Chiroptical spectroscopic studies of polydiacetylenes

Alex F. Drake and Peter Udvarhelyi
Department of Chemistry, Birkbeck College, 20 Gordon Street, London WC1H 0AJ, UK

David J. Ando*, David Bloor and Jasvinder S. Obhi†
Department of Physics, Queen Mary College, Mile End Road, London E1 4NS, UK

and Stephen Mann
GEC–Marconi Research Centre, West Hanningfield Road, Great Baddow, Chelmsford CM2 8HN, UK

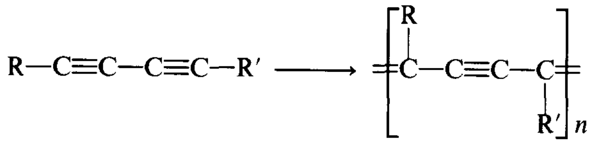
(*Received 15 September 1988; revised 27 January 1989; accepted 2 March 1989*)

A new class of optically pure, chiral, soluble polydiacetylenes have been synthesized. These show both solvato- and thermo-chromism, with behaviours similar to those reported for the well-studied analogous achiral *m*-butoxycarbonylmethylurethane (*m*BCMU) class of polydiacetylenes. Although it is now generally agreed that this chromic behaviour is a direct result of the order–disorder transformation of the dissolved polymer, there still remains disagreement about the conformation and state of aggregation of the various forms. The chiral structure of these new polymers allows these general questions to be addressed through the use of circular dichroism spectroscopy. We report measurements obtained on both solution and thin film samples. These have allowed us to characterize more precisely the various states involved.

(Keywords: polydiacetylene; spectroscopy; characterization; conformation)

INTRODUCTION

Many disubstituted diacetylenes undergo solid state (topochemical) polymerization under the influence of heat, pressure, light or ionizing radiation to form highly perfect, macroscopic, polymer single crystals[1,2] according to *Scheme 1*. However, owing to the insolubility of most polydiacetylenes (PDAs) in common organic solvents, attempts to study their solution properties remained unsuccessful until 1978 when the appropriate choice of sidegroups led to the synthesis of the first class of soluble PDAs. A number of different series of soluble polymers now exist, but of these, the class (**I**) containing the symmetrically substituted butoxycarbonylmethylurethane (BCMU) side group, first reported by Patel[3], has been most extensively studied.



$$\mathrm{R{-}C{\equiv}C{-}C{\equiv}C{-}R' \longrightarrow \left[{=}\overset{R}{C}{-}C{\equiv}C{-}\underset{R'}{C}{=}\right]_n}$$

Scheme 1

I $\mathrm{R = R' = {-}(CH_2)_mO.CO.NH.CH_2.CO.O.(CH_2)_3CH_3}$

*m*BCMU, where $m = 2, 3, 4, 6, 9$

The solvato- and thermo-chromism displayed by these soluble polymers, however, has continued to attract a considerable amount of research effort and controversy. While there is now general agreement that this chromism is a direct feature of the order–disorder transformation of the dissolved polymer, the nature of the polymer conformation and state of aggregation in these phases still encourages active debate[4,5].

In good solvents, e.g. chloroform, a yellow solution is obtained[6]. The chain structure has in this case been described either as a random coil containing sharp discontinuities between linear sequences of the polymer backbone[7] or a worm like chain with only gradual changes in backbone orientation[8]. On addition of a poor solvent, e.g. hexane, or cooling, either a red or a blue polymer is obtained[6]. This transition has been associated with formation of extended polymer chains either as a single chain phenomenon[4] or as a result of aggregation[9]. It has been shown that red and blue forms can exist for a single polymer and that in this instance the red form has disordered side groups[10]. This implies that the red form has an extended but non-planar backbone while the blue form is extended and planar.

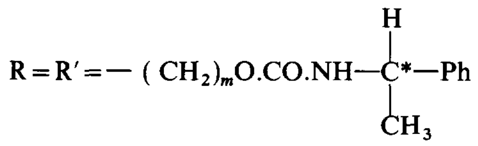
As part of a programme to design new organic materials with potentially useful non-linear optical properties a new class of soluble PDAs containing the symmetrically substituted methylbenzylurethane (MBU) chiral side group (**II**) has recently been synthesized[11]. These optically pure, soluble polymers show both solvato- and thermo-chromism, with features similar to those previously reported for the achiral *m*BCMU analogues. However, the chiral structure of these new PDAs gives us the opportunity to further investigate the nature of the conformational states of the polymers by the use of circular dichroism (c.d.) spectroscopy. In this present work, we have carried out a detailed chiroptical

---

* To whom correspondence should be addressed

† Present address: Department of Physics, University of Nevada, Las Vegas, Nevada 89154, USA

0032-3861/89/061063-05$03.00

II 

$$\mathrm{R=R'=-(CH_2)_mO.CO.NH-\overset{H}{\underset{CH_3}{C^*}}-Ph}$$

$$^*\text{R-(+)-; S-(−)-}$$

$$\left.\begin{array}{l}\text{R-(+)-/R-(+)-; } m\text{RMBU series}\\ \text{S-(−)-/S-(−)-; } m\text{SMBU series}\end{array}\right\} \text{where } m=2, 3, 4, 6, 9$$

spectroscopic investigation of all of the polymers currently available, and subsequent analysis of the results obtained, for both solution and thin film samples, has enabled us to identify and characterize more precisely the various states involved. Selected results are presented in this paper. A preliminary account of this work has already been reported[12].

EXPERIMENTAL

Synthesis

The various urethane monomers were prepared by a condensation reaction between either the R-(+)- or S-(−)- methylbenzyl isocyanate with a suitable diacetylene diol, by a method similar to that used by Patel[3] to produce the related *m*BCMU diacetylenes. A modification of the method of Hay[13], involving the oxidative coupling reaction of terminal acetylenic alcohols, was used to first produce the necessary diols. The polymers were obtained by γ-ray (^{60}Co) irradiation of the respective monomers, using doses of 50 Mrad at room temperature. Unreacted, i.e. residual, monomer was extracted by repeated washing with acetone, the polymer being totally insoluble in this solvent; yields of over 90% conversion to polymer were achieved for a number of the members of this series.

Optical spectroscopy

Circular dichroism spectra were recorded using a JASCO J4OCS CD spectrometer. Ordinary absorption and linear dichroism (l.d.) measurements were made with a Varian 2390 spectrophotometer. A calcite prism polarizer was employed for the l.d. studies.

RESULTS*

We report here our chiroptical spectroscopy measurements of the 9R and 9S enantiomers of the MBU series. Like the other chiral PDAs in this series and the achiral BCMU analogues, these are isolated in the form of fine micro-crystalline powders, by solvent extraction of unreacted monomer from γ-irradiated material, as described above. The addition of solvent, i.e. chloroform, to either the 9R or 9S enantiomer provides a brackish suspension. Gentle heating encourages the formation of a brightly coloured, apparently clear, yellow solution. However, both of these states are in fact highly scattering. In the c.d. spectrometer strong circular intensity differential scattering (c.i.d.s.) is observed (*Figure 1*) with features inside and outside the electronic absorption envelope (550–300 nm) whose shape, sign and intensity are variable, being particularly dependent on the position of the sample cell along the optic axis of the spectrometer[14]. These measurements effectively involve changes in the solid angle of collection of transmitted and scattered light, a feature characteristic of c.i.d.s. This phenomenon has been well characterized for large biological assemblies[15]. Membrane filtration (0.2 μm pore size) further clarifies the yellow solutions which now present no detectable circular dichroism in the 720–340 nm region. This shows unambiguously that the polymer chains adopt a random conformation in the yellow solution. The significance of this result is discussed further below.

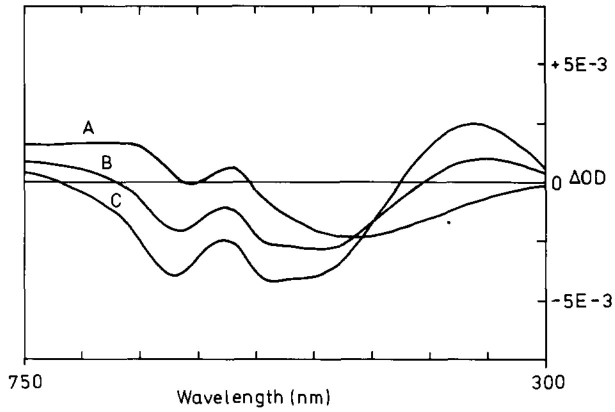


Figure 1 C.d. spectra of 9RMBU polymer scattering solution in chloroform showing variations with position of sample along the instrument optic axis: A, 'near' position, 0.5 cm from sample to photomultiplier (PM); B, 'mid' position, 10 cm from PM; C, 'far' position, 20 cm from PM

The other chiral MBUs are also soluble in chloroform with differing degrees of difficulty. In consequence, we are able to make the general observation that the soluble random form does not display optical activity associated with the visible electronic absorption, for any of these polymers. We wish to emphasize at this point that c.d. spectroscopy provides an excellent technique to identify the random polymer chains expected in a true solution state.

Addition of a non-solvent, e.g. hexane, to filtered solutions of 9R and 9S polymers in chloroform induced the anticipated ordinary absorption changes (*Figure 2*) as has been well established for the achiral BCMU series of soluble PDAs[6–10,16]. This corresponds to a yellow to red colour change of the solutions described above. Strong circular dichroism, lacking c.i.d.s. effects, is now observed (*Figure 3*) which signifies the production of a helical conformation of the polymer. The absence of c.i.d.s. effects indicates that any particles formed are much smaller than the wavelength of light so that filtration at this point would be ineffective. Similar spectra have been recorded for the scattering unfiltered solutions although in this circumstance the induced molecular c.d. is superposed on the c.i.d.s, as can be seen in *Figure 4*.

In an attempt to improve the quality of our spectral data we turned our attention to studies of solid samples. Samples produced as nujol mulls gave c.i.d.s. spectra similar to those found for the scattering solutions with no evidence of the molecular c.d. indicative of the ordered state observed in the solvent mixture (chloroform–hexane).

---

* Unless otherwise indicated, the use of the abbreviations *m*R or *m*S in the text, in all cases, refer to the specific *polymer* enantiomer under discussion.

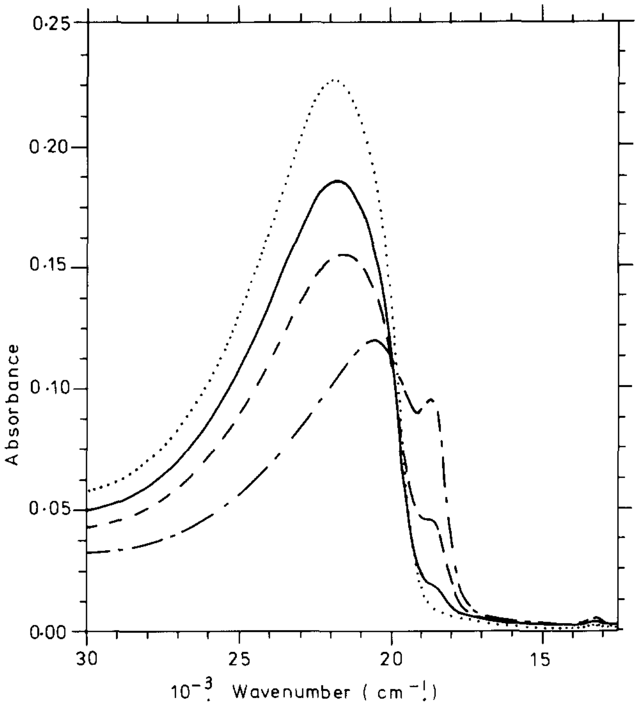


Figure 2 Sequential absorption spectra of 9RMBU polymer in chloroform recorded with increasing addition of hexane: initial $CHCl_3$ solution concentration $\sim 1 \times 10^{-5}$ mol l^{-1}. Spectra shown for $CHCl_3$ mol fractions; (······), 0.86; (———), 0.74; (-----), 0.68; (-·-·-), 0.56

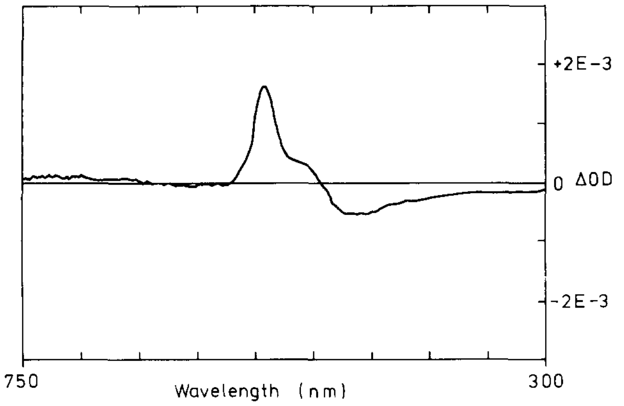


Figure 3 C.d. spectrum of 9RMBU polymer in a filtered chloroform solution (see text), after the addition of hexane to give a 50:50 mixture, % by volume

Polymer films cast from chloroform solution onto glass microscope slides are red in colour and of good optical quality. These gave excellent c.d. spectra (see *Figure 5a* for the 9R species), similar to those of the polymer in chloroform-hexane solvent mixtures. These films did not scatter light, nor were they birefringent: their c.d. spectra were independent of their position along or about the optic axis[14]. Similar results have now been obtained for all of the antipodes of the 2-, 3-, 4-, 6-, and 9-methylbenzylurethane derivatives, and will be reported elsewhere[17].

As discussed below these observations are particularly relevant to our parallel investigations of the optical waveguiding properties of these films, in particular for the 9SMBU polymer[18]. Accordingly we have now measured the spectra of the corresponding high quality films produced by the controlled dipping process[19] that is employed in our waveguiding studies. Again, excellent 'pure' c.d. spectra are observed (*Figure 5b*) similar to that of the polymer in solvent-non-solvent mixtures.

SPECTROSCOPIC ANALYSIS AND CONCLUSIONS

The yellow forms of the 9R and 9S species in filtered chloroform solutions are characterized by a strong ordinary absorption at 456 nm. There is no detectable optical activity associated with the visible electronic absorption of this state. This means that the polymer chains must adopt a random conformation without any locally extended regions. If the latter were to occur they would give rise to c.d. spectra as observed for the red form of the polymer. Thus the model of a worm like chain rather than a sharply kinked chain is favoured by our results.

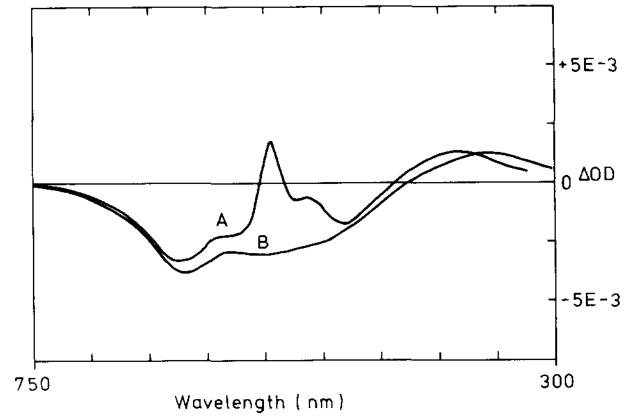


Figure 4 C.d. spectra of 9RMBU polymer in scattering (unfiltered) solutions: A, in chloroform/hexane solvent mixture (50:50 mixture, % by volume); B, in chloroform only

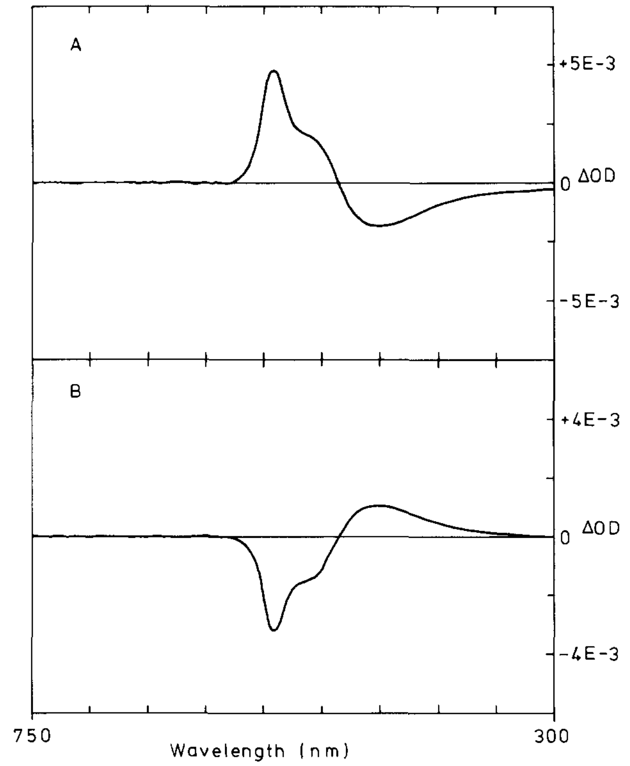


Figure 5 C.d. spectra of 9MBU cast polymer films on glass microscope slides: A, 9R polymer, produced by a simple evaporation technique; B, 9S polymer, high quality film (thickness ~0.4 μm) produced by a controlled dipping process

Upon the addition of the non-solvent, this absorption at 456 nm decreases with the λ_{max} shifting to 488 nm and the emergence of absorption at 538 nm. The underlying c.d. spectrum has two components, but displays three features. A sharp positive differential absorption (for 9R) at 540 nm is followed by a conservative positive bisignate curve with maxima at 525 nm and 465 nm with a crossover close to the ordinary absorption maximum (488 nm). These c.d. observations are reminiscent of exciton coupling although one is left to query the non-conservative nature of the visible absorption manifold as a whole. It is important, therefore, to characterize more clearly the individual c.d. components.

Oriented polymer films of 9R can be obtained by rubbing, as previously reported for the achiral BCMU polymers[20]. These oriented films are highly dichroic about the stroke axis. Dichroic rations $(A_{\parallel} - A_{\perp}/A_{\parallel} + A_{\perp})$ in excess of 10^{-2} are readily achieved. Preliminary l.d. studies indicate differing polarizations for the two c.d. components. The higher energy pair are orthogonally polarized as exciton coupling requires. The sharp low energy c.d. component does not appear to display any associated l.d. This suggests a different molecular origin for the high energy c.d. couplet and the low energy single c.d. band.

This latter conclusion is reinforced by low temperature c.d. spectra obtained for 9R polymer solutions. On cooling, the sharp low energy c.d. component becomes intense with respect to the higher energy c.d. couplet. We have also noted relative intensity variations between the two c.d. band systems when comparing solutions and various films. However, the relative magnitudes of the two c.d. couplet components is always constant and conservative.

Both the l.d. and low temperature c.d. observations will be reported in detail elsewhere[17]. However, they do enable us to propose the existence of more than one state of order for these chiral PDAs.

The sharp single low energy c.d. band is reminiscent of the J-band which is often observed with aggregated dye molecules in solution[21]. This is said to be derived from an excitation to an excited state delocalized over the whole aggregate. This certainly explains its lack of l.d. The higher energy c.d. couplet we ascribe to a classical exciton coupling either between or within discrete polymer chains.

The other members of the chiral MBU series (2-, 3-, 4-, and 6- species) have also been studied, and all seem to show similar behaviours to the 9-MBU derivatives. There is no detectable c.d. associated with the random form and a multi-component c.d. spectrum associated with the helical form[17].

On the basis of these results and comparisons we conclude that the red polymer chains have an extended, helical form associated in either ordered or glassy aggregates. Thus the red solutions consist of either strongly or loosely associated polymer, i.e. particles, and a weak gel network. This conclusion is supported by recent work on neutron scattering[22] and shear flow[23]. The former reveals particle formation, while the latter indicates the presence of a weakly interacting network. Thus the red solutions are inhomogeneous, and not a homogeneous solution. The loosely aggregated chains are able to order and form particles at lower temperatures, i.e. an equilibrium exists between the two forms at room temperature. Evidence for this has been found in recent studies of 9BCMU[24]. Comparison of the ordinary absorption spectra of chiral and achiral BCMUs provide additional evidence for similar behaviour in both classes of polymer.

Low optical loss has been observed in 9SMBU films tested as slab and channel optical waveguides[18]. This indicates either a glassy morphology or a distribution of small ordered particles, with dimensions less than the wavelength of light, in a glassy matrix. The c.d. spectra show that the latter is correct. Thus on solidification the polymer films ‘freeze in’, to a large extent, the structure which exists in the inhomogeneous ‘solution’.

Thus these studies of chiral PDAs lend support to the view that the disorder–order transition in PDAs is from a worm like chain to extended chains in both strong and weak association.

ACKNOWLEDGEMENTS

Part of this work was supported by funding from the Science and Engineering Research Council (SERC) and the Department of Trade and Industry under the Joint Opto-Electronic Research Scheme. The SERC and the University of London (ULIRS) are acknowledged for their funding of the Chiroptical Spectroscopy and Optical Spectroscopy Research Services, respectively. One of us, J.S.O., thanks the SERC for a studentship. We wish to thank Dr D. Bishop of BDH Chemicals, Poole for supplying a number of the precursor terminal acetylene alcohols, and also Dr N. Carr of Plessey Research, Caswell, for providing the 9SMBU controlled dipped thin film. Dr P. Clay of Imperial College, London, is thanked for his help with γ-irradiation of the monomers. These chiral diacetylene materials are the subject of a patent application by the General Electric Company plc[11].

REFERENCES

1 ‘Polydiacetylenes’ (Eds. D. Bloor and R. R. Chance), Martinus Nijhoff, Dordrecht, 1985

2 Bloor, D. ‘Developments in Crystalline Polymers’ (Ed. D. C. Bassett), Applied Science, London, 1982, p. 151

3 Patel, G. N. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1978, **19**, 154

4 Lim, K. C., Sinclair, M., Casalnuovo, S. A., Fincher, C. R., Wudl, F. and Heeger, A. J. *Mol. Cryst. Liq. Cryst.* 1984, **105**, 329

5 Wenz, G., Muller, M. A., Schmidt, M. and Wegner, G. *Macromolecules* 1984, **17**, 837

6 Patel, G. N., Chance, R. R. and Witt, J. D. *J. Chem. Phys.* 1979, **70**, 4387

7 Shand, M. L., Chance, R. R., LePostollec, M. and Schott, M. *Phys. Rev. B* 1982, **25**, 4431

8 Allegra, G., Brückner, S., Schmidt, M. and Wegner, G. *Macromolecules* 1986, **19**, 399

9 Muller, M. A., Schmidt, M. and Wegner, G. *Makromol. Chem., Rapid Commun.* 1984, **5**, 83

10 Bloor, D., Ando, D. J., Obhi, J. S., Mann, S. and Worboys, M. R. *Makromol. Chem., Rapid Commun.* 1986, **7**, 665

11 Ando, D. J. and Mann, S. British Patent Application No. 8714511, 1987

12 Ando, D. J., Bloor, D., Drake, A. F., Udvarhelyi, P. and Mann, S. Poster presentation (No. 18) at Macro-Group UK Meeting ‘Optically Active (Chiral) Polymers’, University of Lancaster, 16 March, 1988

13 Hay, A. S. *J. Org. Chem.* 1962, **27**, 3320

14 Obhi, J. S. PhD thesis, University of London, 1987

15 Dorman, B. P., Hearst, J. E. and Maestre, M. F. *Methods Enzymol.* 1973, **270**, 267

16 Ando, D. J., Bloor, D., Bedford, S. N., Obhi, J. S. and Mann, S. 'Integration of Fundamental Polymer Science and Technology—2' (Eds. P. J. Lemstra and L. A. Kleintjens), Elsevier Applied Science, Barking, Essex, UK, 1988, pp. 173–178

17 Drake, A. F., Ando, D. J. and Bloor, D., in preparation

18 Mann, S., Oldroyd, A. R., Bloor, D., Ando, D. J. and Wells, P. J. 'Non-Linear Optical Properties of Organic Materials' (Ed. G. Khanarian), *Proc. SPIE 971,* International Society for Optical Engineering, Bellingham, 1988, pp. 245–251

19 Ulrich, R. and Weber, H. P. *Appl. Opt.* 1972, **11**, 428

20 Casalnuovo, S. A., Lim, K. C. and Heeger, A. J. *Makromol. Chem., Rapid Commun.* 1984, **5**, 77

21 Gardner, B. J. PhD thesis, University of East Anglia, 1967

22 Rawiso, M., Aime, J. P., Fave, J. L., Schott, M., Muller, M. A. Schmidt, M., Baumgartl, H. and Wegner, G. *J. Phys. France* 1988, **49**, 861

23 Taylor, M. A., Batchelder, D. N. and Odell, J. A. *Polym. Commun.* 1988, **29**, 253

24 Bloor, D., unpublished results