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MOLECULAR MOTION AND ENERGY MIGRATION IN POLYMERS(U)  
ROYAL INSTITUTION OF GREAT BRITAIN LONDON (ENGLAND)  
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MOLECULAR MOTION AND ENERGY  
MIGRATION IN POLYMERS

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Work has continued on three fronts, that of the study of excimer formation in styrene polymers, using laser excitation of fluorescence; the study of time-resolved anisotropy in synthetic polymers and model systems, and on the study of structure-fluorescence correlation in poly(diacetylenes).

#### Excimer Formation in Copolymers of Styrene and Acrylonitrile

The photophysical behaviour of a range of styrene-acrylonitrile (S-A) copolymers has been studied both by steady state and time resolved fluorescence spectroscopy. The objective of the work was to establish the applicability of the photophysical model which has been proposed to describe intramolecular excimer formation in other vinylaromatic copolymer systems<sup>1,2</sup>. The S-A copolymer system was chosen specifically to attain this objective for the following reasons: (i) Copolymerisations of S and A show a tendency towards alternation of the comonomer residues in the resultant macromolecules. Consequently it is to be anticipated that the copolymers will show differing distributions of isolated and nearest neighbour paired chromophores relative to the vinylaromatic copolymers examined to date using methyl methacrylate or methyl acrylate as 'spectroscopically inert' comonomer. (ii) Preliminary studies<sup>3</sup> and literature reports<sup>4,5</sup> have indicated that the excimer forming characteristics of the S-A system as detected by steady state spectroscopy are described by a different intramolecular concentration dependent function from that applicable to the photophysics of vinylaromatic methyl methacrylate<sup>1,2</sup> or acrylate copolymers<sup>6</sup>. In this respect, the S-A copolymer system is expected to form an excellent 'test system' for the general applicability of our photophysical reaction scheme<sup>1,2</sup>.

#### Transient Excitation Spectroscopy

Polymers, dissolved in dichloromethane, were excited by the frequency doubled output of a cavity-dumped, mode-locked 4W Argon ion laser (Spectra Physics 166). The monomer decay in the homopolymer is adequately described by a dual exponential function in agreement with previous observations on high molar mass material<sup>7</sup> and polystyrenes and block copolymers over a wide range of effective polystyrene molar masses<sup>7</sup>. At relatively low aromatic contents, decays in monomer and excimer regions are adequately described by dual exponential decay functions. At intermediate aromatic compositions ( $F_A > 0.65$ ), both monomer and excimer decays require triple exponential functions.

If, following previous arguments, the triple exponential decays are consequent upon the existence of an excimer site distribution  $D^*$  and two types of monomer distribution  $M_1^*$  and  $M_2^*$  where  $M_2^*$  is a 'relatively kinetically isolated' chromophore the following observations may be made: (i) Consistent with the data the decays in the monomer region will be dominated at low aromatic contents by those of  $M_1^*$  and  $M_2^*$  (dissociation of excimer being a relatively unimportant process in styrene polymers) and in the homopolymer by  $M_1^*$  and  $D^*$ . Dual exponential fits will result. (ii) The decay parameter,  $\lambda_3$ , associated with the excimer, is within experimental error, invariant across the composition range. (iii)  $\lambda_3$  is consistently greater in the region of monomer decay compared to that obtained from the excimer decay reflecting the sampling of the total excimer distribution by the monomeric sites resultant upon excimer dissociation. (iv) Consistent with the photophysical kinetic scheme adopted, appropriate combinations of the decay parameters  $\lambda_1$  and  $\lambda_2$  prove to be functions of

the term  $F_{ss}$  (as opposed to other microcompositional descriptors) and allow extrapolation to yield individual rate constants such as  $ak_{DM}$ ,  $k_{MD}$ ,  $k_M$  and  $k_D$ , from which the intramolecular concentration dependence has been removed.

### Conclusions

The styrene acrylonitrile copolymer system has been shown to exhibit a different dependence of its photophysical behaviour from other vinyl-aromatic copolymers studied to date. The system has consequently proved to act as a good test of the validity of the photophysical reaction scheme which we have proposed for the description of the processes governing intramolecular excimer formation in macromolecules containing one type of excimer species.

### Anisotropy

The difficulties in resolving multiple components in time-dependent fluorescence anisotropy in complex systems such as tagged polymers have led us to a critical evaluation of simple systems in order to give some idea of the limits of accuracy of such measurements.

For a spherical molecule rotating freely in a fluid medium, the anisotropy exhibits a single component, related to the rotational diffusion coefficient. It would be pertinent to summarise under what conditions

$$r(t) = \frac{I_{||}(t) - I_{\perp}(t)}{I_{||}(t) + 2I_{\perp}(t)} \quad (1)$$

more than one component would be expected, and to comment upon how realistic it is to expect to extract such components in a real experiment. Given that anisotropy is derived from the difference between fluorescence decays recorded parallel and perpendicular to excitation radiation, with consequent reduction in the signal to noise ratio, it is unrealistic to extract, for example, the five components (not however all independent) anticipated from the rotation of an asymmetric molecule around the three Cartesian axes. It might in favourable cases be possible experimentally to resolve two components, and this has been done, for example, in the case of perylene,

$$D(t) = I_{||}(t) - I_{\perp}(t) \quad (2)$$

which rotates as a disk (oblate) with a slip boundary condition, in which case the anisotropy takes the form where  $\theta_A$  and  $\theta_E$  are the polar

$$r(t) = \frac{2}{5} e^{-6D_{\perp}t} \sum_{k=0}^{\infty} e^{-k^2(D_{||} - D_{\perp})t} F_k(\theta_A, \theta_E, \phi_{AE}) \quad (3)$$

angles between the absorption and emission dipoles, and the unique symmetry axis and where  $\phi_{AE}$  is the difference in their azimuthal angles.

$$F_0 = P_2(\cos \theta_A) P_2(\cos \theta_E) = \frac{1}{4} (3 \cos^2 \theta_A - 1)(3 \cos^2 \theta_E - 1) \quad (4)$$

$$F_1 = \frac{3}{4} \sin 2\theta_E \sin 2\theta_A \cos 2\phi_{AE} \quad (5)$$

$$F_2 = \frac{3}{4} \sin^2 \theta_E \sin^2 \theta_A \cos^2 \phi_{AE} \quad (6)$$

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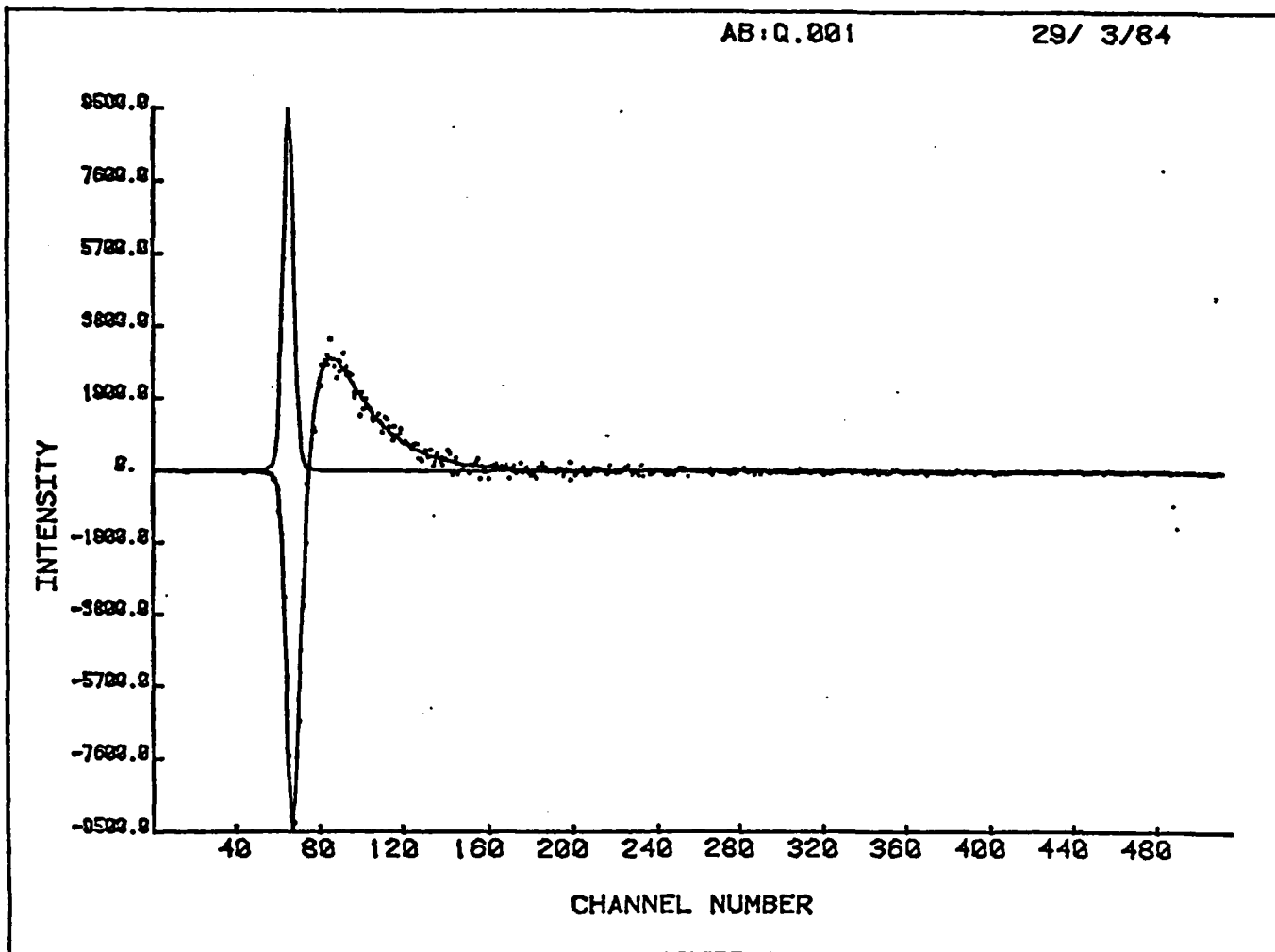


Figure 1

Time-dependent fluorescence anisotropy of perylene in glycerol/water mixture. (See text).

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In perylene both  $\theta_A$  and  $\theta_E = \pi/2$ , and thus  $r(t)$  simplifies to

$$r(t) = 0.10 e^{-6D_{\perp}t} + 0.30 \cos 2\phi_{AE} e^{-(2D_{\perp} + 4D_{\parallel})t} \quad (7)$$

The raw data for an 85% glycerol/15% V/V water solvent mixture are shown in Fig. 1 to be complex. The initial negative anisotropy occurs because at 257.25 nm excitation, the absorption (to  $S_2$ ) and emission (from  $S_1$ ) dipoles are orthogonal. The cross-over to a positive value is due to the fact that rotation within the plane of the aromatic rings is faster than that out-of-phase i.e.,  $D_{\parallel} > D_{\perp}$ .

Analysis of Fig. 1 together with the sum function ( $S(t) = I_{\parallel} + 2I_{\perp}(t)$ ) which yielded a decay time identical to that measured at the magic angle of  $5.17 \pm 0.13$  ns, gave for the anisotropy satisfying exact agreement with Equation (7), and yielding values of  $D_{\perp}$ ,  $D_{\parallel}$  of  $3.37$  and  $16.6 \times 10^7 \text{ s}^{-1}$  respectively, and for  $\phi_{AE}$ ,  $82^\circ$ .

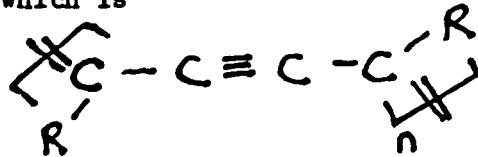
### Conclusion

The results of this study give us greater confidence in the ability to extract complex anisotropies in copolymers, presently being carried out.

### Structure Fluorescence Correlation in Poly(diacetylenes)

The aim of this part of the project is to establish the nature, dynamics and decay of excitons in polydiacetylenes. Little work (both experimentally and theoretically) has appeared concerning the behaviour of excitons in conjugated polymers. This knowledge is an important factor in a proper understanding of the interaction of free carriers and excitons, which have been shown in other materials to form bound states. The project thus necessitates experimentation to elucidate the conformation of PDA chains using light scattering, nmr spectroscopy, Raman spectroscopy; and then separate measurements of fluorescence and absorption spectra, and fluorescence decay measurements. The latter proved difficult, and this aspect of the project remains to be completed fully.

The PDA backbone has in the ground state a conjugated  $\pi$ -bond structure, the absorption of which is



excitonic in character. Macroscopic single crystals of PDA do not fluoresce, but deformed systems have been shown to fluoresce weakly. Thus PDA solutions and films have fluorescence yields in the range 0.001 - 0.003, and absorption spectra in the range 1.6 to 2.5 eV, depending upon the degree of disorder. Absorption and fluorescence spectra, from this work have been reported in three publications<sup>9,10,11</sup> in terms of chromism observed; there being several phases observed, a Y-phase, R-phase, and B-phase.

On the basis of the data presented above one can postulate a correlation relating order/disorder, fluorescence yield, absorption profiles and extent of exciton-phonon coupling for the different backbone conformations.

Y-phase

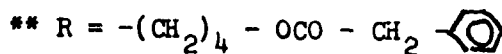
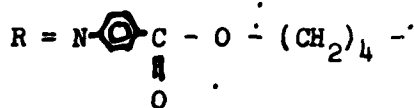
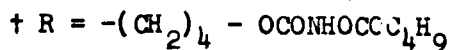
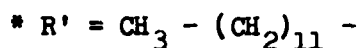
$460 \pm 10 \text{ nm}$

$Y^H$ -exciton

|         |                 |                         |
|---------|-----------------|-------------------------|
| R-phase | 535 $\pm$ 10 nm | R <sup>H</sup> -exciton |
| B-phase | 610 $\pm$ 15 nm | B <sup>H</sup> -exciton |

The different phases will be labelled with different type of excitons associated with them. The H superscript refers to room temperature excitons. The B<sup>H</sup>-excitons are expected to be very anisotropic or coherent since PDA crystals are highly anisotropic. The other excitons are expected to be less coherent so that exciton-migration may occur by hopping as well. Of course, the extent to which these Y<sup>H</sup>-excitons are localised is not known; probably over 6-7 repeat units. (Fig. 2 summarises the conclusions).

X-ray studies reveal that the macroscopic single PDA crystals have the sidegroups attached to the backbone in an all-trans conformation. If one compares the R-phase absorption spectra 4BCMU<sup>†</sup> and 9PA\*\* obtained after addition of a poor solvent (Hexane) to a solution of good solvent (CHCl<sub>3</sub>), it is noticed that the relative intensities of the vibrational sidebands (V.S.'s) compared to the zero-phonon bands (Z.P.B.'s) are different. We can say that the 4BCMU is more ordered than the 9PA since we know, from resonance Raman studies, that the more ordered polymer backbones have weakly associated V.S.'s. Recent studies on PPC\* PDA clearly show that red polymer solutions have different absorption profiles (viz. the ratio of the heights of the Z.P.B.'s to the V.S.'s). Nevertheless, all these spectra show an absorption peak or shoulder at 540 nm. However, one would expect a decrease of the fluorescence yield with an increase in the exciton-phonon interaction. A competition therefore exists between the extent of the exciton-phonon interaction and fluorescence yield or the extent of the localisation of the exciton wavefunction. Despite this competing process, the fluorescence quantum yield measured for the Y + R phases are low, ca. 0.1 - 0.3% and less than 10<sup>-4</sup> for the B-phase. The non-radiative relaxation process in PDA chains is therefore extremely efficient. The nature of this non-radiative decay channel is still not known. One possibility is the occurrence of rapid interpretation crossing from the singlet exciton to the lowest triplet exciton. Results for other linear conjugated macromolecules suggest that this rapid interpretation crossing can only occur by singlet-triplet fission with the resulting triplets likely to decay rapidly by phonon emission since the backbone phonons range up to 0.25 eV in energy.

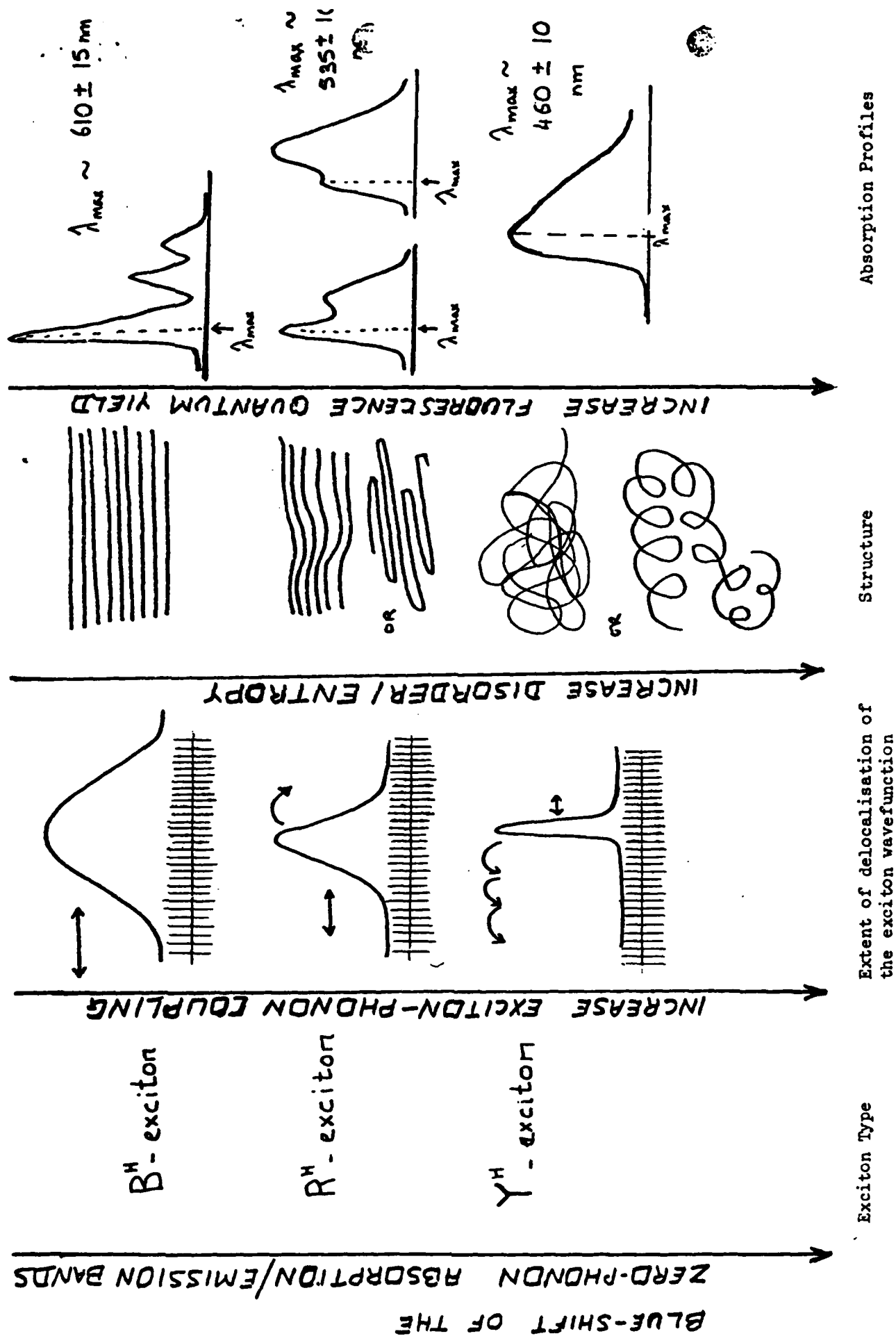


### Conclusion

Further work on the time-resolution of fluorescence of PDA's on a 10 - 100 ps timescale, is in progress.

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CORRELATION RELATING DEGREE OF ORDER, FLUORESCENCE QUANTUM YIELD, ABSORPTION/EMISSION PROFILES AND EXCITON-PHONON INTERACTION

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2.

The remainder of the contract will be carried out on the work specified originally, and described in the report above.

Papers Published or Presented During the Grant Period

1. 'Chromism of a poly(diacetylene) with weakly interacting sidegroups'. S.D.D.V. Rughooputh, D. Phillips, D. Bloor and A.J. Ando, Polymer Communications, 25, (in press).
2. 'Optical absorption and luminescence in poly(4,4'-diphenylene di-phenyl vinylene'. W.J. Feast, R.H. Friend, M.E. Horton, I.S. Millichamp, D. Phillips and G. Rumbles, Synthetic Metals, 10, 181-191, (1985).
3. 'Excited states in polymers'. D. Phillips in 'Excited state probes', Eds., A.G. Szabo and C. Mascotti, Plenum Press, (in press).
4. 'Spectroscopic studies of poly(diacetylene) solutions and glasses of an H-bonding polymer', S.D.D.V. Rughooputh, D. Phillips, D. Bloor and D.J. Ando, Chemical Physics Letters, (in press).
5. Fluorescence polarisation in poly(styrene), J.L. Gardette and D. Phillips, Polymer Communications, (in press).

3.

The principal investigator lectured on the subject of this research at a NATO-ASI held in Acireale, Sicily in September.

4.

Dr J.L. Gardette left the laboratory in September 84 to return to his permanent employment at CNRS Laboratoire de Photocchimie, University de Clermont-Ferrand, France.

Dr Andrew Langley was appointed to a post-doctoral position associated

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