The coil to rod transition in polydiacetylenes: a kinetic study

M. A. Taylor* and J. A. Odell
H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

and D. N. Batchelder
Department of Physics, Queen Mary College, Mile End Road, London E1 4NS, UK

and A. J. Campbell
Department of Materials, Queen Mary College, Mile End Road, London E1 4NS, UK

(*Received 11 August 1989; accepted 25 September 1989*)

The kinetics of the coil to rod transition for polydiacetylene solutions have been followed as a function of concentration and molecular weight. The results indicate that the transition is a single chain phenomenon which is not mediated by the diffusion of molecules towards each other to form intermolecular contacts. The spectral changes observed at the transition can be interpreted in terms of the collapse of isolated molecules onto themselves, possibly forming regular intramolecular contacts.

(Keywords: kinetics; polydiacetylene; coil-to-rod transition; Raman spectroscopy)

INTRODUCTION

Soluble polydiacetylenes (PDAs) exhibit chromism as a function of solvent quality[1]. This chromism is related to structural features of the molecule in solution. In a good solvent, such as trichloromethane or hot toluene, the polymer appears yellow and behaves as a worm-like coil. Reducing the solvent quality, e.g. by cooling the toluene to room temperature, causes a dramatic colour change to red or blue. The chains are thought to uncoil and assume a more extended and highly conjugated rigid-rod type conformation[2]. The word extended is used in this paper to indicate a stiff and substantially extended molecule rather than a molecule which is straight over its full contour length. Wegner and coworkers propose, on the basis of light scattering data, that, in the extended form, molecules associate in solution to form a suspension of aggregates, each consisting of up to 1000 molecules[3]. In contrast, Heeger and coworkers believe that aggregation only occurs above the critical concentration for gelation[2]. Recent neutron scattering data[4] indicate that the yellow solutions are worm-like coils and that the red and blue solutions are indeed large aggregates of extended molecules. The role of aggregation in the coil to rod transition has also been investigated in our laboratory at Bristol[5]. Aggregation of the extended form was studied using an elongational flow technique, which indicated loosely bound aggregates with a conformational relaxation time as large as 4 s, independent of concentration. In addition, Chance and co-workers have some evidence to suggest that aggregation occurs following conformational changes at the transition[6]. This was apparent from dynamic light scattering measurements which indicate a change in hydrodynamic radius associated with formation of macroscopic aggregates. This process is distinct from and subsequent to colour change associated with the transition. These studies are based on the polymers 3BCMU and 4BCMU, where BCMU indicates a butoxycarbonyl methylurethane sidegroup attached to the polydiacetylene backbone.

There has been considerable discussion in the literature on the causes and nature of the conformational transition. It is now clear that solutions may consist of either isolated coils or aggregated extended molecules, but a fundamental question remains about the role of aggregation; it is not known if aggregation is the cause of the transition or if it is just a consequence. Indeed, aggregation may not be necessary for the transition to occur. Relevant data may be obtained from a kinetic study of the transition. Any aggregation must involve the diffusion and subsequent contact of a number of molecules. If the relative proportions of the extended and coil forms can be measured, the kinetics of the transition can be related to variables such as concentration and molecular weight, which would in turn influence the rate of diffusion and molecular contact. In this way, the role of aggregation in the transition may be identified. One such study has been reported by Chance and coworkers[7], who used a stopped flow spectrophotometer to follow the progress of the transition after the rapid addition of the non-solvent hexane to a solution of 3BCMU in trichloromethane. The proportion of the extended form increased logarithmically with time over the range 1 ms to 1000 s and exhibited no concentration dependence over the range 6×10^{-6} to 6×10^{-4} mol l^{-1} (concentrations are expressed in moles of repeat units). Chance concluded that the transition proceeds as a single chain phenomenon independently of any aggregation.

We have completed a more extensive study using Raman spectroscopy to follow the transition kinetics for a range of molecular weights. In addition, the use of a very sensitive low light level detection system allowed us

---

* To whom correspondence should be addressed

0032-3861/90/061116-06

to extend our study to concentrations as low as 3×10^{-8} mol l^{-1} (1.5×10^{-5} g l^{-1}), which were previously considered beyond the range of current experimental techniques.

The transition can be conveniently initiated by rapid cooling of solutions in toluene. For this purpose we have adopted 4BCMU as a model system for study; 3BCMU proved to be rather insoluble in hot toluene and tended to precipitate from solution at room temperature over a timescale of minutes. 4BCMU dissolved much more readily and significant precipitation only occurred over a much longer timescale.

EXPERIMENTAL

4BCMU was synthesized and polymerized in the usual manner[8]. Polymerization was achieved using 3 Mrad of γ (^{60}Co) radiation and low molecular weight residues were removed by solvent extraction.

The stock material was dissolved in trichloromethane and treated in an ultrasonic bath for various times to produce samples with reduced molecular weights. After treatment, the solutions were stabilized by the addition of the radical scavenger triethylamine to prevent any spontaneous degradation. Molecular weight data were then obtained using a gel permeation chromatography (g.p.c.) system equipped with a high performance ultraviolet detector. The trichloromethane was removed under vacuum and the samples were then redissolved in hot toluene at a range of concentrations.

The solutions were maintained at 90°C on a water bath and were transferred in turn to the kinetic apparatus shown in *Figure 1*. Hot solution was drawn into a capillary tube of 2 mm bore mounted in front of a Raman spectrometer. The capillary was placed in a jetstream from a compressed air line to increase the cooling rate of the solution and the cooling function was determined by a thermocouple (*Figure 2*). A survey of the literature reveals that the transition temperature when cooling 4BCMU in hot toluene is centred around 66°C[5,9] and can be as low as 55°C (Reference 10). Accordingly, our apparatus is capable of promoting the transition within 10 s of induction of solution into the capillary.

The capillary was illuminated via a ×10 objective with 50–100 mW of radiation from an argon ion laser tuned to 514.5 nm. Scattered radiation was passed through a dielectric filter to remove Rayleigh scattering and dispersed by a single grating onto a cooled charge-coupled device low light level imaging system[11]. The dedicated software and readout electronics were used to record up to 30 spectra in rapid succession after induction of the sample into the capillary. In this way, the transition was initiated by the cooling of the solvent and its progress could be followed.

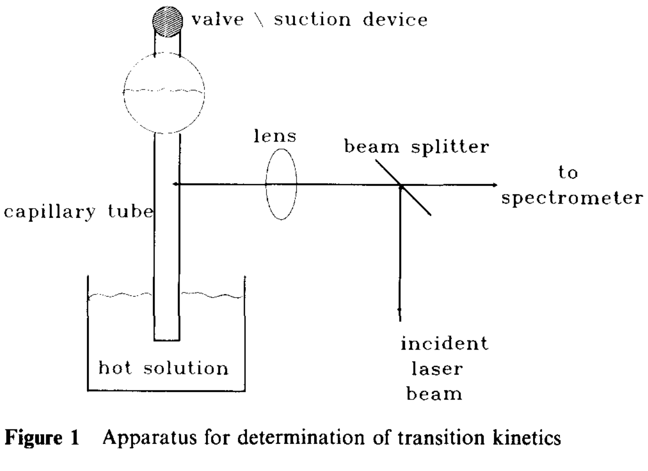


Figure 1 Apparatus for determination of transition kinetics

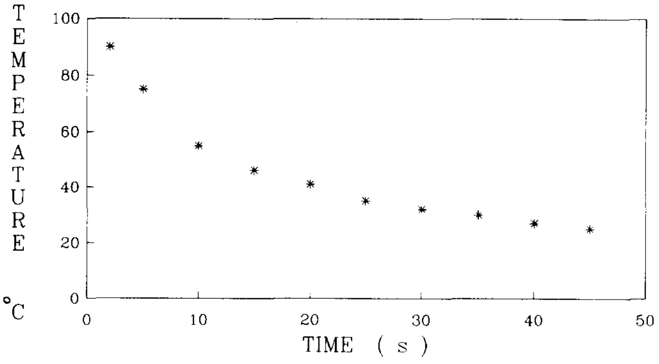


Figure 2 Cooling function of apparatus

For comparison with other forms of 4BCMU, full Raman spectra were taken of fresh solutions (approximately 1 h old) at a concentration of 10^{-4} mol l^{-1} in a 50:50 trichloromethane mixture, the toluene being added to induce the yellow to red transition. Raman spectra were also measured for the three different crystalline phases which have been found by X-ray diffraction for single crystals of 4BCMU: the 'as polymerized' phase I at room temperature, the 'high temperature' phase II, which appears above 388 K, and the 'low temperature' phase III, which appears on cooling the crystal back to 300 K. The details of these transitions will be reported in a later publication.

RESULTS

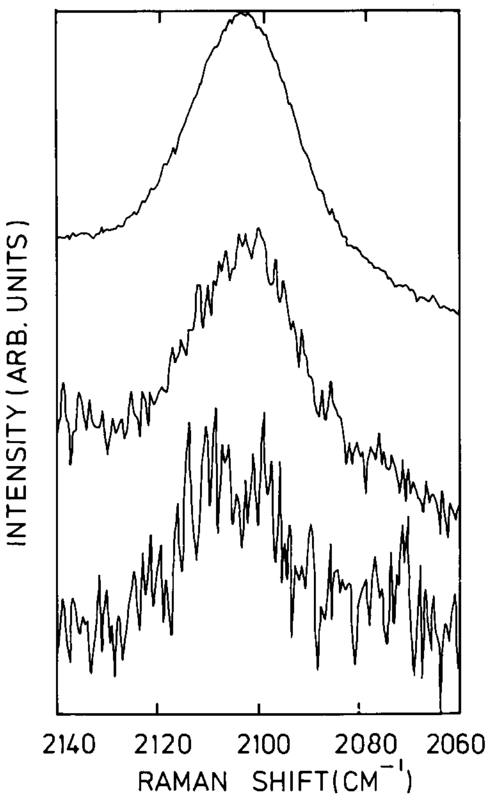
Polymer molecular weight

G.p.c. data was calibrated by an appropriate scaling factor determined from corresponding light scattering data. The weight average molecular weight (M_w) of the stock material was 1.6×10^6 (the monomer molecular weight is 508.61 daltons). Ultrasonic treatment reduced the chain length of the stock material by a factor of about 6 to between 0.2 and 0.33×10^6.

Raman spectroscopy

Photoselection. Raman spectroscopy of PDAs is dominated by resonance enhancement and, for the incident wavelength of 514.5 nm, only relatively long conjugation lengths are associated with sufficient optical absorption to produce a resonantly enhanced Raman signal[12]. Accordingly, at the concentrations studied here there were no strong spectral features associated with the coil form but there were two intense bands near 1500 and 2100 cm^{-1} associated with the extended form. The two bands originate from vibrations along the polymer backbone dominated by stretching of the double and triple bonds, respectively. The total band area in either case is proportional to the amount of the extended form present; however, the region near 1500 cm^{-1} is also associated with a spectral contribution from the toluene. It was therefore decided to follow the progress of the transition by monitoring the increase in band area near 2100 cm^{-1} with time.

Polymer concentration. Some typical Raman spectra recorded at various concentrations are shown in *Figure 3*.



gure 3 Raman spectra recorded at various concentrations (mol l^{-1}): m top to bottom, 10^{-4}; 10^{-6}, 3×10^{-8}

each case, the data are shown before smoothing so at the intrinsic noise is apparent. The exposure time as fixed at 3 s but it was necessary to increase the ectronic gain of the detector together with the laser ower as the concentration was reduced. The very high nsitivity of the detector clearly allows kinetic studies to conducted at concentrations as low as 3×10^{-8} mol l^{-1} d with data points separated by as little as 3 s in time. t these low concentrations it was necessary to clean the pillary with a good solvent such as trichloromethane tween successive runs to remove traces of polymer sorbed onto the glassware which would otherwise ontribute erroneously to the Raman signal.

The scattering volume for these experiments is defined the volume element within the sample from which olecules contribute to the data and is a function of the tical parameters of the system. The value derived from e known laser beam waist and the depth of focus of e lens is $\approx 1\times10^4\,\mu m^3$. At a concentration of $3\times$ $)^{-8}$ mol l^{-1} and molecular weight of 1.4×10^6 this olume would contain only about 70 molecules and this an indication of the high sensitivity of our Raman stem.

Raman frequency. The frequency of the Raman band sociated with vibration of the triple bond was compared r a series of samples at 300 K. The value of 2105 cm^{-1} as invariant with polymer concentration over the range $\times 10^{-8}$ to 10^{-4} mol l^{-1}. In addition, samples which had en left to stand for several months and had formed rge precipitate particles visible to the unaided eye also roduced a Raman band with the same frequency.

Table 1 lists the frequencies of the most prominent aman bands at 300 K for both the 10^{-4} mol l^{-1} solution 4BCMU in 50:50 trichloromethane/toluene and phases II and III of the BCMU single crystal.

Kinetic data

Figure 4 shows a typical set of spectroscopic data which has been subjected to a nine-point smoothing function and stray light background correction by our software package. This data set relates to a 1×10^{-4} mol l^{-1} solution and shows 30 spectra recorded at 3 s intervals. The time axis starts within a few seconds of induction of the solution into the capillary. The development of the extended form is associated with a gradual increase in band area. Band areas for this and other samples have been measured as a function of time and have been plotted as a percentage of the total band area for each sample in *Figures 5* and *6*.

Figure 5 shows data for the initial 90 s with a data interval and spectral exposure time of 3 s. The rate of increase of the extended form is relatively rapid at first but then slows as the transition proceeds to completion at about 60 s. The kinetics do not seem to be influenced significantly by concentration or molecular weight although there is some indication that the initial rapid rise becomes increasingly significant as the concentration is reduced.

Figure 6 shows data over a longer time scale to 200 s for the more dilute samples, with a data interval and

Table 1 Frequencies (cm^{-1}) of the most intense Raman bands for a 4BCMU single crystal in the three phases and a 10^{-4} mol l^{-1} solution of 4BCMU in 50:50 chloroform/toluene mixture at 300 K

Crystal			
I	II	III	Solution
2086	2118	2101	2105
	1513	1514	1507
1460		1486	1499
1358	1332		
1317			
1257	1247	1250	1247
1214	1168	1166	1163
1088	1070	1078	1072
1051	1046	1048	s[a]
	922	963	s
	825	844	841
699	696		

[a] The two bands marked s were masked by solvent bands

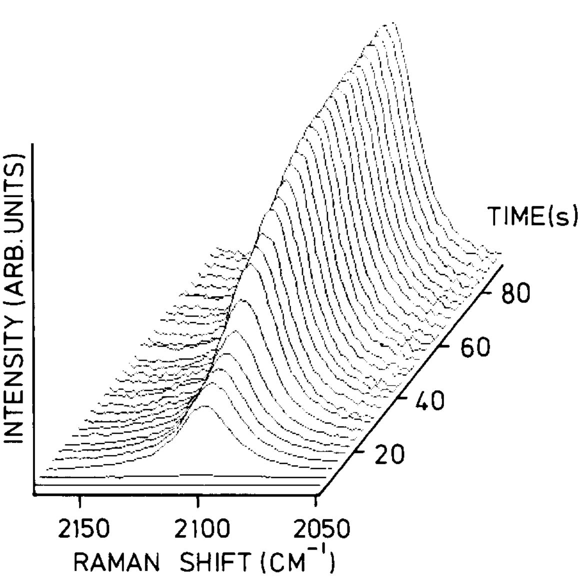


Figure 4 Development of Raman spectrum with time

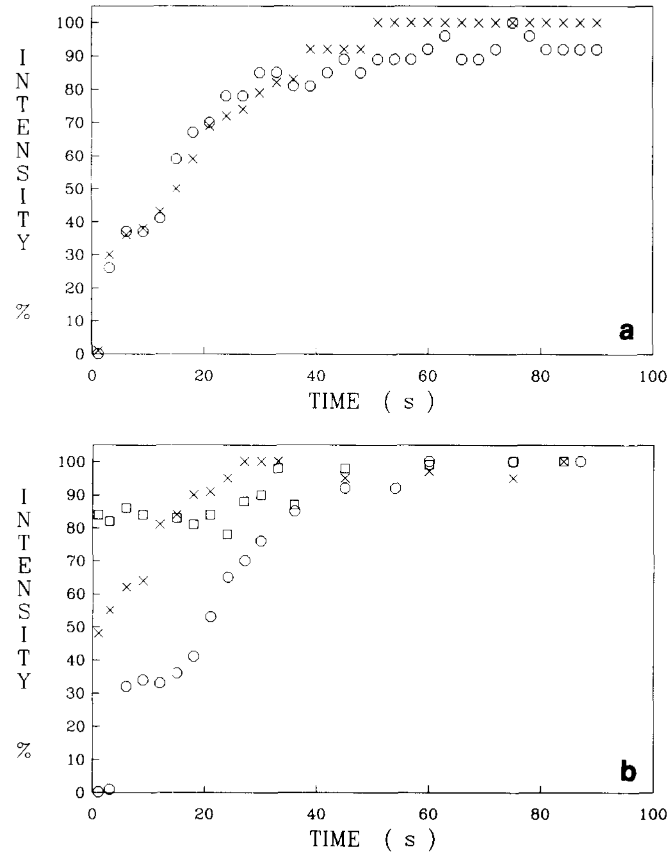


Figure 5 Area of Raman band as a function of time for the following concentrations/molecular weights: (a) ○, $10^{-6}/1.4\times10^{6}$; ×, $10^{-4}/1.4\times10^{-6}$; (b) ○, $10^{-4}/3.3\times10^{5}$; ×, $10^{-6}/2.0\times10^{5}$; □, $10^{-8}/2.2\times10^{5}$

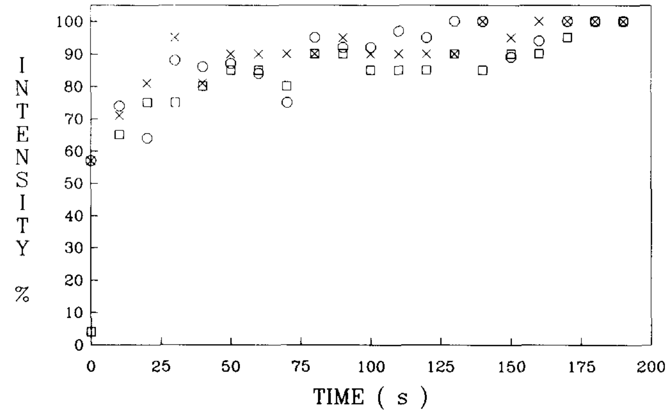


Figure 6 Area of Raman band as a function of time for the following concentrations/molecular weights: □, $10^{-7}/3.3\times10^{5}$; ×, $10^{-7}/1.4\times10^{6}$; ○, $10^{-8}/2.2\times10^{5}$

exposure time of 10 s. At this data interval, the initial rapid rise is less apparent but the results otherwise confirm those of *Figure 5* in that the transition kinetics are not significantly affected by molecular weight or concentration.

In addition to the changes in band intensity discussed above, it was also apparent that the band maximum occurred at lower Raman shift as the transition proceeded. The overall change in band position was $\approx 5\,\mathrm{cm}^{-1}$ and this would be expected for a sample which is subject to cooling from ≈ 360 to 300 K.

To investigate long term effects, a $10^{-4}\,\mathrm{mol\,l}^{-1}$ sample was also followed for 24 h and this revealed that no significant spectral changes occurred after the initial 200 s.

DISCUSSION

Raman spectroscopy indicates that the transition proceeds rather slowly and occurs over a timescale longer than that required for the samples to cool to room temperature. This timescale of some tens of seconds is insensitive to concentration and molecular weight. If aggregation is a fundamental component of the transition, these variables would have significantly affected the transition kinetics because of their influence on diffusion rates.

Calculation of the diffusion rates for the various samples is useful to place these results in perspective. Each sample of known molecular weight and concentration requires a certain time for a number of molecules to diffuse into each other and establish intermolecular contacts to form an aggregate. This time cannot be precisely defined because the size and nature of individual aggregates is uncertain. However, to compare the relative times for the various samples, the expectation value can be calculated of the time required for a molecule to diffuse over the distance to its nearest neighbour and contact. This characteristic time represents the absolute minimum time required to form an 'aggregate', which in this case would consist of two molecules. The implicit assumption is that the characteristic times are dominated by the diffusion times and this seems reasonable for a dilute system. It is not clear at this stage if such diffusion would involve the movement of extended or coil-like molecules because it is not yet clear if the transition involves rod formation before any aggregation. Accordingly, characteristic times are calculated for both conformations.

The problem of calculating the time required for a molecule in dilute solution to contact with another molecule can be separated into two parts. First we must calculate the expected diffusion distance before contact is probable; this is equal to the reciprocal of the probability, P, of interaction during diffusion by unit distance. If the molecule diffuses a distance r (to the surface of a sphere of radius r), then the probability of collision in diffusing a further distance $\mathrm{d}r$, $P\,\mathrm{d}r$, is equal to

$$\frac{\text{area of interaction}}{\text{area of sphere}} \times \text{number of molecules in spherical shell } \mathrm{d}r$$

For extended molecules the area of interaction is of the order of $L^2/4$ (the square of the projected length of the molecule), leading to

$$P\,\mathrm{d}r = \frac{c' M_0 N_A L^2}{4M} \times 10^3\,\mathrm{d}r$$

where c' is the concentration in $\mathrm{mol\,l}^{-1}$, M_0 is the monomer molecular weight, N_A is Avogadro's number and M is the polymer molecular weight. Thus the expected diffusion distance before collision is

$$x_r = \frac{4M}{c' M_0 N_A L^2 \times 10^3} \qquad (1)$$

For coils the argument is the same except that the area of interaction is of order πr_g^2 where r_g is the radius of gyration of the coil. This leads to an expression for the expected diffusion distance for a coil:

$$x_c = \frac{M}{c' \pi r_g^2 M_0 N_A \times 10^3} \qquad (2)$$

The second part of the problem is to calculate, in each case, the corresponding diffusion time τ. In general this is given by $\tau = x^2/D$, where D is the appropriate diffusion coefficient. For extended molecules the diffusion is anisotropic: diffusion is fast along the molecular axis but the probability of interaction is low. The appropriate diffusion coefficient is that perpendicular to the molecular axis D_1. This is given by[13]

$$D_1 = \frac{kT \ln(L/d)}{4\pi\eta L}$$

where d is the diameter of the rod and η is the solvent viscosity. This leads to an expression for the expected time between collisions τ_r:

$$\tau_r = \left(\frac{4M}{c' M_0 N_A L^2 \times 10^3}\right)^2 \times \frac{4\pi\eta L}{kT \ln(L/d)} \qquad (3)$$

Diffusion of coils is isotropic and given by the Stokes–Einstein relation:

$$D = \frac{kT}{6\pi\eta r_g}$$

giving

$$\tau_r = \left(\frac{M}{c' \pi r_g^2 M_0 N_A \times 10^3}\right)^2 \times \frac{6\pi\eta r_g}{kT} \qquad (4)$$

Characteristic times are summarized in *Table 2* and assume the radius of gyration values for the coil conformation reported by Wegner *et al.*[14]. All the other data required were derived from the known properties of the system.

The diffusion of extended molecules is more rapid than that of coils but in either case it is clear that, at concentrations $\leqslant 10^{-6}$ mol l^{-1}, the characteristic time becomes long in relation to the experimental timescale. If the transition is diffusion controlled, dramatic differences in transition kinetics would be apparent as a function of molecular weight and, especially, concentration and this is clearly not the case.

Transition kinetics are thus not determined by diffusion and aggregation but are associated with a single chain phenomenon. The reason why such a conformational change should occur over a timescale of seconds, independent of molecular weight and concentration, is not clear at this stage. However, this must be related to the properties of individual molecules in solution and not a collective phenomenon based around intermolecular interactions.

Such a clear-cut result is only possible at the low concentrations we have examined. The diffusion times calculated in *Table 2* illustrate that in the concentration range where most previous experiments have been performed, the separation of cause and effect would have been exceedingly difficult.

Table 2 Characteristic diffusion times (seconds)

	Molecular weight 1.4×10^6		Molecular weight 2.2×10^5	
Concentration (mol l^{-1})	Extended form	Coil	Extended form	Coil
10^{-4}	3×10^{-3}	1	3×10^{-2}	0.2
10^{-6}	30	1×10^4	3×10^2	2×10^3
10^{-8}	3×10^5	1×10^8	3×10^6	2×10^7

The invariance of Raman frequency with concentration may indicate that the transition involves an intramolecular collapse. Raman frequency is very sensitive to environment for PDAs[15] and the value associated with systems known to be aggregated is clearly comparable with that for the most dilute solutions which cannot be aggregated (see above). The comparable frequencies indicate a comparable molecular environment which must involve molecular segments in close proximity. This is only possible if 'aggregation' can occur in the most dilute case and it must therefore be some form of intramolecular aggregation. At the transition, coil-like molecules may collapse into themselves to form straight conjugated segments folded over into close proximity. This intramolecular collapse model explains the concentration independence of the transition kinetics and the comparable Raman frequencies, and has the additional advantage that it is consistent with the established behaviour of many polymer molecules in solution, which collapse into themselves as the solvent quality is reduced[16].

Once the solution has cooled to 300 K the triple bond vibrational frequency remains constant at 2105 cm^{-1}, even after times sufficiently long for aggregation to occur; the same value was found for the 50:50 chloroform/toluene solutions. This suggests that the structure of the polymer chain remains constant during and after the transition and that the structure is likely to be the same as that of the polymer in the 50:50 chloroform. The red solutions of 4BCMU exhibit Raman photoselection, providing strong evidence that the polymer exists in a range of configurations[12]. Comparison of the Raman data in *Table 1*, however, shows that the dominant component of the polymer in the red solution has a structure which must be very similar to that of a phase III single crystal. An extended polymer chain in solution is very unlikely to have the same Raman features as one of the three possible crystalline structures. The small differences in Raman frequency in *Table 1* between the single crystal and the solution could be due to previously observed size effects[15].

The presence of a degree of crystallinity resulting from intrachain collapse could help explain other features of 4BCMU solutions. On cooling the solutions it is common to observe an isosbestic point in the optical absorption spectra[5], which is evidence that the coil and extended forms are in equilibrium over a range of temperatures. There is some evidence that this effect results from a dependence of the transition temperature on molecular weight, the higher values having higher transition temperatures[17]. If the transition from the coil to the extended form occurred by a crystallization-like process then a dependence of the transition temperature on molecular weight would not be surprising. The necessity to redissolve the partially crystalline molecules on increasing the temperature could also be responsible for the hysteresis observed in the transition.

CONCLUSION

The transition from the coil to the extended form observed in PDA solutions has been demonstrated, at least for 4BCMU, to be a property of an isolated polymer chain. Aggregation is not responsible for the transition although it occurs at later times. The structure of the dominant component of 4BCMU polymer in toluene solution does not change upon aggregation. Raman spectroscopy suggests that this structure is very similar to that of a crystalline phase of the polymer. It is suggested that the transition to the extended form of the polymer in solution involves intramolecular collapse to a crystal-like environment.

ACKNOWLEDGEMENTS

This work was conducted with financial support from the S.E.R.C. Polymers were synthesized by B. Keneghan. We thank Professor G. Wegner for his suggestions on the role of intramolecular collapse in the transition. Light scattering measurements were performed by Dr M. Schmidt of the Max-Planck Institut für Polymerforschung, Mainz, FRG, to whom we are also grateful for communicating experimental results before publication.

REFERENCES

1 Chance, R. R. *Macromolecules* 1980, **13**, 396

2 Lim, K. C., Fincher, C. R. and Heeger, A. J. *Phys. Rev. Lett.* 1983, **50**, 1934

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

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

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

6 Peiffer, D. G., Chung, T. C., Schulz, D. N., Agarwal, P. K., Garner, R. T., Kim, M. W. and Chance, R. R. in 'Non Linear Optical and Electroactive Polymers' (Eds P. N. Prasad and D. R. Ulrich), Plenum Press, New York, 1988, p. 205

7 Chance, R. R., Washabaugh, M. W. and Hupe, D. J. in 'Polydiacetylenes' (Eds D. Bloor and R. R. Chance), *NATO Solid St. Sci. Ser.* Martinus Nijhoff, 1985, p. 239

8 Patel, G. N. *Polym. Prepr.* 1978, **19**, 154

9 Aime, J. P., Fave, J. L. and Schott, M. *Europhys. Lett.* 1985, **1**, 505

10 Lim, K. C. and Heeger, A. J. *J. Chem. Phys.* 1985, **82**, 522

11 Batchelder, D. N. *Euro. Spec. News* 1988, **80**, 28

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

13 Bird, R. B., Armstrong, R. C., Nassager, O. and Curtiss, F. C. 'Dynamics of Polymeric Liquids', Wiley, New York, 1977

14 Enkelmann, V., Wenz, G., Müller, M. A., Schmidt, M. and Wegner, G. *Mol. Cryst. Liq. Cryst.* 1984, **105**, 11

15 Batchelder, D. N. and Bloor, D. in 'Advances in Infrared and Raman Spectroscopy', Vol. 11 (Eds R. J. H. Clark and R. E. Hester), Wiley Heydon, Chichester, 1984, p. 133

16 Dauod, M. and Janninck, G. J. *J. Phys. Paris* 1976, **37**, 973

17 Schmidt, M. private communication