Unusual chromatic properties observed from polymerized dipeptide diacetylenes

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The chromatic properties of a few dipeptide polydiacetylenes were found to change dramatically with very slight structural variations of dipeptides, leading to the proposal of a non-coplanar packing model to explain the chromatic behavior of polydiacetylenes.

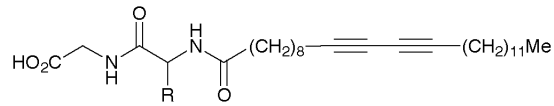
In 1993 Charych *et al.* reported the development of a direct colorimetric detection method of influenza virus based on the chromatic change of polydiacetylene Langmuir–Blodgett films.[1] This work provided a new possibility for diagnostic applications, and the chromatic property of polydiacetylenes has caused extensive attention since then. However, up until now, the precise molecular mechanism of the blue to red color change or transition remains unclear.

At the present time, it is generally accepted that the chromatic difference is based on the difference in the effective π-electron delocalization length along the polymer backbone. The blue form of polydiacetylene, which absorbs light at around 640 nm in the red region, is believed to have a more effective π-electron conjugation length, whereas the red form of polydiacetylene, which absorbs light at around 540 nm in the blue region, has a shorter π-electron conjugation length.[2] However, conflicting explanations for what causes the difference of the effective π-electron conjugation length have been put forward. A model which was generally accepted during the past years attributes the less effective π-electron conjugation of red form polydiacetylenes to conformational disorder or the entangling of the side chains.[3] However, this side chain disorder model is facing more and more challenges from new experimental observations. Recent investigations by FT-IR, electron diffraction[4] and atomic force microscopy[5] have shown that the side chains of red form polydiacetylenes are actually also in an ordered conformation.

Cheng and Stevens reported that the chromatic properties of polydiacetylene liposomes functionalized with amino acids such as Glu, Gln and His as polar moieties were affected by the pH of the aqueous solution.[6] The chromatic change upon pH value variation is attributed to the repulsive Coulombic interactions developed on the surface due to ionization of the amino acid head groups. As a result, the head groups must rearrange themselves to a staggered non-coplanar packing to accommodate the new charge distribution. The staggered non-coplanar packing of diacetylene lipids leads to the formation of a non-linear red form polydiacetylene backbone when irradiated, yet the alkyl chains attached to polydiacetylene backbone remain in their well-ordered conformation.

In the meantime, our recent study of hydrogen bonding effects on the polymerization and chromatic properties of a triaminotriazine diacetylene lipid has led us to the same conclusion.[7] In order for two different diacetylene lipids to attain stable intermolecular hydrogen bonding, the two lipids were packed into a staggered non-coplanar packing mode in the mixed monolayer, leading to the observation of only red form polydiacetylene films.

We now report experimental evidence which further supports this mechanism. Four dipeptides, GlyGly, AlaGly, ValGly and PheGly, were attached to pentacosa-10,12-diynoic acid (PDA) through solid phase peptide synthesis. The four dipeptide



PDA-GlyGly-OH R = H
PDA-AlaGly-OH R = Me
PDA-ValGly-OH R = Pr^i
PDA-PheGly-OH R = Bn

diacetylene lipids have the same molecular skeleton structure, except that they have different hydrophobic side groups on the second amino acid residue. While PDA-GlyGly-OH has no side group, PDA-AlaGly-OH has a methyl side group, PDA-ValGly-OH has an isopropyl side group and PDA-PheGly-OH has a benzyl side group. The surface pressure–area isotherm measurements have shown that the four lipids formed stable monolayers at the air-water interface (Fig. 1). The limiting molecular areas of PDA-GlyGly-OH, PDA-AlaGly-OH, PDA-ValGly-OH and PDA-PheGly-OH are 23, 32, 36 and 40 $Å^2$ $molecule^{-1}$, respectively, which are proportional to the size of the second amino acid side groups in the dipeptides.

The dipeptide Langmuir films were irradiated with UV light (254 nm) at a surface pressure of 20 mN m^{-1} on a pure water subphase (pH 5.80). The *in situ* UV-Vis absorption spectra of the monolayers with different irradiation times are presented in Fig. 2. Tremendous chromatic differences were observed from the four polymerized dipeptide lipid monolayers, despite the very slight structural differences between these molecules. While the PDA-GlyGly-OH monolayer exhibits a typical blue absorption band with a maximum absorption around 640 nm, the polymerization of PDA-AlaGly-OH, PDA-ValGly-OH and PDA-PheGly-OH monolayers leads to the appearance of polymer absorption bands at 570 (purple form), 535 (red form) and 525 nm (red–yellow form), respectively.

The only difference between these peptide amphiphiles is the size of the hydrophobic side groups on the second amino acid residue. It has been reported previously that dipeptide GlyGly derivatized lipids with single hydrophobic alkyl chains tend to form β-sheet structures at the air-water interface, due to strong

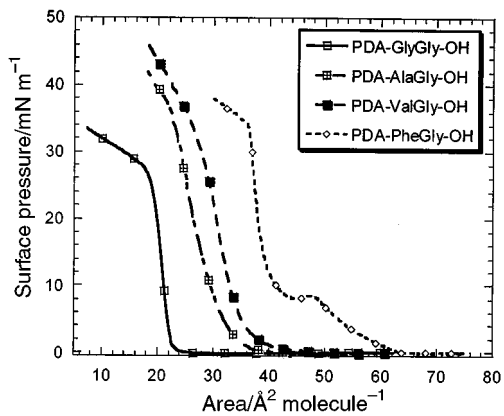


Fig. 1 The surface pressure–area isotherms of the dipeptide diacetylene lipids at the air-water interface.

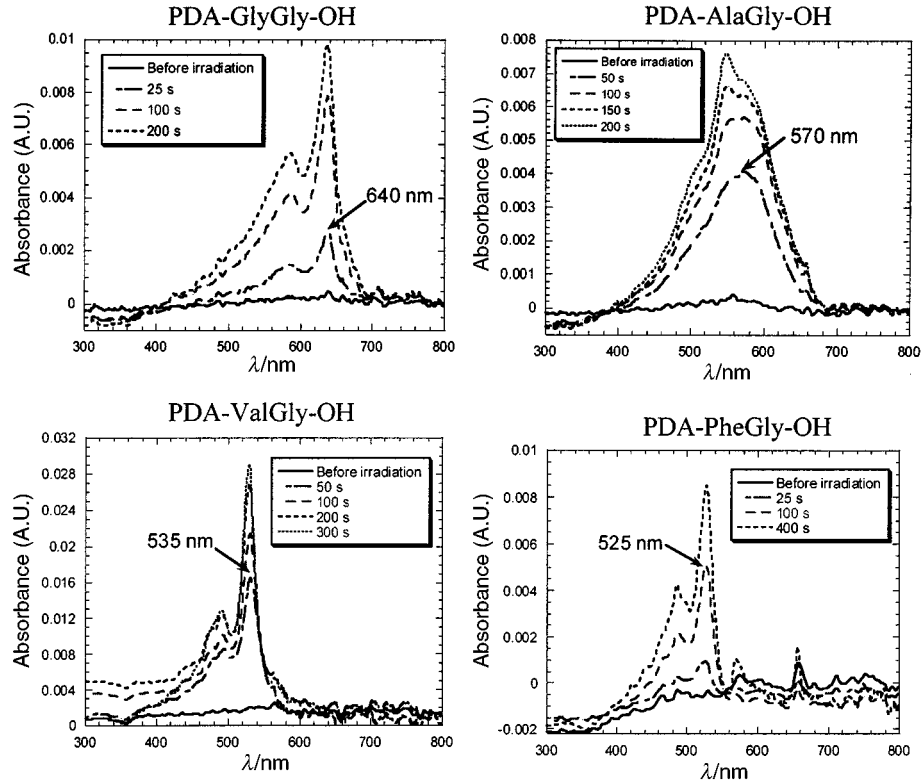


Fig. 2 The UV-Vis absorption spectra of polymerized dipeptide diacetylene monolayers with different irradiation times.

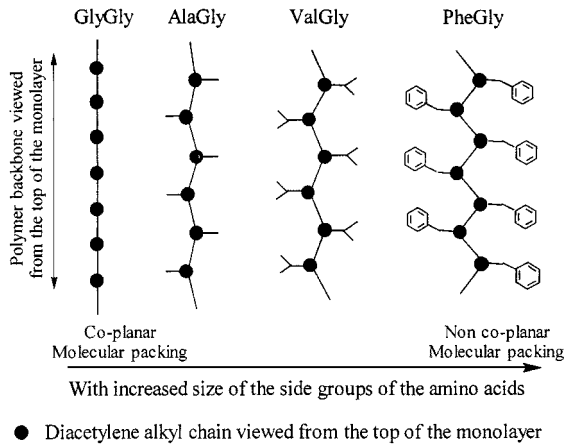


Fig. 3 An illustration of the decreased linearity of the polydiacetylene backbone due to the non-coplanar packing of diacetylene lipids with the increased size of the side groups on the dipeptides.

hydrogen bonding between the GlyGly polar moieties.[8] We believe that the PDA-GlyGly-OH lipids also formed a β-sheet structure at the air-water interface and the lipid alkyl chains are packed in a coplanar mode. As a result, the polymerization of the coplanar diacetylene groups leads to the formation of a linear blue form polydiacetylene backbone, as shown in Fig. 3.

In the case of PDA-AlaGly-OH, due to the presence of a methyl group as a side group on the dipeptide, steric hindrance does not allow the formation of a perfect β-sheet structure. The PDA-AlaGly-OH lipids are obliged to adopt a staggered non-coplanar packing mode. With this staggered non-coplanar packing of diacetylene lipids, the photoirradiation leads to the formation of a non-linear zigzag red form polydiacetylene backbone, as illustrated in Fig. 3. With increased size of the side groups on the amino acid residues, as in the case of PDA-ValGly-OH and PDA-PheGly-OH, the linearity of the polymer backbone is further decreased, leading to a shift of the absorption band towards lower wavelength.

Theoretical calculations have shown that very slight rotations around the C–C bonds of the polymer backbone (5°) are enough to produce a dramatic decrease in the π–π electron conjugation length.[9] When the non-coplanar packed monolayer is polymerized, the C–C single bonds must rotate away from the linear backbone to accommodate the non-coplanar packing of the lipids. Even a slight deviation of lipids from coplanar packing may introduce enough rotations of C–C bonds to produce large chromatic differences, as observed from the four dipeptide lipids. In the meantime, the alkyl side chains attached to the polymer backbone remain in their well-ordered conformation without being disturbed by the slight structural change of the polydiacetylene backbone.

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