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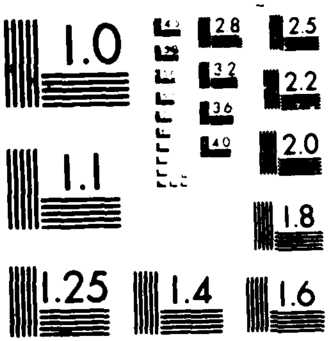
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Molecular motion and energy migration in polymers

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First Periodic Report

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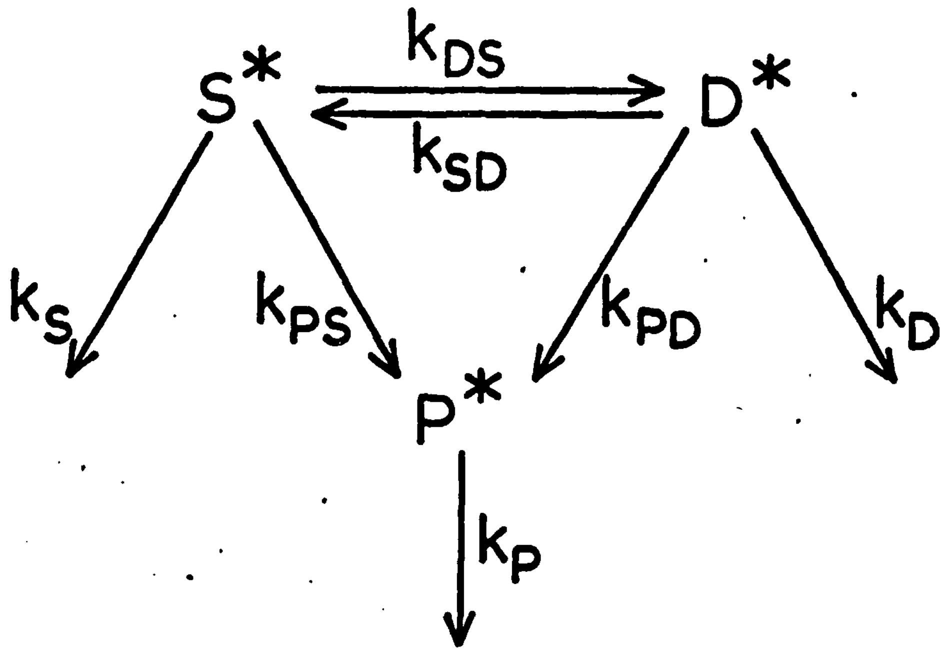
1. The first part of this report is concerned with research the aim of which is to establish whether or not electronic energy migration in synthetic polymers with pendant aromatic chromophores is a facile process or not. This is an area of some controversy, since authors regard the process as rapid, and proven to exist, others claim, largely on the basis of measurement of fluorescence anisotropy, that it does not oocur at all. We have in cooperation with Dr. Ian Soutar, Heriot-Watt University synthesized two copolymer systems in an attempt to devise a more definitive experiment with which to test these conflicting hypotheses. These are polystyrene copolymerized with 0.01 percent of 2,5-diphenyl oxazole (PPO), and styrene-butadiene block copolymers. (Great Britain)

Phenyl oxazole results

A sample of polystyrene containing 0.01 mole percent of 2,5-diphenyl oxazole (PPO) chromophores as intramolecular energy traps was prepared by copolymerization of styrene and 2-phenyl-5-(p-vinyl)phenyloxazole (POS) under high vacuum conditions at 60°C using AIBN as initiator. The polymer was purified by multiple reprecipitation.

Fluorescence from this polymer consists of emission centred at 280nm (styrene momoner); 330nm (styrene excimer), and 370nm, PPO. Decay data from these compounds, described fully in the accompanying preprint, are consistent with Scheme 1, and solution of the kinetics, also described in the preprint, reveals that the rate constant for energy transfer to the PPO from the styrene monomer, k_{PS}, relative to that for the transfer from the excimer, k_{PD}, $>$ 30.



The data presented in these papers offer strong evidence for the existence of energy migration in styrene polymers. The reasoning which leads to this important conclusion is detailed below.

If we assume at the outset that energy migration does not occur in polystyrene then energy is localised at the chromophore at which absorption occurs and excimer emission results solely from sites which can adopt the required orientiation during the excited monomeric lifetime. As a consequence it would have to be argued that the ratio of excimer to monomer fluorescence yields revealed in the fluorescence spectrum of the homopolymer reflects the influence of the twin parameters of relative concentration and quantum efficiency of emission of excimer and monomer. Since the emission spectrum of dilute solutions of polystyrene are dominated by fluorescence from intramolecular excimer sites the logical conclusion in the absence of migration is that excimeric species are relatively abundant and exhibit reasonably high fluorescence efficiency in the polymer. However, these factors allied to the relatively long lived nature of the excimer and the considerable degree of spectral overlap with the PPO absorption band would produce reasonably efficient energy transfer from excimer donors to PPO traps. Since this is incompatible with the observed kinetic behaviour it must be concluded that the initial assumption of energy localisation is wrong.

The relatively minor contribution to the energy received by PPO traps from the excimer implies that intramolecular excimeric species are present in relatively low concentrations in polystyrene. The large contribution to the emission profile made by the excimer must therefore result from energy migration and subsequent trapping at excimer sites in the polymer chain.

The conclusions of the study are thus:-

(1) In intramolecular energy transfer to guest traps in polystyrene the excimer plays an insignificant role as a donor relative to that of excimer monomer.

(2) Energy migration occurs in polystyrene.

(3) Quantitative evaluation of the mechanism of intramolecular energy trapping could only be made subsequent to the determination of the photophysical behaviour of pure polystyrene. This observation emphasises the need to study fundamental photophysics in polymer systems if it is desired that a complete picture of polymer photochemistry (which implies understanding of energy trapping by photo labile species) be obtained.

Block copolymer studies

Full details of this study are given in the accompanying preprint.

A series of styrene homopolymers and styrene-butadiene block copolymers of type SB and SBSB in which the sequence length of styrene chromophores has been varied, have been studied by time resolved fluorescence techniques. It has been shown that the kinetic behaviour of polystyrene fluorescence cannot be attributed to the existence kinetically distinct monomeric species. The dual exponential decays observed in the region of monomer emission are assigned to the influence of quenched monomer and excimer dissociation respectively. The molar mass dependence of the polystyrene photophysics is best explained by models which assume energy migration to occur within (and at low molecular weights be limited by) the chromophore sequence lengths. Thus both of these independent studies support strongly the concept of *facile electronic energy migration in these polymers in solution.* Excimer formation has also been used to further investigate the existence of order in outlines of photo active polymer, in this case a polymer based upon the chromophore 1,2-diphenyl cyclopropene. (See attached preprint 3). In this polymer the absolute quantum yield of crosslink formation approaches the theoretical maximum for a single-step crosslinking process. In the matrix, only a small fraction of chromophores (~4%) are in reactive configurations, and it appears from the fluorescence behaviour of the films that these are associated with excimers.

Chemical analysis reveals the formation of tricyclic dimers in the irradiated films, as anticipated by DeBoer et al[2,3] which indicates that the primary crosslinking step is cycloaddition between the double bonds of two suitably oriented cyclopropene rings. The high initial quantum yield of the photoreaction coupled to a low concentration of reactive sites implies extensive energy migration in the system. From lifetime measurements, the migration range of the triplet excitation in the matrix is estimated at 150A.

Finally, as part of a continuing attempt to improve the resolution of fluorescence decay measurements, we have established standards for decay time measurements, details outlined in the accompanying preprint 4.

2. The remainder of the contract will be spent carrying out work substantially as described in the original application. Work is thus continuing on excimer formation and motion of polymers based upon styrene. Some emphasis is now also being given to fluorescence anisotropy measurements upon vinyl polymers with pendant naphthalene chromophores.

3. The principal investigator attended the International Conference on Spectroscopy in Melbourne, Australia, and the RAC Annual Congress, Canberra, Australia in August 1982, where he lectured on the subject of this research. There have been no significant changes in personnel, or in the direction of the work.

4. None.

Annex

5. a. The balance of unused funds remaining on the contract at the end of December 1982 is $54.166.

b. Replacement plasma tube for Spectraphysics 166 Ion Laser (£4,900)
2 ADP Frequency doubling crystals (£770)
XP2020 Fast photomultiplier tube (£800)

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