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ENERGY MIGRATION MOTION AND ORDER IN SYNTHETIC POLYMERS
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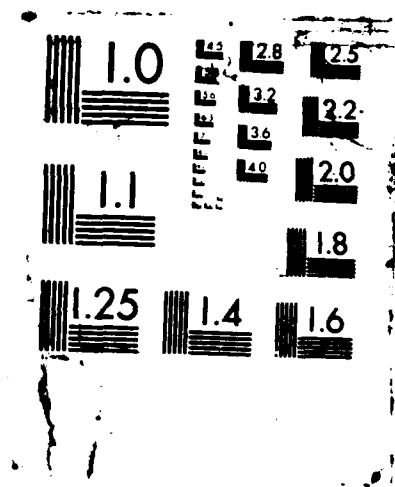
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ENERGY MIGRATION, MOTION AND ORDER IN
SYNTHETIC POLYMERS

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Contract No. DAJA-87-C-0031

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First Periodic Report

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The first two months of this grant have been spent in recruiting staff to the project, and ordering equipment with which to construct the evanescent wave induced fluorescence (EWIF) spectrometer. In addition some steady state fluorescence work on poly(diacetylenes) has been carried out.

Personnel Recruited:

Dr Garry Rumbles (1 August 1987), Ph.D., University of London.

Mr Alan Brown (May 1987), B.Sc. First Class Honours, University of Southampton.

Dr. Rumbles has just returned from the University of California Irvine, and is exceptionally well qualified for this project. Mr Brown is a Ph.D. student of outstanding merit.

Equipment Ordered:

In the early phase of this project, the following items of equipment, funded in part only from this contract, have been ordered.

- | | | |
|-------|--|-----------|
| (i) | 'Antares' Coherent Radiation Mode-locked YAG laser | \$170,000 |
| (ii) | Perkin-Elmer LS-5B spectrofluorimeter | \$20,000 |
| (iii) | 7T11 Sampling Trigger Unit and 7S11 Sampling Unit,
Type S4 Sampling Head. | |
| | 7603 Tektronix Sampling Oscilloscope. | \$20,000 |

Other smaller items of optical equipment necessary for the construction of the EWIF Spectrometer have also been ordered.

It is thus anticipated that the construction of the spectrometer can be begun in the next report period (six months). The principle is shown in Appendix 1.

✓ *Spectroscopy of Urethane-substituted poly(diacetylenes)*
Poly(diacetylenes) may adopt various configurations (Figure 1) in different media, and changes in configuration may be revealed by optical spectroscopy. In PDA crystals and films, the order can be changed by temperature and by compressive stress. In PDA solutions, a change in temperature or solvent leads to a change in the order of the polymer, [1-4].

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TABLE 1

Table 1 shows some common PDA sidegroups and states in what forms they are commonly used.

Abbrev.	Formula	n	forms	solvent
<i>nBCMU</i>	$(\text{CH}_2)_n \text{OCO NH CH}_2 \text{CO C}_4\text{H}_9$	2,3,4,9	Sol, film	CHCl_3
<i>nECMU</i>	$(\text{CH}_2)_n \text{OCO NH CH}_2 \text{CO C}_2\text{H}_5$	3,4	Sol, film	CHCl_3
<i>nKAU</i>	$(\text{CH}_2)_n \text{OCO NH CH}_2 \text{CO}_2^- \text{K}^+$	3,4	sol	H_2O
<i>nKA</i>	$(\text{CH}_2)_n \text{CO}_2^- \text{K}^+$	2,3	sol	H_2O
<i>9PA</i>	$(\text{CH}_2)_9 \text{OCO CH}_2 \text{C}_2\text{H}_5$		sol	CHCl_3
<i>TS</i>	$\text{CH}_2 \text{OSO}_2 \text{C}_6\text{H}_4 \text{CH}_3$		crys sol	$\text{C}_6\text{H}_5\text{NO}_2$
<i>TCDU</i>	$(\text{CH}_2)_4 \text{OCO NH C}_6\text{H}_5$		crys	
<i>10H</i>	$\text{R}' = \text{CH}_2\text{OH}$ $\text{R} = \text{CH}_3$		film crys (fibres)	

cont'd

Table 1 shows poly(diacetylenes) of fundamental and commercial interest. We have initiated a spectroscopic study of the BCMU's substituted in the 2,3,4, and 9 positions (Table 1), the purpose being to correlate observed spectral features with the structures illustrated in Figure 1. Thus in the linear conjugated segments (LCS) or the wormlike structures, the concept of effective conjugation is introduced to explain red/blue shifts in absorption: a red shift in the absorption corresponds to an increase in the conjugation, either by the straightening of a wormlike structure or by the unravelling of a coil to form a rod.

Using this type of argument, spectra of similar PDA's can be compared.

This study has just begun, but the initial results are illustrated in Figures 2 and 3.

A complete discussion of the findings will be presented in the second periodic report.

Figure 1

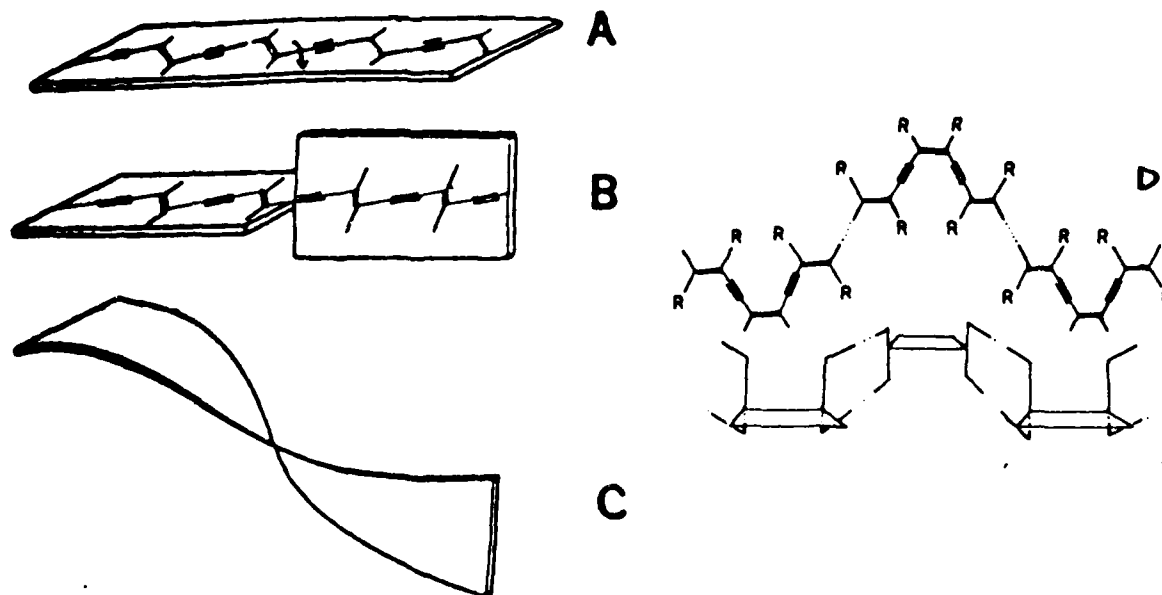


Figure 2

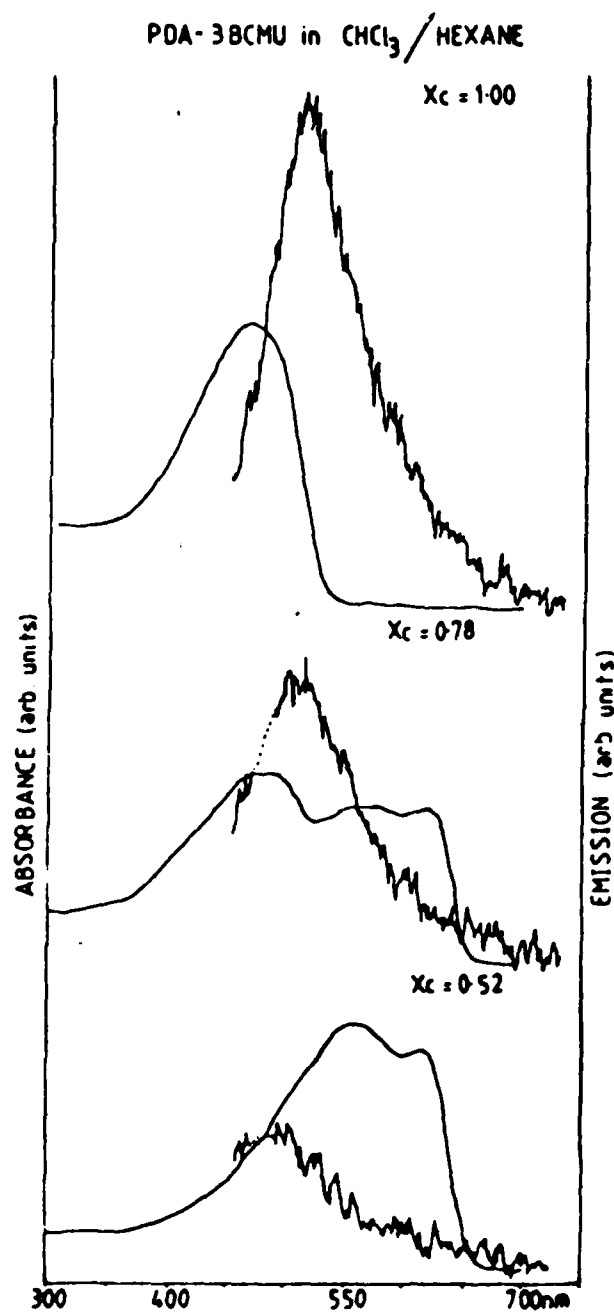


Figure 3 (a)

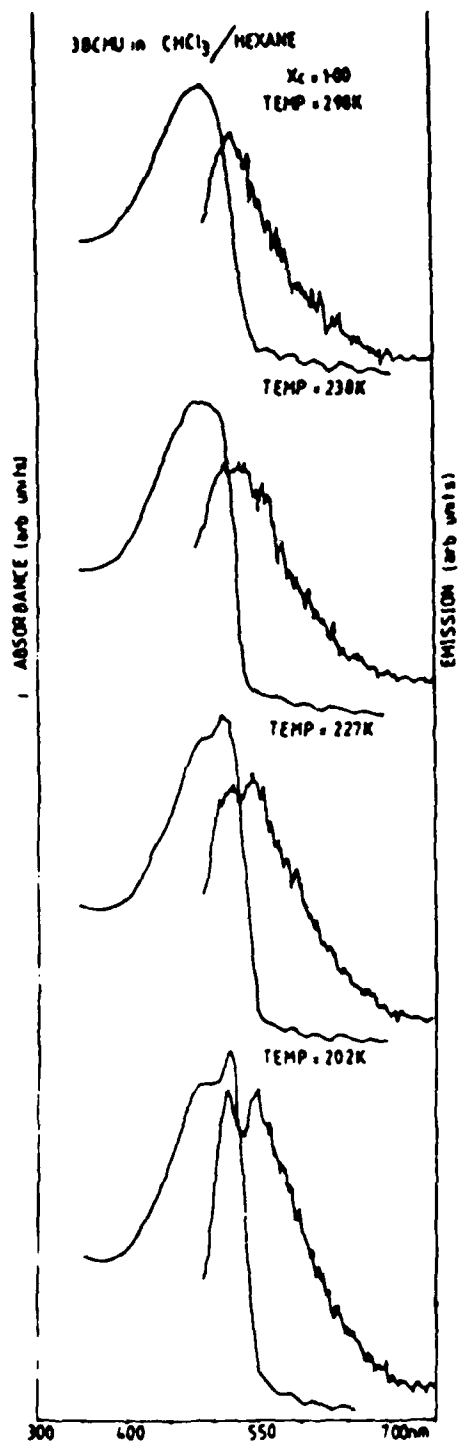


Figure 3 (b)

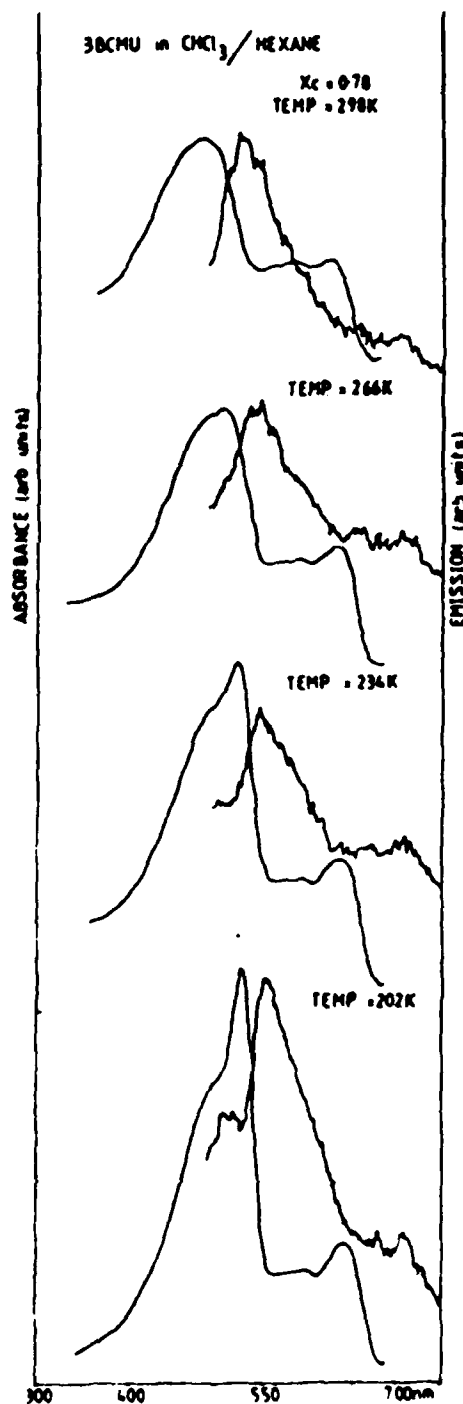


Figure 3 (c)

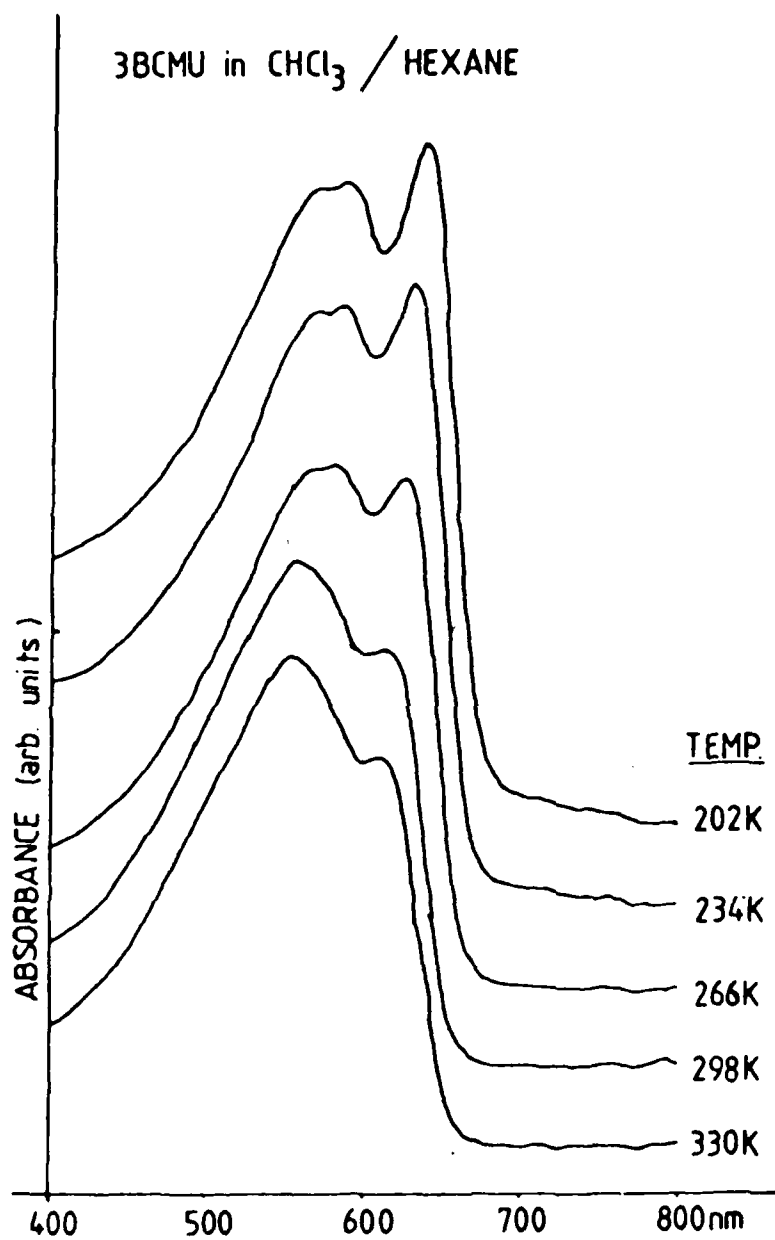


Figure Captions

Figure 1 *Structures of poly(diacetylenes)*

- A** Planar, highly ordered, rigid rod.
- B** Linear conjugated segments.
- C** Wormlike structure.
- D** Coiled structure with large number of cis double bonds, but some trans present.

Figures 2 and 3 detail the chromism of 3BCMU solutions:

Figure 2 Solvatochromism of 3BCMU in CHCl_3 /Hexane - absorption and emission.

Figure 3 (a) Thermochromism of 3BCMU with $X_c = 1.00$
 (b) Thermochromism of 3BCMU with $X_c = 0.78$
 (c) Thermochromism of 3BCMU with $X_c = 0.52$
 - absorption only.

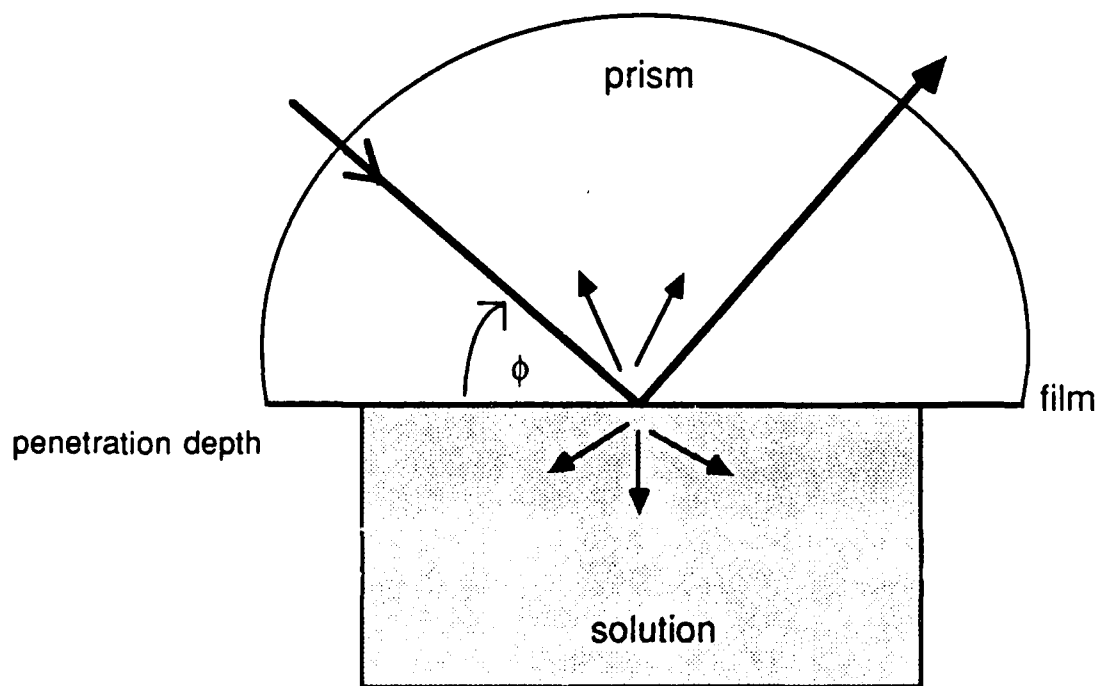
Notice the peaks, depending on solvent or temperature, occurring at 470 nm, 530 nm, 560 nm and 640 nm in absorption, and 520 nm and 540 nm in emission. Unlike 4BCMU, the low X_c form is not fluorescent, and the drop in fluorescence is seen in Figure 2. A low temperature glass emission has also been observed in 3BCMU at about 620 nm.

Appendix 1

Evanescent Wave Induced Fluorescence

This new technique [1] can be used to probe the interaction of PDA solutions and other polymers with repulsive and attractive film/surfaces interactions. By controlling the angle of incidence of a probing laser through a prism, such that the beam is 'totally' internally reflected at the prism/solution interface, the exact penetration of the evanescent wave set up can be determined (Figure A1). The fluorescence from this region can be collected and information on the polymer form and concentration in this region can be derived.

Figure A1



[1] C.Allain, D.Aussere, and F.Rondelez, *Phys.Rev.Lett.*, 1982, 49, 1694.

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