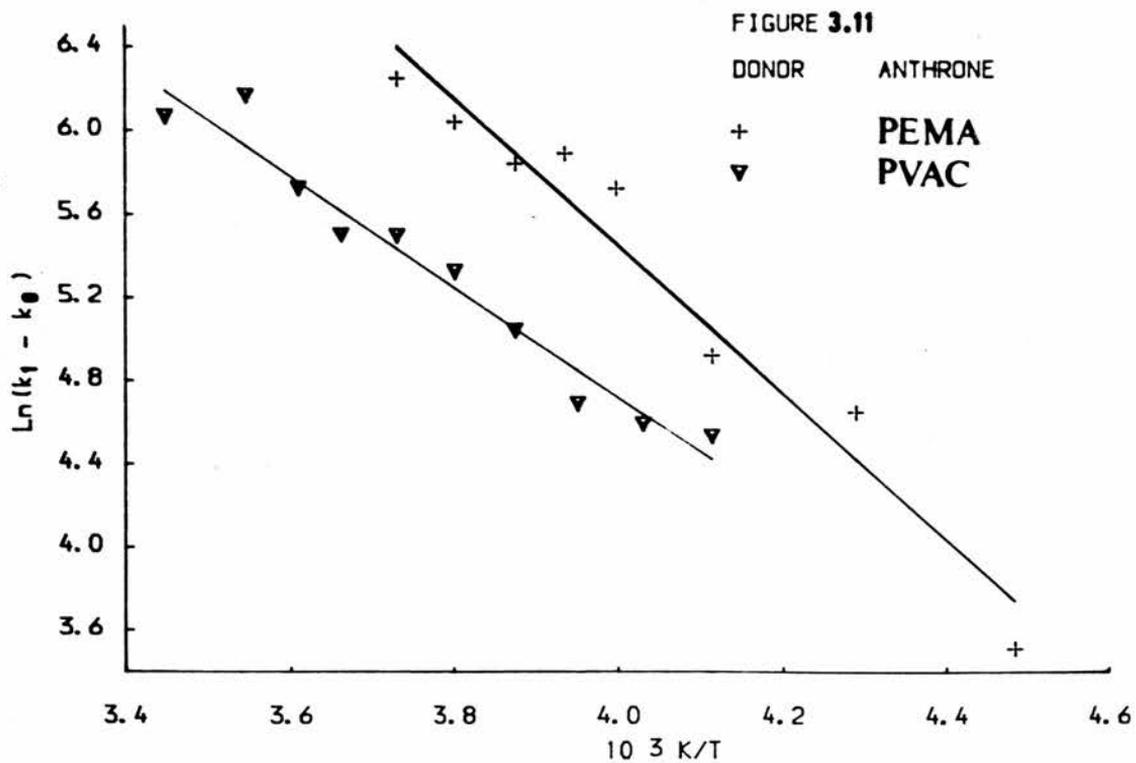


TABLE 3.1

DONOR ANTHRONE

MATRIX	NON EXP. TRANSITION K	k_1 TRANSITION K	k_2 TRANSITION K
POLY(METHYLMETHACRYLATE)	188-200	227-238	283-244
POLY(ETHYLMETHACRYLATE)	193-203	222-233	240-250
POLY(VINYLACETATE)	193-203	233-240	270-277
POLYSTYRENE	168-178	206-212	238-246

TABLE 3.2

DONOR ANTHRONE

MATRIX	E_{a_1} kJ mol ⁻¹	A_1 s ⁻¹	E_{a_2} Below	E_{a_2} Above
POLY(METHYLMETHACRYLATE)	27.5	9.9×10^7	14.0	26.0
POLY(ETHYLMETHACRYLATE)	30.0	3.6×10^8	18.1	35.5
POLY(VINYLACETATE)	23.0	1.6×10^7	19.0	51.0
POLY(STYRENE)	16.9	1.1×10^6	14.5	30.0

3.4.2 Donor : Benzophenone

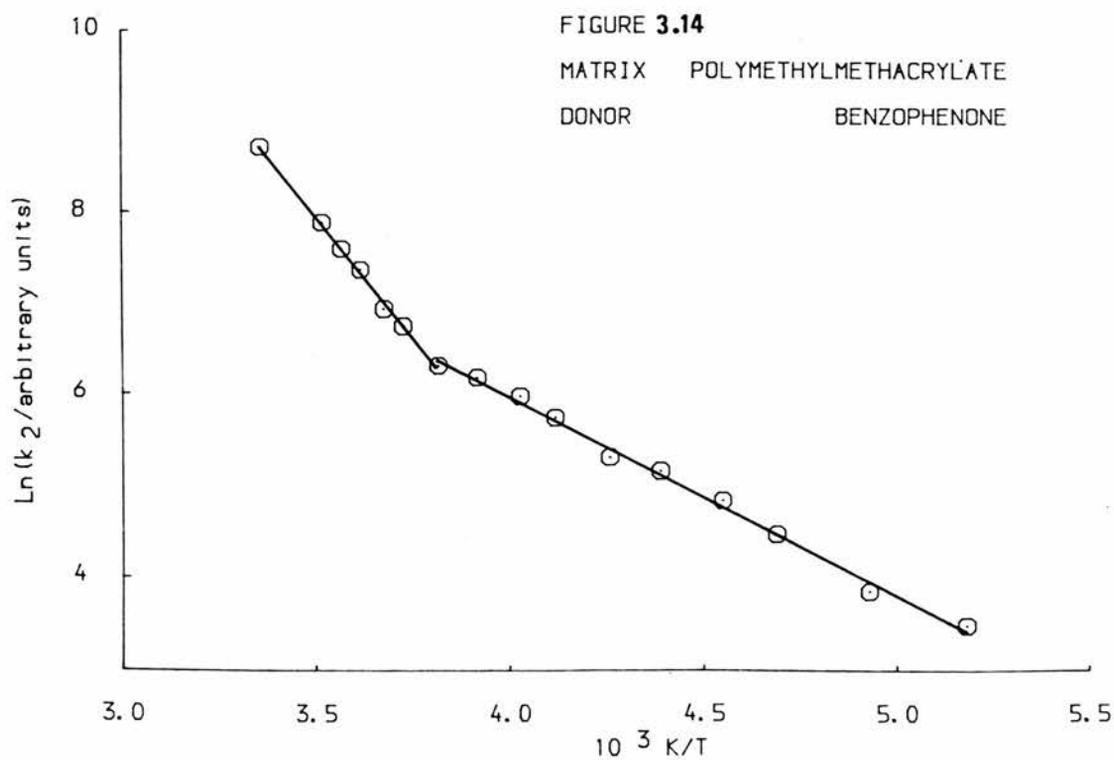
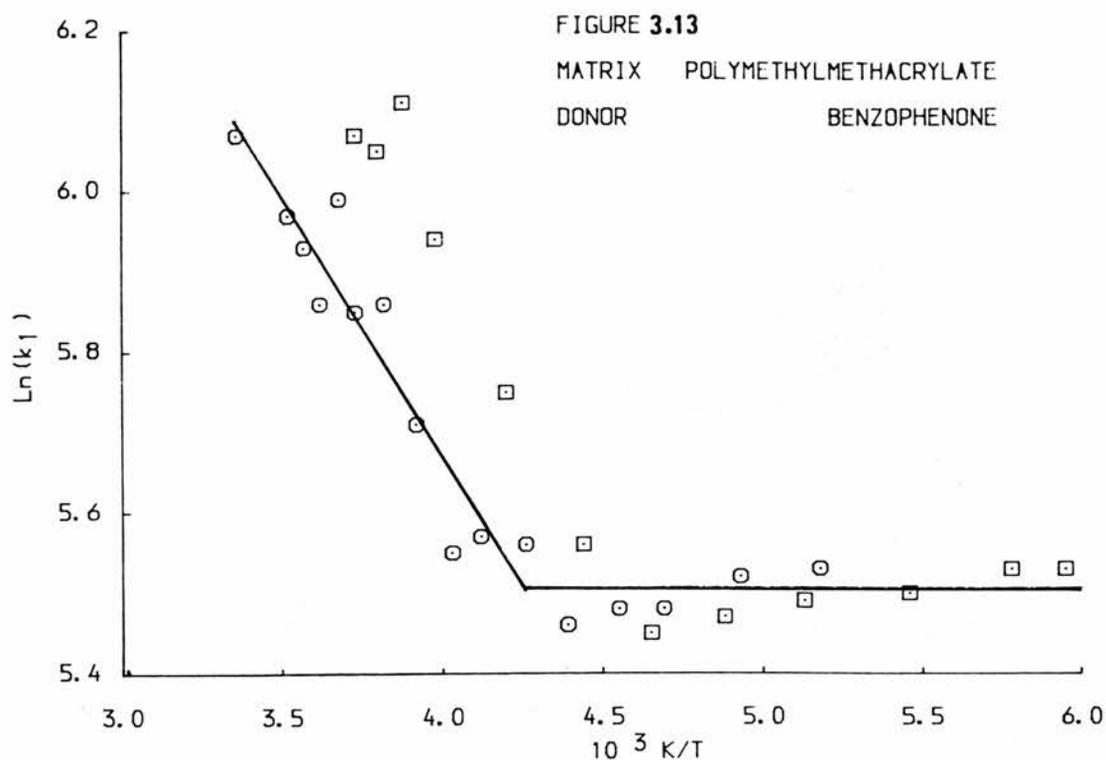
In the case of benzophenone there was an erratic but distinct increase in k_1 on progressing from 77 K to the onset of non-exponentiality, representing a slight reduction in phosphorescence life-time, and making the application of equation 3.2 in the Arrhenius form even less valid. Thereafter, the behaviour was similar to that observed for anthrone.

Figures 3.13-3.16 illustrate the uncorrected Arrhenius plots for k_1 and k_2 . The corresponding temperature transitions, non-exponentiality onset temperatures and activation energies are collated in Tables 3.3 and 3.4 respectively.

3.4.3 Donor : Carbazole

The phosphorescence decay behaviour of carbazole as a function of temperature was similar to that of the aromatic carbonyl compounds in which deviations from single exponentiality were also observed. However, differences were apparent, especially in the low temperature exponential decay region where the life-time decreased as non-exponentiality was approached, highlighting the existence of additional low temperature transitions in the Arrhenius plots.

The uncorrected Arrhenius plots are shown in Figures 3.17-3.18 and the associated transition temperatures are listed in Table 3.5.



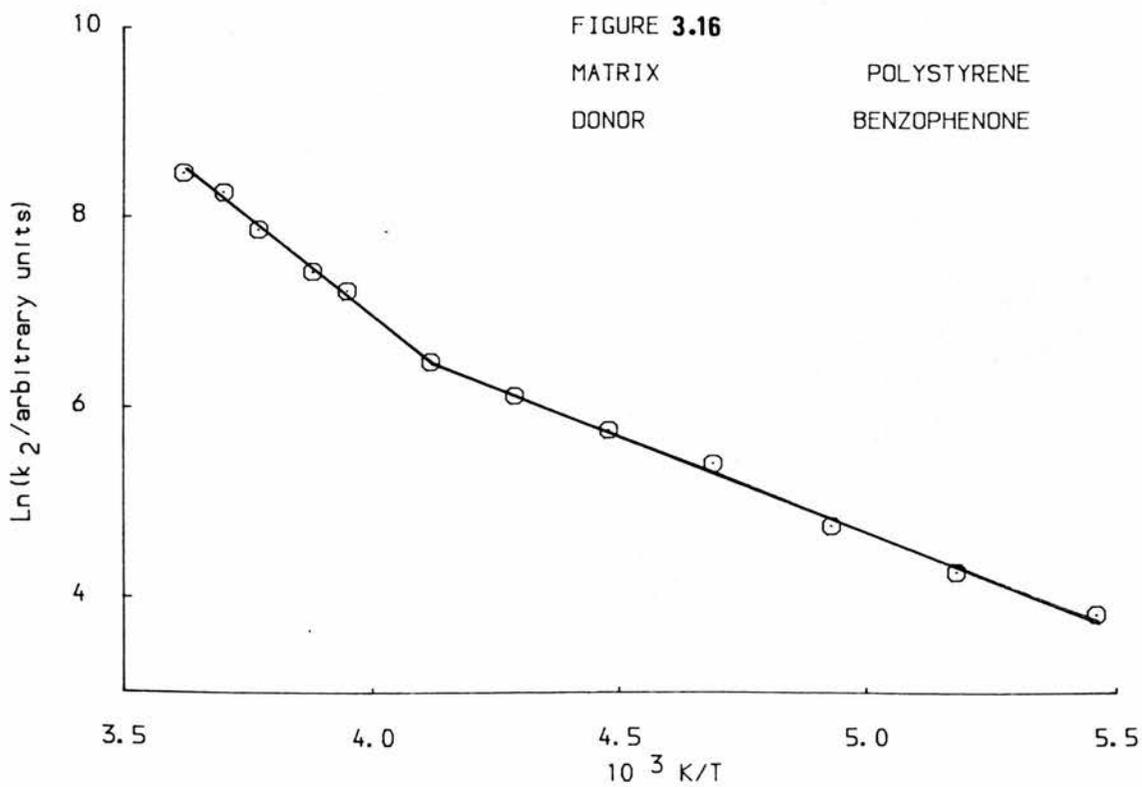
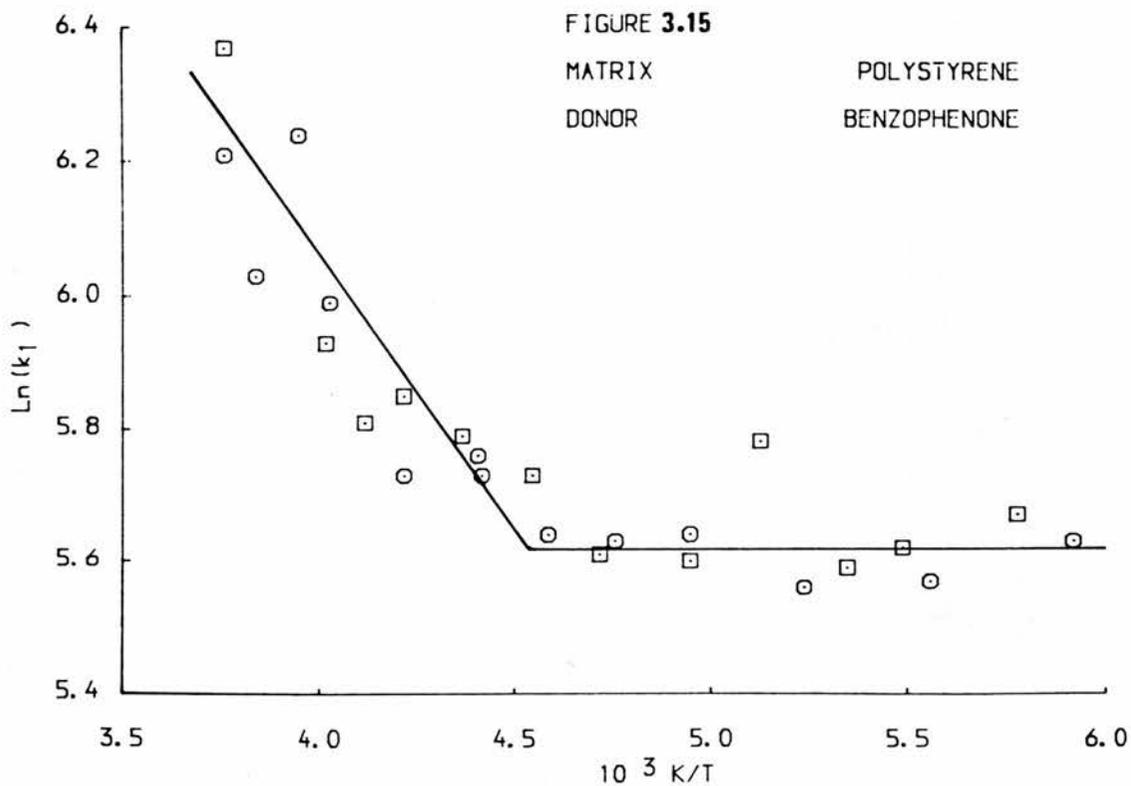


TABLE 3.3

DONOR BENZOPHENONE

MATRIX	NON EXP. TRANSITION K	k_1 TRANSITION K	k_2 TRANSITION K
POLY(METHYLMETHACRYLATE)	193-203	223-244	250-265
POLY(ETHYLMETHACRYLATE)	193-203	233-238	247-255
POLY(VINYLACETATE)	190-200	243-250	270-277
POLYSTYRENE	166-173	217-223	238-243
COPOLYMER 2	175-183	233-238	243-250

TABLE 3.4

DONOR BENZOPHENONE

MATRIX	E_{a1} ± 2 kJ mol ⁻¹	A_1 s ⁻¹	E_{a2} Below ± 2 kJ mol ⁻¹	E_{a2} Above ± 2 kJ mol ⁻¹
POLY(METHYLMETHACRYLATE)	17.2	7.29×10^5	17.5	43.0
POLY(VINYLACETATE)	17.5	3.9×10^5	20.0	36.0
POLYSTYRENE	18.4	1.48×10^6	16.0	33.0

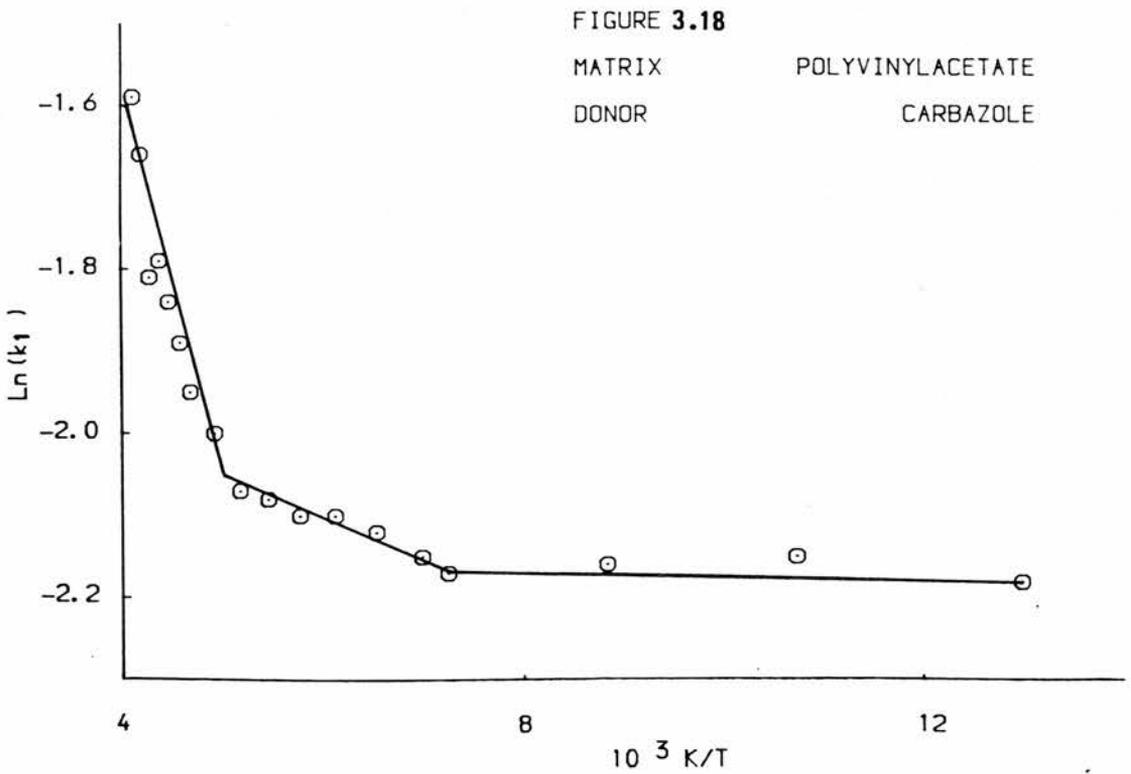
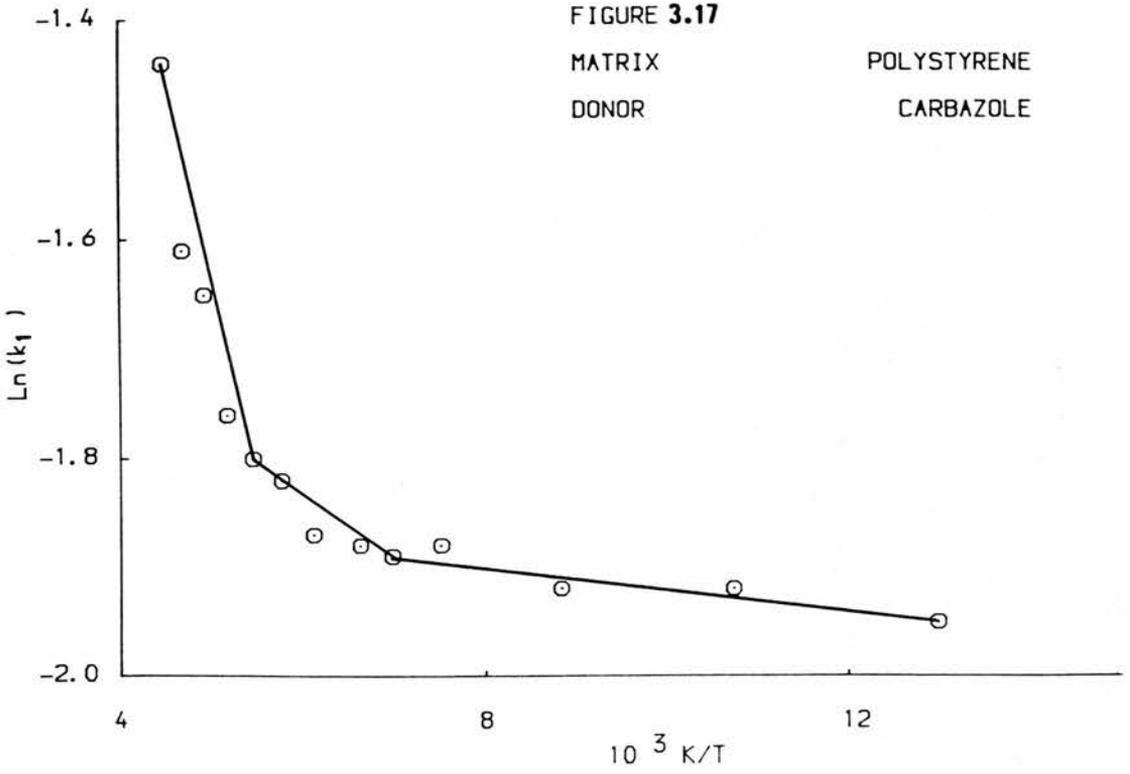


TABLE 3.5
DONOR CARBAZOLE

MATRIX	k_1 TRANSITION K	NON EXP. TRANSITION K
POLY(VINYLACETATE)	138-142	210-220
POLY(VINYLACETATE)	192-200	
POLY(VINYLACETATE)	240-250	
POLYSTYRENE	143-154	190-200
POLYSTYRENE	188-194	
POLYSTYRENE	230-240	

3.5 DISCUSSION OF RESULTS

There are numerous literature reports concerning guest phosphorescence in polymer support matrices, the initial objectives of which often vary, encompassing investigations to test radiative and non-radiative rate theories [164], studies monitoring macromolecular relaxations to yield structural information [173,174] and in the present case, to research possible photophysical interactions between specific additives and the polymer as a precursor to understanding polymer photochemistry.

On the basis of an extensive matrix study and limited temperature data, Chapter Two proposed an electronic interaction between the donor and polymer to explain the observed phosphorescence behaviour and to account for non-exponential decays. However, authors using luminescence techniques to study polymer relaxation generally implicate polymer motions as the principal effect governing the temperature dependence of donor phosphorescence. The data presented in the preceding sections tends to favour the inclusion of additional features to fully explain the decay characteristics, but before discussing the current results further, relaxation phenomena in polymers will be briefly outlined.

3.5.1 Relaxation Effects in Bulk Polymers

The term relaxation is most conveniently defined in terms of a time dependent return to equilibrium of a system which has undergone a change in an applied constraint [175]. The nature of the constraint may include a wide range of effects such as temperature, pressure or chemical change and extend to electric and magnetic induced perturbations.

Polymer molecular relaxations are thermally activated and can range from the chaotic, random, chain motions associated with melts to specific rotational relaxations of chemical moieties attached to monomer repeat units at temperatures well below the T_g . The subject of polymer relaxations is an active area of research and as such has been extensively reviewed [176]. Tables 3.6-3.7 summarize the secondary relaxation temperatures obtained from mechanical studies on poly(methylmethacrylate) and polystyrene.

Studies utilizing the temperature dependence of phosphorescence emission intensity, life-time, and polarization to detect polymer relaxations have become more prevalent [168,169,170,173]. The onset of relaxation is considered to occur at the temperature at which there is a resultant increase in the rate of radiationless depletion of the triplet state probe; the exact transition or relaxation temperature obtained from the point of discontinuity in the Arrhenius plot [173]. Transitions generally become observable when the time scale of the experimental arrangement is comparable with the relaxation time of the molecular processes responsible. In addition, relaxation temperatures have been shown to be influenced by a variety of effects such as, the

structure of the repeat unit, crystallinity, cross-linking and the presence of diluents or plasticizers [177]. Using luminescence techniques, I.Soutar et al. [173] characterized two distinct relaxation transitions in poly(methylmethacrylate) whereas K.P.Ghiggino et al. [168] claimed the presence of at least three transitions over the same temperature region. The latter authors, using two different types of indole based probe, identified two separate transitions in poly(vinylalcohol), but only one was common to each. Furthermore, K.P.Ghiggino et al. [168] located only one transition in polystyrene over a temperature domain in which both β and γ transitions have been characterized [176].

In a comprehensive study J.E.Guillet et al. [170] investigated the phosphorescence temperature dependence of ketone and naphthalene groups in a wide range of polymers, also observing discontinuities in Arrhenius plots. The polymer films were not degassed, leading the authors to attribute the decrease in phosphorescence intensity of the films with rising temperature to the increased mobility of oxygen giving rise to enhanced triplet state quenching. However, the regions of discontinuity were considered coincident with temperatures for the onset of specific sub-group motions in polymers.

Hence, when using the temperature dependence of luminescence to study polymer relaxations, the picture is not entirely consistent and often yields conflicting results.

TABLE 3.6

POLYMER	POLY(METHYLMETHACRYLATE)			
SECONDARY RELAXATION	Temp. K	Ea kJ mol ⁻¹	MOLECULAR MOTION	Ref
T _α '	301	177	local mode relax.	176
T _β	273	78	ester group rot.	176
T _γ	100	13	methyl group rot.	176

TABLE 3.7

POLYMER	POLY(STYRENE)			
SECONDARY RELAXATION	Temp. K	Ea kJ mol ⁻¹	MOLECULAR MOTION	Ref
T _g	377	335	Main chain relax.	176
T _β	300	126	local mode relax.	176
T _γ	153 - 138	33.5	restricted phenyl group rot.	176

TABLE 3.8

POLYMER	PROBE	SECONDARY RELAXATION	Temp. K	Ea kJ mol ⁻¹	Ref
PMMA	I	β	250	14	173
PMMA	I	γ	153	7	173
PMMA	II	β	263	19	173
PMMA	II	γ	159	5	173
PMMA	III	β	253	20	173
PMMA	III	γ	173	9	173
PMMA	IV	—	157	8	168
PMMA	IV	—	240	14.5	168
PMMA	IV	—	270	26.7	168
PS	IV	—	166	12.6	168
PVA _λ	IV	—	169	4.7	168
PVA _λ	IV	—	205	10.5	168
PVA _λ	V	—	215	8.9	168
PVA _λ	V	—	268	18.3	168

PMMA ≡ Poly(methylmethacrylate)
 PS ≡ Polystyrene
 PVA_λ ≡ Poly(vinylalcohol)
 I ≡ Naphthalene
 II ≡ 2-vinylnaphthalene(copolymerized)
 III ≡ acenaphthylene
 IV ≡ β-carboline(9H-pyrido[3,4]indole)
 V ≡ indole-3-acetic acid

3.5.2 Temperature Transitions : Results

In view of section 3.5.1 it is important to recognise that the ketone and carbazole donors will be differentially susceptible to time dependent relaxation effects when used as probes.

3.5.2.1 Short Life-Time Probes

The temperature dependence of anthrone and benzophenone phosphorescence was considered in terms of two composite rate constants, k_1 and k_2 , both of which displayed irregularities when plotted in the Arrhenius form. The transitions observed for each donor in a given polymer were similar and no transitions in either k_1 or k_2 Arrhenius plots were located at temperatures < 200 K, which contrasts with the results of I.Soutar et al. [173] for poly(methylmethacrylate) and K.P.Ghiggino et al. [168] for poly(methylmethacrylate) and polystyrene; both groups used long-lived phosphorescent probes. However, the higher temperature transitions reflected in k_1 Arrhenius plots for poly(methylmethacrylate) compare favourably with those outlined in Table 3.8 and with the transition located by light scattering techniques [178]. Neither the present study or the experiments by I.Soutar et al. [173] could detect the high temperature transition at 270 K reported for poly(methylmethacrylate) by K.P.Ghiggino et al. [168]. The present work also detected a high temperature transition occurring in polystyrene at 206-220 K, a transition not observed by K.P.Ghiggino et al. [168] but confirmed by T.Conner [179] using proton n.m.r spin

lattice relaxation methods, which G.E.Roberts [176] attributed to the ν relaxation process.

The temperature transitions established in the poly(methacrylates) were similar, but the corresponding k_1 and k_2 Arrhenius transitions in poly(vinylacetate) occurred at slightly higher temperatures. Moreover, the relevant transitions in polystyrene occurred at lower temperatures than those reported for the aliphatic polymers. In the case of k_1 , the composite rate constant containing a contribution from k_{et} , this latter observation is consistent with the proposal of thermally activated energy transfer to the lower level of polystyrene.

3.5.2.2 Long Life-Time Probes

Three temperature transitions in both poly(vinylacetate) and polystyrene were detected using the donor/probe carbazole; an observation contrasting with the number observed using ketone probes. The transitions occurring at < 195 K in both polymers were essentially coincident, indicating their origin to be an intrinsic property of the molecule. However, the high temperature transitions, located at the temperature where the emission intensity could no longer be detected, appeared to be matrix specific and agreed with the k_1 transitions found using the aromatic carbonyl donors.

3.5.3 Temperature Transitions : Discussion

There would appear to be a correlation between the discontinuities observed in the Arrhenius plots from luminescence temperature dependence studies using polymer hosts and the temperatures associated with polymer relaxations. However, invocation of polymer mechanical motion as the sole explanation for the temperature dependence of phosphorescence fails to adequately interpret all the experimental features and results in certain unresolved anomalies.

For example, the onset of donor non-exponentiality is not associated with polymer relaxations, and as discussed in Chapter Two, was only observed for the high energy triplet donors within the temperature range 77-298 K. However, polymer relaxations have been detected by both high and low triplet energy level donors. The phosphorescence decay of carbazole, although apparently detecting two low temperature transitions in polystyrene, one of which could be attributable to phenyl group rotation, remained strictly exponential in this temperature region and only deviated from exponentiality at higher temperatures. In support, the decay of the low triplet energy donor phenanthrene possessing a similar life-time, displayed exponential behaviour in the temperature range 77-298 K in both poly(vinylacetate) and polystyrene; a range containing at least two structural relaxations for polystyrene as characterized by mechanical studies [176]. In addition, the donor anthracene has both a low triplet energy level and a short phosphorescence life-time and in view of section 3.5.1 would be susceptible to be influenced by polymer

relaxations occurring on a different time scale, but it also decays exponentially in poly(methylmethacrylate) over the same temperature range [111]. Furthermore, the onset of non-exponentiality associated with the aromatic ketones occurs at temperatures below the k_1 transitions. Hence, the triplet energy level of the donor and not the applicability of the donor life-time to reflect polymer mechanical motion, remains the common link with donor non-exponentiality.

The extent of polymer main chain and sub-group motion is undoubtedly associated with temperature and polymer chemical composition but in studies utilizing luminescence techniques to probe polymer relaxations there is rarely an attempt to explain how such effects can enhance the initial rate of triplet state deactivation. However, in a rationalization of why the room temperature decay of naphthalene-d-8 was exponential in poly(methylmethacrylate) but non-exponential in polystyrene, the authors P.F.Jones and A.R.Calloway [180] proposed that at 300 K in the softer polystyrene host the nuclear conformations of the molecule are no longer constrained by the matrix, resulting in an enhanced initial decay rate. This explanation is incompatible with the observation of exponential naphthalene-d-8 decay in poly(vinylacetate) at 295 K presented in Chapter Two. At such a temperature, only 4 K below the T_g [154], main chain motions are extensive and the polymer assumes rubber like properties, exposing the dopant to an unconstrained environment which does not influence the mode of decay. Moreover, J.L.Kropp and W.R.Davidson [114] found that the phosphorescence decay of coronene in poly(methylmethacrylate) and DER 332 epoxy resin remained similar even though in the temperature range studied the former polymer undergoes a secondary transition whereas the latter

remains rigid. It follows that the mechanical motion of the host polymer did not significantly affect the phosphorescence.

An additional anomaly arises by acknowledging that experimental studies into polymer relaxations require the operational frequency of the measuring device, mechanical or photophysical, to be comparable with the time scale of relaxation [173]. Consequently, if phosphorescence is to be quenched by some process related to polymer relaxation, this process must occur within the life-time of the triplet state. On this basis, it is difficult to rationalize a polymer mechanical motion, governed by a distinct relaxational time or frequency for a given temperature, being equally susceptible to detection by anthrone and carbazole possessing the markedly different "test" frequencies of 10^3 and 0.2 Hz respectively. However, both these molecules indicated the presence of a discontinuity or transition in their k_1 Arrhenius plots occurring at 240-250 K in poly(methylmethacrylate). In this context, it is important to note that both these molecules have high triplet energy levels (see Table 2.1) which again serves as a common link between the spectral characteristics of the probe and the observation of a temperature transition.

Hence, a photophysical scheme containing only unimolecular deactivation routes coupled with an allowance for the inclusion of additional excited state decay pathways due to relaxations in polymer structure, still cannot adequately account for all the features of the phosphorescence temperature behaviour of high triplet energy level molecules in polymer hosts.

3.6 ASSESSMENT OF KINETIC SCHEME

Section 3.2 introduced a kinetic scheme to interpret the temperature dependence of donor phosphorescence in a range of polymers; the results were presented and discussed in the preceding sections in which emphasis was given to the discontinuities in the Arrhenius plots. However, the current section will review the relative merits of the scheme in terms of the nature of the the decay curves and by comparing the predicted and experimental activation energies obtained from the composite rate constants k_1 and k_2 .

3.6.1 Phosphorescence Decay Curves

Under the influence of increasing temperature anthrone and benzophenone were shown to exhibit non-exponential decays for short time intervals (<1 ms) after the excitation flash and approximately exponential decays thereafter. This behaviour is consistent with triplet-triplet annihilation at early times following the excitation pulse in which mixed uni- and bimolecular processes operate competitively on the triplet excited state. After cessation of the exciting light, the triplet state concentration would be optimized for bimolecular interactions; their occurrence more probable during a subsequent limited time period.

Similar decay behaviour has been reported for benzophenone [137] and other molecules [158] as a function of concentration in which triplet-triplet annihilation was established by successfully resolving P-type delayed fluorescence from the total emission spectra, the

contribution of which increased with exciting light intensity and donor concentration. Unfortunately in the present study, due to the technical difficulties outlined, P-type delayed fluorescence was not unequivocally observed and an intensity effect could not be established.

However, the nature of the phosphorescence decay curves and the confirmation that the degree of non-exponentiality was temperature dependent, resulting in an increased k_2 contribution to the initial part of the decay curve, as reflected by the fitting routine, certainly supports the proposal of thermally activated transfer from the donor to the polymer followed by subsequent triplet-triplet interactions and thus emulating the effects observed by other workers [137] on varying the donor ground state concentration.

3.6.2 Activation Energies

The kinetic model for thermally activated energy transfer predicts that the activation energy for transfer plus the triplet energy level of the donor should equal the triplet energy level of the polymer host. Consultation of Table 3.2 clearly demonstrates the activation energies E_{a_1} for anthrone to be greater in the aliphatic polymers than in polystyrene, a fact consistent with the lower triplet level of the latter. Moreover, the difference between the activation energies found in polystyrene and poly(methylmethacrylate) agrees with the difference in their triplet energy levels quoted in Table 2.3. However, when added to the triplet energy level of anthrone the resultant values predict higher polymer triplet energy levels than those given in Table 2.3. The problem of reliably locating polymer

triplet levels has been mentioned, and in view of the additional complications introduced in Chapter Four, this result proves less surprising. In addition, when using equation 3.2 no provision was made to subtract non-radiative temperature dependent contributions from the intensity data. The E_{a_1} activation energies found for anthrone are considered to be in accord with the proposed mechanism.

Table 3.4, listing the relevant data for benzophenone, displays smaller E_{a_1} activation energies than anthrone and fails to distinguish between the different polymers. These facts are not consistent with the proposed mechanism and is tentatively attributed in this instance to the invalidity of equation 3.2 due to the increase in benzophenone life-time as 77 K was approached.

The activation energies obtained from k_2 rate parameters are of less diagnostic value and no mechanistic significance was attached to their magnitude. The relative size of k_2 is predicted to be concentration dependent and this could be associated with temperature induced polymer relaxations giving rise to favoured orientations of polymer pendant groups surrounding the donor molecules.

In the final assessment of the mechanism the results presented in this section are not conclusively in support but collective consideration of all the available evidence substantiates the concluding comment of section 3.5.3 and favours the inclusion of bimolecular processes in any photophysical scheme presented to satisfactorily explain all the temperature effects encountered.

3.7 CONCLUSION

This chapter investigated the temperature dependence of donor phosphorescence in polymer hosts with a view to testing the proposal of thermally activated triplet energy transfer by analysing the decay data in terms of a model based on triplet-triplet annihilation kinetics, yielding relevant rate constants and corresponding activation energies.

The rate constants displayed irregularities when plotted in the Arrhenius form which enabled two distinct linear regions to be defined. The observation of such effects is not unprecedented and the point at which the linear sections intersect is generally assumed to reflect a polymer structural relaxation. Although when correlating the temperature transitions acquired from a range of donors with varying spectral properties, some did indeed coincide with reported polymer relaxations, others highlighted certain anomalies. This led to the conclusion that polymer structural relaxation was not the sole factor governing the temperature dependence of donor phosphorescence.

Another complicating feature was the observation of donor non-exponential decays, shown to be both temperature dependent and matrix specific. This facet of decay behaviour was common to all the high energy triplet donors but absent in low energy triplet donors and ascribed to a bimolecular interaction between triplet states as a consequence of triplet energy transfer from the donor to the polymer.

The applicability of the kinetic scheme was assessed in terms of activation energies derived from k_1 Arrhenius plots and on the nature of the phosphorescence decay curves. The activation energies obtained

for anthrone were consistent with the scheme in that they distinguished between aliphatic and aromatic polymers but predicted higher polymer triplet energy levels than previously reported. Treatment of benzophenone data in a similar fashion failed to reflect the effect of varying polymer environment on the predicted E_{a1} activation energies. The nature of the decay curves was in agreement with the proposed mechanism although P-type delayed fluorescence was not unequivocally observed.

Collective consideration of the experimental results presented in this chapter generally favours the proposed mechanism, but not without some qualification, and the view that unimolecular processes alone cannot adequately explain the temperature dependence of donor phosphorescence when studied in polymer hosts.

Energy Transfer

in

Polymer Hosts

at

77 K

CHAPTER FOUR

4.1 INTRODUCTION

Electronic energy transfer in polymeric systems has received considerable attention in the literature [181,182,183,] and the topic has been extensively studied in both liquid solution [184] and solid film [184]. Emission spectroscopic techniques, both steady state and time resolved, have been utilized to investigate the numerous photophysical processes which occur in organic polymers [183,186,187]. More recently a variety of experiments have been reported which have increased the understanding of the dynamic aspects of exciton migration and the nature of the various excited state interactions that can occur in polymers [188].

4.1.1 INFLUENCE of POLYMER STRUCTURE on PHOTOPHYSICS

An extensive volume of data has been assembled from photochemical and photophysical studies of small molecules [189], the conclusions of which can generally be extended to polymers. However, in practical terms the situation is more complicated with polymeric materials owing to their peculiar structural features. In this respect, it is necessary to be cognisant of how these features can influence polymer photophysical behaviour.

The complication of polymer chain entanglement and the close proximity of adjacent chromophores enhances the probability of specific inter- and/or intra-chain photophysical

interactions [181,190,191] and can result in the formation of excimers, complexes of electronically excited molecules with molecules of the same species in the ground state [192]. For example, in solutions of polystyrene both monomer and excimer emission is observable [193,194], whereas in the solid state both inter- and intra-chain excimer formation is possible [195].

In addition to these implicit structural features of the polymer, there are certain other adventitious chemical factors which play a role in macromolecular structure, and as such could interfere with photophysical events; their presence being essentially unavoidable, originating in the initial polymerization or in subsequent commercial manipulation. Physical defects, due to chain folding or strain points, have also been proposed to act as traps or centres capable of dissipating energy radiatively or non-radiatively [193].

4.1.2 CONCEPT OF ENERGY TRANSFER

Electronic energy transfer involves interaction, either radiatively or non-radiatively, between an electronically excited donor molecule with a ground state acceptor molecule, such that the donor is de-excited and the acceptor raised to an excited electronic state [197,198]. The non-radiative mechanisms are most relevant to this study and indeed, the contribution of the radiative mechanism to energy transfer, involving sequential donor emission and re-absorption of the emitted photon by the acceptor, was purposely minimized by using very thin polymer films. There are two important non-radiative mechanisms; one coulombic in origin and the other involving electron exchange interactions, both of which can be represented by:



where D and A depict donor and acceptor respectively and * denotes an excited state.

Each mechanism requires a specific resonance between the donor and acceptor energy and both are governed by symmetry, multiplicity and overlap restrictions. These factors and their significance to the mechanism of energy transfer will be discussed in detail. In the case of polymeric support matrices the situation is further complicated by the possibility of an energy migration mechanism among chromophores attached to the polymer backbone. Indeed, it has been proposed that energy migration of this nature occurs in the singlet level of poly(1-vinylnaphthalene) [199] and polyacenaphthalene [200] and in the triplet level in poly(vinylbenzophenone) [201,232] and poly(vinylcarbazole) [202]. Consequently, it is important to distinguish energy transfer from energy migration, which is a special case of the former phenomena [3], involving electronic energy transfer between chemically identical chromophores.



The non-radiative mechanisms of electronic energy transfer will be reviewed, quoting relevant formulae, listing assumptions implicit in their derivation, stating the limitations of their application and outlining factors which influence their efficiency.

4.2 NON-RADIATIVE MECHANISMS OF ELECTRONIC ENERGY TRANSFER

Electronic energy transfer experiments are most often characterized by one or more of the following parameters, k_{et} , the rate constant for transfer, Q_{et} , the efficiency of transfer or R_0 , the critical transfer distance.

4.2.1 The Dipole-Dipole Mechanism

As the name suggests this mechanism is electrostatic in origin and can be considered in terms of a multipole expansion of potentials between the electrons of the donor and acceptor; in this expansion the dipole-dipole contribution most often dominates [89,198,203]. The first complete derivation of a relationship between the specific rate of electronic energy transfer and experimentally available parameters was formulated by Th.Forster [204], proposing the following expression [3]:

$$k_{et} = 8.79 \times 10^{-28} \frac{\kappa^2 \phi_D}{n^4 \tau_D R^6} \int f_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4} \quad \dots 4.1$$

where κ is an orientation factor, ϕ_D the donor emission quantum yield, n the refractive index of the medium, τ_D the emission life-time of the donor in the absence of the acceptor, R the donor-acceptor separation, f_D the donor emission spectrum and ϵ_A the acceptor extinction coefficient.

It is convenient to define a specific donor-acceptor separation

R_0 , such that the probability of electronic energy transfer is equal to that of decay by radiative and non-radiative processes [204]. Hence, for this condition,

$$k_{et} \tau_D = 1.0 \quad \dots 4.2$$

thereby allowing equation 4.1 to be written as:

$$(R_0)^6 = 8.79 \times 10^{-28} \frac{\kappa^2 \phi_D}{n^4} \int f_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4} \quad \dots 4.3$$

Consequently, an estimation of R_0 can be obtained from the spectroscopic properties of the donor and acceptor under investigation [3].

Th. Forster [204] then applied averaging techniques to equation 4.1, encompassing a random ensemble of donor-acceptor pairs, leading to an expression relating the donor luminescence intensity as a function of time and acceptor concentration, both directly measurable parameters. Thus,

$$I_D(t)/I_D(0) = \phi(t) = \exp(-(t/\tau_D) - \sqrt{\pi B} \cdot (t/\tau_D)^{\frac{1}{2}}) \quad \dots 4.4$$

where $I_D(t)$ and $I_D(0)$ represent the donor luminescence intensity at time $t=t$ and time $t=0$ respectively. The parameter $B=C/C_0$, where C is the acceptor concentration and C_0 represents the critical transfer concentration, defined under the same conditions as for R_0 , such that,

$$R_0 = 0.7346/C_0^{1/3} \text{ (nm)} \quad \dots 4.5$$

Equation 4.4 is relevant to the experimental condition of flash excitation; a requirement satisfied in the present study.

The important energy transfer parameter R_0 can also be obtained by measuring the yield of donor emission in the presence of acceptors relative to that in their absence [89]. According to M.Inokuti and F.Hirayama [205], the yield of donor emission may be calculated by integration of the decay function,

$$\eta/\eta_0 = 1/\tau_D \int \phi(t) dt \quad \dots 4.6$$

where η and η_0 are the donor emission yields in the presence and absence of acceptor respectively. In terms of this theory, the relative yield of donor emission is related to C_0 when $C/C_0 < 0.75$, according to [89],

$$\eta/\eta_0 = \exp(-0.5\pi C/C_0) \quad \dots 4.7$$

Hence, under certain experimental conditions and by judicious application of intensity time experimental data, the parameters R_0 and C_0 can be obtained from two different equations, thus allowing comparison.

4.2.2 The Exchange Mechanism

The exchange mechanism of energy transfer operates up to relatively small distances (1.5 nm) and involves the overlap of the molecular orbitals of the donor and acceptor [205]. This interaction arises from the antisymmetry requirements of the electronic wave function of the donor/acceptor system [206,207]. Consequently, the rate constant for energy transfer by this mechanism is expected to fall off exponentially as the separation between the excited donor and the ground state acceptor increases.

D.L.Dexter [206] proposed the following expression for the rate of energy transfer by this mechanism,

$$k_{et} = (2\pi/h) z^2 \int f_d(\bar{\nu}) \epsilon_A(\bar{\nu}) d\bar{\nu} \quad \dots 4.8$$

$$z^2 = Y \exp(-2R/L)$$

where h is Planck's constant, Y a constant with the dimensions of energy and L represents the effective average Bohr radius of the excited and unexcited states of the donor and acceptor. The integral is termed the spectral overlap and in the case of the exchange mechanism is normalized to unity.

By a similar technique to that applied by Th.Forster to extend the induced dipole treatment over a random ensemble of donor-acceptor pairs, M.Inokuti and F.Hirayama [205] derived the following expression for the decay of donor emission in the presence of varying acceptor

concentrations,

$$I_D(t) / I_D(o) = \phi(t) = \exp[(-t/\tau_D) - \mathcal{V}^{-3} \cdot B \cdot g(z)] \quad \dots 4.9$$

where

$$z = \exp(\mathcal{V} \cdot (t/\tau_D))$$

$$\mathcal{V} = 2Ro/L$$

$$B = C/Co$$

The symbol $g(z)$ represents an integral function and can be approximated by the following expression,

$$g(z) = (\ln z)^3 + k_1(\ln z)^2 + k_2(\ln z) + k_3 \quad \dots 4.10$$

where k_1 , k_2 and k_3 are numerical constants. The function $g(z)$ will be discussed in greater detail in section 4.3.1. Hence, it can be appreciated from equation 4.9 that energy transfer parameters can be directly related to the experimentally accessible variables of luminescence intensity, acceptor concentration and time. This equation is strictly applicable to conditions of flash excitation.

In addition, M.Inokuti and F.Hirayama [205] have suggested that the efficiency of energy transfer by this mechanism could be discussed in terms of the following expression, recognising that the donor life-time will be influenced by the presence of the acceptor.

$$\phi_F = 1 - [\tau_D^{-1} \int \phi(t) dt] \quad \dots 4.11$$

Similarly, emission yield data may be used to derive values of R_0 for the exchange mechanism and in this case it has been shown that the relative emission yield can be represented by,

$$\eta/\eta_0 = \exp(-\alpha C/C_0) \quad \dots 4.12$$

for all values of λ where $0.05 < C/C_0 < 1.0$; α is a constant.

4.2.3 Assumptions Inherent to Equations

In common to most theoretical models there are certain constraints to which the system must comply before attempting to establish a mathematical base from which equations can be derived, and the energy transfer mechanisms are no exceptions. Below is a list of assumptions implicit to the derivation of the energy transfer equations quoted in the previous sections.

- (i) The donor and acceptor are randomly distributed in an inert medium.
- (ii) Diffusional movement during donor life-time is negligible.
- (iii) Energy transfer occurs such that donor-donor transfer is minimal.
- (iv) The donor is exclusively excited in the presence of the acceptor.
- (v) There is no ground state donor-acceptor interaction.

The details of the theoretical and mathematical treatment can be found in many literature sources [205,206,207].

4.2.4 Comparison of Mechanisms

Spectral overlap between donor emission and acceptor absorption is necessary for both mechanisms, but only in the exchange mechanism is the overlap integral normalized to unity. Consequently, the rate constant for exchange transfer is independent of the oscillator strength of the acceptor transition and therefore, this mechanism is expected to predominate in systems where the acceptor transition is forbidden. Another point of difference is the distance over which each mechanism is expected to operate; typical R_0 values being < 1.5 nm and > 1.5 nm for the exchange and dipole mechanisms respectively [197].

The decay functions for both mechanisms, represented by equations 4.4 and 4.9, are non-exponential. The first term of each gives the life-time of the donor as a single dopant whereas the second terms reflect the intensity lost by energy transfer [208]. The magnitude of the second term in relation to the first diminishes as time increases, making its contribution to the decay function less significant. To further underline the mechanistic comparison, a computer program was written to generate theoretical decay curves to enable the effects of varying specific parameters within each equation to be readily appreciated in graphical form. The authors M.Inokuti and F.Hirayama performed a similar analysis for the exchange mechanism only [205].

Consider first decay curves derived from equation 4.9 corresponding to exchange energy transfer, shown in Figures 4.1-4.3. The curves depict a plot of \ln (Luminescence Intensity) against t/τ_D for varying values of C/Co for a given value of \mathcal{V} . It is evident that deviation from exponentiality for a given \mathcal{V} is more pronounced for larger values of C/Co . In addition, the area under the decay curve, which is related to the yield of donor emission, is also markedly reduced for an increase in C/Co . In each case the curves show a rapid initial drop, the severity of which rises with an increase in \mathcal{V} . The curves also clearly illustrate that for small values of \mathcal{V} , the time interval that must elapse before exponential decay is approached is correspondingly larger.

Figures 4.4 and 4.5 demonstrate the effect of varying C/Co on the decay characteristics of the dipole mechanism. The observations are consistent with equation 4.4 in that the larger the value of C/Co the more rapid the initial drop in the donor intensity, resulting in a pronounced deviation from exponentiality.

Finally, it is important to recognise the similarity in the exchange and dipole curves for small values of \mathcal{V} , < 10 , covering the same range of C/Co . In such an area it is exceedingly difficult to differentiate between the mechanisms. However, as \mathcal{V} increases distinct differences appear in the the decay curves.

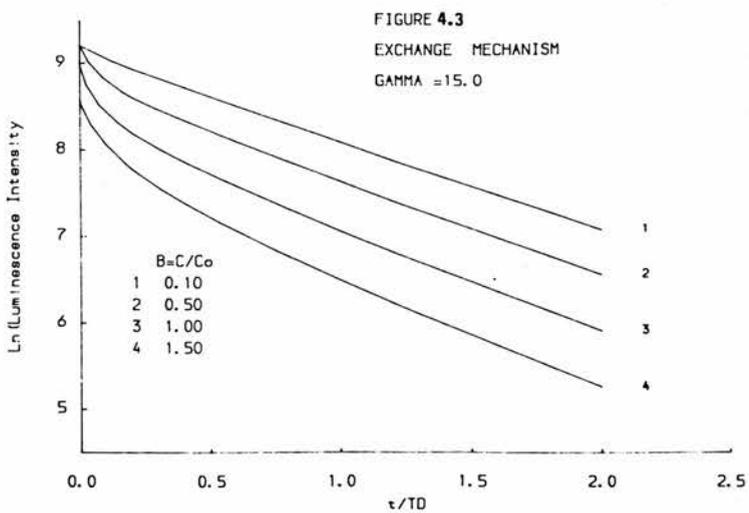
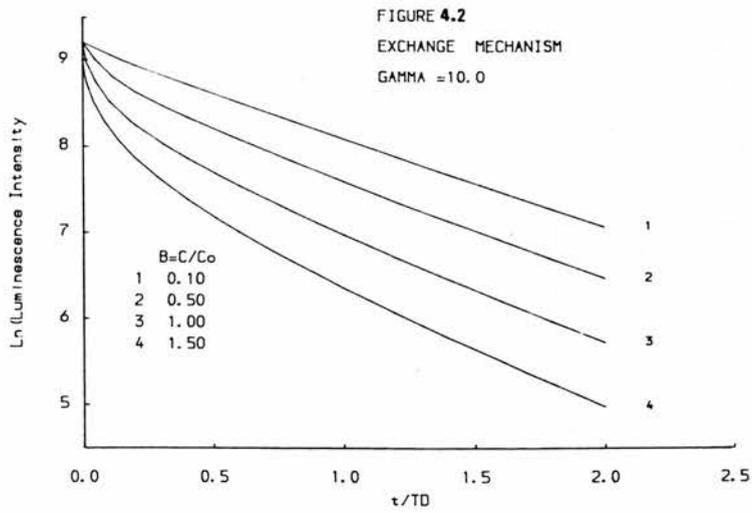
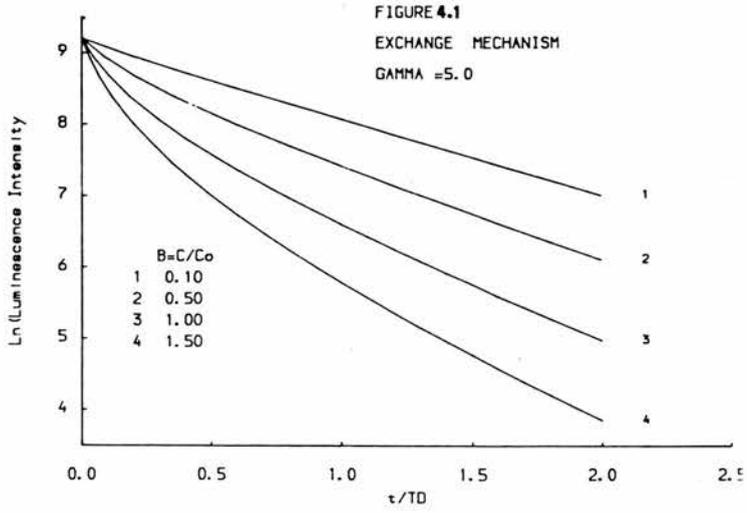


FIGURE 4.4
DIPOLE-DIPOLE MECHANISM

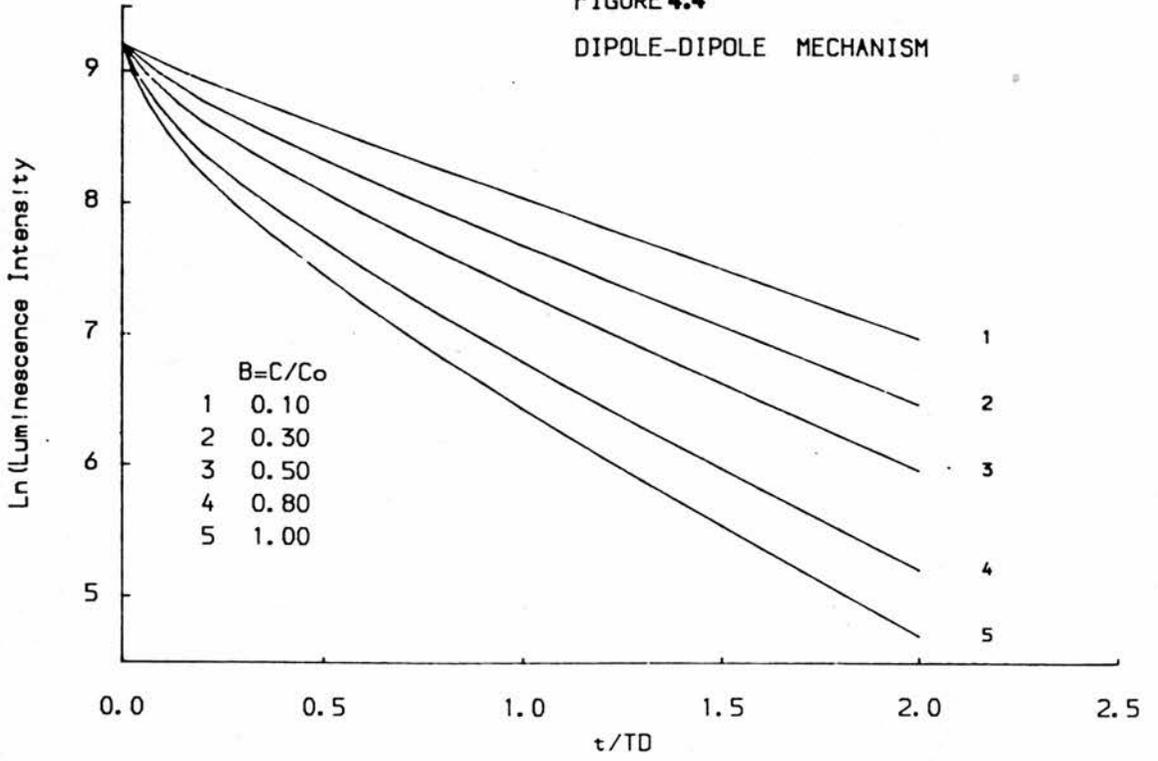
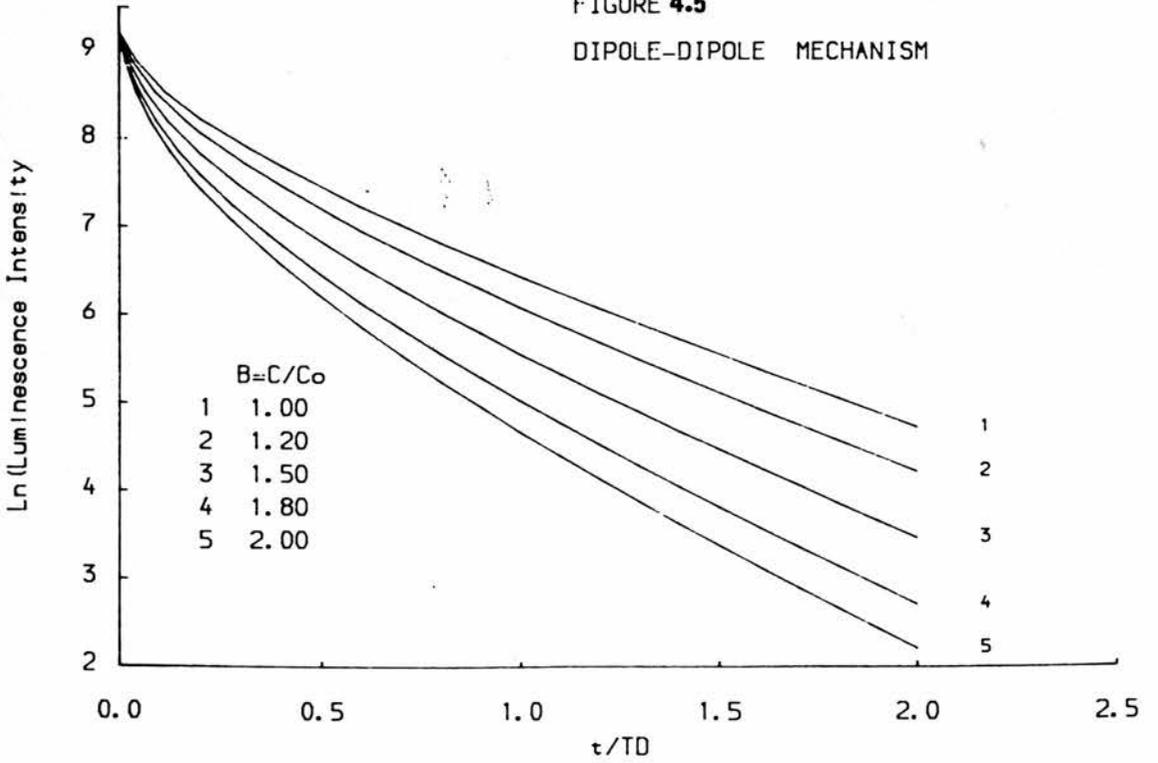
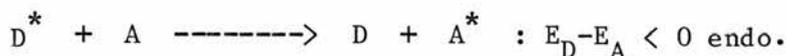
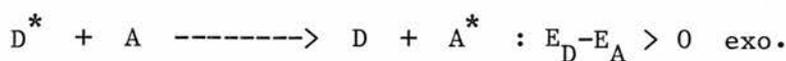


FIGURE 4.5
DIPOLE-DIPOLE MECHANISM



4.2.5 Factors Influencing Transfer Efficiency and Applicability

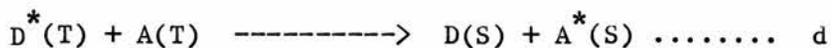
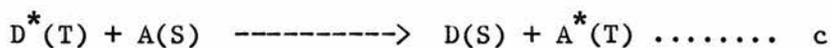
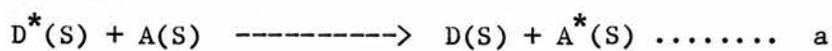
Electronic energy transfer processes, irrespective of the mechanism, require an exact resonant energy matching between the energy levels of the donor (D^*) and acceptor (A). This factor is illustrated in Figure 4.8, which depicts energy level matching in terms of the overlap between donor emission and acceptor absorption. Consequently, energetics exercise a constraint over the efficiency of transfer and allows the definition of exothermic and endothermic transfer processes [197].



A second important feature in influencing the efficiency of transfer are the spin selection rules applied to donor and acceptor. In the case of the induced dipole mechanism, spin conservation laws apply to the donor and acceptor molecules individually, prohibiting a change in spin multiplicity in either during transfer [209]. However, with the exchange mechanism the less restrictive Wigner spin conservation laws apply [209]. If S_1 and S_2 are the initial spin quantum numbers of donor and acceptor respectively, the resultant quantum number of the donor plus acceptor must have one of the values,

$$S_1 + S_2, S_1 + S_2 - 1, \dots, S_1 - S_2.$$

Knowledge of the type of multiplicities involved in the transfer process is important in deciding which mechanism is valid. Consider the following transfer modes, where S and T denote singlet and triplet states respectively.



Hence, in view of the aforementioned spin selection rules, transfers a and b are more tenable by the dipole mechanism, whereas transfers c and d are more feasible by the exchange mechanism [3].

4.3 DATA ANALYSIS

Investigation into the relationship between donor emission intensity and acceptor concentration provides a means of quantifying energy transfer parameters. Experimentally, either steady state intensity or decay profiles are measured as a function of acceptor concentration. If the latter approach is chosen the decay curves are analysed in terms of either equation 4.4 or 4.9, thereby raising the problem of how to abstract meaningful data from a curve. To overcome this problem, in the case of the exchange mechanism, M.Inokuti and F.Hirayama [205] devised a comprehensive procedure by which R_0 and C_0 could be obtained, involving a comparison of experimental decay curves and those predicted by theory for a given set of variables. The method has also been outlined by C.O.Hill and S.H.Lin [210]. However, due to the advance in computer facilities, an alternative procedure based on an iterative curve fitting analysis, has attracted attention in the literature [67,87], and this method was used in the present study. However, before considering the basic principles of such a technique, it is necessary to discuss the properties of the function $g(z)$ appearing in equation 4.9, one of the equations to which the method was applied.

4.3.1 The Function g(z)

The exchange energy transfer equation, 4.9, has been shown to contain the function g(z), which can be represented in terms of a Taylor's series,

$$g(z) = 6z \sum_{m=0}^{\infty} \frac{(-z)^m}{m!(m+1)^4} \quad \dots 4.13$$

However, when utilized in conjunction with equation 4.9, g(z) is not used in the above form but in terms of an approximation, given by equation 4.10.

$$g(z) = (\ln z)^3 + k_1(\ln z)^2 + k_2(\ln z) + k_3 \quad \dots 4.10$$

where the coefficients have been shown to equal [205],

$$k_1 = 1.731, \quad k_2 = 5.934, \quad k_3 = 5.444$$

It is evident from equation 4.13 that g(z) is positive and monotonically increases for any value of z > 0 and for small values of z the Taylor's series rapidly converges. It has been claimed [205] that for large values of z the approximation, that is, equation 4.10 gives g(z) with excellent accuracy, but is not valid for small values

of z . The purpose of the present section is to substantiate this claim and further, to explore the limits of the validity of equation 4.10 for a range of experimental conditions.

As stated, the Taylor's series will rapidly converge for small values of z and convergence is considered to be achieved when the difference between the m^{th} and the $m^{\text{th}-1}$ value of $g(z)$ is zero or negligibly small. Let this difference be denoted by X . Hence, one can dictate when convergence has been attained by comparing X with a desired value Y ; choosing Y to be the stipulated limit of convergence. Obviously, the smaller the value of Y the greater will be the value m , as an increase in the desired accuracy is achieved at the expense of including more terms in the summation.

To investigate this problem a computer program was written with the facility for varying Y and noting the value of m , whilst comparing the resulting $g(z)$ given by the Taylor's series with the corresponding $g(z)$ calculated by the approximation. The symbols GAP and GAC represent $g(z)$ calculated using the approximation and the Taylor's series respectively. The data was acquired over a large range of z and is listed in Table 4.1. The results prove that when z is < 0.1 the approximation is not valid as it yields negative values of $g(z)$ which must always be positive. Furthermore, for z such that $0.5 < z < 1.0$ the approximation, whilst giving positive values, is not sufficiently accurate to merit its use. However, for $z > 5.0$, the approximation proved to be very accurate, confirming that it should only be used when the latter condition is satisfied. Hence, the predictions concerning the accuracy of the approximation [205] have been shown to be correct.

Having answered the question on when to use the approximation, it

is worthwhile commenting upon why the Taylor's series is not used for all values for z . For small values of z convergence is rapid but for large values of z ; experimentally more realistic, convergence is tedious, involving numerous summation terms and requiring excessive computation time. Hence, for such cases, the use of the Taylor's series would be impracticable; this being the region in which the approximation is most valid.

There are certain experimental factors which can influence the magnitude of z , the value of which is not constant but changes as a function of time during the course of the transfer process. This changing value of z could necessitate the use of both the Taylor's series and the approximation in the computation of $g(z)$. Consider the following experimental situation in which the smallest practical \mathcal{V} is taken as 5, the donor life-time as 10 s and the luminescence sampling rate equal to 0.1 s. Under such conditions z is given by,

$$z = \exp(5) \times 0.1 / 10.0 = 1.5$$

Consequently, to calculate the corresponding value of $g(z)$ over the first four sampling points the Taylor's series is recommended; thereafter the approximation is valid as $z > 5.0$. In the present study, the first intensity data acquisition points for both donors benzophenone and anthrone, using \mathcal{V} equal to 5, predict the smallest values of z to be 40 and 50. Hence, in both examples, at all times during the donor decay the approximation is valid.

In conclusion, this section confirms the analytical approximation to the Taylor's series to be valid but demonstrates the existence of certain conditions that must be fulfilled for its proper use.

TABLE 4.1

Z	Y	M	GAP	GAC
0.01	0.1	1	-82.82427	0.05996
0.01	0.00001	2	-82.82427	0.05996
0.10	0.1	1	-11.24649	0.59625
0.10	0.00001	3	-11.24649	0.59625
0.50	0.1	1	1.83045	2.90625
0.50	0.00001	3	1.83045	2.91063
1.00	0.1	1	5.44487	5.62500
1.00	0.00001	4	5.44487	5.65853
5.00	0.1	3	23.65019	22.81322
5.00	0.001	9	23.65019	23.64618
5.00	0.00001	13	23.65019	23.65030
10.00	0.1	12	40.49826	40.11427
10.00	0.001	19	40.49826	40.48921
10.00	0.00001	24	40.49826	40.49833

4.3.2 Curve Fitting

Curve fitting is the process of finding a mathematical formula for approximating a set of data values or for approximating another mathematical formula. The following section briefly outlines the basic ideas behind the technique; the precise mathematical detail is described by R.La Fara [211].

4.3.2.1 Mathematical Principles

For a set of data points where each observed quantity Y_i is dependent upon one or more variables X_1, X_2, \dots, X_n , a functional relationship can be written such that

$$Y_i = f(X_1, X_2, X_3 \dots X_n) \quad \dots 4.14$$

It is necessary to derive some mathematically expressible function of the independent variables, say

$$U_i = g(X_1, X_2, X_3 \dots X_n) \quad \dots 4.15$$

such that when g is evaluated for each set of values of the independent variables, all errors

$$\epsilon_i = Y_i - U_i \quad \dots 4.16$$

are necessarily small.

In the present context the mathematical form of the function is

known, thereby reducing the problem to one of evaluating the parameters of the function g consistent with experimental data.

Rewriting equation 4.15,

$$U_i = g(a_1, a_2, a_3 \dots a_n) \quad \dots 4.17$$

it can be seen that it is necessary to find a set of a_i 's such that the term

$$\sum (Y_i - g(a_1, a_2, a_3 \dots a_n)) \quad \dots 4.18$$

is a minimum

The function g is expanded as a Taylor's series in which only the first order terms are retained, allowing each value of a_i in equation 4.17 to be written in terms of an initial guess a_i^0 , an increment value Δa_i and a partial derivative of the function g with respect to a_i . The algorithm given by R. La Fara [211] uses a numerical method to solve for the Δa_i and these increments can then be added to the original guess (relevant a_i^0) to give a new approximate a_i which can then be used to find the new values of the function. Hence, an iterative procedure is performed correcting the initial guesses of the unknowns (the a_i^0) until the coordinates generated by the correct a_i values equal, within a stipulated error, the experimental coordinates. If such a condition is satisfied, convergence is achieved, yielding the relevant numbers represented by the $a_1, a_2, \dots a_n$ parameters necessary to reproduce the experimental data.

4.3.2.2 Using the Algorithm

The method of curve fitting can be readily understood by illustrating the operation of the algorithm with reference to the dipole expression, equation 4.4, in which the two unknowns (a_1 and a_2) are $\ln I_0$ and B , denoted by A and B respectively. The algorithm, written in the computer language Fortran, is shown in Figure 4.6 and is divided into numbered sections for ease of explanation.

The function (equation 4.4) is shown in section 1 and equation 4.16 is outlined in section 2. The partial derivatives of the function g with respect to the unknowns, Y_A and Y_B , are shown in section 3. Section 4 illustrates the numerical procedure used to obtain the values of the increments (DA and DB) and section 5 corrects the current value of the unknowns by these increments. Finally, section 6 dictates the conditions for successful convergence in terms of the errors between experimental and fitted data points and the number of iterations allowed. Such a routine is easily incorporated into a larger program designed to analyse a kinetic model. Indeed, during the course of the present study, computer programs were written to interpret data based on dipole, exchange and triplet-triplet annihilation mechanisms.

Figure 4.6

```
DO 40 I=1,M
FUNCT(I)=A-T(I)/TD-(SQRT(PI)*B*SQRT(T(I)/TD) ..... 1
DY=YLN(I)-FUNCT(I) ..... 2
YA=1.0 ..... 3
YB=-(SQRT(PI)*SQRT(T(I)/TD))

S1=S1+YA*YA
S2=S2+YA*YB
S3=S3+YB*YB
S4=S4+YA*DY ..... 4
S5=S5+YB*DY

40 CONTINUE
D=S1*S3-S2*S2
DA=(S3*S4-S2*S5)/D
DB=(S1*S5-S2*S4)/D

A=A+DA ..... 5
B=B+DB

X=ABS(DA/A) + ABS(DB/B)
IF(X.LE.0.0001) GOTO 50
IF(K.LT.100) GOTO 60
GOTO 100 (terminate loop) ..... 6

60 K=K+1
GOTO 31 (continue round loop)

50 CONTINUE (convergence successful)
```

4.3.3 Curve Fitting Routines

Having written computer programmes to execute curve fitting routines for dipole and exchange energy transfer processes, it was necessary to test each respectively with genuine dipole and exchange decay data, thus establishing whether or not each routine could reliably reproduce energy transfer parameters consistent with theory. The tests were implemented by choosing realistic values of the unknowns such that R_0 would equal 1.59 nm for successful convergence. In both cases the fitting routines produced values of the unknown parameters in exact agreement with those used to generate the simulated data.

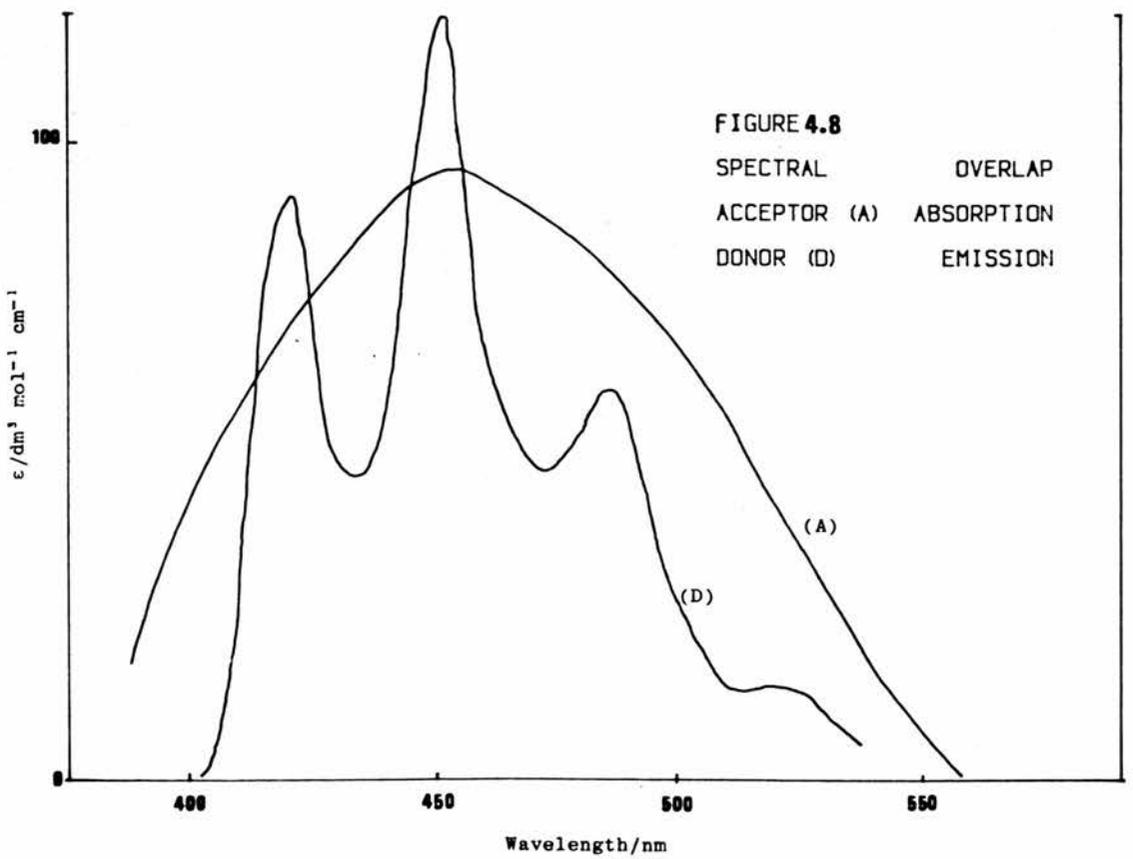
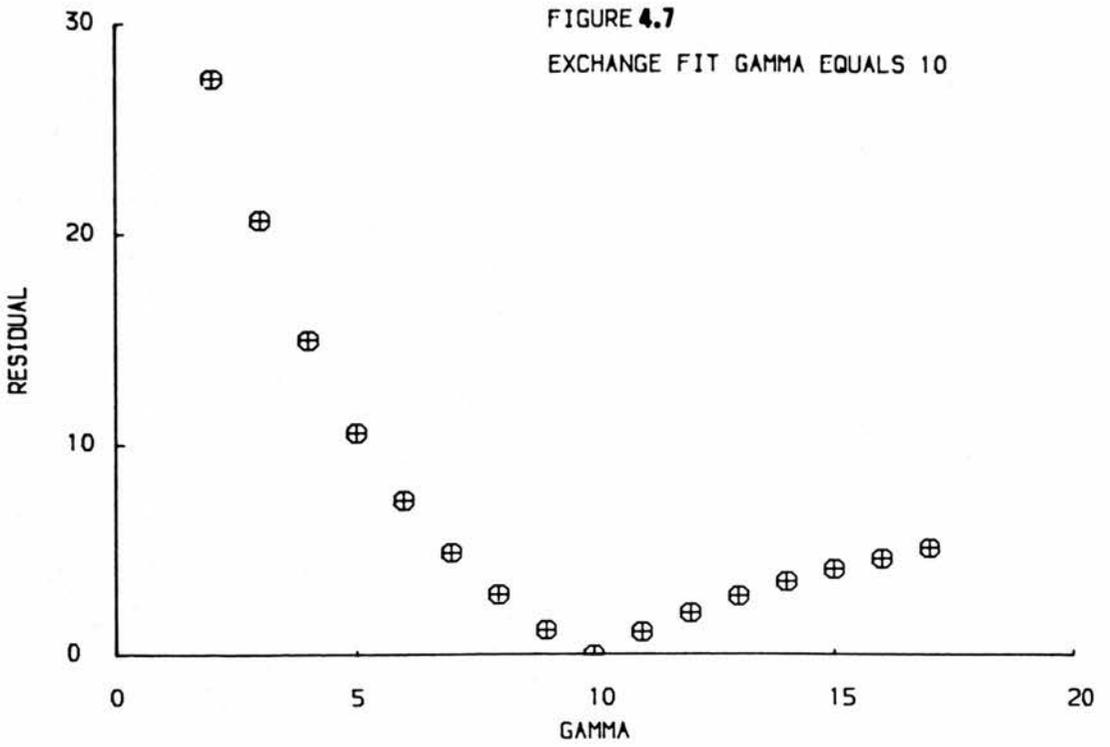
4.3.4 The Exchange Equation

The equation describing energy transfer by the exchange mechanism, 4.9, contains three experimental quantities; namely, I_0 , B and \mathcal{V} . In addition, the expression is further complicated by the analytical function $g(z)$, in which \mathcal{V} appears as variable. Due to such complexity, it was decided to curve fit this equation for the unknowns $\ln I_0$ and B , whilst varying \mathcal{V} over a fixed range. Ideally, it would have been advantageous to have had an accurate value of I_0 , allowing the fitting routine to determine B and \mathcal{V} . However, experimentally the true value of I_0 is unattainable, but in systems where the donor life-time is in seconds and the data acquisition rate is in milliseconds, a good approximation to I_0 can be obtained. Unfortunately, this approach was not valid in the present study for

two reasons. Firstly, due to experimental problems the first 5-8 % of any sweep had to be neglected and secondly, the donor phosphorescence life-times were also in the millisecond region.

To illustrate that the above procedure will converge to the correct value of the unknowns, a set of simulated exchange decay data was generated using $\ln I_0=10$, $B=1$ and $\mathcal{V}=10$. Figure 4.7 shows a plot of residual, that is, the sum of the squares of the differences between simulated and fitted intensity points against \mathcal{V} . It is clearly demonstrated that the residual is zero for the fitted value of $\mathcal{V}=10$, indicating successful convergence and only this value produced the correct input values of $\ln I_0$ and B .

Experimentally, the final choice of \mathcal{V} was not arbitrarily chosen but decided by observing the most physically sensible fit to the data and by consideration of literature evidence.



4.4 SPECTRAL CONSIDERATIONS

The probability of electronic energy transfer occurring is favoured when the donor emission spectrum overlaps the acceptor absorption spectrum. It is the purpose of the present section to confirm that the donor/acceptor systems investigated conform to such a requirement and to comment upon the triplet level of ferrocene.

Initially there was doubt whether or not ferrocene exhibited phosphorescence and this concern is reflected in the uncertainty of the value that ought to be ascribed to its lowest triplet level. Ferrocene was first reported to phosphoresce by D.R.Scott and R.S.Becker [212] but the authenticity of the report was later challenged by S.P.McGlynn et al. [213] and subsequent work has not satisfactorily resolved the matter [214]. However, F.Wilkinson et al. [89] categorically stated that ferrocene does not show any emission. Experimental evidence argues against the the triplet level of ferrocene being much above 168 kJ mol^{-1} [215,216,217] and such an estimate finds theoretical corroboration [218]. Hence, such studies establish the lowest triplet level of ferrocene to be considerably lower than the T_1 of both anthrone and benzophenone.

Figure 4.8 shows the phosphorescence emission spectrum of benzophenone superimposed on the absorption spectrum of ferrocene, thus demonstrating spectral overlap. Importantly, there exists a convenient spectral window in the absorption spectrum of ferrocene between 300-370 nm where the molecule has a low extinction coefficient, < 10 , thus allowing selective excitation of the carbonyl donors.

4.5 ENERGY TRANSFER RESULTS

This section is concerned with the presentation of results obtained from energy transfer experiments involving the donor/acceptor systems benzophenone/ferrocene and anthrone/ferrocene. The experiment entailed recording the donor triplet decay as a function of acceptor concentration in different polymer matrices and the results were analysed in terms of equations 4.4 and 4.9.

4.5.1 System : Donor Benzophenone / Acceptor Ferrocene

This donor acceptor system was investigated in three different polymeric host media and the results pertaining to each will be presented separately. However, the following comments and observations relating to experimental data obtained are equally applicable to each matrix and to each case in the anthrone/ferrocene system.

Without exception the experiments were carried out at 77 K, a temperature at which both donor decays are exponential in the absence of acceptor. Such a condition is necessary for the application of equations 4.4 and 4.9 but is not always adhered to [90,221]. It is evident from the figures depicting the mode of donor decay in the presence of acceptor that departures from exponentiality are observed, becoming more apparent as the concentration of the latter increases. Such a feature is noted for each matrix and is entirely consistent with theory. It is also apparent that the decay approaches exponentiality at long time values; a fact in accord with

equations 4.4 and 4.9. The time period over which meaningful data could be recorded was generally equal to two first order life-times; a time scale commonly adopted [89,219]. At longer time periods the emission intensity was exceedingly weak and subject to noise and background error. Consequently, the kinetic parameters quoted in this section were calculated over such a time interval, although the decay curves are shown over a smaller time domain.

In each set of decay curves the effect of at least three different acceptor concentrations is shown but the resulting values of R_0 and C_0 were averaged over five different ferrocene concentrations. Acceptor concentrations in excess of $5 \times 10^{-2} \text{ mol dm}^{-3}$ were not considered, thus minimising the possibility of solute aggregation. For each individual decay curve the analysis yields a value of $B (=C/C_0)$ for a given concentration of acceptor C . In order to obtain an averaged value of R_0 for the system, a plot of B against C was made which is expected to be linear, passing through the origin with gradient equal to $1/C_0$. It was from this value of C_0 that an averaged value of R_0 was acquired. In each case the parameters obtained for the exchange mechanism are relevant for $\nu = 5$.

4.5.1.1 Matrix : Poly(methylmethacrylate)

Donor emission intensity decay data was analysed by both curve fitting routines and Figure 4.9 illustrates the result for the dipole fit; the solid line representing the theoretical fit to the experimental data. The resulting fitted values of B for both mechanisms are shown in Table 4.2 and for the dipole mechanism, plotted against acceptor concentration in Figure 4.10. The average

value of R_0 and C_0 for both mechanisms is shown in Table 4.3.

4.5.1.2 Matrix : Polystyrene

Figure 4.11 shows the effect of increasing ferrocene concentration on the phosphorescence decay of benzophenone, again the solid line represents the dipole fit. The corresponding values of B for both mechanisms are listed in Table 4.4 and for the dipole mechanism, plotted against ferrocene concentration in Figure 4.12. The average value of R_0 and C_0 for both mechanisms is shown in Table 4.5.

4.5.1.3 Matrix : Poly(vinylacetate)

The solid line Figure 4.13 represents the dipole fit to the experimental decay data for this system and the calculated values of B for both mechanisms are displayed in Table 4.6. Figure 4.14 shows the graphic relationship between dipole B values and acceptor concentration. The average value of R_0 and C_0 is shown in Table 4.7.

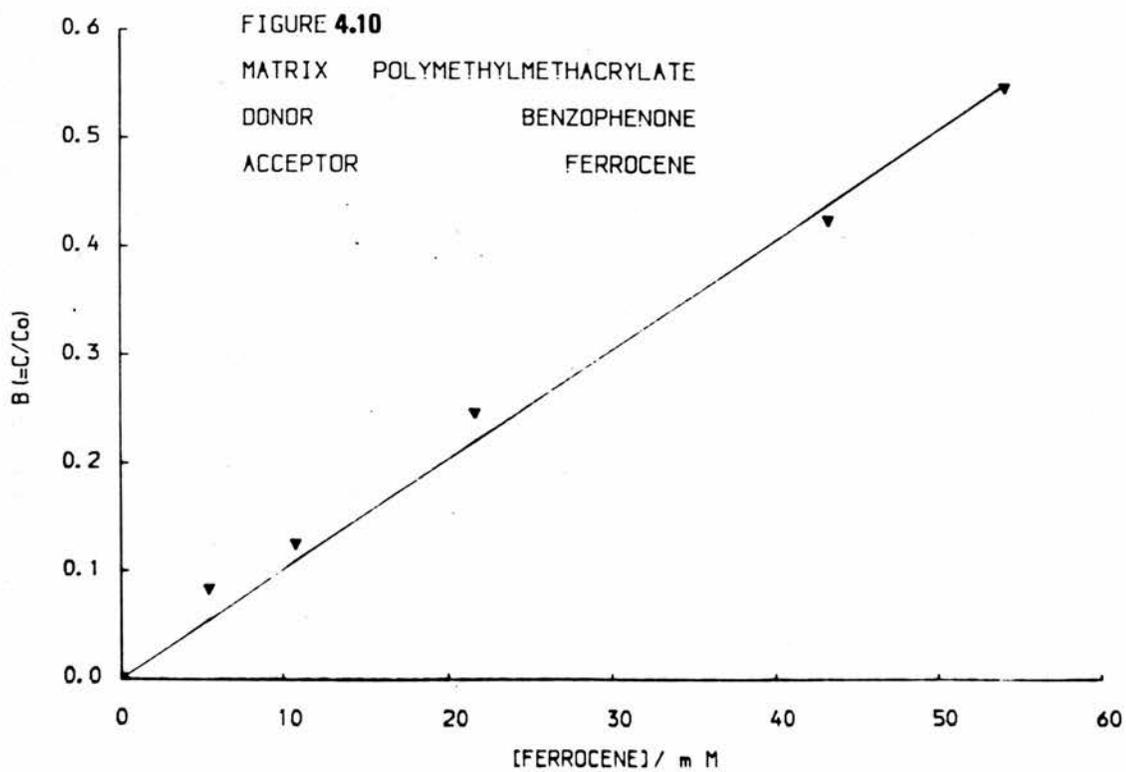
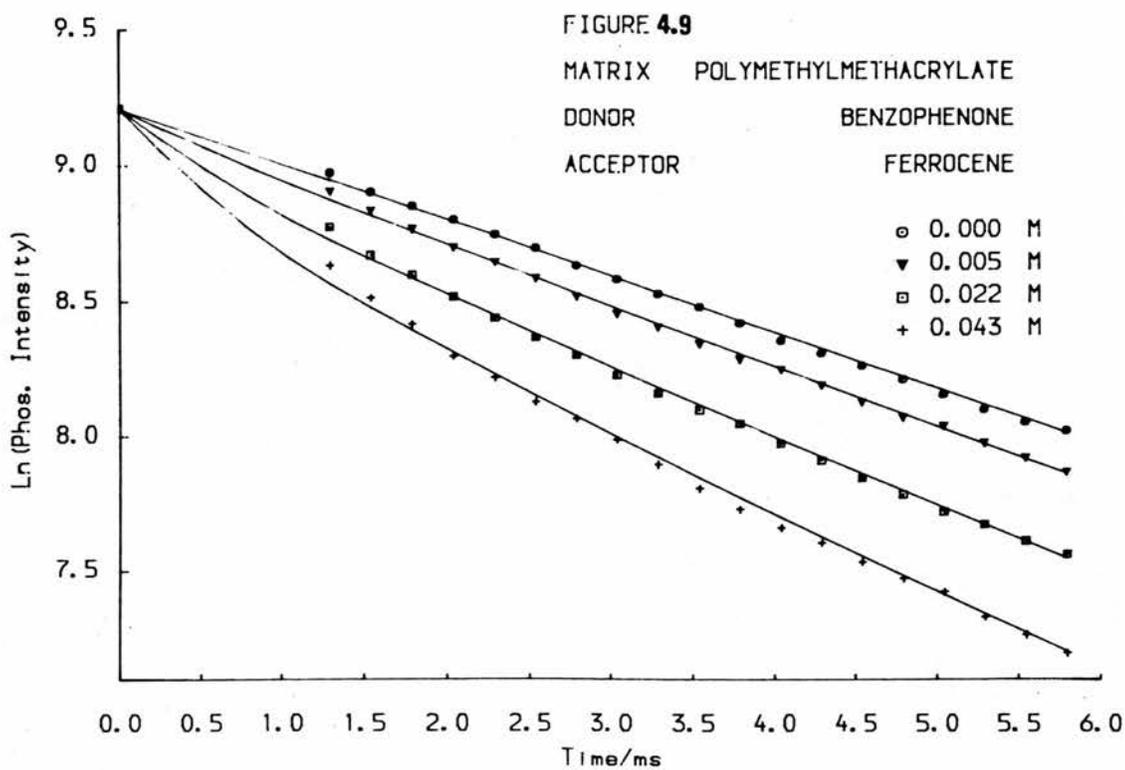


TABLE 4.2

DONOR BENZOPHENONE

MATRIX POLY(METHYLMETHACRYLATE)

[FERROCENE] mol dm ⁻³	DIPOLE MECH. B	EXCHANGE MECH. B
0.0054	0.083	0.092
0.0108	0.124	0.137
0.0217	0.245	0.269
0.0433	0.423	0.465
0.0542	0.545	0.599

TABLE 4.3

DONOR BENZOPHENONE

MATRIX POLY(METHYLMETHACRYLATE)

MECHANISM	R ₀ ± 0.10 nm	C ₀ Mol dm ⁻³
DIPOLE	1.59	0.099
EXCHANGE	1.64	0.090

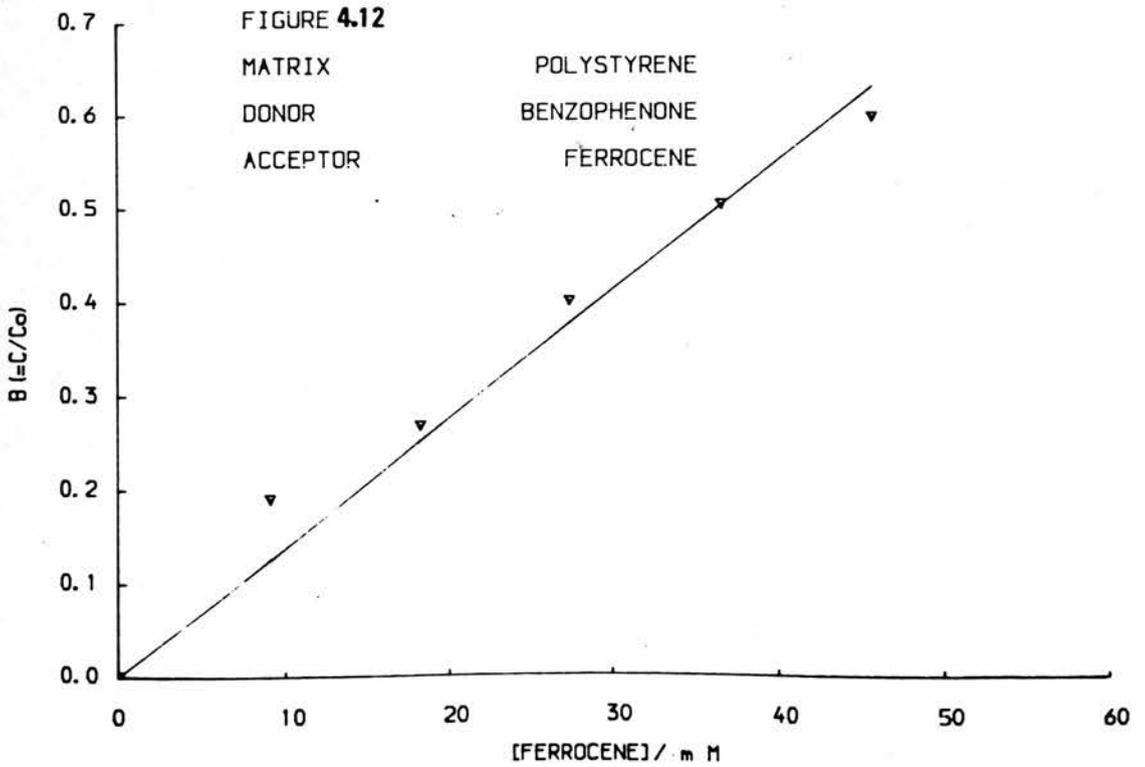
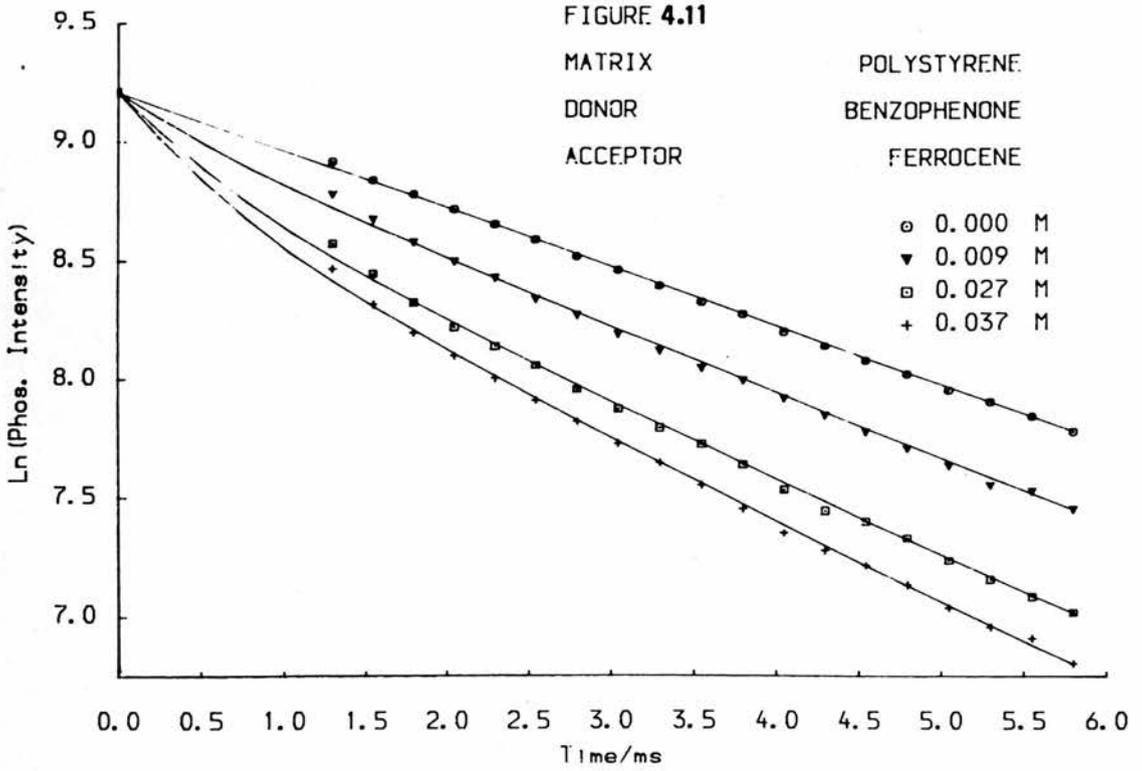


TABLE 4.4

DONOR BENZOPHENONE

MATRIX POLYSTYRENE

[FERROCENE] mol dm ⁻³	DIPOLE MECH. B	EXCHANGE MECH. B
0.0092	0.191	0.215
0.0183	0.269	0.302
0.0275	0.402	0.451
0.0366	0.505	0.565
0.0458	0.600	0.673

TABLE 4.5

DONOR BENZOPHENONE

MATRIX POLYSTYRENE

MECHANISM	R ₀ ± 0.10 nm	C ₀ Mol dm ⁻³
DIPOLE	1.76	0.072
EXCHANGE	1.83	0.065

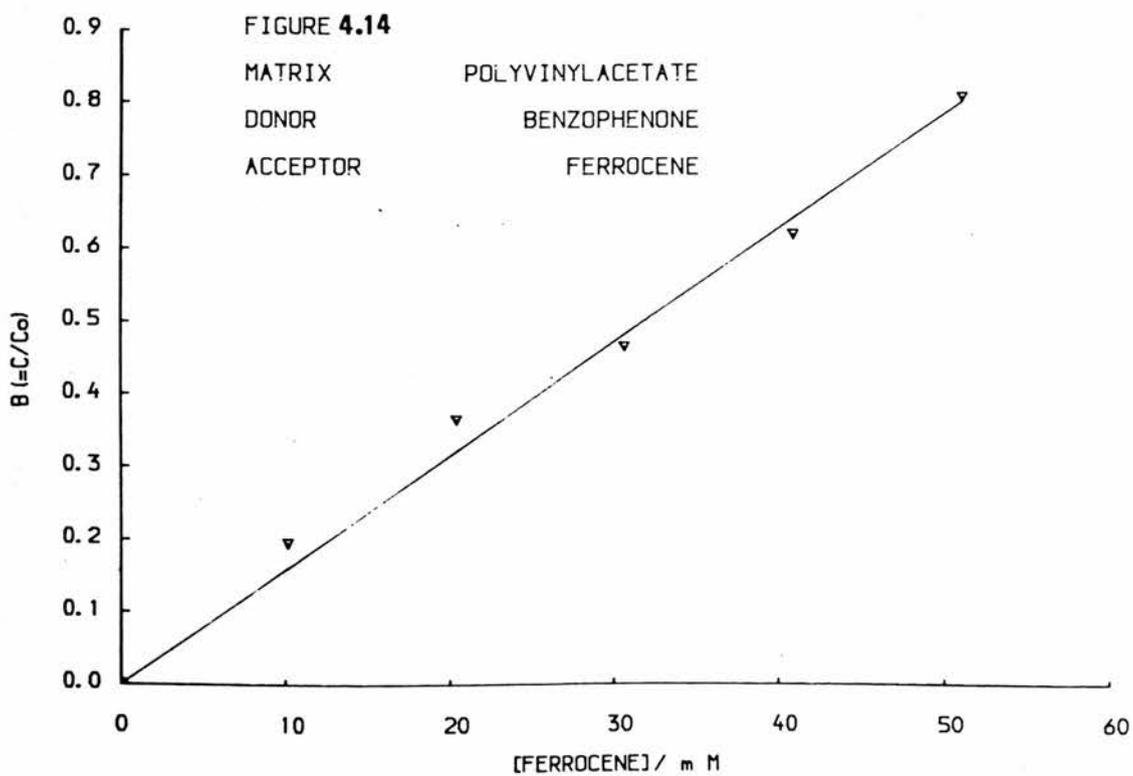
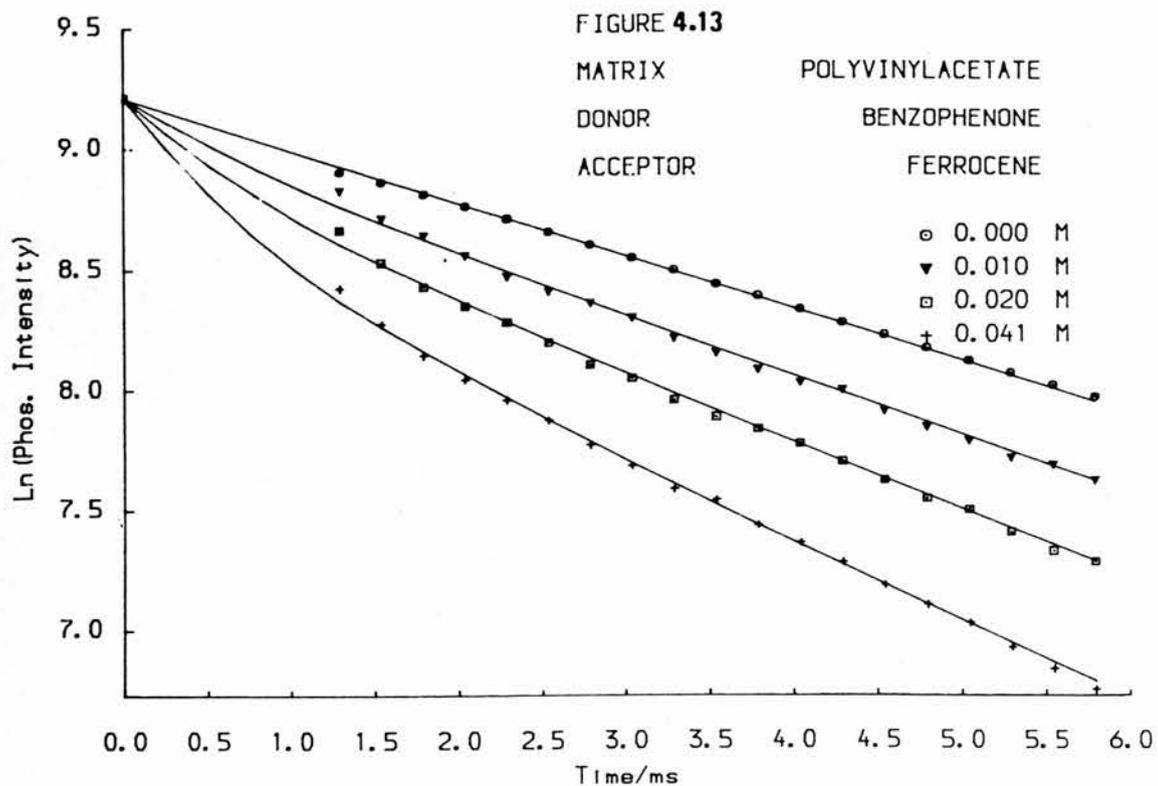


TABLE 4.6

DONOR BENZOPHENONE
MATRIX POLY(VINYLCETATE)

[FERROCENE] mol dm ⁻³	DIPOLE MECH. B	EXCHANGE MECH. B
0.0102	0.194	0.215
0.0205	0.364	0.400
0.0307	0.465	0.512
0.0409	0.620	0.681
0.0512	0.810	0.890

TABLE 4.7

DONOR BENZOPHENONE
MATRIX POLY(VINYLCETATE)

MECHANISM	R ₀ ± 0.10 nm	C ₀ Mol dm ⁻³
DIPOLE	1.79	0.069
EXCHANGE	1.84	0.063

4.5.2 System : Donor Anthrone / Acceptor Ferrocene

This system was investigated in four different polymeric host media, and results will be presented in graphical and tabular form; each individually labelled and numbered. The format is universal to each polymer and consists of intensity decay plots, plots of B against acceptor concentration, tabulated B values and a table displaying the average value of R_0 and C_0 found for each polymer. The donor intensity decay curves shown refer specifically to the dipole mechanism. The R_0 and C_0 values for the donor/acceptor system in poly(n-butylmethacrylate) are shown in Table 4.18.

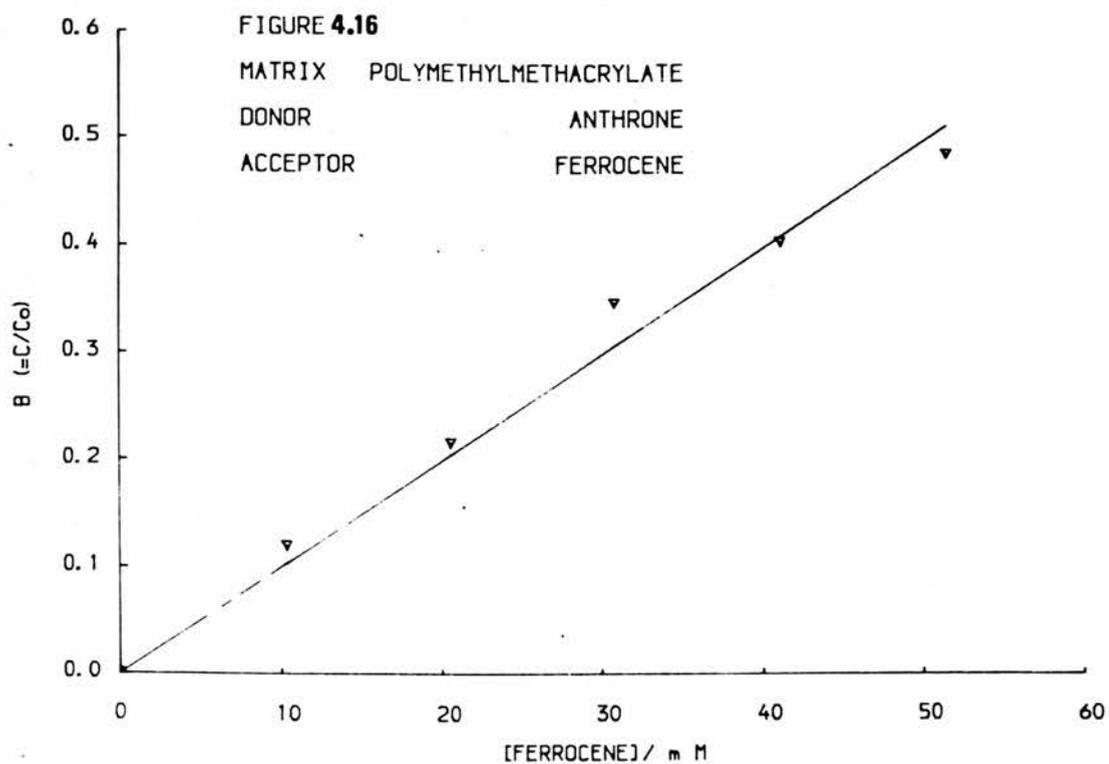
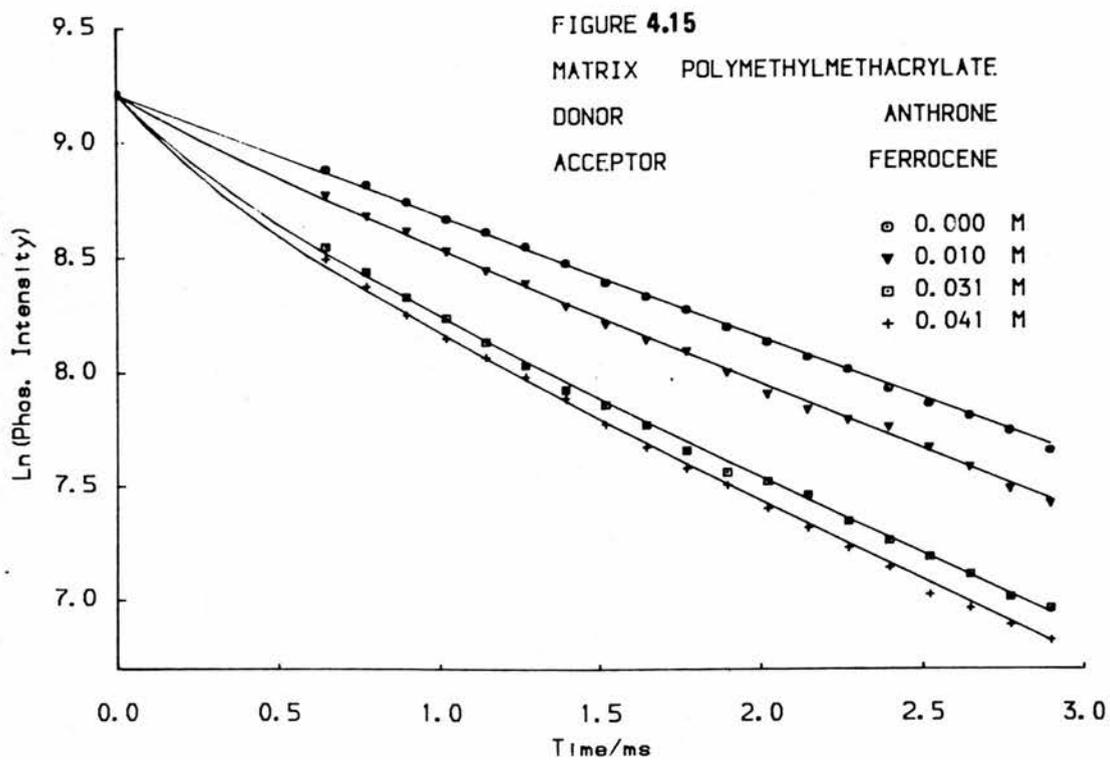


TABLE 4.8

DONOR ANTHRONE

MATRIX POLY(METHYLMETHACRYLATE)

[FERROCENE] mol dm ⁻³	DIPOLE MECH. B	EXCHANGE MECH. B
0.0104	0.119	0.136
0.0206	0.215	0.245
0.0309	0.346	0.393
0.0412	0.403	0.459
0.0515	0.485	0.551

TABLE 4.9

DONOR ANTHRONE

MATRIX POLY(METHYLMETHACRYLATE)

MECHANISM	R ₀ ± 0.10 nm	C ₀ Mol dm ⁻³
DIPOLE	1.58	0.101
EXCHANGE	1.65	0.089

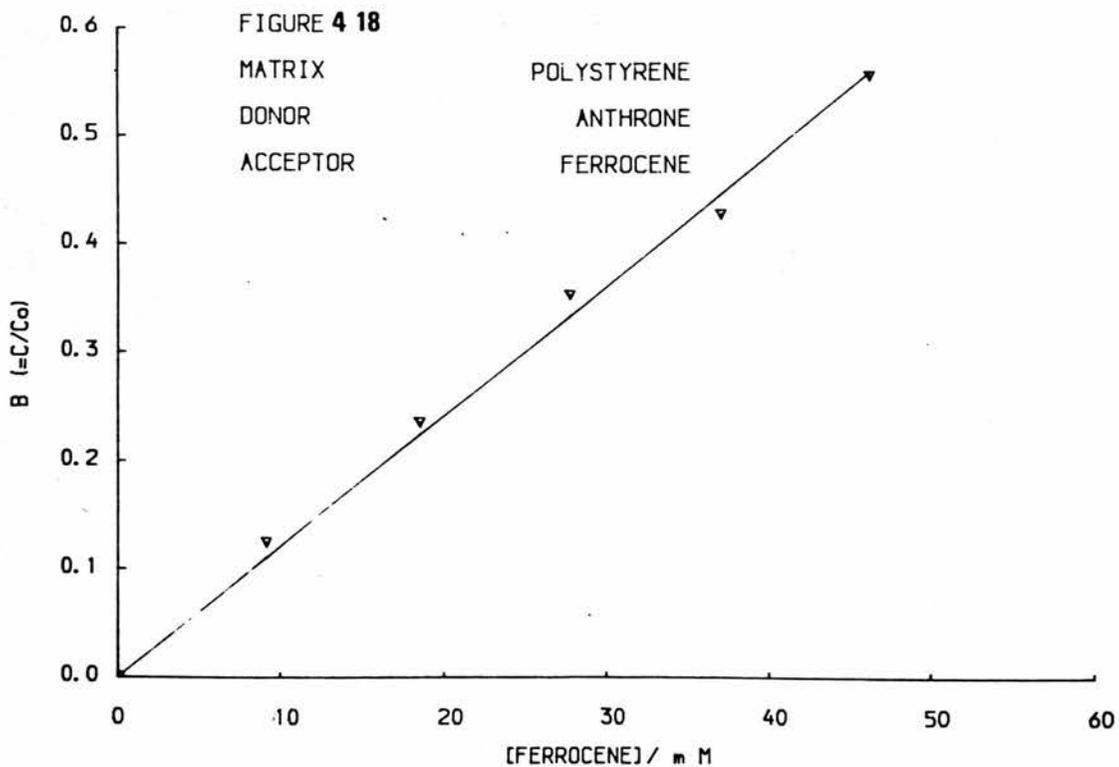
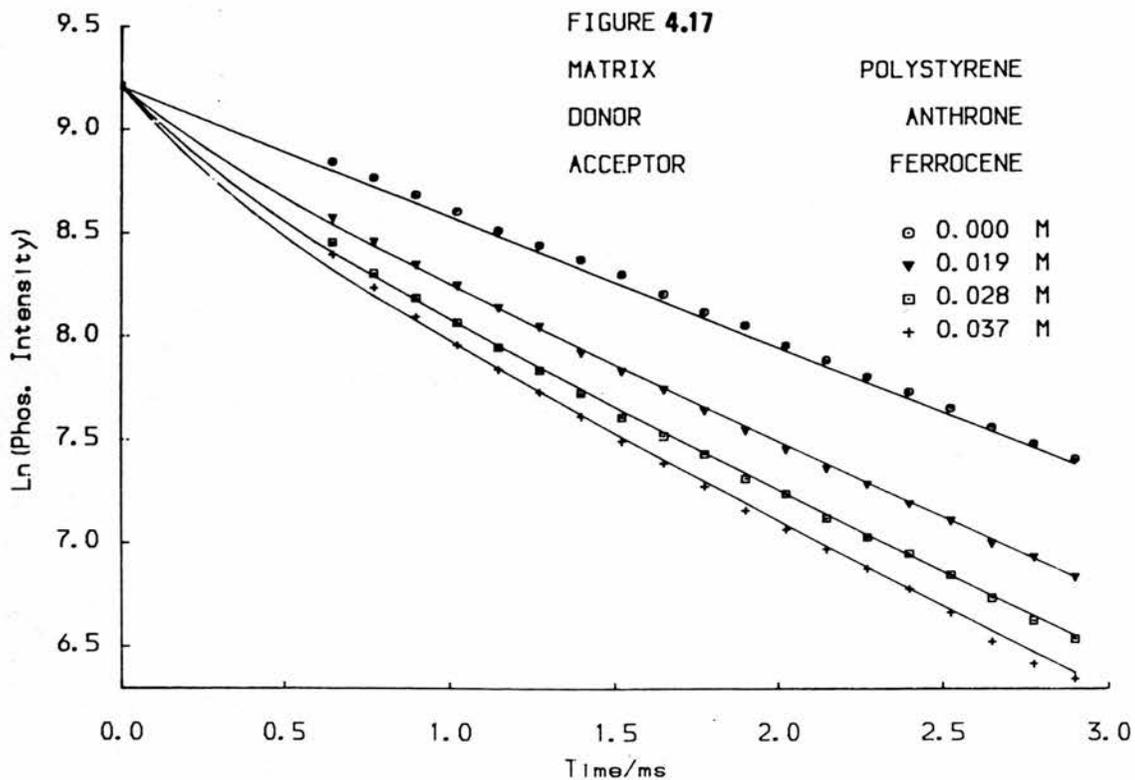


TABLE 4.10

DONOR ANTHRONE

MATRIX POLYSTYRENE

[FERROCENE] mol dm ⁻³	DIPOLE MECH. B	EXCHANGE MECH. B
0.0092	0.125	0.146
0.0186	0.236	0.277
0.0278	0.355	0.416
0.0371	0.429	0.504
0.0464	0.556	0.649

TABLE 4.11

DONOR ANTHRONE

MATRIX POLYSTYRENE

MECHANISM	R ₀ ± 0.10 nm	C ₀ Mol dm ⁻³
DIPOLE	1.69	0.083
EXCHANGE	1.78	0.071

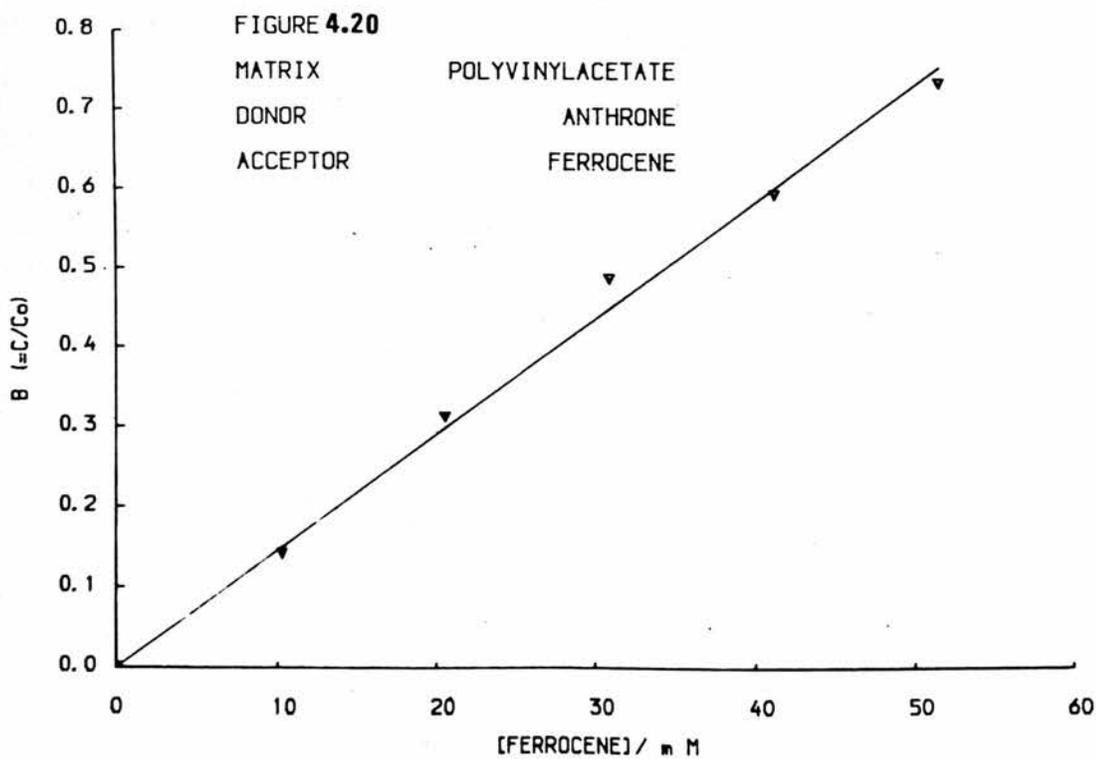
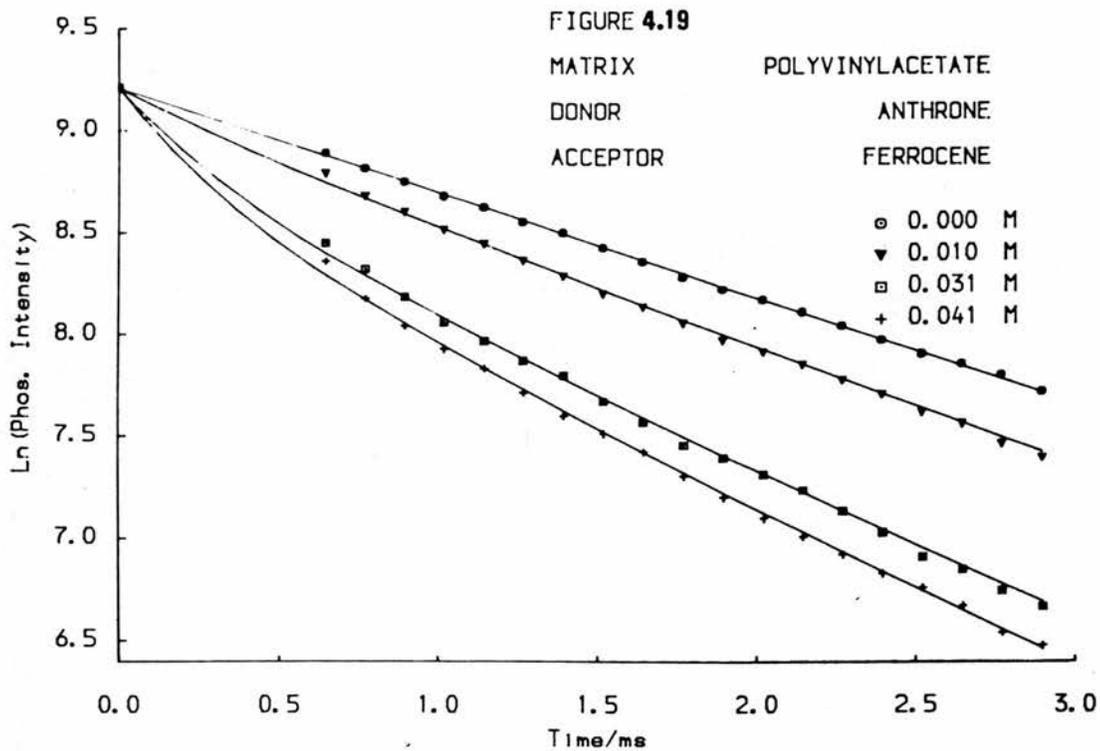


TABLE 4.12

DONOR ANTHRONE

MATRIX POLY(VINYLCETATE)

[FERROCENE] mol dm ⁻³	DIPOLE MECH. B	EXCHANGE MECH. B
0.0103	0.1423	0.1613
0.0207	0.3139	0.3520
0.0310	0.4878	0.5289
0.0414	0.5927	0.6666
0.0517	0.7312	0.8221

TABLE 4.13

DONOR ANTHRONE

MATRIX POLY(VINYLCETATE)

MECHANISM	R ₀ ± 0.10 nm	C ₀ Mol dm ⁻³
DIPOLE	1.77	0.071
EXCHANGE	1.84	0.063

4.6 LITERATURE REVIEW

Electronic energy transfer experiments have been performed in an extensive array of liquid, glass and polymeric host media, resulting in the publication of a considerable volume of kinetic data. Hence, it is the purpose of the present section to collate and review a representative sample of such data in order to compare the magnitude of R_0 obtained in solid glass solution with typical values of R_0 acquired from energy transfer experiments utilizing polymers as solvents. The special case in which the polymer assumes the role of donor will also be considered. This approach will ensure a fair, critical assessment of the results presented in section 4.5

4.6.1 Solid Glass Solvents

Table 4.14 summarizes a selection of data obtained by applying the exchange mechanism to triplet-triplet energy transfer experiments carried out in hydrocarbon/alcohol glasses at 77 K. In the examples where the decay curves are shown [89,222], the extent to which the decay departs from single exponential behaviour was related to the acceptor concentration; a fact consistent with theory and in accord with the current work. The quality of the theoretical fit to experimental data was encouraging, although at the highest donor concentrations the accuracy was slightly diminished. Such is also the case with the decay curves shown in section 4.5.

It is now necessary to comment upon the magnitude of the experimental values of R_0 found for triplet energy transfer processes

in solid glass solution and to consider the range of \mathcal{V} observed for the different donor/acceptor systems. Table 4.14 clearly and consistently demonstrates that R_0 is generally located in the region 1.0-1.5 nm and rarely exceeds 1.5 nm. It is important to note that the data presented in Table 4.14 extend to both n, π^* and π, π^* triplet state donors, so encompassing a wide magnitude of donor phosphorescence life-time. In addition, when both donor and acceptor are organic molecules the value obtained for \mathcal{V} is large, whereas when the acceptor is a transition metal ion the value of \mathcal{V} is relatively small. F. Wilkinson *et al.* [89] have commented upon such an observation, emphasizing that exchange transfer between two organic molecules involves 2p orbitals, the electron density of which falls off rapidly, whilst in the case of transfer to a transition metal a 3d or 4d orbital is involved, which exhibit a more gradual fall off in electron density with increasing distance from the orbital centre. Consequently, this results in comparatively large values of the parameter L, giving rise to small values of \mathcal{V} .

4.6.2 Polymeric Media

Electronic energy transfer experiments involving polymers can be conveniently classified into two types in which the polymer is either employed as a host support matrix or is utilized as a donor.

4.6.2.1 Polymer : Support Matrix

Table 4.15 illustrates a selection of R_0 values obtained for energy transfer experiments using polymers as host matrices and it is evident from a comparison with Table 4.14 that R_0 values found for such experiments in polymers are generally larger. In this context, when the R_0 value derived by experiment exceeds that predicted by theory, it is considered as evidence for the occurrence of energy migration [3]. Indeed, it has been suggested for the exchange mechanism that when R_0 is greater than 1.5 nm energy migration is likely to be operative [226].

There are numerous publications implicating the involvement of polymers in energy transfer processes [87,90,190,217,228,229,230]. J.R.MacCallum [190] emphasizes the likelihood of triplet energy migration occurring in the room temperature photophysical behaviour of certain polycyclic aromatic hydrocarbons suspended in polymers. Furthermore, polymers also appear to influence energy transfer occurring via singlet multiplicity modes, as Ya.A.Terskoi et al [228,229] observed a deviation between experimental transfer efficiencies and those predicted by the Forster equation.

4.6.2.2 Polymer : Donor

Table 4.16 depicts R_0 values derived for energy transfer experiments in which polymer donors were doped with small molecule acceptors, indicating the magnitude to be larger than the upper predicted limit of 1.5 nm for the exchange mechanism. The table can be further qualified by noting that the R_0 values associated with aromatic polymer donors are larger than those obtained for aliphatic polymer donors. This has led to the suggestion that energy migration, preceding the final transfer step to the acceptor, is more prevalent in aromatic polymers [226]. An important contribution to the understanding of energy migration in polymers has been made by C. David et al. [232,233,234,235].

Further supporting evidence has been provided by J.E. Guillet et al. [236] who investigated the possibility of triplet energy migration in poly(phenylvinylketone) and poly(methylisoprenylketone) using the triplet acceptors 1-cis, 3-cis, cyclooctadiene and piperylene, proposing it to be operative in the former but absent in the latter. Extending this type of work to polyketone donors, J.E. Guillet et al. [191,237] have recently produced evidence implicating polymer tacticity in energy transfer. They studied poly(phenylvinylketone) doped with naphthalene, finding R_0 to be 2.25 nm and 2.03 nm for the isotactic and atactic configurations respectively, leading them to conclude that energy transfer is more important in the former matrix.

Evidence of photophysical events occurring as a consequence of triplet energy migration have been documented for a series of polymers [238,239,195]. Delayed fluorescence (P-type) is a direct result of triplet-triplet annihilation, and in solid polymer films

where the translational motion of pendant chromophores is restricted, the observation of P-type delayed fluorescence must imply the involvement of triplet energy migration. Such a rationale was proposed by R.F.Cozzens and R.B.Fox to explain their results in poly(1-vinylnaphthalene) [238] and in other polymers [241]. In an extension of this work [242], these authors studied triplet energy migration and trapping in a range of copolymers using the monomers styrene, methylmethacrylate and 2-vinylnaphthalene. Incorporation of energy traps in these copolymers was used to demonstrate that intra-chain triplet migration in alternating copolymers was also possible. Significantly, sequences of a few methylmethacrylate units were sufficient to impede the transfer efficiency through aromatic groups on the same chain.

TABLE 4.14

DONOR TRIPLET	ACCEPTOR	γ	Ro nm	Ref
Benzophenone	Naphthalene	25	1.37	219
Benzophenone	Naphthalene	18	1.29	205
Benzophenone	1-Bromopaphthalene	19.5	1.30	205
Benzaldehyde	1-Naphthol	17	1.42	220
Carbazole	Naphthalene	28	1.51	221
Acetophenone	Naphthalene-d-8	25	1.24	223
Acetophenone	Indole	32	1.18	222
Naphthalene-d-8	Co^{2+}	4.4	1.24	210
Naphthalene-d-8	Cu^{2+}	12.0	1.78	210
Naphthalene-d-8	Ni^{2+}	7.0	1.10	210
2-Acetylfluorene	Eu^{3+}	5.75	1.04	224
Triphenylene	Tm^{3+}	4.6	1.00	225
Triphenylene	Er^{3+}	7.1	1.09	225

TABLE 4.15

DONOR	ACCEPTOR	MODE	MATRIX	Ro nm	Ref
Acetone	DBN	T-T	PS	2.1	90
Acetophenone	DBN	T-T	PS	1.5	90
Acetone	DBN	T-T	PMMA	1.7	90
Acetophenone	DBN	T-T	PMMA	1.7	90
Cyclohexanone	DBA	T-S	PS	3.5	231
Cyclohexanone	DBA	T-S	PMMA	2.1	231
Triphenylene	Ferrocene	T-T	PMMA	1.59	89
Triphenylene	Ruthenocene	T-T	PMMA	1.54	89

TABLE 4.16

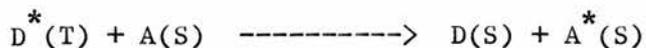
DONOR	ACCEPTOR	MODE	Ro nm	Ref
Poly(vinylbenzophenone)	Naphthalene	T-T	2.9	232
Poly(phenylvinylketone)	Naphthalene	T-T	2.6	233
Poly(methylvinylketone)	Naphthalene	T-T	1.1	234
Poly(styrene/vinyl- benzophenone [77%])	Naphthalene	T-T	3.1	235
Poly(phenylvinylketone)	Naphthalene	T-T	2.25	191
Poly(phenylvinylketone)	Naphthalene	T-T	2.03	191

4.7 DISCUSSION OF RESULTS

It is evident from the results presented in the preceding section that electronic energy transfer is occurring from the aromatic carbonyl donors to the acceptor ferrocene. However, it is the purpose of the present section to investigate the extent to which the polymer solvent becomes involved in the transfer process.

4.7.1 Choice of Mechanism

Consideration of section 4.2.5, reviewing the criteria governing the choice of which mechanism was most applicable to a particular study, led to the decision to analyse the experimental decay data by both the mechanisms outlined. The magnitude of the ferrocene oscillator strength in the region of spectral overlap has prompted the suggestion that the dipole mechanism would be the most dominant for such systems [89]. However, in addition to accessible triplet levels, ferrocene also has allowed singlet transitions in the area of overlap, giving rise to the possibility of the following transfer modes, both of which are more tenable by the exchange mechanism.



Consequently, the decay data was analysed in terms of both mechanisms as the principal aim was to distinguish between the effect of polymer

matrices on the transfer characteristics of a given donor/acceptor pair and not solely to ascribe a particular mechanism to the process. In this respect, F.Wilkinson et al. [89] have commented that both mechanisms may occur simultaneously in some systems.

4.7.2 Comments and Observations

The following comments were made with respect to Tables 4.17 and 4.18 in which the R_0 values obtained for both the systems studied are summarized.

1. The critical transfer distances in polystyrene are larger than those found for the polymethacrylates.
2. There is no significant difference between the R_0 values found for the donors anthrone and benzophenone; a fact consistent with their similar triplet energy levels.
3. For each system the exchange mechanism yields a larger R_0 than the dipole mechanism.
4. Dipole and exchange mechanisms fitted equally well to the decay data, yielding kinetic parameters in the range where legitimate distinction is difficult.
5. The R_0 values for the donor/acceptor systems in poly(vinylacetate), irrespective of mechanism, would appear to be anomalously high.

This latter result was not expected and is inconsistent with the overall trend. In the case of poly(methylmethacrylate) and polystyrene, each possessing a T_g well above room temperature [154], dopant concentrations were not corrected for polymer contraction on cooling to 77 K as the ambient value of the coefficient of thermal expansion predicts negligible volume shrinkage; a consideration endorsed by others [89]. However, for poly(vinylacetate) with its T_g located near room temperature [154], the coefficient of expansion changes more rapidly on cooling to 77 K and if this were appreciable, the concentration of the dopants used to determine C/C_0 would be artificially too low resulting in erroneously high R_0 values.

TABLE 4.17
DONOR BENZOPHENONE

MATRIX	ACCEPTOR FERROCENE			
	DIPOLE		EXCHANGE	
	Ro ± 0.10 nm	Co mol dm ⁻³	Ro ± 0.10 nm	Co mol dm ⁻³
POLY(METHYLMETHACRYLATE)	1.58	0.101	1.65	0.089
POLY(n-BUTYLMETHACRYLATE)	1.59	0.099	1.63	0.090
POLYSTYRENE	1.69	0.083	1.78	0.071
POLY(VINYLACETATE)	1.77	0.071	1.84	0.063

TABLE 4.18
DONOR BENZOPHENONE

MATRIX	ACCEPTOR FERROCENE			
	DIPOLE		EXCHANGE	
	Ro ± 0.10 nm	Co mol dm ⁻³	Ro ± 0.10 nm	Co mol dm ⁻³
POLY(METHYLMETHACRYLATE)	1.59	0.099	1.64	0.090
POLYSTYRENE	1.76	0.072	1.83	0.065
POLY(VINYLACETATE)	1.79	0.069	1.84	0.063

4.7.3 Results : Analysis

The values of R_0 obtained for triplet-triplet energy transfer processes in solid glass solvents have been shown to be < 1.40 nm, whereas similar systems studied in polymers yield larger values; a point highlighted in Tables 4.17 and 4.18. The magnitude of R_0 reflects the extent of quenching and so it would appear that polymer solvents provide additional non-radiative deactivation routes enhancing energy transfer. Furthermore, the size of R_0 is also dependent on the nature of the polymer. Tables 4.15-4.18 demonstrate that R_0 values obtained for systems involving aromatic polymers are generally larger than the corresponding values in aliphatic polymers. A comparison of Figures 4.9 and 4.11 illustrates that for approximately the same acceptor ferrocene concentration, the reduction in donor emission yield is greater in polystyrene than in poly(methylmethacrylate).

F.Wilkinson et al. [89] studied electronic energy transfer from the triplet donor triphenylene to the acceptor ferrocene dispersed in poly(methylmethacrylate). The authors found that application of the dipole equation 4.4 satisfactorily fitted their decay data, giving $R_0 = 1.59$ nm and $C_0 = 0.096$ mol dm⁻³. However, their results did not obey equation 4.7 even though $C/C_0 < 1$. This led the authors to investigate the system in a hydrocarbon glass, resulting in a substantial improvement to the fit, in addition to the results now complying with equation 4.7, giving $R_0 = 1.62$ nm and $C_0 = 0.093$ mol dm⁻³. On the basis of this discrepancy, the authors concluded that although the dipole mechanism is operative, an

additional transfer channel is provided or caused by the polymer solvent.

In a series of papers N.J.Turro et al. [90,242] studied triplet-triplet energy transfer between the donors acetone and acetophenone to the acceptor 1,4 dibromonaphthalene in poly(methylmethacrylate) and polystyrene. The largest R_0 value, 2.1 nm, was obtained in polystyrene for transfer from acetone and this led the authors to invoke triplet energy migration among polystyrene phenyl groups as an explanation, even though the initial transfer step from acetone to the polymer is allegedly endothermic by approximately $12-20 \text{ kJ mol}^{-1}$. Extending this argument to rationalize the lower values of R_0 found for transfer from acetophenone to 1,4 dibromonaphthalene in polystyrene and for both donor/acceptor systems in poly(methylmethacrylate), the authors proposed that the donor-polymer host triplet energy level difference was too endothermic, thereby excluding the possibility of energy transfer to, and subsequent energy migration in, the polymers.

However, the situation is not as simple, as the value quoted by these workers for the triplet level of polystyrene ($338-347 \text{ kJ mol}^{-1}$), essentially taken to be equivalent to the triplet level of toluene, warrants closer examination. The authors correctly point out that the triplet level of poly(methylmethacrylate) should be higher than that of polystyrene, but the problem arises by observing that the currently accepted triplet level of the former polymer is recognised to be approximately 300 kJ mol^{-1} [87], a value commonly quoted by other workers [88,89]. If this latter estimate is correct, the triplet level of polystyrene must be $< 300 \text{ kJ mol}^{-1}$, which is considerably lower than the value quoted by N.J.Turro et. al. [90]. Consequently,

this evidence places the triplet level of both polymers lower than that of the donors acetone and acetophenone. Hence, the objection to energy transfer occurring in the above systems on the basis of excess endothermicity must be reappraised. The R_0 values derived for the donor/acceptor systems in either matrix are still larger than those associated with similar experiments in rigid glass solution, and as such, can still be considered consistent with the proposal of triplet energy migration involving the matrix.

This problem raises a very interesting point, suggesting that the triplet level of the polymer is significantly lower in energy than the isolated chromophore, which is essentially one of the conclusions arrived at in an earlier study by S.P.McGlynn et al. [87]. The proposal is not unprecedented for R.D.Buckhart et al. [244] offered a similar conclusion concerning the triplet level of poly(vinylcarbazole) in relation to the monomer vinylcarbazole. Supporting evidence in the case of polystyrene was produced by C.W.Frank and L.A.Harrah [245] who characterized polymer phosphorescence at 4.2 K, locating the 0,0 transition at $24\ 000\ \text{cm}^{-1}$, corresponding to $287\ \text{kJ mol}^{-1}$, which is appreciably lower than the analogue toluene [246].

The reason explaining this energy mis-match is not immediately obvious, but R.D.Buckhart et al. [244] offered two suggestions. The possibility of the existence of a triplet state in the solid phase arising from collective contributions from numbers of chromophores rather than individual ones would appear reasonable and would resemble the characteristics of an excitonic state. Alternatively, the dielectric environment of the chromophores in the film could be markedly different from that in rigid solutions causing a shift in the

triplet level to lower energies. This problem further illustrates the complexity of interpreting photophysical phenomena in the solid state.

Electronic energy transfer is not necessarily limited to a direct interaction between the donor and the acceptor but may encompass an indirect involvement via the virtual excited states of the solvent. F. Wilkinson et al. [89] explored this approach in terms of a model for exciton transfer discussed previously by H. Sternlicht et al. [160], an important feature of which is the magnitude of ΔE_{D-H} , that is, the energy gap between the donor and host excited states. The dependence upon such an energy gap is relevant to the present study, which has shown the observed behaviour of donor/acceptor systems to be related to the triplet energy difference between a given donor and polymer host. The excitation transfer could be enhanced by both the donor and acceptor coupling with the virtual electronic levels of the polymer.

4.8 CONCLUSIONS

This chapter has provided experimental evidence demonstrating triplet energy transfer from two different ketone donors to the acceptor ferrocene. The extent of quenching, under controlled conditions, has been shown to be dependent on the polymer host and to be more pronounced in polystyrene. Furthermore, the application of two energy transfer mechanisms differentiated between the effects of aromatic and aliphatic polymers.

Within the context of the analysis, this difference was attributed to the lower lying triplet level of polystyrene, allowing an additional weak energy transfer channel to the polymer. The correlation between the experimental observations and the energy gap between the excited states of donor and host, led to the tentative suggestion that transfer could be enhanced by an indirect electronic coupling between the donor/acceptor system and the virtual state of the polymer. In view of the present work and the literature evidence quoted, polymers are likely to interfere with energy transfer events when used as host matrices.

General Overview

GENERAL OVERVIEW

The initial aim of the current research project was to establish the suitability of certain polymers as inert hosts for use in photophysical studies by investigating the phosphorescence behaviour of specific types of guest molecules and in particular, those associated with polymer photodegradation and photostabilization, thereby introducing practical overtones. The problem was considered in terms of guest phosphorescence as a function of polymer environment and temperature and by performing donor/acceptor energy transfer experiments. This short section will review the salient features highlighted by such studies.

The choice of solvent, whether liquid or solid, for use in luminescence studies must comply with a number of desired specifications such as optical transparency, the lack of any obvious source of electronic perturbation and must, in general, be considered photophysically inert. On first inspection the polymers investigated would appear to conform with such criteria, however, during the course of the present study the importance of additional factors became apparent.

The phosphorescence life-time of the donors at 77 K was shown to be matrix dependent and illustrated the difference between aliphatic and aromatic polymer hosts. Furthermore, the mode of donor phosphorescence decay was also demonstrated to be both temperature and matrix dependent. The common link between these observations was the triplet energy level difference between guest (donor) and host (acceptor). To rationalize these results a non-radiative energy transfer mechanism was postulated to be operative between the donor

and the polymer, the latter assuming the role of acceptor. The efficiency of the transfer mechanism could be enhanced by temperature and lower lying polymer triplet energy levels. This latter point is in accord with the shorter phosphorescence life-time and reduced quantum yields observed in polystyrene, serving to distinguish between the effects of aliphatic and aromatic polymers and discriminating against the use of polystyrene as a support matrix for luminescence studies.

The onset of donor non-exponential decay was attributed to a triplet-triplet annihilation process occurring as a consequence of triplet energy transfer between the additive and polymer. Donor non-exponentiality, within the temperature range considered, was not observed for those molecules possessing low lying triplet energy levels relative to the host triplet level: a donor/acceptor combination for which triplet energy transfer would be improbable. This led to the conclusion that the efficiency of triplet energy transfer and the likelihood of subsequent photophysical events was associated with the magnitude of the triplet energy level difference ΔE_{D-A} and that polymer host interference with guest phosphorescence was only possible when the value fell within a certain range. An upper limit of 35 kJ mol^{-1} has been suggested from work carried out in doped crystal phosphorescence studies.

In recent years the temperature dependence of phosphorescence has been used to measure and characterize polymer main chain and pendant group relaxations. These temperature induced motions are considered to enhance probe triplet state non-radiative deactivation. Arrhenius plots of the rate constants representing probe phosphorescence decay exhibited irregular behaviour, allowing the definition of two separate

linear regions the intersect of which yielded a transition temperature. In some cases such transition temperatures correlated with specific polymer relaxations. However, the merits of this technique are not free from criticism and in this respect, the present work uncovered certain anomalies on applying this approach as the principal explanation for the temperature dependence of phosphorescence.

Hence, when choosing a polymer as a host medium for a photophysical study at the triplet level, in addition to satisfying the conditions outlined previously, it is necessary to select the molecule/polymer pair such that the combination produces a prohibitively endothermic triplet energy level difference. If the study involves varying the temperature it is also necessary to ensure that the triplet life-time of the molecule used does not overlap with the frequency of reported polymer relaxations.

In an attempt to further differentiate between the influence of aliphatic and aromatic polymers as host media, donor/acceptor energy transfer experiments were carried out at 77 K using ferrocene as an acceptor. The quenched phosphorescence intensity decay data was analysed by two different mechanisms both of which implicated the polymer in the energy transfer process and in particular polystyrene. This was attributed to the lower lying triplet level of the latter. These experiments clearly demonstrated the efficiency with which ferrocene quenched aromatic ketone phosphorescence; molecules known to be involved in polymer photodegradation. Polymer stabilizers can function by a variety of methods, such as, by preferentially absorbing destructive radiation and harmlessly dissipating it non-radiatively. Indeed, ferrocene has been studied in such a role [17] and to explain

its superior efficiency, the authors proposed that ferrocene was also involved in polymer stabilising energy transfer mechanisms. Additional work combining photophysical and photochemical techniques to investigate ferrocene and its derivatives in the role of polymer stabilizers would appear to be an attractive prospect.

In conclusion, it is the contention of this thesis that under certain circumstances energy transfer processes at the triplet level can occur between randomly dispersed donors and polymer support matrices.

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Appendix I

LASER7.FOR

```
C      PROGRAM LASER 7
C *****
      INTEGER SAMPLE(4097), TOTAL(1000)
      DIMENSION TIME(950), FTOTAL(950), YCALC(950)
      INTEGER TITLE1(10), TITLE2(5), TITLE3(5), TITLE4(10)
      INTEGER DPER
      BYTE PRIME, ARM, TRIGER, XFER, TOTSAM, OPTION, ERROR
C *****
      MM=1
      WRITE(3,10)
10     FORMAT('0 TO EXECUTE COMMAND, TYPE IN OPTION NO. WHEN PROMPTED')
199    CONTINUE
      WRITE(3,20)
20     FORMAT('0 OPTIONS TABLE')
      WRITE(3,30)
30     FORMAT('0 1. ENTER SWEEP TIME')
      WRITE(3,40)
40     FORMAT('0 2. INPUT EXPERIMENTAL DETAILS')
      WRITE(3,41)
41     FORMAT('0 3. TO OBTAIN BACKGROUND DATA')
      WRITE(3,50)
50     FORMAT('0 4. TO OBTAIN DECAY DATA')
      WRITE(3,51)
51     FORMAT('0 5. TO CORRECT DATA & CORRELATE ARRAYS')
      WRITE(3,60)
60     FORMAT('0 6. TO CALCULATE LEAST-SQUARES LIFE-TIME')
      WRITE(3,70)
70     FORMAT('0 7. TO PRINT OUT RESULTS')
      WRITE(3,80)
80     FORMAT('0 8. TO END EXPERIMENT')
      WRITE(3,90)
90     FORMAT('0 SELECT OPTION NOW')
      READ(3,100) JOPT
100    FORMAT(I4)
      GOTO(11,22,33,44,55,66,77,88), JOPT
11     CONTINUE
C      OPTION NUMBER    1 .....
      WRITE(3,110)
110    FORMAT('0 TYPE IN SWEEP TIME IN SECS/')
      READ(3,120) SWEEP
120    FORMAT(F10.6)
      WRITE(3,121)
121    FORMAT('0 INPUT % DELAY NOW/')
      READ(3,122) DPER
122    FORMAT(I4)
```

```

C          TO CALCULATE TIME ARRAY
C *****
      WRITE(3,140)
140     FORMAT('0 CALCULATING TIME ARRAY')
      TSTEP=SWEEP/4096.00
      IF(DPER.EQ.0) GOTO 123
      FDPER=FLOAT(DPER)
      NS=DPER*41
C NS = THE NUMBER OF CHANNELS IGNORED
      FNS=FLOAT(NS)
      TIME(1)=FNS*TSTEP
124     DO 150 I=2,950
      K=I-1
      TIME(I)=TIME(K)+(TSTEP*4.0)
150     CONTINUE
      GOTO 199
      22     CONTINUE
C          OPTION NUMBER      2 .....
      WRITE(3,160)
160     FORMAT('0 SAMPLE DETAILS')
      READ(3,170) TITLE1
170     FORMAT(10A4)
      WRITE(3,180)
180     FORMAT('0 TEMPERATURE')
      READ(3,170) TITLE2
      WRITE(3,190)
190     FORMAT('0 EMISSION WAVELENGTH')
      READ(3,170) TITLE3
      WRITE(3,200)
200     FORMAT('0 MISCELLANEOUS DETAILS')
      READ(3,170) TITLE 4
      GOTO 199
      33     CONTINUE
      44     CONTINUE
C          OPTION NUMBERS      3 & 4 .....
      WRITE(3,208)
208     FORMAT('0 TYPE IN NUMBER OF AVERAGES')
      READ(3,100) TOTSAM
      SAMPLE(4097)=5
      PRIME=1
      ARM=2
      TRIGER=3
      XFER=4
      WRIRE(3,210)
210     FORMAT('0 VARIABLES SET/ INITIALISING DRIVER ROUTINES')
      WRITE(3,220)
220     FORMAT('0 PRIMING RECORDER')
C *****
      CALL T6502
      OPTION=PRIME

```

```

ERROR=PRIME
CALL TRANRC(OPTION,SAMPLE(1))
IF(OPTION.NE.0) GOTO 700
WRITE(3,230)
230  FORMAT(`0 INITIALISING ARRAYS/`)
      DO 240 I=1,4096
      SAMPLE(I)=0
240  CONTINUE
      DO 250 I=1,1000
      TOTAL(I)=0
250  CONTINUE
      DO 260 I=1,TOTSAM
      OPTION=ARM
      ERROR=ARM
      CALL TRANRC(OPTION,SAMPLE(1))
      IF(OPTION.NE.0) GOTO 700
      OPTION=TRIGER
      ERROR=TRIGER
      CALL TRANRC(OPTION,SAMPLE(1))
      IF(OPTION.NE.0) GOTO 700
      WRITE(3,270)
270  FORMAT(`0`)
271  WRITE(3,272) I,OPTION
272  FORMAT`+`,2I3)
      OPTION=XFER
      ERROR=XFER
      CALL TRANRC(OPTION,SAMPLE(1))
      IF(OPTION.EQ.32) GOTO 271
      IF(OPTION.NE.0) GOTO 700
      DO 290 K=NS,4000,4
      SAMPLE(MM)=SAMPLE(K)
      TOTAL(MM)=TOTAL(MM)+SAMPLE(MM)
      MM=MM+1
290  CONTINUE
      MM=1
260  CONTINUE
      NB=0
      IF(JOPT.EQ.4) GOTO 292
      DO 291 I=1,950
      NB=NB+(TOTAL(I)/TOTSAM)
291  CONTINUE
      MB=NB/950
      WRITE(3,293) MB
293  FORMAT(`0 BACKGROUND CURRENTLY READING`,I6)
      WRITE(3,298) TOTAL(500)
298  FORMAT(`0 BACKGROUND CHECK = `,I6)
      IF(MB.LE.10) GOTO 199
      WRITE(3,294)
294  FORMAT(`0 ADJUST OFFSET SLIGHTLY & READ IN BACKGROUND AGAIN`)
292  CONTINUE

```

```

GOTO 199
55 CONTINUE
C OPTION NUMBER 5 .....
XF=FLOAT(TOTSAM)
FMB=FLOAT(MB)
WRITE(3,262)
262 FORMAT('0 BACKGROUND CORRECTION IN PROGRESS')
DO 300 J=1,950
FTOTAL(J)=((FLOAT(TOTAL(J)))/XF)-FMB
300 CONTINUE
WRITE(3,301)
301 FORMAT('0 ARRAY CORRELATION ? YES=1, NO=0')
READ(3,404) KANS
IF(KANS.EQ.1) GOTO 302
XCOR=1.0
WRITE(3,305)
305 FORMAT('0 PROCESSING ARRAYS')
GOTO 303
302 XCOR=10000.00/FTOTAL(1)
WRITE(3,304)
304 FORMAT('0 ARRAY CORRELATION IN PROGRESS')
303 CONTINUE
DO 310 J=1,950
FTOTAL(J)=ALOG(FTOTAL(J)*XCOR)
310 CONTINUE
GOTO 199
66 CONTINUE
C OPTION NUMBER 6 .....
WRITE(3,320)
320 FORMAT('0 CALCULATION OVER CHANNELS 1 TO MN, LIMITS 1 TO 950')
WRITE(3,330)
330 FORMAT('0 TYPE IN THE VALUE OF MN')
READ(3,100) MN
WRITE(3,331)
331 FORMAT('0 ENTER VALUE CALCULATION INCREMENT')
READ(3,100) KM
WRITE(3,332) KM
332 FORMAT(1H , 'CHOSEN INCREMENT = ',I6)
WRITE(3,340)
340 FORMAT('0 CALCULATION IN PROGRESS')
FS=FLOAT(MN/KM)
C TO CALCULATE GRADIENT
C *****
SUMX=0.0
SUMY=0.0
SUMXY=0.0
SUMX2=0.0
SUMY2=0.0
DO 350 I=1,MN,KM
SUMX=SUMX+TIME(I)

```

```

SUMY=SUMY+FTOTAL(I)
SUMXY=SUMXY+TIME(I)+FTOTAL(I)
SUMX2=SUMX2+TIME(I)**2
SUMY2=SUMY2+FTOTAL(I)**2
350 CONTINUE
A=SUMX*SUMY-(FS*SUMXY)
B=SUMX**2-(FS*SUMX2)
GRAD=-(A/B)
DIME=-(B/A)
C=(SUMX*SUMXY)-(SUMY*SUMX2)
G=SUMX**2-(FS*SUMX2)
CINT=C/G
C TO CALCULATE BEST STRAIGHT LINE
C *****
DO 360 I=1,MN,KM
YCALC(I)=CINT-GRAD*TIME(I)
360 CONTINUE
C TO CALCULATE CORRELATION COEFFICIENT
C *****
R1=(SUMXY-((SUMX*SUMY)/FS))**2
R2=SUMX2-((SUMX**2)/FS)
R3=SUMY2-((SUMY**2)/FS)
CORCO=R1/(R2*R3)
WRITE(3,370) DIME
370 FORMAT('OLIFE-TIME OF TRANSIENT = ',F12.6,' s')
WRITE(3,380) CORCO
380 FORMAT('O CORRELATION COEFFICIENT EQUALS ',F8.4)
GOTO 199
77 CONTINUE
C OPTION NUMBER 7 .....
WRITE(3,390) TITLE1
WRITE(2,390) TITLE1
390 FORMAT(1H ,10A4)
WRITE(2,270)
WRITE(3,390) TITLE2
WRITE(2,390) TITLE2
WRITE(2,270)
WRITE(3,390) TITLE3
WRITE(3,398) TITLE3
WRITE(2,270)
WRITE(3,390) TITLE4
WRITE(2,390) TITLE4
WRITE(2,270)
WRITE(2,370) DIME
WRITE(3,270)
WRITE(2,280) CORCO
WRITE(2,277) SWEEP
277 FORMAT('O DECAY RECORDED OVER SWEEP TIME',1X,F12.8,1X,'S')
WRITE(2,281) DPER
281 FORMAT('O % DELAY SET AT ',I4)

```

```

WRITE(2,400) TOTSAM
400  FORMAT('0 LIFE-TIME CALCULATED AFTER ',I6,' AVERAGES')
      WRITE(2,401) MN
401  FORMAT('0 LIFE-TIME CALCULATED OVER CHANNELS 1 --',I6)
      WRITE(2,270)
      WRITE(3,402)
402  FORMAT('0 DO YOU WISH INTENSITY DATA PRINTED ?')
      WRITE(3,403)
403  FORMAT('0 YES=1 OR NO=0/')
      READ(3,404) MANS
404  FORMAT(I1)
      IF(MANS.EQ.0) GOTO 199
      CONTINUE
      WRITE(3,410)
410  FORMAT('0 TYPE IN INCREMENT OF DATA POINTS TO BE PRINTED')
      READ(3,100) JN
      WRITE(3,420)
420  FORMAT(1H ,5X,'TIME(I)',8X,'EXP.INT',5X,'CALC.INT')
      WRITE(3,430)
430  FORMAT(1H0,44(1H-))
      WRITE(3,440)
440  FORMAT(45H !      TIME      !      EXP.INT      !      CALC.INT      !)
      WRITE(2,430)
      DO 450 I=1,MN,JN
      WRITE(3,460) TIME(I),FTOTAL(I),YCALC(I)
460  FORMAT(1H ,2X,F10.7,5X,F10.6,3X,F10.6)
      WRITE(2,470) TIME(I),FTOTAL(I),YCALC(I)
470  FORMAT(1X,'!',1X,F10.7,2X,'!',2X,F10.6,2X,'!',2X,F10.6,1X,'!')
450  CONTINUE
      WRITE(2,480)
480  FORMAT(1H ,44(1H-))
      WRITE(2,270)
      GOTO 199
700  CONTINUE
C    ERROR ROUTINE .....
      WRITE(3,500) OPTION,ERROR
500  FORMAT('0 ERROR CODE =',I3,' OPTION NO. =',I3)
      GOTO 199
      88  CONTINUE
C    OPTION NUMBER      8 .....
      WRITE(3,510)
510  FORMAT('0 EXPERIMENT WILL NOW END')
      END

```