

Figure 6 E.s.r. spectra of PBN-labelled LDPE at various temperatures. (a), -110°C ; (b), 90°C ; (c), 110°C

the spectrum has a broad asymmetric line shape, indicating that the label is in an immobilized state (Figure 6a). The line becomes sharper and the line separation narrows as temperature increases (Figure 6b). At 110°C the triplet changes into a triplet of doublets (Figure 6c).

This doublet may be caused by the β -proton in the label, whose interaction is masked by the line width of the triplet below 110°C .

Figure 7 shows the temperature variation of the separation of the triplet. The result of the spin probe method is shown in the same figure. It is found that a small narrowing takes place at about -20°C and rapid one at 67°C . Comparing the result of the spin label with that of the spin probe, it is noted that the narrowing temperature is considerably shifted to higher temperatures by formation

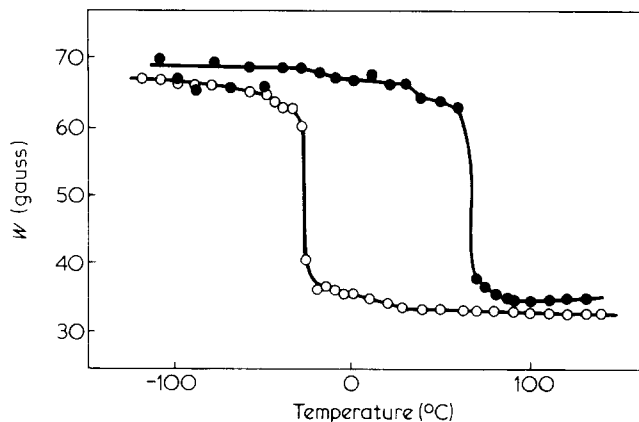


Figure 7 Change of line separation with temperature. O, spin probe; ●, PBN-labelled

of a chemical bond between the radical and the host polymer. In the previous paper we proposed a theory on the relation among the narrowing temperature T_n ($\approx T_{50G}$, T_g and the molar volume ratio of the segment of the host polymer to the probe⁸ and this theory was experimentally proved.^{9,10} According to this theory, this increase in T_n value is attributed to the mechanism that larger activation volume for jumping of the radical site into an adjacent hole becomes necessary for formation of spin labelled segment of host polymer.

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Excimer and charge transfer complex trapping of excitons in carbazole containing polymers

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The carbazolyl chromophore can confer photo-activity on a polymer, and a number of such polymers have been studied.¹ Of these poly(N-vinyl carbazole) is the most important technically, and shows very efficient excimer formation and exciton migration characteristics. When the carbazolyl chromophore is attached to the backbone by a spacing group (as in a series of carbazolyl substituted methacrylate polymers) both excimer formation and exciton migration are reduced. Poly(2-(9-ethyl) carbazolyl methyl methacrylate), I, exhibits excimer formation without long range exciton migration¹, and as such forms a useful reference

material for the study of excimer trap characteristics. Poly(9-carbazolyl methyl methacrylate), II, forms charge transfer complexes with tetracyano ethylene (TCNE), but exhibits no appreciable excimer emission or exciton migration.

In this preliminary communication we report the progress of continuing study of these phenomena.

Excimer characteristics

The absorption and emission spectra of the polymer are illustrated in Figure 1. The fluorescence from 'monomeric'

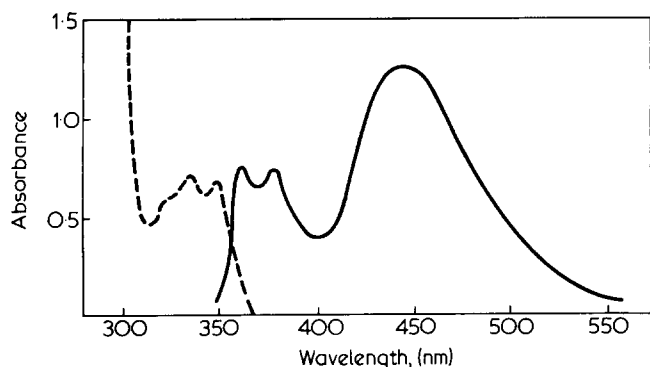


Figure 1 Absorption (broken line), and fluorescence (full line) in arbitrary units spectra of polymer I in methylene chloride, 2×10^{-4} m in monomer units.

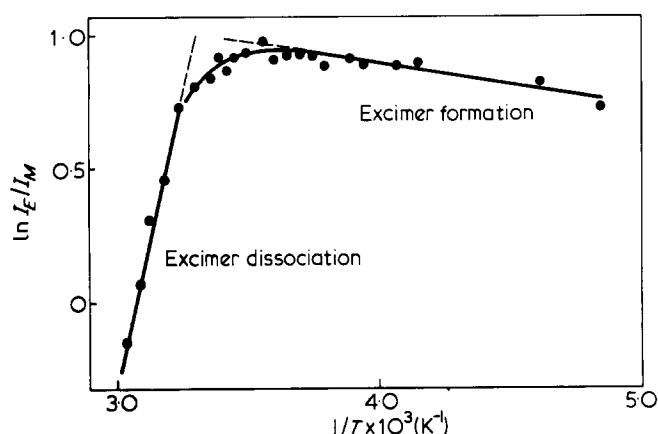
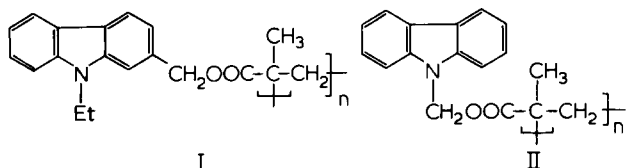


Figure 2 Ratio of excimer to monomer emission, I_D/I_M , as a function of reciprocal temperature in methyl tetrahydrofuran, 9.5×10^{-5} m in monomer units.



chromophores is evident as the structured mirror image of the ${}^1L_b \leftarrow {}^1A$ absorption, and the excimer fluorescence forms an unstructured band centred about 450 nm. The ratio of excimer to monomer fluorescence is constant between monomer unit molarities 2×10^{-5} and 3×10^{-4} , indicating that the excimer is intramolecular in origin.

The temperature dependence of the ratio of excimer to monomer fluorescence is illustrated in Figure 2. The maximum in such a curve is usually interpreted² in terms of thermally activated conformational change into the excimer site geometry determining the rate of excimer formation at low temperatures, and thermal dissociation of rapidly formed excimer sites determining the excimer population at high temperatures. In this context we note that time dependent studies¹ at 298 K gave a rapid excimer rise time. The slope of the low temperature section of Figure 2 yields an Arrhenius activation energy $0.14 \text{ kJ mole}^{-1}$, in line with the easy formation (or virtual pre-formation) of excimer sites deduced from earlier work¹. The fact that excimer formation is rapid compared with radiative and decay processes at high temperatures

simplifies analysis of the high temperature regime, which reflects simply the almost unperturbed equilibrium concentration of excimer balanced between conformational formation of excimer sites and thermal dissociation of such sites. The slope of the graph then represents the conformational energy difference between the excimer state and the normal ground state, which is 40 kJ mole^{-1} , so that the excimer binding energy is $40.1 \text{ kJ mole}^{-1}$ (0.4 e.v.).

A reason for the lack of energy migration in this polymer is thus seen to be the large concentration of excimer traps which are easily formed and have an appreciable binding energy or trap depth. Thus a puzzling feature of the earlier work¹, that the geometrical requirements for energy migration should be less severe than those for excimer formation, is explained. The localization of the energy arises from trapping and not because of any fundamental improbability of exciton migration between monomeric chromophores.

A variety of important photophysical and photochemical phenomena depend on the ability of electronic excitation energy to move from the site of primary absorption of a photon, from molecule to molecule until the position of final activity is reached. In polymer systems this process is assisted by the migration of an exciton along polymer molecules containing chromophoric repeat units. The efficiency of this migration is affected by the presence of trapping sites on the molecule, and in this context excimers (dimeric complexes formed between two chromophores one of which is in the excited state) form shallow traps which may be capable of thermal dissociation. Charge transfer complexes are often intermediates in photoprocesses, and the presence of a charge transfer complex in a chain of chromophores usually constitutes a deep trap, or quenching centre, from which the mobile exciton cannot be re-energized by thermal means.

Charge transfer complex traps

A charge transfer acceptor, such as tetracyanoethylene, can quench the fluorescence of an excited charge transfer donor either by a bimolecular collisional interaction with the excited state, or by arrival of the excitation energy at a preformed ground state charge transfer complex. If we consider that only uncomplexed donor is available for fluorescence, we define the charge transfer complex formation by

$$K = \frac{[C]}{[D][A]} \quad (1)$$

where D , A , C represent donor, acceptor, complex (ground states) respectively. The Stern-Volmer collisional quenching of the donor fluorescence by acceptor (when $[A] \gg [D]$) yields

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [A] \simeq 1 + k_q \tau_0 [A]_0 \quad (2)$$

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} \frac{[D]_0}{[D]} \simeq (1 + k_q \tau_0 [A]_0) / (1 + K [A]_0) \quad (3)$$

Thus the quenching characteristics measured in intensity and lifetime yield different Stern-Volmer plots, comparison of which yields information on the equilibrium constant for formation of the complex.

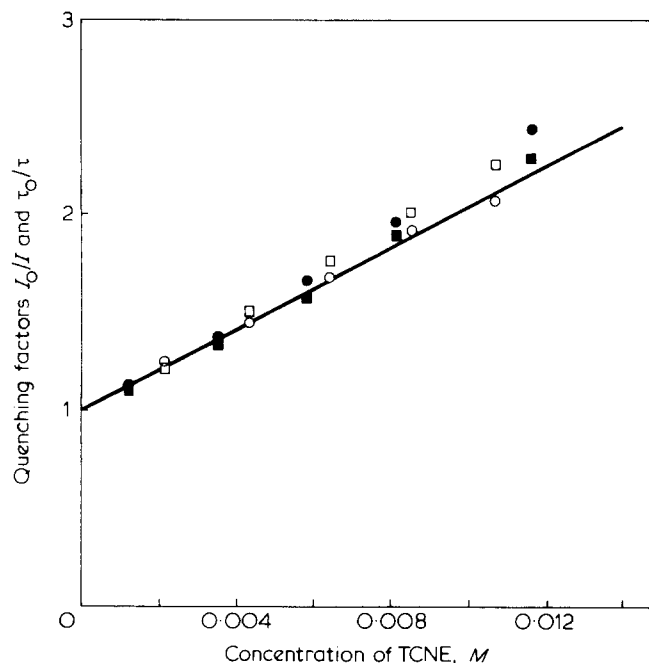


Figure 3 Quenching of carbazole fluorescence by TCNE in methylene chloride at 298 K. ● I_0/I , ■ τ_0/τ both for carbazole 1.6×10^{-4} M; ○ τ_0/τ , □ I_0/I both for carbazole 8×10^{-4} M.

Quenching of fluorescence of carbazole by tetracyanoethylene in methylene chloride is illustrated in Figure 3. The lifetimes were measured using apparatus described previously¹. In this case there is no detectable difference between steady state intensity and lifetime data. In quantitative terms this means that less than ten percent of the carbazole is complexed at these concentrations so that the complexing equilibrium constant is less than $9(\text{M}^{-1})$. Data for 9-ethyl carbazole are similar, and so agree with literature values³⁻⁵ which range between 2 and 7.

Quenching of fluorescence of poly(9-carbazolyl methyl methacrylate) by tetracyanoethylene is illustrated in Figure 4. The quenching efficiency (slope of the τ_0/τ plot) is about a factor of two greater than for the small molecules (carbazole and 9-ethyl carbazole). There is also a marked difference between the lifetime (τ_0/τ) and steady state intensity (I_0/I) data. Analysis of this difference using equations 2 and 3 yields $K = 45.7$. This differs from literature reports which, using absorption in *much* more concentrated solutions, suggest that the complexing constant is *smaller* for polymers than for small molecules.

Similar measurements on collisional quenching by hexachlorobenzene produce coincidence of τ_0/τ and I_0/I Stern-Volmer plots as expected, again with quenching efficiencies about twice those observed for the small molecules.

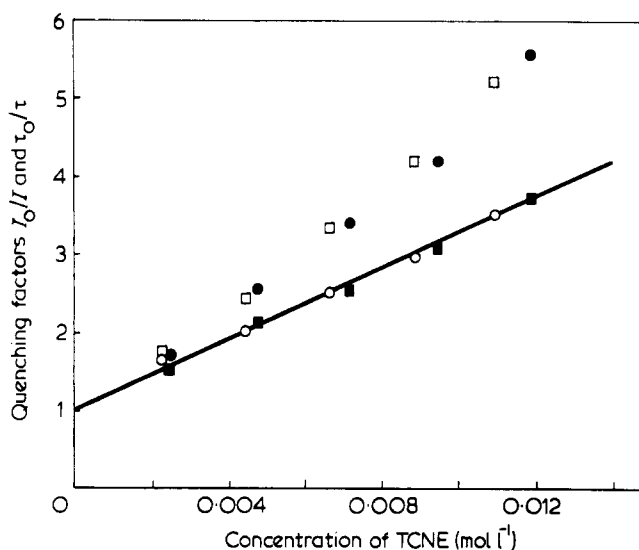


Figure 4 Quenching of polymer II 380 nm fluorescence by TCNE in methylene chloride at 298 K. ● I_0/I , ■ τ_0/τ both for 4.4×10^{-5} M monomer units; ○ τ_0/τ , □ I_0/I both for 8.8×10^{-5} M monomer units.

There are two possible explanations. The first is that in this polymer with the carbazolyl chromophore spaced away from the backbone, steric barriers to complex formation are eased, and of course, the entropy of complex formation will be less unfavourable with a polymeric substrate, so that K is genuinely larger than for small molecules. Alternatively, if K is similar to that observed for small molecules, each acceptor interacts with energy initially localized on about 8-9 donor chromophores. This might be by way of very limited excimer migration (2 or 3 'hops') or by rapid dissociation - reformation of the acceptor - donor complex so that 8 or 9 donor chromophores may complex with a single acceptor; indeed the complex may have a D_nA stoichiometry.

Studies on these questions are continuing.

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Entanglement effects in the segmental motion of two flexible chain polymers

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When the concentration of a dilute polymer solution is increased, interchain interactions occur first by hydrodynamic forces transmitted by intervening solvent mole-

cules, and then by direct intersegment interactions. When this interaction has sufficient strength and lasts sufficiently long to reduce the motional freedom of the participating