

## The Colors of Polydiacetylenes: a Commentary

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Polydiacetylenes (PDA) can take several colors, mostly “red” and “blue”, and blue-to-red color transitions are usually considered as transitions from a well ordered state to a disordered one. Recent work on single isolated PDA chains shows that this is not correct: red chains can be quasi-perfect quantum wires. The transition is between two different chain conformations, and each may, or may not, be perfectly ordered. Disorder, when it occurs, is a side-product of the transformation

### Introduction

It has been known since the early days of research on polydiacetylenes (PDA) that PDA chains in bulk polymer crystals can have either of two different structures, with different absorption spectra, so-called “blue” and “red” phases (see, for instance, ref 1). Usually, PDA crystals are either blue or red at all temperatures  $T$ . In some cases, however, a first-order reversible transition between a lower  $T$  blue phase and an upper  $T$  red one is observed, with a large hysteresis, up to 60 degrees.<sup>2–4</sup> The crystal quality degrades after each transition, so the blue phase produced after a temperature cycle is less well ordered than the original one, but still blue.<sup>5</sup> In these transitions, the conjugated chain remains in its electronic ground state, since the lowest energy excited state, a triplet, is near or slightly above 1 eV.<sup>6</sup>

Less well ordered condensed phases, cast films or gels for instance, and Langmuir–Blodgett mono and multilayers, films on water, membranes, and vesicles, also show blue and red phases. These two phases can sometimes be reversibly inter-converted into each other (see, for instance, refs 7 and 8). But generally, a blue phase is irreversibly converted into a red one, either as polymerization proceeds (hence as a function of polymer content  $x_p$ ), or by heating a completely polymerized film. These changes are called “color transitions”. Early work of LB films and similar structures was reviewed by Tieke.<sup>9</sup> Several recent works try to use these transitions in LB films to develop biological sensors, using suitably derivatized diacetylene monomers (see, for instance, refs 10–13).

Chains in the blue single-crystal phases are known to be planar with the so-called “enyne” bond alternation  $=C-C\equiv C-C=$ .<sup>1,14</sup> But the conformation of red chains, and the nature of the color transitions, have been debated, and there is still no general agreement on this. Moreover, other “colors” have been sometimes observed, particularly the so-called “purple” phase, and it is not clear how this phase fits into the overall picture of the transitions. A recent review<sup>15</sup> has dealt with some of these questions.

Recently, we have studied isolated PDA chains, either blue or red, dispersed in their single crystal monomer matrix, essentially that of the diacetylene 3BCMU (with side group formula  $-(CH_2)_3-OCNHCH_2-COO-C_4H_9$ ). A review of all

results up to 2004 can be found in ref 16: it is possible to study a *single* isolated red chain; the dominant optically accessible electronic transition (which spectrum is at the origin of the red color in transmission that gives the phase its name) is an exciton, belonging to a well-behaved one-dimensional exciton *band*; the absorption line is very narrow (down to 300  $\mu$ eV at 6 K); its radiative properties are those expected for a perfect quantum wire,<sup>17</sup> in the whole investigated temperature range, 3–80 K; and in addition, this exciton is a quantum state that is spatially coherent (at low temperature) over the whole chain length<sup>18</sup> (none of these properties have been observed to-date in semiconductor quantum wires, which are not perfect enough). This length is up to more than 20  $\mu$ m, or 4  $10^4$  repeat units.<sup>16,19</sup>

All this points to a very highly ordered polymer chain. The purpose of this note is to explore the logical consequences of this fact for the red chain structure and for the color transitions. It is not meant to be a review, and only papers I felt typical of the question discussed are cited. We shall concentrate on the most frequent transition, between blue and red, and conclude with some remarks about other, less often observed, colors.

PDA solutions in good solvent are yellow ( $\lambda_{max}$  near 470 nm), and a decrease of solvent quality, either by decreasing the temperature through the theta point, or by adding a non solvent, produces red or blue “solutions” at low concentration, and gels at higher ones.<sup>20</sup> These solutions are, in fact, suspensions of red or blue aggregates,<sup>21,22</sup> with optical properties quite similar to those of solid phases of the same color. These color transitions involving PDA solutions are outside our scope here.

**The Blue-to-Red Transition is Not Caused by a Loss of Order.** The spectroscopy of red isolated chains demonstrates that they are a perfect quasi-1D electronic system.<sup>16</sup> Therefore, the formation of the red phase *is not related to a decrease of order* which would cause a shortening of the conjugation length, as is often claimed (see, for instance, ref 23). Conjugation length is not a precisely defined quantity, but it is usually taken as the length of the oligomer that would absorb at the same wavelength as the polymer sample considered. In the isolated poly-3BCMU red chain, which is a perfect extended 1D system, this is meaningless: the exciton is an excitation of the whole chain, it is spatially coherent over thousands of repeat units of the chain, and the two meaningful lengths are as follows: first, the exciton size, or Bohr radius, which is quite small, of the order of 2–3 nm, due to the strong lateral confinement of the wave function<sup>24</sup>

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(about 1 nm in the PDA studied to-date), and second, the total chain length.

That the notion of (disorder-limited) conjugation length, is not appropriate is further demonstrated by consideration of vibrational frequencies. The double-bond stretching frequency of red isolated poly-3BCMU chains is  $\approx 1525 \text{ cm}^{-1}$ <sup>16</sup> (slightly temperature dependent). In the dispersive resonance Raman scattering spectrum (RRS) of yellow solutions of isolated poly-3BCMU chains in good solvent, at room temperature, this frequency occurs for an excitation wavelength  $\approx 475 \text{ nm}$ , corresponding to a “conjugation length” of 6–7 monomer units; and the triple bond stretching frequency at this excitation wavelength is  $2122 \text{ cm}^{-1}$ .<sup>25</sup> Yet, absorption by isolated red chains occurs at 530 nm and the triple bond stretching frequency is  $2160 \text{ cm}^{-1}$ .<sup>16</sup>

This clearly shows that there is no unique correspondence between vibrational frequencies and electronic absorption energy. The conjugation length concept, as it has been applied to PDA chains in good solvent<sup>25</sup> or to polyacetylene films,<sup>26</sup> is not a valid concept when comparing blue and red phases.

Thus the red phase is an electronic structure of the perfect chain, different from that of the blue chains, but unrelated to disorder. Indeed, a recent study demonstrated highly ordered red chains in a pentacosanoic acid multilayer.<sup>27</sup> It may happen that after a blue  $\Rightarrow$  red transition, the red phase is found to be less ordered than the blue one, but this must be a consequence of the transition, not its cause. Disorder is neither necessary nor sufficient to form a red phase, and the B $\Rightarrow$ R transition may correspond to an increase of order.<sup>28</sup>

**The Red Chain is Likely to be Non-Planar.** The blue chain is known to be planar, with an enyne-type alternation of C–C bond lengths.<sup>1,14</sup> The red chain is known to have the same enyne-type bond lengths and the same repeat unit length,<sup>29</sup> so it cannot be planar too.

The fact that its exciton energy (about 2.282 eV at 10 K for red poly-3BCMU isolated chains) is larger than that of the blue chains (1.901 eV in the same crystal)<sup>16</sup> indicates that the intrachain transfer integrals between neighboring repeat units are smaller in the red phase. A natural explanation is that successive repeat units are no more coplanar as they are in the blue chains; for instance,<sup>16</sup> they can be rotated alternatively by an angle  $\pm\theta$  relative to the average plane.<sup>30</sup> Such a structure would agree with the results of solid-state NMR on poly-ETCD crystals.<sup>30–32</sup>

The ground-state energy of the chain will also depend on  $\theta$ . However, the ground-state potential for rotation around a chain bond is very flat<sup>33,34</sup> so a rotation will only marginally increase the ground-state energy.

The exciton energy is a continuously increasing function of  $\theta$ . The fact that the wavelength of maximum absorption for many red systems clusters around 540 nm implies a relatively well defined  $\theta$ , but there is no local energy minimum for the chain itself for any  $\theta$  except  $\theta = 0$ ; the existence of a well-defined red phase cannot be explained by the properties of the chain itself.

In other words, one should look for an energy minimum of the system as a whole chain plus its side groups; this minimum corresponding to a well-defined chain geometry is different from that of the blue chain. The existence of two (at least) chain geometries should be considered as a consequence of side group packing.

**Both Blue and Red Conformations are Compatible with Imperfect Order.** Isolated BCMU chains, and some bulk PDA crystals, particularly poly-DCH,<sup>35</sup> can be considered as almost

perfectly ordered. But the existence of blue and red colors does not require perfect order at all. LB films are not perfectly ordered, and other, even less ordered, solid phases can be blue or red, in the sense that they have an absorption threshold near 640 and 550 nm, respectively. Disordered films of soluble PDA can be cast or spin-coated from solutions; gels can be formed by decreasing the solvent quality.

For instance, the absorption spectrum of a poly-4BCMU red gel in Toluene<sup>20,21</sup> is very similar to the one calculated from the reflectivity spectrum on bulk TCDU polymer crystal.<sup>36</sup> The gel is made of a 3D network of polymer fibrils, and even if these fibrils were perfectly ordered between their connecting points (which is unlikely), the corresponding length cannot be more than a few tens of nm. Blue or red cast films are even more disordered, but the first absorption maximum is still near 620 or 540 nm.

This is not too surprising, since the exciton size is so small: all mesoscopic coherence properties are, of course, lost in disordered samples, but the exciton energy is not much affected as soon as the “conjugation length” is much larger than the exciton size,  $\approx 2 \text{ nm}$ , provided the local geometry of the chain stays the same; hence the existence of disordered blue or red phases. Note, however, that particularly in spin-cast films, there is an excess absorption at shorter wavelengths, corresponding to a more disordered fraction of the film, similar to the yellow solution case. Indeed, resonance Raman spectra excited in that wavelength range show larger vibrational frequencies.

The robustness of the difference between blue and red chains in disordered samples suggests that it has to do with *local* properties, at the level of at most a few repeat units.

**The Most Stable Conformation May be Either Blue or Red Depending on the Side-Groups.** PDA isolated chains in solution are continuous curvature (“wormlike”) chains with a persistence length of 16 nm. The most thoroughly studied, and very instructive, cases are those of poly-3BCMU and poly-4BCMU.<sup>21</sup> In these chains, the hydrogen bonds between successive side groups are all broken. So, both polymer chains have identical geometries in good solvent, but films cast from these solutions, or gels, of poly-3BCMU are blue, while those of poly-4BCMU are red.<sup>20,21</sup> Apparently, the lowest energy state is the blue one in the former, and the red one in the latter. In the latter case, the red phase corresponds to the minimum energy of the system, even though it is not that of the chain itself.

But both polymer crystals, obtained by topotactic polymerization of the corresponding monomer crystals, are blue. So, poly-4BCMU chains in 4BCMU monomer crystal are forced to be in a metastable configuration, the blue state, due to geometrical constraints from the surrounding crystal lattice.

There are other ways to remove, or at least weaken, these constraints, without going in solution. One possibility is to remove, by selective dissolution, the residual monomer from incompletely polymerized samples. This creates “voids” which allow relaxation of elastic energy. Both red  $\Rightarrow$  blue<sup>9</sup> and blue  $\Rightarrow$  red<sup>37</sup> transitions have been observed in that way.

The only difference between the molecular formulas of 3BCMU and 4BCMU is that the side-groups are connected to the chain by a  $-(\text{CH}_2)_3-$  group in 3BCMU and a  $-(\text{CH}_2)_4-$  group in 4BCMU. This is enough to invert the order of the ground state energies of the two conformations, possibly because it affects the geometry, hence the energy, of hydrogen bonds connecting the side-groups.

This is another indication that the color is in fact governed by geometrical constraints from the side groups.<sup>30,38</sup>

**The Role of Side Groups.** It is well established that the reactivity of a monomer DA crystal is dependent on the geometry at the reactive site: distance and relative orientation of two neighboring  $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$  groups.<sup>14,39,40</sup> DA crystals are usually molecular crystals for which van der Waals interactions play a major role in the packing, and since the side groups contain many more atoms than the reactive center, their packing will dominate the crystal structure. In Langmuir films, there is an additional constraint due to the charge at the end of one side group, but the packing within the layer is again due to van der Waals interactions between alkane chains.

One geometrical condition is that two neighboring C4 groups are related by a translation vector  $d_m$  whose length is close to the polymer equilibrium repeat distance  $d_p = 4.9 \text{ \AA}$ .<sup>1,14</sup> In the case of Langmuir films on water, or of LB mono- and multilayer films of fatty acids or salts, the details of the structure vary widely, as evidenced in recent reviews.<sup>41–43</sup> But, as shown for instance in Figure 13 of ref 41, one unit cell parameter of the local packing is often  $4.8 \pm 0.1 \text{ \AA}$ . Replacement of four  $\text{CH}_2$  groups by a diacetylene group will locally change the rigidity and somewhat affect the packing, but the “fact” that, in films of saturated acids, one condition for topotactic reaction is already “met” certainly favors the reactivity of diacetylene films. There are not many structural studies of the latter films, but an early study of multilayers of the Cd salt of the 12/8 acid yielded distances of  $4.86\text{--}4.90 \text{ \AA}$ .<sup>43</sup> In several DA crystals, neighboring side groups are connected by hydrogen bonds which form linear chains in the crystal; for average strength H-bonds, the repeat distance will be close to  $4.9 \text{ \AA}$ .<sup>44,45</sup> favoring the reaction.

However,  $d_m - d_p \approx 0$  only means that a chain growing in its monomer matrix will experience a small longitudinal strain, favoring chain propagation.<sup>46,47</sup> Side group motion (and possibly deformation) induced by the displacement of the reacting C atoms to which they are attached can produce lateral strain of the polymer chain.

The first polymer chains are formed within the monomer structure, and consequently, there is an irreversible energy gain due to the formation of a delocalized  $\pi$ -conjugated system, but stresses build up in the solid since the relaxed geometry of the chain with its side groups is not identical to that of the monomers it replaces.

As polymerization proceeds, the accumulated stress increases. The stress is not principally longitudinal, since the repeat unit length is close to a unit cell parameter of the monomer, and is almost the same in the blue and red phases, as deduced from single-crystal X-ray diffraction;<sup>14,29</sup> it is mostly lateral. So, it forces a geometrical change onto the side groups, which in turn may provoke a geometrical change on the chain itself. Buildup of stresses is a possible cause for a phase transition. LB films of pure fatty acids exhibit a relatively rich polymorphism,<sup>41–43</sup> and it is likely to be true also of diacetylene LB films. This indicates that there are several crystal structures with comparable lattice energies.

A blue  $\rightleftharpoons$  red color transition is a phase change. It is not a conformational change of the chain alone, on the contrary, the color change may be a visible indication of the phase change of the system as a whole.

One might propose the following scenario: There is a competition between the chain geometry governed by chain electronic properties alone, and a constraint imposed at some point on the side groups. This may be, in the examples given above, the presence of H-bonds, or the preferred geometry of the ionized interface, or else a distortion at the free film surface generated by binding of a bulky group (in biological sensors

applications), or by shearing under an AFM tip.<sup>48,49</sup> It may also be that the monomer matrix undergoes a phase change as a function either of temperature or pressure, or of polymer content at partial polymerization. The stress corresponding to that constraint is transmitted to the chain via the alkyl chains, long enough to allow possible rotational isomerizations. Such isomerizations generate a small number of possible chain conformations only, each of which corresponds to a defined out of plane distortion of the chain. Indeed, the amount of gauche bonds in the side groups changes at the color transition of the poly-ETCD crystal.<sup>30</sup>

**Color Transitions Triggered by Electronic Excitation of the Chain.** The color transitions in LB films as a function of  $T$  or the polymer content  $x_p$  all occur with the chain in its electronic ground state. Similarly, thermally induced  $\text{B} \rightleftharpoons \text{R}$  transitions in PDA single crystals do not imply electronic excitation. However, transitions triggered by light have been reported in bulk PDA crystals showing a thermal reversible transition;<sup>52</sup> in addition, an irreversible  $\text{B} \rightarrow \text{R}$  transition has been reported in solid films of the LB film forming PDA 12/8.<sup>53</sup> I am not aware of any similar result in Langmuir or LB films.

The  $\text{B} \rightleftharpoons \text{R}$  thermal transition in PDA crystals usually shows a large hysteresis. Within the  $T$  range of the hysteresis cycle, it is possible to achieve the  $\text{B} \rightarrow \text{R}$  transition or, less efficiently, the  $\text{R} \rightarrow \text{B}$  one by an intense enough light pulse. The microscopic mechanism has not been completely elucidated, but the transitions are not related to heating. Whatever the details, this is apparently a process in which the chain geometry is first affected, and the corresponding distortion is enough to overcome the barrier between the two conformations and trigger the geometrical change in the side-groups that leads to the transformed state. But very high excitation densities, thus large changes in the chain electron configuration, are required to trigger such transitions, which thus appear quite different from those discussed in this comment, which all occur in the chain electronic ground state.

**The Purple Phase.** The existence of a phase absorbing at a wavelength ( $\approx 590 \text{ nm}$ ) intermediate between the blue ( $\approx 630 \text{ nm}$ ) and the red ( $\approx 540 \text{ nm}$ ) phases has been noted early on.<sup>54</sup> But it has been more thoroughly studied only more recently.<sup>49,55,56</sup> Not enough is known yet to allow a detailed model, but some comments are possible.

It was pointed out above that red chains can be perfectly regular. If purple chains can be too, the same reasoning as above leads to the conclusion that they are not planar. A distortion similar to that postulated for the red chains is possible, but the distortion angle must be smaller, since the purple phase absorbs at longer wavelengths. It has been proposed<sup>49</sup> that the blue-to-red transition sometimes proceeds in two steps, the first blue  $\rightleftharpoons$  purple one being easily reversible. Since this occurs in partially polymerized samples, it would be interesting to correlate this behavior with structural changes in the monomer layer crystal structure.

Since it has not been proved that purple chains are regular, they could, in principle, be planar chains in which (reversible) structural defects would interrupt the conjugation, that is, restore a bona fide “conjugation length”, leading to a blueshift of the absorption, and to an increase of the Raman frequencies.<sup>25</sup> But since the purple spectrum may be as well resolved as the blue one, it requires that the defects are equally spaced in order to have a single value of the conjugation length.

At first sight this may seem very odd, but there is, in fact, a mechanism able to produce such a situation: the Frenkel–Kontorowa model (see for, instance, ref 57). It has been shown

that when a 1D periodic system is subjected to a periodic potential, which differs slightly from the natural period of the system, the lowest energy state may correspond to the formation of regularly spaced defects, named discommensurations. Their distance depends on the mismatch of the two periods. Therefore, if the film has a phase transition significantly affecting the parameter in the direction of the PDA chain axis, so that it becomes more different from the equilibrium value of ca. 4.90 Å, the chain experiences a compressive or a tensile strain: the conditions for the appearance of discommensurations may be met. These defects will define “boxes” all of the same length; hence, a single conjugation length. As the film is further heated, the mismatch period will vary, so one would expect in this model a small shift of the “purple” absorption and Raman frequencies with  $T$ . The process is, of course, reversible: upon cooling, the film returns to its initial structure and the discommensurations disappear.

An order of magnitude of the size of the boxes that would be implied by the experimental values of Raman frequencies and optical transition energies can be estimated using the empirical relations between these quantities and the number  $N$  of monomers in a conjugation length.<sup>25,33</sup> Depending on the particular PDA considered, one finds values for  $N$  from  $\sim 20$ <sup>58</sup> to  $\sim 30$ ,<sup>49</sup> that is, a distance between defects of 10–15 nm, with at least one indication of energy shift with  $T$ .<sup>58</sup> This is not a ridiculous value, but it is not enough to support that model, which remains unlikely.

Still, this discussion of the purple phase may serve to illustrate two ideas. If the model of chain torsion is correct, it shows that PDA chains are “adaptable” and may take various conformations of comparable energies. The Frenkel–Kontorowa model illustrates the fact that a stress does not always produce random disorder, and that such a system may sometimes prefer a periodic deformation.

## Conclusion

A PDA chain can have at least two types of ground state conformations, corresponding to the blue and red phases. Both may be perfectly ordered, in fact the perfect order has been better characterized in red chains.<sup>16</sup> Only one of these conformations (the blue one) corresponds to the minimum ground-state energy of the conjugated chain itself, the other (the red one) is not even a local minimum of that energy; the red transition energy does not vary much among red PDA, and not more than the blue one.<sup>16</sup> Thus, in the red phase, the chain has a fairly well defined (non planar) geometry. It is determined by the side groups, which must have two different, well defined, geometries in the two phases.

The red phase produced in a color transition is not inevitably disordered. In fact, it may even be better ordered than the initial blue one. The different transition energies only reflect the fact that the chains have different geometries, and they should not be analyzed in terms of “reduced conjugation length”.

Disorder can be introduced in both phases without producing a color change, that is without much affecting the transition energies. For instance, a red poly-4BCMU gel has a well-resolved absorption spectrum,<sup>21</sup> not much different from that of a red PDA single crystal at room temperature.<sup>36</sup> This is probably related to the small exciton size.<sup>16,35</sup> But this small size has nothing to do with a reduced conjugation length: a red chain can be so perfect that a macroscopic spatial coherence of the exciton is observed.<sup>18</sup> Rather, the small exciton size is a natural consequence<sup>24</sup> of the reduced dimensionality: a PDA chain is possibly as close to an exact one-dimensional quantum wire as is physically possible, with a width smaller than 1 nm.

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## References and Notes

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