

## Characterization of solid polymers by luminescence techniques

Graeme A. George

Department of Chemistry, Queensland Institute of Technology, Brisbane,  
4000, Australia.

**Abstract** - The characteristic features of luminescence from solid polymers are compared with the emission from the isolated 'monomer'. The dominance of excimer emission in the solid enables this to be used for the characterization of polymer blends, relaxation processes and transport properties. These may also be studied by electronic energy transfer and the incorporation of a luminescent probe enables the characterization of non-luminescent polymers. While fluorescence and phosphorescence are of limited application for the identification of polymers and additives, they are of particular value in studying degradation and stabilization. Chemiluminescence observed during polymer oxidation can be used to study molecular relaxations, oxidation rates and the process of deformation and failure.

### INTRODUCTION

The study of the luminescence properties of small organic molecules has provided a vast amount of information about the symmetry of the molecule and its electronic excited states, the way that it may dissipate electronic excitation energy and the way it interacts with other molecules in its environment. This is achieved through studies of the intensity and lifetime of the luminescence as well as excitation and emission spectra and polarization properties (ref. 1).

Such detailed molecular information also forms the basis for the characterization of organic polymers. For many years the luminescence properties of polymers have been measured and compared to those of the small molecule analogue - the polymer repeat unit. The extreme sensitivity of luminescence has led to much valuable information about the role of trace impurities, the processes of interchain and intrachain interactions and the temperature dependence of polymer properties (ref. 2,3).

New developments in luminescence spectroscopy such as the use of picosecond lasers to study lifetimes have been immediately applied to polymers (ref. 4). While many of the present active areas of research involve the use of time-resolved fluorescence to study polymer conformation and dynamics in solution, there are many exciting applications of luminescence in studying the solid state properties of polymers.

These include:

- . Identification of polymers, additives and impurities
- . Phase separation and polymer miscibility
- . Glass Transition Temperature and other relaxations
- . Transport properties including permeability
- . Polymer degradation
- . Polymer deformation and failure.

In this review we will be interested in the use of luminescence to provide information about these particular solid state properties.

### THE POLYMER LUMINESCENCE EXPERIMENT

In the broadest sense, polymer luminescence is the light emitted by a polymer after it has been excited in some way. This light is characterized as either fluorescence or phosphorescence depending on the emitting state being either a Singlet or a Triplet state. Because of the high efficiency of energy transfer in the solid state, the emitting species is very often not the chromophore that was originally excited. It may be the repeat unit of the polymer, an impurity or oxidation product on the polymer chain, or a foreign molecule

trapped in the matrix.

The excitation process may involve the absorption of high energy radiation, UV-visible radiation or even the excess energy of a chemical reaction (chemiluminescence). In a particular case, light emission is not measured until the polymer is heated to temperatures higher than that at which it was irradiated (thermoluminescence).

The apparatus necessary to obtain luminescence data in all cases requires a very sensitive and rapid method for measuring light intensity, but otherwise depends on the mode of excitation and information required (ref. 3,5). The main types of information obtained are:

- . the dependence of emission intensity on exciting light wavelength (excitation spectrum)
- . the intensity of emitted light as a function of emission wavelength (fluorescence or phosphorescence spectrum)
- . the polarization properties of the excitation and emission spectra
- . the decay of luminescence intensity after excitation ceases - ranging from nanoseconds for Singlet states (fluorescence) to several seconds for Triplet states (phosphorescence) or several minutes for chemiluminescence decay
- . the increase in luminescence intensity as a function of temperature and time; ranging from minutes to hours depending on the rate of reaction (chemiluminescence and thermoluminescence).

In Fig. 1 are shown typical emission spectra from a 'pure' vinyl aromatic polymer in the solid state. The fluorescence from the polymer is dominated by excimer emission. This broad, structureless emission occurs at lower energy than the structured molecular emission spectrum of the repeat unit or 'monomer' which may be weak or even absent in the solid.

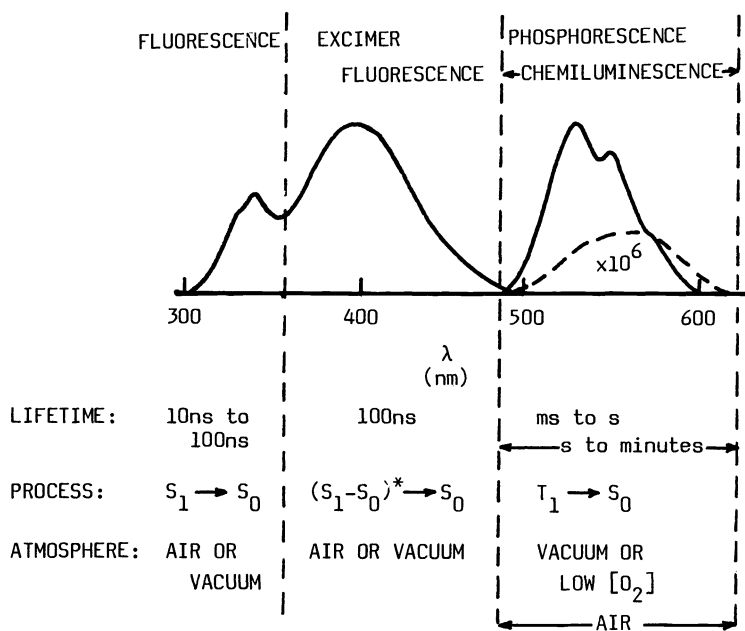


Fig. 1. Typical luminescence spectra from a solid vinyl aromatic polymer following UV excitation. The lifetime, spectral process and atmosphere for the observation of each are indicated.

Excimer fluorescence in both solution and the solid state has been intensely investigated (ref. 6) and arises from the interaction of an excited chromophore (e.g. the phenyl group in polystyrene) with an adjacent unexcited chromophore to form a transient excited dimer. As the dimer does not exist in the ground state, the emission is structureless. Since excimer formation requires the electronic excitation energy to be trapped at a rate faster than the rate of monomer emission, longer lived states are more prone to excimer formation. The geometrical requirements for excimer formation are a planar sandwich with a separation of

$\sim 3\text{\AA}$ . In the solid state either the abundance of available excimer forming sites or the rapid energy transfer results in this dominating the fluorescence spectrum. The fraction of excimer forming sites in polystyrene has been reported to be about 40% (ref. 6).

The phosphorescence spectrum may show triplet excimer emission as well as monomer phosphorescence. However, the solid state spectrum is often found to be dominated by impurity emission. For example, in polystyrene the phosphorescence arises from phenyl alkyl ketone end groups formed by trace oxidation during polymerization and processing (ref. 7). This results from the efficient energy transfer in the long-lived triplet manifold in the solid state. A further consequence of this is that paramagnetic quenching molecules such as oxygen must be removed if strong phosphorescence is to be observed. Thus quenching impurities may be either on the polymer backbone or merely dissolved in the solid.

Also shown in Fig. 1 is a very weak emission (here amplified by  $\sim 10^6$ ) that is observed to last for very long times in the presence of oxygen at elevated temperatures. This is generally found to be spectrally equivalent to the phosphorescence from a ketone oxidation product. Kinetic and energetic analysis of this emission suggests it arises from the bimolecular termination of alkyl peroxy macroradicals formed during the trace oxidation of the polymer, initiated in this case by the UV radiation used to stimulate photoluminescence (ref. 8). The long lifetime results from the slow decay of the alkyl peroxy radicals in the solid polymer after UV irradiation ceases. Because of the low quantum yield of chemiluminescence ( $\phi \sim 10^{-9}$ ) compared to phosphorescence ( $\phi \sim 10^{-1}$  to  $10^{-3}$ ) it is normally not observed in routine spectral measurements. Recent developments in stable photon counting techniques for measuring low light levels have enabled this emission to be studied (ref. 8,9).

#### APPLICATIONS OF POLYMER LUMINESCENCE

The following applications of luminescence studies of solid polymers exploit a particular photophysical phenomenon e.g. excimer formation, energy transfer, quenching to characterize the material. The wide range of excited state lifetimes allows kinetic process to be studied with rate constants from  $10^8 \text{ s}^{-1}$  to  $10^{-2} \text{ s}^{-1}$ .

##### Identification of polymers, additives and impurities

The inherent sensitivity of luminescence has led to its attempted application for the identification of thermoplastic and thermosetting polymers through combined measurements of excitation spectra, fluorescence spectra and lifetimes (ref. 5). Pigments, antioxidants and other stabilizers have also been studied following their extraction from the polymer (ref. 5). As a general analytical method for polymers, luminescence spectroscopy suffers from the same problem as UV-visible absorption spectroscopy - the level of information obtained is coarse because of the close similarity in energy of the electronic transitions and their vibronic progressions, in which substituent effects are either absent or not resolved. The technique has been particularly powerful, however, in detecting trace amounts of oxidation products. A typical sensitivity for quantitative analysis of carbonyl chromophores by phosphorescence spectroscopy is  $2 \times 10^{-5}$  mol/mol compared with common spectroscopic techniques of IR:  $3 \times 10^{-4}$  mol/mol; UV:  $5 \times 10^{-4}$  mol/mol and  $^{13}\text{C}$  NMR:  $9 \times 10^{-4}$  mol/mol (ref. 10,11,12). Balanced against this sensitivity is the experimental difficulty in measuring quantitative spectra in the absence of oxygen and, in some polymers, at low temperature.

##### Phase separation and polymer miscibility

The application of luminescence to the problem of compatibility of polymer blends utilizes the strong dependence of the photophysical processes of intermolecular energy transfer and excimer formation on the chain conformation. The efficiency of interchain singlet energy transfer on the one hand and the extent of disruption of the excimer forming sites on the other depends on the degree of chain interpenetration and thus the miscibility of the two polymers. These two approaches will be considered separately.

Donor - acceptor energy transfer. The process of singlet-singlet energy transfer from an excited molecule with a higher electronic level (the Donor molecule, D) to another, different molecule with a lower lying singlet energy level (the Acceptor molecule A) will occur with an efficiency that depends on the separation of D and A and the spectral overlap between the emission from D and the absorption by A. This energy transfer process appears as a decrease in  $I_D$  the luminescence intensity of the Donor and, if A is luminescent, an increase in  $I_A$ . Since the transfer efficiency depends on  $r_{DA}^{-6}$  where  $r_{DA}$  is the separation of D and A, the emission intensity ratio  $I_D/I_A$  is a sensitive probe of the local concentration and extent of mixing of D and A. Thus if two polymers contain chromophores that meet the electronic energy requirements for a Donor and an Acceptor their miscibility may be studied by measuring the ratio  $I_D/I_A$ . Since most polymers of interest will be unlikely to meet these requirements, it is necessary to label the polymers with D and A fluorophores

of high quantum efficiency. This may be achieved by copolymerization of fluorescent vinyl aromatic or aromatic acrylate compounds having the appropriate energy levels. A suitable donor chromophore is naphthalene or carbazole and a suitable acceptor is anthracene (ref. 13). In more recent studies this has been achieved by light chloromethylation of the polymers to be studied followed by attachment of the fluorescent labels (ref. 14).

In a typical study of the compatibility of poly(methyl methacrylate), (PMMA) with styrene-acrylonitrile copolymers (SAN), equal weights of carbazole-labelled SAN and anthracene-labelled PMMA were cast as films (ref. 15). The films were irradiated in the carbazole absorption band at 296 nm and  $I_D/I_A$ , the ratio of emission intensity at 347 nm from carbazole to that at 413 nm from anthracene, was measured as a function of the acrylonitrile content of the SAN. Polymer miscibility is detected as a minimum in  $I_D/I_A$  i.e. maximum energy transfer efficiency and as shown in Fig. 2 this occurs when the SAN contains 30 to 40% acrylonitrile, in agreement with other methods. A limitation to this method occurs if the phase domains in an incompatible blend are sufficiently small to allow significant energy transfer across the boundary. The gradual transition from compatibility to incompatibility in Fig. 2 is thought to be due to interpenetration at the phase boundary.

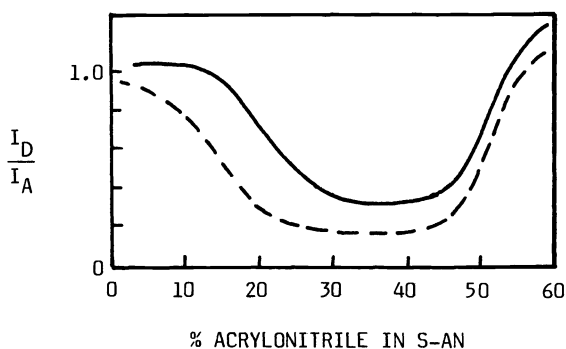


Fig. 2. The dependence of the compatibility of PMMA and SAN on AN content by the donor-acceptor fluorescence intensity  $I_D/I_A$ . The dotted line is for lower MW PMMA (adapted from ref. 15).

An interesting recent extension of this technique has been in polarized fluorescence microscopy in which, by use of a hot stage, the initial process of phase separation and boundary formation may be studied (ref. 16).

**Excimer fluorescence.** An alternative fluorescence method for studying energy transfer exploits the strict conformational requirements for excimer emission. Excimer fluorescence is observed from a polymer only if the aromatic rings can form a sandwich separated by  $\approx 3.5\text{\AA}$  within the excited state lifetime. Any chain interpenetration occurring in a miscible blend that decreases the number of available excimer forming sites will decrease the excimer fluorescence intensity. Phase separation therefore gives the greatest emission intensity.

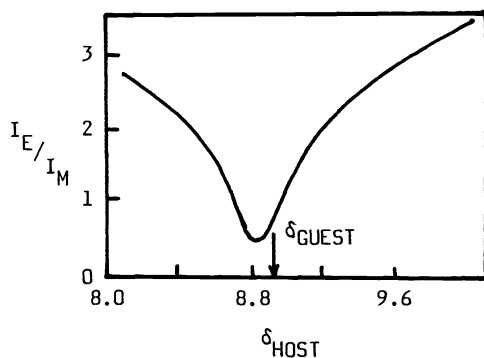


Fig 3. Dependence of P2-VN excimer fluorescence ratio,  $I_E/I_M$ , on solubility parameter,  $\delta_{\text{HOST}}$ , of a series of methacrylate host polymers.  $\delta$  of the P2-VN guest occurs near the minimum (adapted from ref. 18).

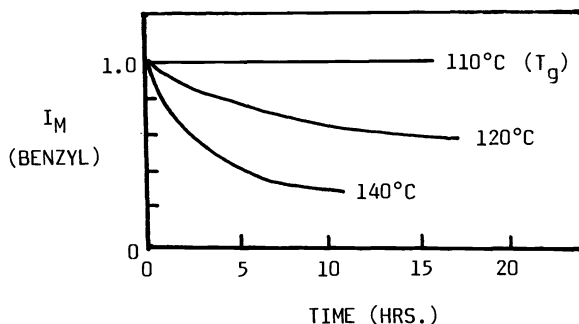


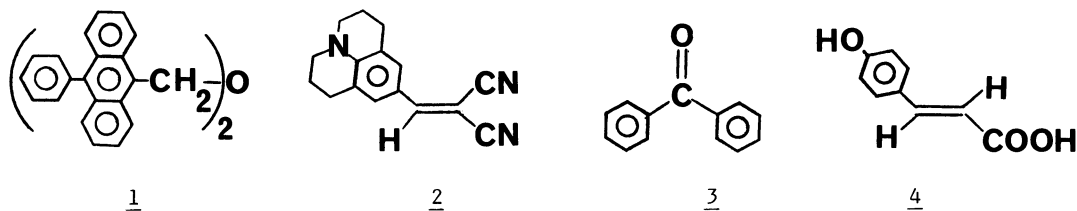
Fig. 4. Decay of 'monomer' benzyl emission from a PBzMA/PMMA blend with time of heating at the temperature indicated (adapted from ref. 15).

In a number of studies Frank *et al* (ref. 6,17,18) have used  $I_E/I_M$ , the ratio of excimer emission intensity to monomer emission intensity as a criterion for phase separation. To support this it was shown that  $I_E/I_M$  for poly(2-vinyl naphthalene) (P2-VN) dispersed in a series of methacrylates showed a minimum where the solubility parameters,  $\delta$ , of the two polymers were closest (Fig. 3). The underlying physical process is still under investigation, particularly as a function of molecular weight and concentration, and recently it has been suggested that changes in  $I_E/I_M$  at low concentration results from a decrease in guest polymer (P2-VN) coil size with increasing concentration because of the trend toward segregation (ref. 19).

Morawetz (ref. 15) has recently reported on the use of excimer emission to monitor phase separation of blends of poly(benzyl methacrylate), PBzMA and PMMA. As shown in Fig. 4, heating below  $T_g$  results in no change in  $I_M$ , but above  $110^\circ\text{C}$  where phase segregation can occur there is a decrease in  $I_M$  as excimer emission from the phenyl groups of PBzMA is observed.

#### Relaxation and transport processes

The wide range of lifetimes of the luminescence from solid polymers summarized in Fig. 1' enables polymer relaxations and transport processes to be studied from  $10^{-2}$  Hz to  $10^8$  Hz. A particular problem arises if the polymer is not intrinsically luminescent, but is easily overcome by incorporating a luminescent probe molecule either at synthesis, when processing, by casting from a solvent or simply by soaking the polymer in a swelling solvent containing the probe. The use of the probe can be turned to advantage as it can be chosen specifically to monitor particular properties e.g. 5-dimethyl amino-1-naphthalene sulfonate has been used to study polar interactions in cationic copolymers of styrene and vinyl benzenetri-alkylammonium halides (ref. 20). An excimer forming probe that has been widely used in studying the change in free volume with temperature is 10, 10' diphenyl-bis-9-anthryl methyl oxide or 'diphant' 1 (ref. 21,22). From lifetime studies it was found that the rotational process of the probe reflects the segmental motions of the polymer.



The probe molecule, julolidene malononitrile, 2 has been shown to have a fluorescence quantum yield that decreases with an increase in polymer free volume (ref. 23,24). This, and similar molecules based on the malononitrile structure have a first singlet excited state with substantial charge transfer character that undergoes radiationless decay at a rate dependent on the free volume. The radiationless rate constant increases with free volume, resulting in a sharp decrease in fluorescence intensity at the glass transition temperature. It has recently been shown that the fluorescence from 2 is sensitive to the tacticity of PMMA (ref. 24). It may also be used to study network formation in epoxy resins (ref. 25).

The probe molecules 3 and 4 show triplet state emission properties that are sensitive to relaxation processes of the host polymer. In the case of benzophenone, 3, the triplet decay kinetics change at a transition and this has been attributed to quenching by side-chain ester groups (ref. 26). The coumaric acid derivative, 4, similarly shows an increase in the radiationless rate constant with the onset of side group motion, so leading to a decrease in emission intensity at a characteristic temperature (ref. 27). These applications are extensions of the early work of Guillet (ref. 28) in which the quenching of phosphorescence was attributed to the increased accessibility of trace molecular oxygen to the emitting chromophore as the polymer becomes more mobile. The apparent relaxation temperature depends on the partial pressure of oxygen above the film. The range of polymers and the relaxations that have been studied using the above probes are summarized in Table 1.

Luminescent probe molecules have also been used to study transport properties. For example, the permeability of a polymer to oxygen may be obtained by continuously monitoring the change in either emission intensity or excited state lifetime with the time of exposure to oxygen of a previously evacuated film. This requires a uniform distribution of the fluorescent or phosphorescent species in the film. Quenching of luminescence will occur at the diffusion controlled rate, so the Stern-Volmer equation (1) will apply, where  $k_q$  is

the quenching rate constant and  $\tau$  the excited state lifetime.

$$I_0/I-1 = k_q \tau [O_2] \quad (1)$$

TABLE 1. The use of probe molecules to monitor relaxation processes in polymers

Probe	Polymer	Relaxation	Mechanism
<u>1</u>	Polyisoprene Polybutadiene SBR Polysiloxanes	$T_g$	Excimer formation increases with free volume (ref. 21,22).
<u>2</u>	PMMA PVC-P(vinyl acetate) PS Epoxy resins	$T_g$	Radiationless rate constant increases with free volume (ref. 23,24,25).
<u>3</u>	PMMA PMA	$T_\beta$ $T_{\alpha'}$ $T_g$	Triplet lifetime decreases due to ester quenching (ref. 26).
<u>4</u>	PMMA PS PVA	$T_\beta$ $T_\gamma$	Radiationless rate constant increases with side group motion (ref. 27).

The concentration of oxygen in the film at any time compared to the equilibrium concentration can be determined from the emission intensities since  $k_q$  and  $\tau$  are constants (ref. 29). As shown in Fig. 5 for the quenching of perylene excimer fluorescence in polystyrene, the luminescence quenching data yields a straight line plot. The slope of this line is  $(\frac{4D}{\ell\tau})^{1/2}$  where  $\ell$  is the film thickness. In this example  $D$ , the diffusion coefficient of oxygen in polystyrene was obtained as  $1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  at  $20^\circ\text{C}$  (ref. 29). Similarly, by using the fluorescent probe 2, the sorption of trichloroethane by poly (vinyl chloride co-vinyl acetate) has been followed by the decrease in fluorescence intensity with time (ref. 30). A numerical analysis of the data was not presented.

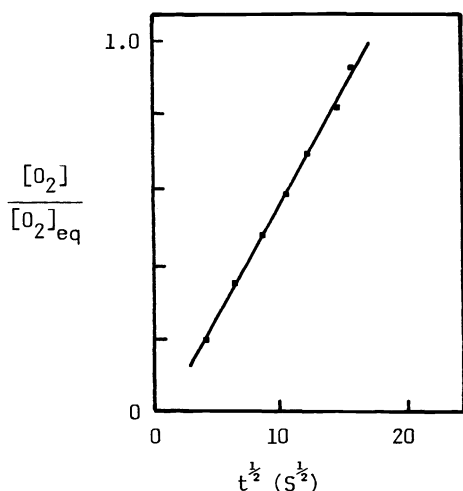


Fig. 5. Determination of  $D_{O_2}$  by oxygen quenching of perylene excimer fluorescence.  $[O_2]$  is determined from equation (1). (Adapted from ref. 29)

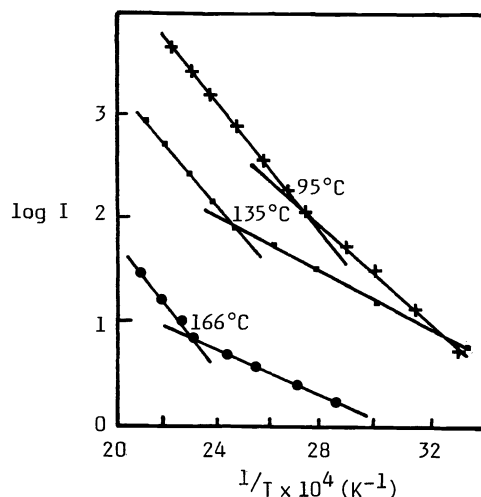


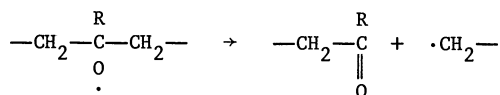
Fig. 6. Measurement of  $T_g$  of an epoxy resin by the temperature dependence of CL intensity.

- + : 17% curing agent
- : 27% curing agent
- : 27% curing agent, postcured at  $170^\circ\text{C}$

Polymer relaxations may also be studied by thermoluminescence (ref. 31) - particularly at low temperatures in vacuum - and by chemiluminescence - particularly at elevated temperatures in air. Thermoluminescence (TL) is the weak light emitted following the heating of a sample that has previously been irradiated at very low temperatures. Free electrons from  $\gamma$ - or X-ray ionization of the polymer are trapped by structural or chemical defects in the solid. When the polymer is heated through a molecular relaxation the electrons recombine with ions of the chromophore resulting in an excited state and thus the emission of luminescence (ref. 32). In many polymers the emissive centres may be trace amounts of impurities such as aromatic hydrocarbons trapped in the polymer (ref. 33). Chemiluminescence (CL) may similarly be used to monitor polymer relaxations since the bimolecular peroxy radical termination reaction responsible for light emission will be sensitive to polymer free volume. Fig. 6 shows a plot of the CL intensity as a function of temperature from an epoxy resin (MY720-Ciba Geigy) cured with diamino diphenyl sulfone (DDS) at 135°C. There is a sharp increase in CL intensity at a temperature that is sensitive to both the concentration of curing agent and the final cure temperature. From dynamic mechanical measurements and DSC this is found to be characteristic of  $T_g$  of this resin. The CL technique offers a rapid non-contact method for measuring  $T_g$  of epoxy resins but it is noted that the material must undergo at least trace oxidation over the temperature range of interest which sets a lower limit of around 290K. Thus CL and TL are complementary techniques as TL is generally not observed above 260K because of the energy loss through collisional rather than radiative processes (ref. 32).

#### Polymer Degradation

Luminescence may be used to study changes in both the chemical and physical properties of a solid polymer during environmental degradation. In the luminescence studies by Allen (ref. 5) the thermal oxidation products of several polyolefins and polyamides have been found to include  $\alpha,\beta$  unsaturated carbonyls - a possible consequence of the competition between alkyl radical and alkyl peroxy radical reactions in these polymers. If chain scission occurs during polymer oxidation as a result of the alkoxy radical reaction below



then the increase in terminal ketone groups should be directly related to the number of chain scission events. This has been shown to be so by a comparison of quantitative phosphorescence spectroscopy of polystyrene (ref. 7) and nylon 66 (ref. 34) and chain scissions as measured by solution viscosity.

The change in the phosphorescence spectrum of nylon 66 fibres with time of thermal ageing in air at 80°C is shown in Fig. 7 (ref. 34). There is a significant emission from the unaged material - a result of oxidation during processing. The integrated emission intensity increases systematically with time of ageing.

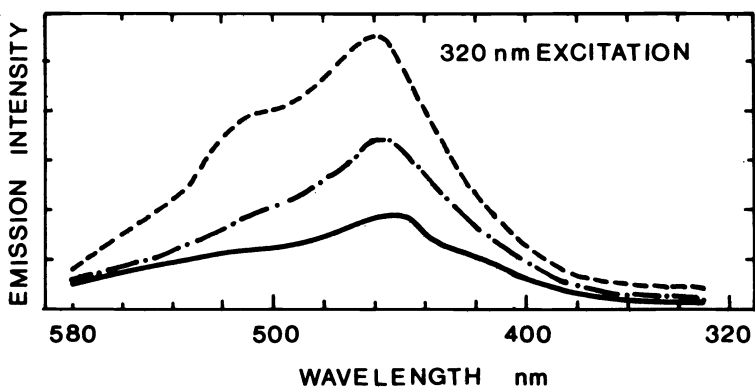


Fig. 7. The phosphorescence spectrum from nylon 66 fibres after ageing at 80°C in air for

0 days : ———  
 90 days : - · - · -  
 300 days : - - - - -

A further extension of this use of phosphorescence spectroscopy has been to correlate the increase in phosphorescence emission intensity due to the accumulation of oxidation products during degradation with the increase in tensile strength of the material (ref. 34, 35). This arises since in many polymers, the tensile strength is related to molecular weight ( $\bar{M}_n$ ) by the relation

$$\sigma = A - \frac{B}{\bar{M}_n}$$

A plot of the phosphorescence emission intensity from nylon 66 fibres as a function of the decrease in tensile strength is shown in Fig. 8 for thermal ageing of the polymer at 80°C. This general relation has been found to hold for nylon 66 oxidized below  $T_g$  and has been used as a non-destructive test method to predict strength losses from materials aged under storage conditions for times up to 30 years (ref. 34).

One interesting observation with nylon 66 fibres is that phosphorescence from the oxidation products can be observed at room temperature in air (conditions which normally quench polymer phosphorescence). This is believed to arise from the low solubility and diffusion coefficient of oxygen in nylon 66 that leads to a value for the term  $k_q \tau [O_2]$  in the Stern Volmer Equation (1) of about 10. This is not observed for the polyolefins and polystyrene.

This property of nylon 66 probably also explains the high intensity of chemiluminescence observed during oxidation (ref. 8). Unlike the phosphorescence previously described which measures the extent of oxidation at any point during the degradation of the material, chemiluminescence has the potential to measure the rate of oxidation. This occurs since the weak light emitted arises from the termination step in the oxidation reaction, so an increase in oxidation rate also increases the emission intensity. The technique is not an absolute method for measuring oxidation rate and an independent measurement of the quantum yield of chemiluminescence or rate of initiation is required. It can however be used for ranking antioxidants since the chemiluminescence intensity is directly proportional to the alkylperoxy radical concentration in the polymer, so any radical scavenging additive will affect the emission intensity. The use of non-stationary chemiluminescence methods such as gas switching or UV irradiation, (ref. 8,36) enables kinetic information to be obtained in the limit of zero extent of oxidation, so allowing a rapid characterization of the oxidative stability of a polymer.

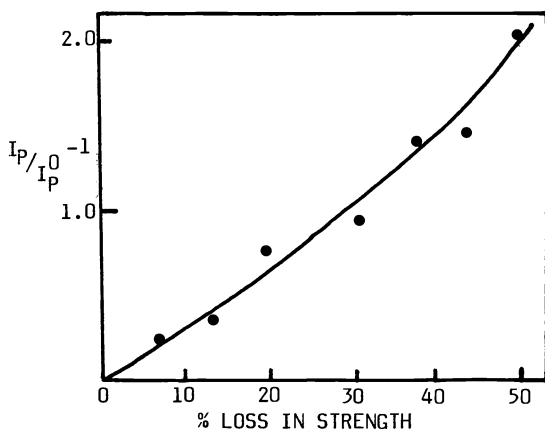


Fig. 8. Relation between phosphorescence intensity from nylon 66 fibres and the loss in strength during oxidation.

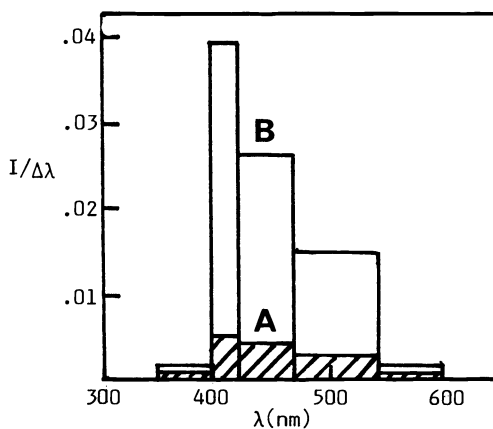


Fig. 9. Spectral distribution of  
A : Thermal CL at 90°C  
B : Stress CL at 60°C.

#### Deformation and Failure

The polarized fluorescence from a probe molecule has been used extensively to study the orientation occurring during polymer deformation (ref. 3). While the experiment yields the orientation of the probe alone, if its location and orientation with regard to the polymer segments are known, the actual segmental orientation may be determined. Suitable probes are diphenyl polyenes and stilbenes. Comparison of probe orientation in PVC and polycarbonate during deformation has shown higher orientation factors in PVC due to deviations from pseudo affine deformation in polycarbonate (ref. 37).

The chemiluminescence accompanying the deformation of a number of polyamides and crosslinked



epoxy resins has been investigated recently (ref. 38,39,40). The effect of applied stress is to enhance the chemiluminescence intensity and while the mechanism in epoxy resins is uncertain at present (ref. 39) the reported results for nylon 66 fibres can be interpreted within a framework of stress enhanced oxidation. At low stress levels repetitive strain cycling results in a reproducible enhancement in luminescence intensity that increases linearly with stress. At stress levels above 60% of ultimate, the emission increases exponentially with stress and on repetitive load cycling is not observed until the previous stress encountered by the polymer is exceeded. This is consistent with esr results during loading of nylon 6 and the luminescence in this region is considered to result from free radical formation due to the progressive rupture of the fully extended tie molecules in the amorphous region that connects the crystalline blocks of the polymer. The equations governing light intensity are identical to those for thermal chemiluminescence and, as shown in Fig. 9, the spectral distribution is also identical suggesting that the effect of stress is to lower the activation energy for the degradation of the polymer (ref. 38). The studies reported so far indicate that the stress chemiluminescence decay curves contain much information about the processes of stress relaxation and the rates of free radical reactions in a stressed polymer.

#### CONCLUSION

While luminescence spectroscopy cannot provide the detailed molecular structure information that, say, FT-IR spectroscopy reveals, it does have the advantage of simplicity and sensitivity. The rapid and efficient electronic energy transfer in the solid state can be turned to advantage in the application of excimer fluorescence and donor-acceptor transfer to the study of blends. The wide range of excited state lifetimes enables relaxations up to the glass transition to be monitored and the diffusion of gases and solvents in films may also be measured. The chemistry of solid polymers may also be studied - particularly the trace oxidation during processing and subsequent environmental degradation and mechanical failure.

The papers cited are only selected examples from an area of very active research. New techniques from small-molecule spectroscopy are soon applied to polymers. Picosecond lasers have revolutionized the study of biopolymers and the conformation of macromolecules in solution and similar advances may be expected in applications to the solid state. For example lasers have been used to study, by total internal reflection, the sub-nanosecond time resolved luminescence of polymer surfaces (ref. 41). The authors believe that this will provide a valuable adjunct to techniques such as ESCA as it can probe depths of  $\sim 100\text{\AA}$ .

#### ACKNOWLEDGEMENT

The financial support of the Australian Research Grants Scheme for studies of polymer chemiluminescence is gratefully acknowledged.

#### REFERENCES

1. J.B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, 1970.
2. D.A. Holden and J.E. Guillet, Developments in Polymer Photochemistry - 1, Ed. N.S. Allen, Applied Science, 1981, Chapter 3.
3. S.W. Beavan, J.S. Hargreaves and D. Phillips, Adv. Photochem., **11**, 207, 1979.
4. K.P. Ghiggino, A.J. Roberts and D. Phillips, Adv. Polym. Sci., **40**, 71, 1981.
5. N.S. Allen, Analysis of Polymer Systems, Ed. L.S. Bark and N.S. Allen Applied Science, 1982, Chapter 4.
6. C.W. Frank and S.N. Semerak, Adv. Polym. Sci., **54**, 31, 1984.
7. G.A. George and D.K.C. Hodgeman, Eur. Polym. J., **13**, 63-71, 1977.
8. G.A. George in Developments in Polymer Degradation - 3, Ed. N.S. Grassie, Applied Science, 1981, Chapter 6.
9. E.S. O'Keefe and N.S. Billingham, Dev. Polym. Deg., **10**, 137-146, 1985.
10. J.L. Koenig, Adv. Polym. Sci., **54**, 89-154, 1984.
11. G.A. George and D.M. Pinkerton in Proceedings of the Critical Review: Techniques for the Characterization of Composite Materials AMMRC MS 82-3, May 1982.
12. L.W. Jelinski, J.J. Dumais, J.P. Luongo and A.L. Cholli, Macromolecules, **17**, 1650-1655, 1984.
13. F. Amrani, J.M. Jung and H. Morawetz, Macromolecules, **13**, 649-653, 1980.
14. F. Mikes, H. Morawetz and K.S. Dennis, Macromolecules, **17**, 60-63, 1984.
15. H. Morawetz, Polym. Eng. Sci., **23**, 689-692, 1983.
16. J.L. Halary, J.M. Ubrich, J.M. Nunzi, L. Monnerie and R.S. Stein, Polymer, **25**, 956-962, 1984.
17. S.N. Semerak and C.W. Frank, Macromolecules, **14**, 443-449, 1981.
18. M.A. Gashgari and C.W. Frank, Macromolecules, **14**, 1558-1567, 1981.
19. J.M. Tarkelson, M. Tirrell and C.W. Frank, Macromolecules, **17**, 1505-1512, 1984.

20. W.G. Herkstroeter, J. Polym. Sci. (Polym. Chem. Edn.), 22, 2395-2412, 1984.
21. L. Bokobza, E. Pajot, L. Monnerie, H. Bouas-Laurent and A. Castellan, Polymer, 22, 1309-1311, 1981.
22. E. Pajot-Augy, L. Bokobza, L. Monnerie, A. Castellan and H. Bouas-Laurent, Macromolecules, 17, 1490, 1984.
23. R.O. Loutfy, J. Polym. Sci. (Polym. Phys. Edn.), 20, 285, 1982.
24. R.O. Loutfy and D.M. Teegarden, Macromolecules, 16, 452-456, 1983.
25. R.L. Levy, Polym. Mater. Sci. Eng., 50, 124, 1984.
26. K. Horie, K. Morishita and I. Mita, Macromolecules, 17, 1746-1750, 1984.
27. K.R. Smit, R. Sakurovs and K.P. Ghiggino, Eur. Polym. J., 19, 49-53, 1983.
28. A.C. Somersall, E. Dan and J.E. Guillet, Macromolecules, 7, 233-244, 1974.
29. J.R. MacCallum and A.L. Rudkin, Eur. Polym. J., 14, 655-6, 1978.
30. K-Y Law, Polymer, 25, 399-402, 1984.
31. V.G. Yerkin, G.A. Mikhail'chenko and A.A. Persinen, Polym. Sci., USSR, 23, 255-258, 1981.
32. R.J. Fleming and J. Hagekyriakau, Radiat. Prot. Dosim., 8, 99-116, 1984.
33. Z. Osawa, H. Kuroda, Y. Kobayashi, J. Appl. Polym. Sci., 29, 2843, 1984.
34. G.A. George and N. McM. Browne, Materials Research Laboratories Report MRL-R-691, 1977.
35. G.T. Egglestone and G.A. George, Materials Research Laboratories Report MRL-R-950, 1985.
36. G.A. George, G.T. Egglestone and S.Z. Riddell, Polym. Eng. Sci., 23, 412-418, 1983.
37. H. Springer, R. Neuert, F.D. Muller and G. Hinrichsen, Coll. Polym. Sci., 26, 800-804, 1983.
38. G.A. George, G.T. Egglestone and S.Z. Riddell, J. Appl. Polym. Sci., 27, 3999-4018, 1982.
39. R.L. Levy and D.L. Fanter, McDonnell Douglas Research Laboratories Report MDRL 79-27, 1979.
40. S.B. Monaco and J.H. Richardson, Polym. News, 9, 230-234, 1984.
41. H. Masuhara, N. Mataga, S. Tazuke, T. Murao and I. Yamazaki, Chem. Phys. Letts., 100, 415, 1983.