Study of the correlation between the backbone conformation and the electronic structure of polydiacetylenes by solid state ^{13}C n.m.r.

H. Tanaka†, M. Thakur, M. A. Gomez‡ and A. E. Tonelli§
AT&T Bell Laboratories, Murray Hill, New Jersey 07974, USA

The relationship between the conformation and the electronic structure of the backbones in polydiacetylene (PDA) has been investigated by high resolution, solid state ^{13}C nuclear magnetic resonance (n.m.r.). We have studied four different PDAs: PTS in its blue phase, the red phase of PTCDU, PTCDU in the stress-induced blue phase, and the thermochromically related blue and red phases of PETCD and P4BCMU. We have not detected the presence of a stable butatrienic structure in any of these PDAs. Instead, we have found that there are two kinds of backbone conformations, or structures, one which is unique to the blue phase and the other unique to the red phase. For all the blue phase PDAs studied here, the –C≡ resonance appeared at c. 107 ppm, while for all the red phase PDAs the same resonance occurred at c. 103 ppm. The backbone structure of the blue phase was found to be more planar than that of the red phase based on the overall –C≡ chemical shift positions. These backbone structures appear to be general for PDAs. This study shows that the chemical shift position of –C≡ can be utilized as a fingerprint for the extent of planarity, or conjugation length, of any PDA system.

(Keywords: conformation; electronic structure; polydiacetylene; n.m.r.)

INTRODUCTION

The optical properties of polydiacetylenes (PDAs) have often been studied[1,2], because several PDAs show large optical non-linearities and several exhibit thermochromic phase transitions. Compared to their optical properties, studies[3-8] of the related structural and conformational properties of PDAs are relatively rare. In general, the electronic state of conjugated polymers like polyacetylene has a one-dimensional character, and the coupling between the electronic structure and longitudinal distortions causes a Peierls transition. It was in this connection that the butatrienic structure of PDA was proposed[7]. However, in the case of substituted PDAs, the coupling of electronic structure to conformational changes seems to be potentially much more important because of the presence of single bonds in their backbones.

Some PDAs, such as PTS (*Figure 1*), form[9] extremely well-ordered single crystals, and X-ray analysis[3] can give precise information concerning their entire geometrical structure. However, for many PDAs, such as PTCDU and PETCD (*Figure 1*), their single crystal perfection is not sufficient for the precise determination[4] of their structures. From X-ray analysis[3,4], optical absorption[6,7], and Raman scattering[6,7], the red phases of PTCDU and PETCD were thought to have a butatrienic backbone

structure as shown in *Figure 2*. On the other hand, the backbone structure of their blue phases are thought to be acetylenic (*Figure 2*).

The electronic state and the π-electron conjugation length of PDAs, are directly related to the conformation of the PDA backbone and are strongly correlated with its non-linear optical properties. As an example, the magnitude of the third-order non-linear optical coefficient, $\chi^{(3)}$, is proportional[10] in the first approximation to the sixth power of the conjugation length. Therefore, a detailed understanding of the backbone conformations of PDAs is very important for our knowledge of their non-linear optical properties.

We have recently studied[8,11,12] the thermochromic phase transition in PETCD and P4BCMU by solid state
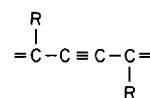
PTS	R = CH$_2$OSO$_2$C$_6$H$_4$CH$_3$	BLUE
PTS12	R = (CH$_2$)$_4$OSO$_2$C$_6$H$_4$CH$_3$	BLUE
PTCDU	R = (CH$_2$)$_4$OCONHC$_6$H$_5$	RED, BLUE
PETCD	R = (CH$_2$)$_4$OCONHC$_2$H$_5$	BLUE, RED
P4BCMU	R = (CH$_2$)$_4$OCONHCH$_2$COO(CH$_2$)$_3$CH$_3$	BLUE, RED

Figure 1 Chemical structures of PDAs

R
|
=C—C ≡ C—C=
|
R

(a)

R
|
—C=C=C=C—
|
R

(b)

R = CH₂—CH₂—CH₂—CH₂—OCONH—CH₂—CH₃
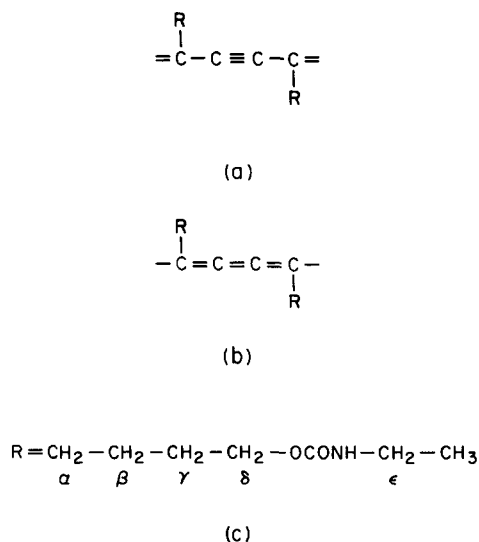   α   β   γ   δ   ε

(c)

Figure 2 (a) Acetylenic and (b) butatrienic backbone structures, and (c) the side chain structure of PETCD

^{13}C nuclear magnetic resonance (n.m.r.). There we observed the absence of a stable butatrienic structure (see *Figure 2*) and the transition was associated with the change from a planar to a less planar backbone conformation. Solid state, high resolution ^{13}C n.m.r. is a powerful method for determining the backbone and side chain conformations of PDAs, because the observed chemical shift positions reflect the shieldings of magnetic fields due to the electronic environments of the carbon nuclei. In addition, we may also study the dynamics[11,12] of molecular motion through the line widths and relaxation times observed in the n.m.r. experiments.

Here we apply solid state ^{13}C n.m.r. to study the backbone conformations of four PDAs: PTS, PTCDU, PETCD and P4BCMU. Among these PDAs, only PTS has side chains incapable of hydrogen bonding. The connections between side chain and backbone conformations are also explored, because the organization of side chains, including their ability to hydrogen bond, may affect the backbone conformation through the strain they place on the backbone.

EXPERIMENTAL

The PDAs (P4BCMU, PETCD, PTCDU, and PTS) were obtained by the solid state polymerization of 4BCMU [5,7-dodecadiyne-1,12-diol-bis((butoxy-carbonyl) methyl urethane)], ETCD [5,7-dodecadiyne-1,12-diol-bis(ethyl urethane)], TCDU [5,7-dodecadiyne-1,12-diol-bis(phenyl urethane)], and TS [2,4-hexadiyne-1,6-diol-bis(*p*-toluene sulphonate)], respectively. The syntheses of these PDA monomers were performed by the procedure reported in the literature[13]. Polymerizations were accomplished by irradiation with 50 Mrad of ^{60}Co γ-rays at room temperature, and unreacted monomers were removed by extraction with acetone.

^{13}C n.m.r. spectra were recorded on a Varian XL-200 spectrometer operating at a static magnetic field of 4.7 T. Magic angle sample spinning (MAS) at a speed of *c.* 3 kHz was achieved with a Doty Scientific variable temperature probe, which utilizes a double air bearing design. The temperature was varied from 20 to 135°C by use of a heated N₂ flow and maintained within ±1°C with the standard Varian temperature control unit.

Polydiacetylenes in powder and film forms were packed in aluminium oxide rotors with Kel-F [poly(chlorotri-fluoroethylene)] end caps. A 45 kHz radio frequency field strength was used for dipolar decoupling (DD), with a decoupling period of 200 ms. The optimum cross-polarization (CP) time was found to be 2 ms for all the PDAs at room temperature, and we used this value at all temperatures. The spectra were referenced to the resonance of poly(oxymethylene) (POM) (89.1 ppm from TMS)[14].

The blue phase of PTCDU was obtained[15] by unidirectionally pressing the red phase powder at a pressure of 10 000 kg cm^{-2}. The resulting blue phase PTCDU sample was a film. The transformation from the red to the blue phase was incomplete, resulting in a sample containing a mixture of both the red and blue phases.

RESULTS AND DISCUSSION

Figure 1 shows the chemical structures of the four PDAs studied here, plus that of PTS12, whose ^{13}C chemical shifts are available in the literature[16]. PETCD, P4BCMU, and PTCDU have very similar molecular structures, the only difference being the terminal portions of their side chains. All three are capable of hydrogen bonding through their side chains. On the other hand, PTS and PTS12 do not have side chains capable of forming hydrogen bonds. Both PETCD and P4BCMU undergo thermochromic phase transitions at *c.* 120 and 90°C, while PTCDU has its transition at *c.* −200°C. However, PTS shows no transition other than decomposition at temperatures higher than 200°C. The difference in the thermochromic phase transition temperatures of P4BCMU, PETCD, and PTCDU may be attributed to the difference in the terminal portions of their side chains, i.e. the difference between CH₂–(C=O)–O–(CH₂)₃–CH₃, ethyl, and phenyl groups. The bulkiness of the terminal phenyl groups in PTCDU may cause the energy stored in the alkyl group portion of the side chain to be released at a lower temperature than in the side chains of PETCD or P4BCMU (see below).

PTS has a blue colour. The low temperature phases of P4BCMU, PETCD, and PTCDU are also blue, while their high temperature phases are red. The blue phases are thought to have an acetylenic structure[8,9,17] (*Figure 2a*), and the red phases were thought to have a butatrienic structure[7] (*Figure 2b*). Recently[8,11,12] however, we were able to clearly demonstrate the absence of a stable butatrienic structure in the red phases of PETCD and P4BCMU by high resolution, solid state ^{13}C n.m.r. spectroscopy. Recent X-ray studies[5,18] suggest the absence of the butatrienic structure in the red phase of PTCDU in contrast to the previous results[4]. The colour of a PDA is directly associated with the electronic structure of its backbone. Here we study the general relation between colour and backbone conformation in PDAs by solid state ^{13}C n.m.r..

Table 1 shows the π–π* transition absorption peak positions[19], which correspond to the excitonic excitation energies, for the PDAs studied in the present work. Note the similarity among the blue and red phase peak positions.

Figure 3 presents the solid state ^{13}C n.m.r. spectra of the PDAs studied: PTS (blue), and PETCD, P4BCMU, and PTCDU (blue and red). The resonances were

Table 1 First optical absorption peak wavelength (cm^{-1}) of polydiacetylenes at room temperature[19]

PDA	Reflection peak (cm^{-1})	(nm)
PTS (blue phase)	16 100	621
PETCD (blue phase)	15 750	635
PETCD (red phase)	18 500	540
PTCDU (blue phase)	15 300	654
	15 170	659
PTCDU (red phase)	18 470	541
	18 800	532
P4BCMU (blue phase)	15 800	634
P4BCMU (red phase)	18 500	540

assigned as indicated in *Figure 3*, and the chemical shifts of the backbone carbons are listed in *Table 2*. Let us compare the spectra of the as-polymerized (red) and pressed (red and blue) PTCDU samples. The pressed sample shows a small resonance at 107.3 ppm corresponding to the blue phase –C≡ carbon, in addition to the primary red phase –C≡ resonance at 102.9 ppm. The spectrum of the pressed sample suggests the coexistence of the red and blue phases. Conversion of the PTCDU red phase to the blue phase appears to be less than 50%, probably because of the modest[15] pressure employed. However, we clearly see the presence of a –C≡ resonance at 107.3 ppm, which corresponds closely to the blue phase –C≡ resonances observed in PETCD and P4BCMU. The details of our studies on PTCDU, including the conformation and packing of side chains, will be presented elsewhere[20].

Let us focus our attention on the chemical shifts of the backbone carbons observed in a variety of PDAs (*Table 2*). The values for PST12 are taken from reference 16. It is apparent from *Table 2* that no resonance corresponding to a stable butatrienic structure (=C=), which should appear[21,22] at c. 136–171 ppm from TMS, is observed in any of the PDAs listed. The chemical shift of =C= should be more downfield than that of –C≡ because the π-electron cloud around =C= is more delocalized than that around –C≡. This also clearly indicates the absence of a stable butatrienic structure, which is consistent with theoretical calculations[23–27] showing that the lowest energy backbone electronic structure is basically the acetylenic structure and the butatrienic structure is higher in energy by 0.5–0.6 eV. Thus, all of these PDAs possess the acetylenic backbone structure independent of whether they are in their blue or red phases. The –C≡ chemical shift for the blue phases of PTS, PTS12, PETCD, P4BCMU and PTCDU is c. 107 ppm, while for the red phase PDAs (PETCD, P4BCMU and PTCDU) it occurs at c. 103 ppm.

From a comparison of the results presented in *Tables 1* and *2*, we can conclude that the colour, and therefore the electronic structure of the backbone, is directly related to the backbone conformation. Most likely there are two predominant backbone conformations for PDAs, one unique to the blue phase and the other unique to the red phase. As discussed in our study[8,11,12] of the thermochromic phase transition of PETCD and P4BCMU, the blue PDAs have a more planar backbone conformation than the red phase PDAs. We found[8,11,12,28] the side chain conformation to become more extended, with more *trans* bonds, during the transition from the blue to the red phase. Transition of the backbone from a planar to a non-planar conformation is affected by rotations about

Figure 3 CP MAS/DD C n.m.r. spectra of PDAs. (a), (b) Blue, red phases of PETCD. (c), (d) Blue, red phases of P4BCMU. (e), (f) Red, pressed (red and blue) phases of PTCDU. (g) PTS (blue phase)

Table 2 ^{13}C chemical shifts of polydiacetylenes, δ ^{13}C (ppm) versus TMS

	C=O	>C=	-C≡	α-CH$_2$	β-CH$_2$, γ-CH$_2$
PETCD (blue)	157.5	131.6	107.4	37.3	24.5
PTS (blue)	–	131.3	107.1	–	–
PTS12 (blue)	–	131.0	106, 108	36	28, 31
PTCDU (blue)	–	–	107.3	–	–
P4BCMU (blue)	158.6	132.2	107.6	37.7	24.9, 24.9
PETCD (red)	158.3	132.0	103.6	37.8	26.4
PTCDU (red)	155.8	131.5	102.9	37.9, 32.3	25.9, 21.8, 28.0, 30.8
P4BCMU (red)	158.5	131.8	102.9	37.2	27.3, 30.9
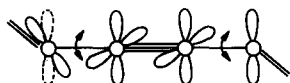
Figure 4 Schematic drawing of π-electron orbitals along a PDA backbone

Figure 5 Chemical bond structure around the backbone >C= carbon

the backbone C–C single bonds (see *Figure 4*). The energy required for these rotations[29], which is contributed by the overlapping of π-electrons, is small. The value of the overlap integral corresponding to the single C–C bond depends on its angle of rotation through a cosine function. Consequently the electronic structure is very sensitive to this kind of conformational change. For PDAs with large side chain substituents, account[11,12] should also be taken of the barriers and conformational energies of the side chains.

According to calculation of overlap integrals[29], the lowest energy backbone conformation is a planar structure. The energy required for the rotation about the backbone C–C single bonds is a continuous cosine function of the rotation angle. Therefore, it would appear that the sharp transition in PDA backbone conformation accompanying the thermochromic phase transition does not originate solely from the backbone energy, but must come from the change in side chain conformation. The thermochromic phase transitions in PETCD, P4BCMU and PTCDU are associated with a conformational transition in their side chains. In the blue phase[11,12] the backbones of PETCD and P4BCMU are in their lowest energy state, while the alkyl portions of their side chains are in a high energy, *gauche* bond conformation. The high conformational energy of the alkyl groups in blue phase PETCD and P4BCMU is compensated by the hydrogen bonding of side chains and the residual memory of the monomer crystal structure. (Detailed studies of the thermochromic phase transitions in PETCD and P4BCMU, including the conformations and motions of their side chains and backbones, are published elsewhere[11,12]).

The chemical shift of the backbone >C= carbons in the PDAs considered here are very similar (131–132 ppm, see *Table 2*), independent of the side chains and the phases. Conformational differences, such as produced by rotations about the backbone single bonds and the first two side chain bonds are expected to affect the chemical shift of >C=. In *Figure 5*, the chemical shift of the >C= carbon C^A is potentially affected by rotations around bonds 2, 3, 4 and 6. Rotations around bonds 2, 3 and 6 may affect the chemical shift of >C= through the usual γ-gauche effects, while rotations around bonds 3 and 4
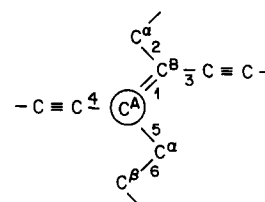
may affect it through the redistribution of the π-electron cloud. The single bonds in the backbone have partial double-bond character. Rotations around bonds 3 and 4 disturb the conjugation of π-electron clouds. Rotations around bonds 3 and 4 probably cause a localization of π-electrons on >C=, which shield >C= causing its resonance to move upfield, as is the case for –C≡, where a 4 ppm upfield shift results (see *Table 2*). This is consistent with the results of theoretical calculations[26], which indicate that a decrease of electron density about >C= occurs with an increase in the degree of delocalization. We think that rotation around the backbone single bonds, such as the rotation around bond 3, is too small to produce a shielding γ-gauche effect on >C=.

Rotations around bonds 2 and 6 can also affect the chemical shift of >C=. There is the possibility that the constancy of the >C= chemical shifts is a result of the cancellation between the localization of π-electrons and the rotations around bonds 2 and 6 via the γ-gauche effect. If this is the case, then bonds 2 and 6 should become more *trans* in the red phase compared to the blue phase, which is consistent with the n.m.r. and X-ray diffraction observations on PETCD and P4BCMU[8,11,12,30–32]. The remarkable constancy of the >C= chemical shifts implies that the cancellation between these two effects is nearly perfect.

The >C= carbon shows only a single resonance, indicating that the angles of rotation around the backbone single bonds are the same on both sides of the acetylenic triple bond (see *Figure 6*). The >C= carbon resonance is a singlet both in its chemical shift position and its mobility. The single >C= resonance peak does not necessarily mean the same rotation angle around all the backbone single bonds, because there is no difference in the >C= chemical shift even between the blue and red phases. However, the motional homogeneity[11,12] of >C=, with a single T_1 (^{13}C), strongly indicates the existence of only a single kind of >C=. This would require a symmetric backbone structure even though it may be non-planar in the red phase.
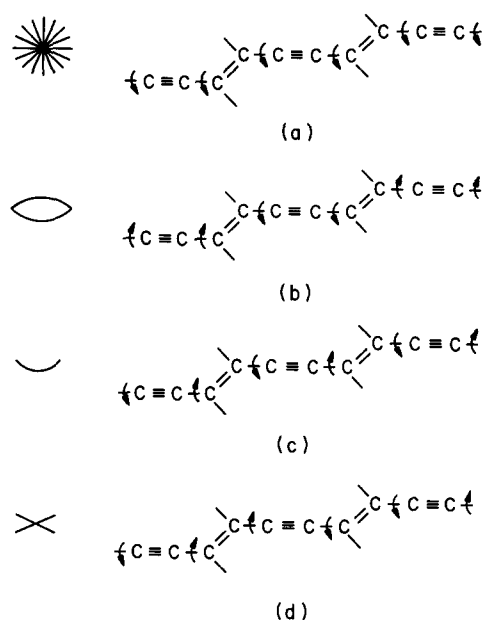
(a)

(b)

(c)

(d)

Figure 6 Models for the rotations around the backbone single bonds in PDAs. The left column shows schematically the direction of the C=C bonds in projection perpendicular to the backbone

The above consideration permits only those types of rotations around the backbone single bonds shown in *Figure 6*. Among these models, (a) is not realistic because, as indicated on the left side of the figure, the direction of the backbone double bonds rotates completely around the molecular axis, which is not consistent with the crystalline packing and the observed fibre repeat unit. In an exact sense, only model (c) has a fibre repeat unit which is about the same as the chemical repeat unit, while models (b) and (d) have fibre repeat units potentially twice as long as the chemical repeat unit. X-ray observations show the fibre repeat unit to be about the same as the chemical repeat unit in both the blue and red phases of PETCD[30,31] and PTCDU[5]. In this sense, model (c) seems most probable however, careful consideration is necessary since the rotation angles around the backbone single bonds are likely to be very small.

Model (b) is not consistent with the retention of inter-side chain hydrogen bonding now known to occur in both the red and blue phases of PETCD, P4BCMU, and PTCDU. Though we favour model (c), because of the symmetry of its single bond rotations which insures equality between the fibre and chemical repeat units, it is difficult to completely rule out model (d).

The chemical shift of the -C≡ carbon is presumably dominated by the magnetic shielding produced by the π-electrons and is sensitive to the delocalization length. Wenz et al.[16] studied the relation between the chemical shift of -C≡ and the delocalization length in several model compounds and found a linear relationship. They also studied the relation between the optical excitation energy, E, and the delocalization length, N, and found it to be well-described by the following Kuhn[33] equation:

$$E = V_0 + [(h^2/4mL_0^2) - (V_0/4)] \times [1/(N + 0.5)]$$

where h is Planck's constant, m is the electron mass, L_0 is the length of the conjugation unit, and V_0 is the amplitude of a sinusoidal potential correcting the free electron gas model for bond length alternation. This

suggests a strong correlation between the colour and the -C≡ chemical shift in the model compounds, which may be generalized to conjugated polymers. From the above relationship we can roughly estimate the conjugation length as 20 (10 repeat units) for the red PDAs and 100 (50 repeat units) for the blue PDAs assuming that their -C≡ chemical shifts are also principally influenced by the π-electrons (*Figure 7*). In *Figure 8*, $N = 20$ and 100 lead to optical excitation wavelengths (λ) of 540 and 680 nm which are in agreement with those observed for red and blue phase PDAs (*Table 1*). However, these estimates of the conjugation length may be inaccurate, because Wenz et al.[16] did not consider the role of backbone planarity in their analysis and furthermore the model they used is probably an oversimplification. It may be more important to estimate the degree of conjugation rather than the conjugation length especially in the case of solid state thermochromic transitions.

The -C≡ resonance of P4BCMU occurs at 101 ppm when dissolved to form a yellow solution[12] in CDCl₃.

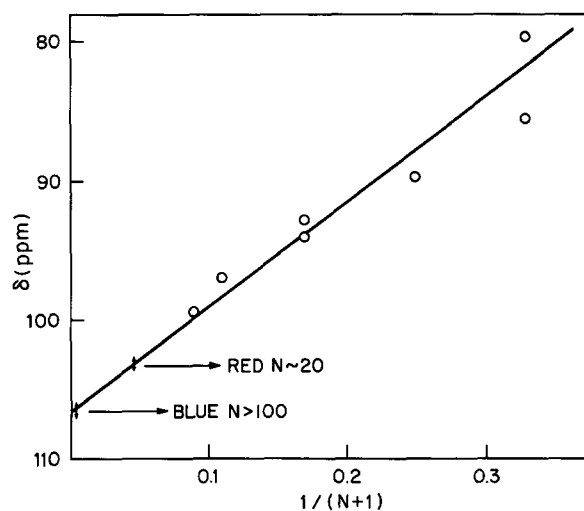**Figure 7** Plot of the observed [13]C n.m.r. chemical shifts, of -C≡ carbons versus $1/(N + 1)$, where N is the conjugation length, for PDAs (‡) and model compounds (○)[16]

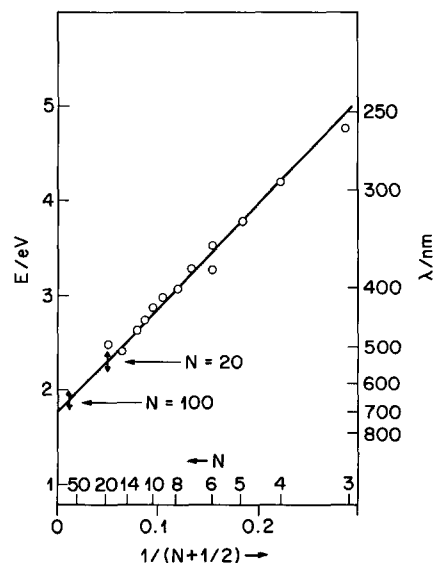**Figure 8** Plot of the optical excitation energy, E, and wave length, λ, versus $1/(N + 0.5)$, where N is the conjugation length, for PDAs (‡) and model compounds (○)[16]

According to the correlation diagram in *Figure 7*, this $-C\equiv$ chemical shift implies a solution conjugation length $N = 12$. When $N = 12$ is placed on the correlation line of *Figure 8*, an optical excitation wavelength $\lambda = 480$ nm is obtained, which agrees closely with that observed[16] for the solutions of soluble PBCMUs where their backbones deviate even further from planarity than their solid red phases.

A precise crystal structure analysis[3] of PTS has clearly established that this PDA has a planar backbone conformation. Our [13]C n.m.r. studies show that the $-C\equiv$ resonance of PTS occurs in the same region (c. 107 ppm) as other blue phase PDAs. This observation provides additional support for the planarity argument, introduced earlier to explain the thermochromism. The extent of planarity decreases at higher temperature and this causes a decrease in the conjugation length, leading to the colour change from blue to red. The decrease in the conjugation length is attributed to the decrease in the backbone planarity based on the following facts:

1. the bond conjugation pattern remains unaltered through the transition;
2. the conjugation length depends only weakly on the backbone valence angles;
3. changes in the bond lengths are energetically too expensive;
4. the band gap is extremely sensitive to the change in planarity achieved by small rotations about the backbone single bonds.

A recent study[31] of a less ordered, melt-crystallized PDA has shown that the $-C\equiv$ resonance occurs at c. 102 ppm, which is further upfield compared to red phase PDAs, and is consistent with a greater loss of planarity. Interestingly as this study suggests, the chemical shift of $-C\equiv$ can be utilized as an indicator of the extent of backbone planarity in any PDA.

Finally, let us consider the origin of the generality in the backbone electronic states among the various PDAs. It is apparent that there are two types of backbone structures which are unique, respectively, to the blue and red phase. As indicated in *Figure 9* there are three models which may explain the generality.
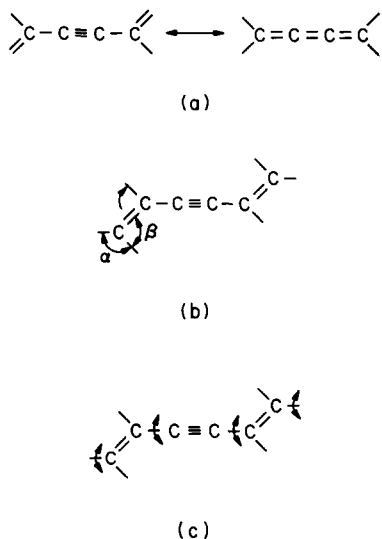

(a)

(b)

(c)

Figure 9 Models for the thermochromic phase transition in PDA. (a) Change in molecular valence structure. (b) Change in valence bond angles. (c) Backbone single bond rotation

Model (a) is based on the difference between two kinds of molecular valence structures, that is the acetylenic and the butatrienic structures. In this case, the origin of the thermochromic transition is thought to be in the backbone itself. All calculations[23-27] indicate that the acetylenic structure is much lower in energy than the butatrienic one. The difference in energy between the two structures is about 0.6 eV (ref. 27) and it is too large to be thermally activated. Furthermore, there is no minimum in the energy map at the butatrienic structure according to the most recent theoretical calculations[27], in contrast to the previous calculation[23]. This clearly indicates the origin of the transition is not in the backbone itself. The absence of the red phase in PTS and PTS12 also suggests that the effect of side chains is more significant than that of the backbone itself for the thermochromic transition. The absence of the butatrienic structure is also apparent from the n.m.r. results[8,11,12] we have already discussed. Furthermore, all calculations[23-27] predict that the butatrienic form would have a lower band gap than the acetylenic form, contrary to the results of optical measurements. A narrower energy gap generally reflects greater delocalization along a chain backbone, which is inconsistent with our n.m.r. results. For these reasons, model (a) appears unrealistic.

Models (b) and (c) are both based on the distortion or slight change of the backbone structure without a change in the bonding pattern. The observed optical spectral shift and n.m.r. chemical shifts in thermochromic PDA crystals can be explained by a small redistribution of electrons along the chain induced by the strain from side chains rather than the change in the molecular valence structure (model (a)). These changes are thought to be caused by the change in the side chain organization which is induced thermally. In particular, the strain from the side chains may play an important role[18,26,34].

In model (b), the degree of conjugation is altered by a change in the valence bond angles[18]. In model (c), on the other hand, it is changed by the rotations around the backbone single bonds. According to Kollmar and Sixl[27], the lowest energy state is the partially delocalized acetylenic structure. They used a bond alternation parameter q, which reflects the bond alternation within the conjugated π system. The state $q > 0$ corresponds to the acetylenic structure, $q < 0$ to the butatrienic structure, and $q = 0$ to the completely delocalized structure. The energy has a minimum at $q = 0.348$, indicating the lowest energy state of PDA is a partially delocalized acetylenic structure. They fixed the planarity of the backbone throughout their calculations. However, the effects of rotation around the single bonds and the valence geometry should be studied theoretically in more detail.

Both the change in the valence bond angles and the rotations around the single bonds probably reduce the delocalized character of bonds. The rotation around a single bond is more likely than the change in the valence bond angle as discussed in a previous paper[11]. In both cases, higher strain causes less delocalization. The distortion of valence bond angles caused by strain seems to be inconsistent with the drastic increase of the mobility of the backbone above the transition point[11,12]. Recent theoretical calculations[29] which neglect the effect of side chains on the rotational barrier show that the barrier for $\pi/2$ rotation around the single bond in the backbone is less than 0.07 eV, therefore, small rotations about the single bonds should be very facile. At the present stage

we believe, that among these models, model (c) is most probable. The chromic transition in PDA solutions is well explained by a planar–non-planar transition. We think the chromic transition in PDA is generally a result of planar to less-planar transition both in the solid state and in solution. It should be checked theoretically whether or not there are potential minima for rotations around the backbone single bonds. Qualitative considerations suggest there may be a local minimum in the total energy at a certain rotation angle around the backbone single bond. The rotation induced by strain probably releases the energy stored in the side chains. On the other hand, the side chains whose rotation is restricted by hydrogen bonding prevent large rotations around the backbone single bonds. These two conflicting factors might make a local minimum in the total energy of PDA at a certain angle for backbone single bond rotation.

Red phases are commonly observed in PETCD, P4BCMU and PTCDU, and all three PDAs have similar structures including the alkyl portions and hydrogen bonding of their side chains. The generality of the red phase should be checked in more PDAs. On the other hand, the blue phases are common in several PDAs. Their generality is better established than that of the red phases, and is probably based on the fact that in the blue phase, PDA is in the lowest energy backbone structure, which is not perturbed by the side chains.

Slight changes of the backbone structure, such as those in models (b) and (c), are probably very difficult to detect by conventional diffraction techniques, and n.m.r. may be the only technique which can tell what kinds of structural and motional changes occur through the transition.

CONCLUSIONS

We have established a correlation between the conformations and the electronic structures (colours) of PDAs through a study of high resolution, solid state ^{13}C n.m.r. spectra of several PDAs in different coloured, crystalline phases. The observation that all blue phase PDAs show $-C\equiv$ resonances at c. 107 ppm, while $-C\equiv$ carbons in red phase PDAs resonate at c. 103 ppm, implies a single blue phase backbone conformation (planar) and a single red phase backbone conformation (slightly non-planar and produced by small rotations about the backbone single bonds). The fact that in all PDAs, the $>C=$ resonances were observed between 131 ppm and 132 ppm suggests that two competing effects resulting from the conformational changes in the backbone and side chains cancel out almost perfectly. The results show that the chemical shift position of $-C\equiv$ can be utilized as a finger print of the extent of backbone planarity in any PDA. In this way, n.m.r. provides a clear correlation between the delocalization along the polydiacetylene backbone and the chain conformation. Such information concern-

ing the PDA chain conformation should be important for understanding the large optical non-linearities exhibited by these materials.

REFERENCES

1 Bloor, D. and Chance, R. R. (Eds) 'Polydiacetylenes', NATO ASI Series E, Applied Science, Martin Nijhoff Publishers, 1985
2 Chance, R. R. 'Encyclopedia of Polymer Science and Engineering', Vol. 4, John Wiley and Sons, New York, 1986, p. 767
3 Kobelt, V. D. and Paulus, E. F. *Acta Cryst.* 1974, **B30**, 232
4 Enkelmann, V. and Lando, J. B. *Acta Cryst.* 1978, **B34**, 2352
5 Kobayashi, A., Kobayashi, H., Tokura, Y., Kanetake, T. and Koda, T. *J. Chem. Phys.* 1987, **87**, 4962
6 Exarhos, G. J., Risen, W. M. Jr and Baughman, R. H. *J. Am. Chem. Soc.* 1976, **98**, 481
7 Chance, R. R., Baughman, R. H., Muller, H. and Eckhardt, C. J. *J. Chem. Phys.* 1977, **67**, 3616
8 Tanaka, H., Thakur, M., Gomez, M. A. and Tonelli, A. E. *Macromolecules* 1987, **20**, 3094
9 Wegner, G. *Discuss. Faraday Soc.* 1980, **68**, 494
10 Agrawal, G. P., Cojan, C. and Flytzanis, C. *Phys. Rev. B* 1978, **17**, 776
11 Tanaka, H., Gomez, M. A., Tonelli, A. E. and Thakur, M. J. *Macromolecules* 1989, **22**, 1208
12 Nava, A. D., Thakur, M. and Tonelli, A. E. *Macromolecules* 1990, **23**, 3055
13 Sandman, D. J., Samuelson, L. M. and Velazquez, C. S. *Polym. Commun.* 1986, **27**, 242; Patel, G. N. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 1591
14 Earl, W. L. and VanderHart, D. L. *J. Mag. Reson.* 1982, **48**, 35
15 Muller, H. and Eckhardt, C. J. *Mol. Cryst. Liq. Cryst.* 1978, **45**, 373
16 Wenz, G., Muller, M. A., Schmidt, M. and Wegner, G. *Macromolecules* 1984, **17**, 837
17 Rubner, M. F., Sandman, D. J. and Velazquez, C. S. *Macromolecules* 1987, **20**, 1296
18 Eckhardt, H., Boudreaux, D. S. and Chance, R. R. *J. Chem. Phys.* 1986, **85**, 4116
19 Schott, M. and Wegner, G. 'Nonlinear Optical Properties of Molecules and Crystals' (Eds D. S. Chemla and J. Zyss), Vol. 2, Academic Press, New York, 1987, p. 28
20 Tanaka, H., Gomez, M. A., Tonelli, A. E. and Thakur, M. to be published
21 van Dongen, J. P. C. M., de Bie, M. J. A. and Steur, R. *Tetrahedron Lett.* 1973, 1371
22 Sandman, D. J., Tripathy, S. K., Elman, B. S. and Samuelson, L. M. *Synth. Met.* 1986, **15**, 229
23 Karpfen, A. *J. Phys. C* 1980, **13**, 5673
24 Sixl, H., Neumann, W., Huber, R., Denner, V. and Sigmund, E. *Phys. Rev. B* 1985, **31**, 142
25 Boudreaux, D. S. and Chance, R. R. *Chem. Phys. Lett.* 1977, **51**, 273
26 Orchard, B. J. and Tripathy, S. K. *Macromolecules* 1986, **19**, 1844
27 Kollmar, C. and Sixl, H. *J. Chem. Phys.* 1988, **88**, 1343
28 Lovinger, A. J., Davis, D. D., Tanaka, H., Gomez, M. A., Thakur, M. A. and Tonelli, A. E. in preparation
29 Dobrosvavljevic, V. and Stratt, R. M. *Phys. Rev. B* 1987, **35**, 2781
30 Downey, M. J., Hamil, G. P., Rubner, M., Sandman, D. J. and Velazquez, C. S. *Makromol. Chem.* 1988, **189**, 1199
31 Tanaka, H., Gomez, M. A., Tonelli, A. E., Lovinger, A. J., Davis, D. D. and Thakur, M. *Macromolecules* 1989, **22**, 2427
32 Iqbal, Z., Murthy, N. S., Khana, Y. P., Szobata, J. S., Dalterio, R. A. and Owens, F. J. *J. Phys. C., Solid State Phys.* 1987, **20**, 4283
33 Kuhn, H. *Fortsch. Chem. Org. Naturst.* 1959, **17**, 404
34 Sandman, D. J. *Mol. Cryst. Liq. Cryst.* 1990, **189**, 273