Chain length effects in polydiacetylene yellow solutions

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Polydiacetylene yellow solutions of the derivatives 2-, 3- and 4BCMU and 9PA in chloroform were prepared with a range of different molecular weights. The measured wavelength of the optical absorption spectrum peak maximum λ_{max} showed a continuous increase with increasing chain length up to lengths of nearly 5000 repeat units. A theory is proposed that this is due to the excluded volume effect. The persistence lengths of the polymer chains in the solutions were calculated from λ_{max}, using small angle neutron scattering data from the literature. The persistence length is shown to obey a direct power-law relationship with physical chain length, which is in good agreement with the theory. Numerical parameters in equations derived from these results, using the theory, are in good agreement with those calculated from independent light scattering and intrinsic viscosity measurements in the literature for other polydiacetylenes and polymers. Furthermore, it is shown that realistic values for the expansion coeficient α_n can be calculated from the derived equations.

(Keywords: polydiacetylene; solution; chain conformation)

INTRODUCTION

Polydiacetylenes are highly conjugated polymers (*Figure 1*) produced by the solid state topochemical polymerization of macroscopically sized single monomer crystals. Certain polydiacetylene derivatives with very long sidegroups such as the BCMUs, 9PA and PTS-12 (*Figure 2*) are soluble in common organic solvents such as chloroform[1–3]. These soluble polydiacetylenes have attracted great interest due to their dramatic thermochromic and solvatochromic properties[2,4–6]. In a good solvent the polydiacetylene polymer solutions are coloured yellow. However, upon cooling or upon the addition of a non-solvent such as hexane, the polydiacetylene polymer solutions undergo a rapid colour change from yellow to red or from yellow to blue. The strong absorption of polydiacetylenes in the visible region of the spectrum is due to their highly delocalized π-bonding system which extends along the whole length of the backbone. Colour changes in polydiacetylenes can therefore be directly linked to changes in the conformation of the polymer backbone. There is good evidence to support the contention that the yellow to red or yellow to blue colour changes in solution involve the backbone undergoing a non-planar to planar conformational transition[4,5,7–11].

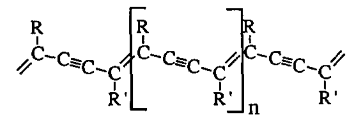

Figure 1 Molecular structure of the polydiacetylene backbone

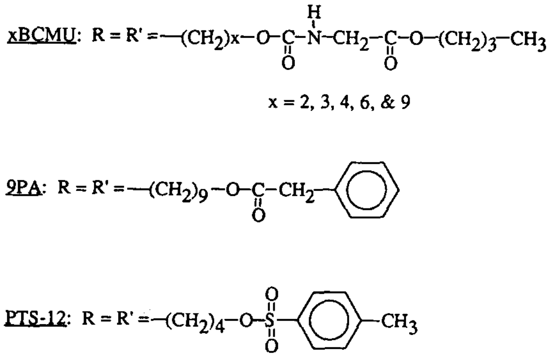

Figure 2 Molecular structure of the polydiacetylene sidegroups R and R′

Integrated and quasi-elastic light scattering, viscosity and field induced birefringence studies all show that the polydiacetylene chains behave as relatively stiff random coils in the yellow solutions[8,9,12–18]. Two different structural models exist for this coiled conformation[4,7,9,13,14,19]. The Kuhn model envisages that the backbone is broken up by exact 90° bond rotations about the backbone single bonds into a series of short but highly ordered planar segments of varying length. The alternative Porod–Kratky model envisages that the polydiacetylene chain has a 'worm-like' configuration, where the backbone has a continuous and smooth curvature which is maintained by each bond being slightly twisted and distorted.

Integrated and quasi-elastic light scattering, viscosity, small angle neutron scattering and high-pressure optical

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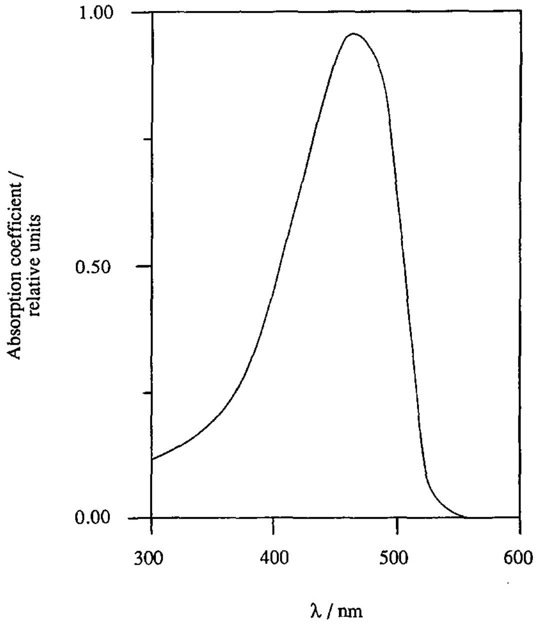

Figure 3 Optical absorption spectrum of the 4BCMU polydiacetylene yellow solutions in chloroform

absorption studies all strongly support the Porod–Kratky model[9,14,18–21]. The 90° bond rotations about the backbone single bonds in the Kuhn model were originally suggested because they were believed to be energetically favourable, but new theoretical results suggest that this is untrue[22,23]. Also, 90° bond rotations about the backbone single bonds cannot actually cause the polydiacetylene backbone to change direction and form a coil[16]. A butatrienic form of backbone conjugation and *trans* to *cis* isomerization of the backbone double bonds have both been suggested to allow the backbone to coil in the Kuhn model, but small angle neutron scattering, ^{13}C n.m.r., photochemical and chemical studies along with theoretical calculations all indicate that neither of these forms of backbone structure occur in the polydiacetylene solutions[8–11,14,15,18,19].

The optical absorption spectrum of the yellow solutions (*Figure 3*) is considerably broadened and contains none of the vibrational side band detail found in that of the freshly polymerized highly ordered polydiacetylene crystals[24]. It has been suggested that this broadening is homogeneous and is due to shorter excited-state lifetimes[25]. However, the blue shift of this spectrum from that of the crystals, along with resonant Raman spectroscopy and ^{13}C n.m.r. results, have been taken to indicate that the backbone's highly delocalized electronic system has been broken up into a distribution of short conjugated segments with an average length of about seven repeat units[7,9]. A theoretical model based on such a distribution of completely discrete and decoupled conjugated segments and using the Kuhn backbone structure has been successful in predicting the shape and position of the optical absorption spectrum, but has been criticized as being unrealistic and requiring the use of physically unjustifiable large linewidths to explain the complete lack of structure in the absorption spectrum[4,7,26]. Alternative theoretical models based on the weakly disordered backbone structure of the Porod–Kratky model have also been successful in predicting the broadening and the blue shift of the optical absorption spectrum, along with the localization of the states along the backbone[23,27].

If the backbone's electronic structure in the yellow solutions is assumed to be broken up into short conjugated segments, then these have an effective length of about seven repeat units[4,7,9]. Alternatively, a theoretical model based on a weakly disordered worm-like chain predicts that the wave functions should be localized over about eight repeat units[23]. Also, the main electronic transition which produces the optical absorption of polydiacetylenes involves the creation of excitons, and the polydiacetylene backbone exciton is localized over about three to six repeat units[26]. All of these results suggest that in the yellow solutions the optical absorption spectrum should be independent of chain length at lengths greater than about 10 repeat units. This would appear to be confirmed by the measurements on polydiacetylene oligomers in solution, which show no appreciable shift in the optical absorption spectrum beyond about 10 repeat units[28–30].

However, u.v. photodegraded yellow solutions of PTS-12 show significant shifts in the optical absorption spectrum from 20 to 1500 repeat units[31]. This is supported by results for 3BCMU and for a derivative similar to 9PA[31,32]. Furthermore, small angle neutron scattering studies show that in the yellow solutions the optical absorption spectrum peak maximum can be directly related to the curvature of the polydiacetylene backbone as measured by the persistence length[20]. Taken together, these results suggest that the curvature of the backbone may vary with chain length over a wide range of lengths. If this does occur, then a possible explanation for the effect could be provided by invoking excluded volume effects on the polydiacetylene random coils in solution.

EXPERIMENTAL

To investigate the excluded volume hypothesis a series of 4BCMU solutions containing molecular weights from 80 to nearly 3000 repeat units were prepared. A smaller number of solutions were also prepared of the derivatives 2- and 3BCMU and 9PA to investigate the effect of different sidegroup structures.

The 2-, 3- and 4BCMU and 9PA samples were synthesized and polymerized as described in the literature[1–3]. Polymerization was achieved using different levels of γ-ray (^{60}Co) irradiation. The 4BCMU (equivalent number of repeat units, $n_w = 83$), 2BCMU ($n_w = 140$), 3BMCU and 9PA samples in this work were prepared using 45 Mrad. The 4BCMU ($n_w = 2800$) and 4BCMU ($n_w = 2200$) samples were prepared using 3 and 5 Mrad, respectively. The 4BCMU ($n_w = 1380$) was prepared by ultrasonic treatment of the 4BCMU ($n_w = 2800$) sample. The 2BCMU ($n_w = 17$) sample was prepared from the 2BCMU ($n_w = 140$) sample by chromotographic separation using a silica gel column as described elsewhere[2].

The yellow solutions in chloroform were prepared to a concentration of 10^{-4} M (in terms of moles of monomer repeat units). The optical absorption spectra of the yellow solutions were recorded on a Perkin–Elmer Lambda 9 u.v./vis./n.i.r. spectrophotometer between 600 nm and 350 nm. The wavelength of the peak maximum in the optical absorption spectrum, λ_{max}, was measured at the point of maximum intensity of that peak. λ_{max} could be measured to an accuracy of ±0.1 nm, but repeated measurements of the same solution suggested a relative accuracy of ± 1 nm.

Molecular weights were measured using g.p.c. The g.p.c. results were calibrated against the molecular weight of the 4BCMU ($n_w = 2800$) sample determined by light scattering data. Average molecular weights were calculated to have an accuracy of ±5% of the measured value.

RESULTS AND DISCUSSION

The molecular weight M_w, n_w and λ_{max} of the yellow solutions in chloroform are listed for all of the samples in *Table 1*. Also included are five values from the literature. Only literature values for which measurements of both M_w and λ_{max} exist are listed. It is expected that some variation in λ_{max} will almost certainly result from the use of different spectrophotometers, so values from the literature are estimated to have a possible variation of ±2 nm. Furthermore, uncertainties in the polydispersity of these samples makes the comparison less sound.

Table 1 M_w, n_w and λ_{max} in the yellow solutions in chloroform for different polydiacetylene derivatives

Derivative	M_w ($\times 10^5$ g mol^{-1})	n_w	λ_{max} (nm)	Ref.
4BCMU	0.42	83	456.4	This work
	1.2	240	460	36
	7.0	1380	465.6	This work
	11.2	2200	467.1	This work
	14.0	2800	468.5	This work
	16.7	3280	470	37
	24.0	4700	468	36
2BCMU	0.078	17	446	This work
	0.65	140	450	This work
3BCMU	4.5	940	470.6	This work
	13.6	2830	483	37
9PA	7.47	1310	467.4	This work
	13.4	2300	473	3, 13

The values of λ_{max} for 4BCMU are plotted against n_w in *Figure 4a*. The seven samples show a continuous increase in λ_{max} with increasing n_w up to nearly 5000. Initially λ_{max} increases very rapidly with increasing n_w, but beyond $n_w \approx 1500$ the rate of increase slows to about 1 nm per 1000 repeat units.

The values of λ_{max} for 2- and 3BCMU and 9PA are plotted against n_w in *Figure 4b*. The results in the literature[31] for the photodegraded PTS-12 yellow solutions in chloroform are also plotted in *Figure 4b*. The results for PTS-12 are almost identical to those for 4BCMU, and show the same variation of λ_{max} with n_w up to 1500. Only two experimental data points exist for 2- and 3BCMU and 9PA, but these all show that λ_{max} increases with increasing n_w up to chain lengths of nearly 3000 repeat units.

Therefore, λ_{max} increases with increasing n_w for a whole range of different polydiacetylene derivatives over all measured chain lengths up to nearly 5000 repeat units.

Small angle neutron scattering and optical absorption spectroscopy studies show that the persistence length b of the polymer chains can be directly related to the optical absorption peak maximum wavelength λ_{max} of the polydiacetylene yellow solutions[20]. The persistence length is a measurement of the decay of orientational order along a coiled polymer chain in solution. It can be

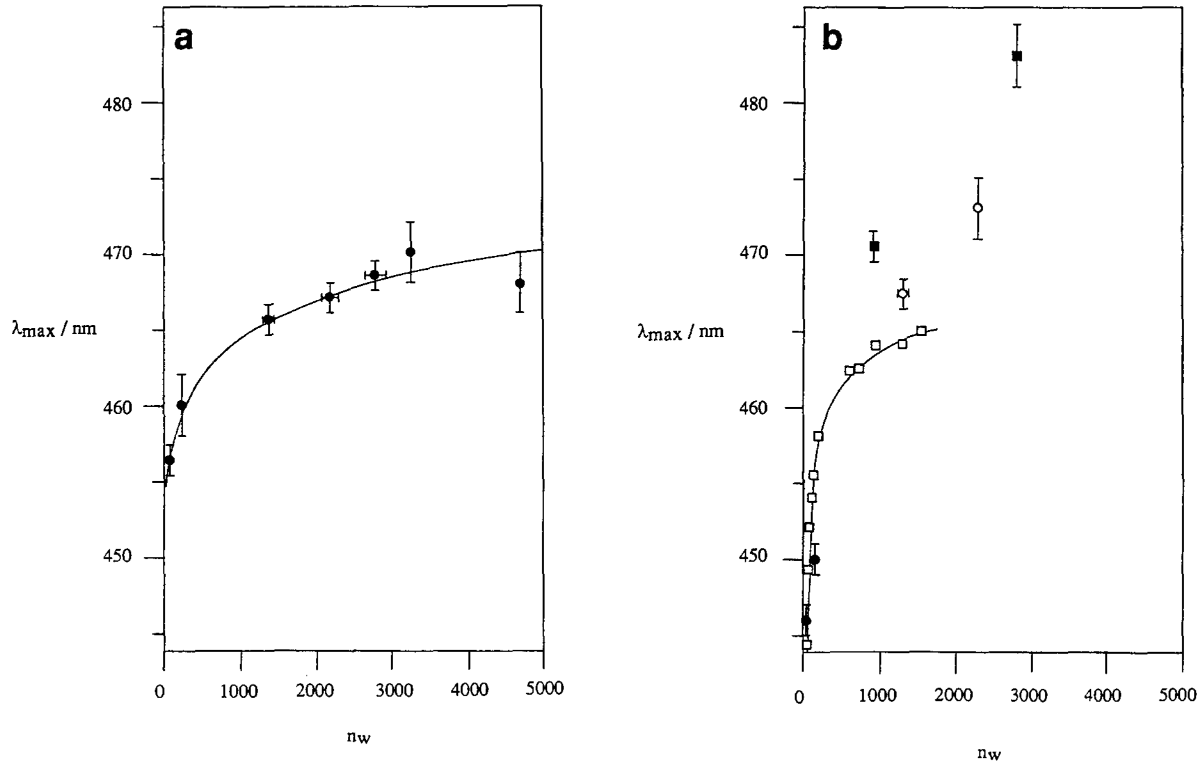

Figure 4 Wavelength of the optical absorption spectrum peak maximum λ_{max} plotted against weight average chain length n_w for the polydiacetylene yellow solutions of (a) 4BCMU and (b) 2BCMU (●), 3BCMU (■), 9PA (○) and PTS-12 (□)[31]

Table 2 n_w and b calculated from equation (3) for different polydiacetylene derivatives

Derivative	n_w	b (nm)	Ref.
4BCMU	83	23.8	This work
	240	26.0	36
	1380	29.3	This work
	2200	30.2	This work
	2800	31.0	This work
	3280	31.8	37
	4700	30.7	36
2BCMU	17	17.3	This work
	140	19.8	This work
3BCMU	940	32.2	This work
	2830	39.1	37
9PA	1310	30.3	This work
	2300	33.5	3, 13

related to the angle ϕ between the directions of two consecutive chain segments by the equation:

$$b = l/(1 - \langle \cos \phi \rangle) \qquad (1)$$

where l is the length of each chain repeat unit and $\langle \cos \phi \rangle$ is the average value of $\cos \phi$. The persistence length is therefore a direct measurement of the level of curvature along the polymer chain or backbone. The smaller the persistence length, the greater the curvature.

The small angle neutron scattering results[20] show that b is related to the wavenumber E of the optical absorption peak maximum by an equation of the form:

$$b = \mathrm{k}_1 - \mathrm{k}_2 E \qquad (2)$$

where k_1 and k_2 are constants. Such an equation has been fitted to the results by the present authors, giving:

$$b = 301.4 - 1.267 \times 10^5/\lambda_{\max} \qquad (3)$$

where b and $\lambda_{\max}$ are both measured in nm. Hence, $\lambda_{\max}$ can be directly related to the level of curvature of the polydiacetylene backbone as measured by the persistence length b.

The persistence length b of the different samples used in this study are calculated from their $\lambda_{\max}$ values in *Table 1* using equation (3). The calculated values of b are listed in *Table 2*. The results demonstrate a continuous increase in persistence length with increasing chain length up to n_w values of 5000 repeat units.

Intrinsic in this analysis is the assumption that $\lambda_{\max}$ is purely dependent on the curvature of the backbone as measured by b. It is assumed that in the yellow solutions changes in the solvent, temperature or sidegroup structure will mainly affect the electronic structure of the backbone by changing the level of backbone curvature. Such factors as polarization interactions between the backbone and the solvent molecules after the chains have coiled will vary between different solvents, but it is assumed that this effect is negligible compared to the effect different solvents have on the electronic structure by varying the backbone curvature via solvent–sidegroup and solvent–backbone interactions. This is supported by small angle neutron scattering results, which show that changes in $\lambda_{\max}$ produced by varying the solvent or the temperature can be directly linked to changes in b[20,33]. Likewise, polarization interactions between the backbone and the sidegroups will vary between the polydiacetylene derivatives due to differences in sidegroup structure, but again it has to be assumed that this is negligible compared to the effect different sidegroup structures have on the electronic structure by varying the backbone curvature via solvent–sidegroup and sidegroup–sidegroup interactions. This seems reasonable given that polarization interactions drop off very rapidly with distance and that the nearest units to the backbone for all the sidegroup structures shown in *Figure 2* consist of identical chains of methyl groups.

In solution a polymer chain can be described as a Flory type random coil, where the root mean square radius of gyration of the coiled chain $\langle S_g^2 \rangle^{1/2}$ can be related to l and n_w by:

$$\langle S_g^2 \rangle^{1/2} = (1/6)^{1/2} \alpha_n (C_n)^{1/2} (n_w)^{1/2} l \qquad (4)$$

where C_n is the characteristic ratio and indicates the amount of short range steric hindrance due to overlapping electron orbitals causing restrictions on the possible bond rotation angles of the chain in solution. C_n varies with n_w at very short chain lengths due to chain statistics, but quickly tends to a limiting value for most polymers[34]. α_n is the expansion factor caused both by long range excluded volume effects between different parts of the random coil and by osmotic swelling of the coil by solvent–polymer interactions. Under theta conditions $\alpha_n = 1$.

The expansion factor increases with increasing n_w over a wide range of chain lengths[34]. As n_w increases the random coil tends to expand because of the physical exclusion of one polymer segment from the space occupied by another, statistically favouring a more expanded conformation. The expansion factor at a given temperature and in a given solvent can be directly measured from light scattering measurements or indirectly from intrinsic viscosity measurements. Over a given range of molecular weights α_n experimentally follows the relationship:

$$\alpha_n = \alpha_0 (n_w)^m \qquad (5)$$

Values of m lie between 0.00 for a polymer in a θ-solvent to about 0.12 for a linear randomly coiling vinyl polymer in a very good solvent[35].

In the Porod–Kratky model the persistence length can be directly related to the characteristic ratio C_n and the expansion factor α_n by the equation:

$$b = 1/2 C_n (\alpha_n)^2 l \qquad (6)$$

Therefore, because α_n increases with increasing n_w, b should also increase with increasing n_w. This is exactly the effect shown by the present results (*Table 2*). The excluded volume effect may therefore be responsible for the variation of the optical absorption peak maximum with chain length in the polydiacetylene yellow solutions.

If excluded volume effects are responsible for the variation in b with n_w, then from equations (5) and (6) the persistence length should vary with chain length according to:

$$b = 1/2 C_n [\alpha_0 (n_w)^m]^2 l \qquad (7)$$

Therefore, b should vary as some power m of n_w.

Figure 5a is a log–log plot of b against n_w for all the 4BCMU results listed in *Table 2*. The seven values lie on a straight line with a correlation coefficient of 0.984. This is strong evidence that b varies simply as some power of n_w.

Figure 5b is a log–log plot of b against n_w for all the

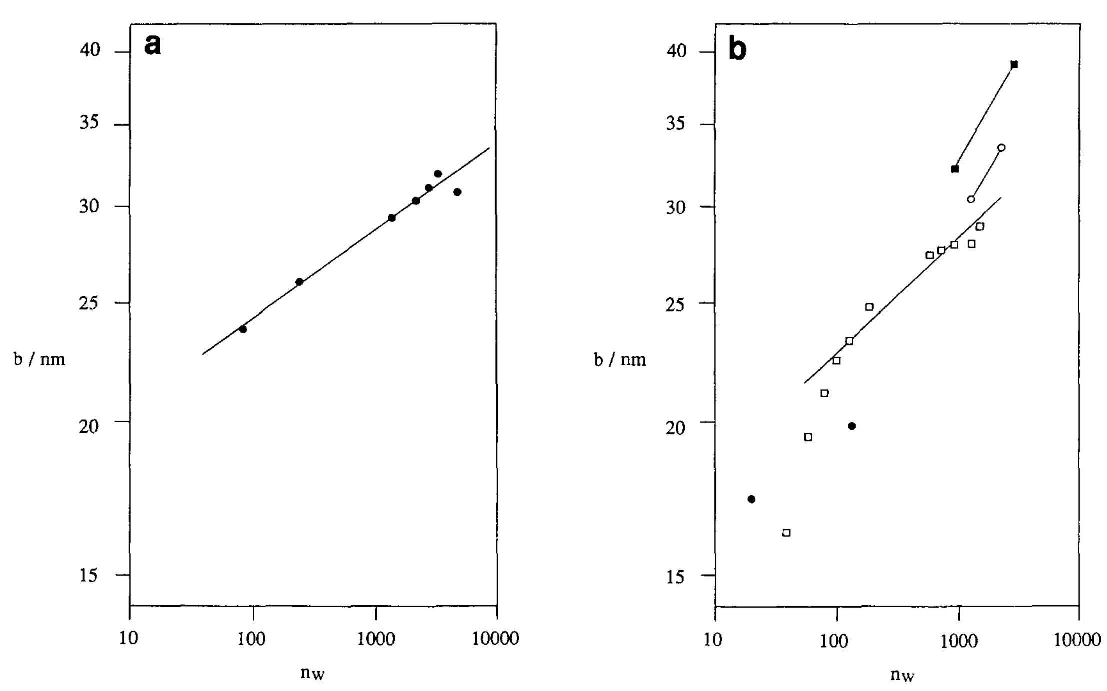

Figure 5 Small angle neutron scattering derived persistence length *b* plotted against weight average chain length n_w for the polydiacetylene yellow solutions of (a) 4BCMU and (b) 2BCMU (●), 3BCMU (■), 9PA (○) and PTS-12 (□)[31]

Table 3 Values of α_0 and *m* in equation (5) for different polymers

Polymer	Measurement technique	Solvent	α_0	*m*	Ref.
4BCMU	U.v.-vis. spectroscopy	$CHCl_3$	0.959	0.035	This work
3BCMU	U.v.-vis. spectroscopy	$CHCl_3$	0.71	0.09	This work
9PA	U.v.-vis. spectroscopy	$CHCl_3$	0.66	0.09	This work
PTS-12	U.v.-vis. spectroscopy	$CHCl_3$	0.861	0.05	31
Polystyrene	Intrinsic viscosity	$CHCl_3$	0.593	0.107	35
Polystyrene	Intrinsic viscosity	Cyclohexane	0.713	0.074	35
Poly(α-methylstyrene)	Intrinsic viscosity	Toluene	0.661	0.091	35
PTS-12	Light scattering	CH_2ClCH_2Cl	–	0.05	9
PTS-12	Intrinsic viscosity	$CHCl_3$	–	0.14	9

2- and 3BCMU and 9PA results listed in *Table 2*. Values of *b* have been calculated for the results in the literature[31] for the photodegraded PTS-12 yellow solutions in chloroform, and these are also plotted against n_w in *Figure 5b*. For chain lengths above 80 repeat units the results for PTS-12 lie on a straight line with a correlation coefficient of 0.981. This is further conformation of the 4BCMU results.

Table 3 shows the values of α_0 and *m* for 4BCMU and PTS-12 calculated from the data shown in *Figures 5a* and *b* using equation (7). These were calculated using values of C_n and *l* of 78 and 0.491 nm, respectively. The value of C_n is that derived from light scattering measurements of the yellow solutions of 3BCMU in chloroform[9]. Also shown are the values of α_0 and *m* for 3BCMU and 9PA calculated from the two points available for these derivatives. Although caution must be expressed in taking these values for 3BCMU and 9PA too seriously, they do lie close to those for 4BCMU and PTS-12. Differences in the values of α_0 and *m* between the four derivatives indicate that the way in which the polymer random coils expand in solution with increasing chain length varies between the three polydiacetylenes. This is presumably due to variations in the level of polymer–solvent interaction and backbone stiffness caused by the differences in the solvent–sidegroup and sidegroup–sidegroup interactions between the three derivatives.

Values of α_0 and *m* have not been calculated from the two points available for 2BCMU because the chain lengths are too small. When n_w falls as low as 17 repeat units excluded volume effects are unlikely to occur and any variations in λ_{max} with n_w are expected to be dominated by the effect of the physical chain length approaching the same dimensions as the polydiacetylene backbone exciton. This is confirmed by the results for PTS-12 in *Figure 5b*, which show that for chain lengths below about 80 repeat units *b* decreases very rapidly with decreasing n_w and ceases to obey the power-law relationship[31].

Also listed in *Table 3* are values of α_0 and *m* for polystyrene in chloroform, polystyrene in cyclohexane and poly(α-methylstyrene) in toluene[35]. These were calculated from intrinsic viscosity measurements using:

$$[\eta] = K_v(M)^{\nu} = (\alpha_\eta)^3 K_{v\theta}(M)^{1/2} \qquad (8)$$

where $[\eta]$ is the intrinsic viscosity, K_v and υ are the viscosity constant and exponent in the Mark–Houwink equation, α_η is the expansion factor pertaining to viscosity measurements and $K_{v\theta}$ is K_v under theta conditions[35]. Considerable experimental evidence shows that[35]:

$$(\alpha_\eta)^3 = (\alpha_\eta)^{2.43} = [\alpha_0(n_w)^m]^{2.43} \qquad (9)$$

Table 3 also lists values of m for the polydiacetylene PTS-12 in 1,2-dichloroethane and chloroform[9]. These were calculated from intrinsic viscosity measurements using equations (8) and (9) and from light scattering measurements using:

$$\langle S_g^2\rangle^{1/2} = K_s(M)^a = \alpha_n K_{s\theta}(M)^{1/2} \qquad (10)$$

where K_s and a are a constant and an exponent, experimentally derived from light scattering measurements and $K_{s\theta}$ is K_s under theta conditions[34]. Values for α_0 cannot be calculated for PTS-12 because values of $K_{v\theta}$ and $K_{s\theta}$ are not available. Also, modelling of the light scattering results for PTS-12 suggests that in polydiacetylenes C_n asymptotically tends to its limiting value at relatively large chain lengths compared to other polymers[9,19]. If this is so then the values of m calculated for PTS-12 will be slightly too large, but it will have no effect on the general conclusions of this work.

As can be seen, all the numerical values of m in *Table 3* for 4BCMU, 3BCMU, 9PA and PTS-12 lie between 0.00 and 0.12 as found for linear randomly coiling polymers in solution in the literature[35], which is exactly as expected if equations (3) and (7) are valid and the excluded volume effect theory is correct. They also lie very close to the values of m found for PTS-12 derived from completely independent experimental techniques[9,35], which gives added support to the fact that the variation of λ_{max} with n_w is indeed due to the excluded volume effect.

All the numerical values of α_0 for 4BCMU, 3BCMU, 9PA and PTS-12 are very similar to those for polystyrene and poly(α-methylstyrene), which again is exactly as expected if equations (3) and (7) are valid and the excluded volume effect theory is correct. Using equation (5) and the values from *Table 3*, it is possible to calculate that for 4BCMU α_n is equal to 1.12 and 1.29 when n_w is equal to 83 and 4700 respectively. These are realistic values of α_n, which agree well with those found for other polymers such as polystyrene which lie in the range between 1.0 and 1.6[34].

All of these results strongly suggest that the excluded volume effect is indeed responsible for the variation of the optical absorption peak maximum with chain length in the polydiacetylene yellow solutions.

CONCLUSIONS

It has been demonstrated that in the yellow polymer solutions in chloroform the wavelength of the optical absorption spectrum peak maximum λ_{max} shows a continuous increase with increasing chain length up to lengths of nearly 5000 repeat units for at least four different polydiacetylene derivatives. It is postulated here that this continuous increase occurs as a result of the continuous increase in radius of curvature of the coiled polymer backbone with increasing total physical chain length due to excluded volume effects. Utilizing this idea and Flory simple coil chain statistics, and using persistence lengths as measured by neutron scattering as a measure of curvature, it has been shown that λ_{max} varies with physical chain length as would be expected if due to excluded volume effects. Furthermore, the numerical values of parameters in equations derived utilizing these ideas are shown to be in good agreement with the values of the parameters derived from independent light scattering and viscosity measurements.

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