

Fluorogenic Conjugated Polymer Fibers from Amphiphilic Diacetylene Supramolecules

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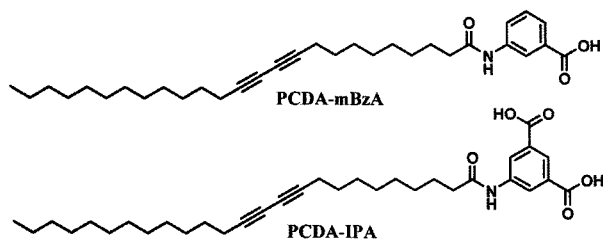
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Introduction

Polydiacetylenes (PDAs),¹⁻¹³ a family of intriguing molecules that have the unique characteristics of self-assembly and π -conjugation, are prepared by irradiation of molecularly ordered diacetylene monomers. The polymer backbone of PDAs, comprised of alternating ene-yne groupings, is responsible for an intriguing stress-induced chromic (blue-to-red) transition. As such, PDAs have been extensively investigated as potential chemosensors.

PDAs prepared in aqueous or organic solvents from most of amphiphilic diacetylene monomers are amorphous vesicles. Although much effort has been given to the development of PDA-based wires/fibers,¹⁴ the majority of reported methods require multistep syntheses of the monomeric diacetylene starting materials. Recently, the efficient preparation of PDA wires from aliphatic amino acid-derived diacetylene monomers was reported.¹⁵ Another important feature of PDAs that has not been much addressed thus far is the fluorescence. Although it has been known that PDAs in 'blue-phase' are nonfluorescent, while their 'red-phase' counterparts fluoresce,¹⁶ little effort has been focused on the fluorescence-based PDA sensor systems until recently.^{10,17} In this note, we describe facile synthesis of fluorogenic PDA nanoribbons generated from UV irradiation of supramolecularly-assembled functional diacetylenes.



During our investigations toward colorimetrically reversible PDA systems, we discovered the PDAs prepared with

the amphiphilic diacetylene monomer PCDA-mBzA show complete colorimetric reversibility during heating and cooling cycles.¹⁸ Scanning electron microscope (SEM) images demonstrate that the PDAs, derived from PCDA-mBzA, exist as spherical vesicles and that no wire/ribbon forms are present. Surprisingly, addition of one more carboxylic acid group to the phenyl ring of PCDA-mBzA afforded completely different morphologies of the resulting PDAs. Thus, the isophthalic acid (IPA)-derived diacetylene PCDA-IPA was found to form almost exclusively fiber forms under specific self-assembly conditions.

Experimental

Materials. 10,12-Pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals. 5-Aminoisophthalic acid was obtained from Aldrich.

Synthesis of PCDA-IPA. To a solution containing 1.00 g (2.67 mmol) of PCDA in 20 mL of methylene chloride was added dropwise 0.81 g (8.01 mmol) of oxalyl chloride and a catalytic amount of DMF at room temperature. The resulting solution was stirred at room temperature for 2 h, concentrated in vacuo, giving a residue which was redissolved in 10 mL of methylene chloride. The resulting solution was added dropwise to the solution containing 0.58 g (3.20 mmol) of 5-aminoisophthalic acid in 15 mL of pyridine. The resulting mixture was stirred for 12 h at room temperature and poured into cold water to yield a precipitate containing the desired diacetylene monomer PCDA-IPA as an off-white solid (0.96 g, 67%).

PCDA-IPA: mp 224 °C; ¹H-NMR (300 MHz, DMSO-d₆): δ = 0.84 (t, 3H), 1.23-1.75 (m, 36H), 2.25-2.33 (m, 6H), 8.13 (s, 1H), 8.43 (s, 2H), 10.26 (s, 1H); ¹³C-NMR (75 MHz, DMSO-d₆): δ = 13.93, 18.27, 22.09, 24.95, 27.70, 28.16, 28.33, 28.39, 28.58, 28.71, 28.87, 29.01, 31.30, 36.40, 65.34, 77.92, 123.39, 124.29, 131.64, 139.90, 166.50, 171.75; IR 1407, 1463, 1546, 1604, 1668, 1693, 2848, 2921, 3272 cm⁻¹.

Results and Discussion

The diacetylene monomer PCDA-IPA was readily prepared by reaction of an acid chloride, formed from commercially available 10,12-pentacosadiynoic acid (PCDA), with 5-aminoisophthalic acid in pyridine. Pouring of the reaction mixture into cold water affords PCDA-IPA as a solid. A clear solution is obtained when a dispersed mixture containing 4 mg of PCDA-IPA in 4 mL of 30% H₂O-EtOH is heated to 50 °C. Upon cooling this solution to room temperature, a white solid was formed in high yield (> 90%).

The optical (A) and (B) and SEM (C) and (D) images (Figure 1) of the diacetylene monomer PCDA-IPA formu-

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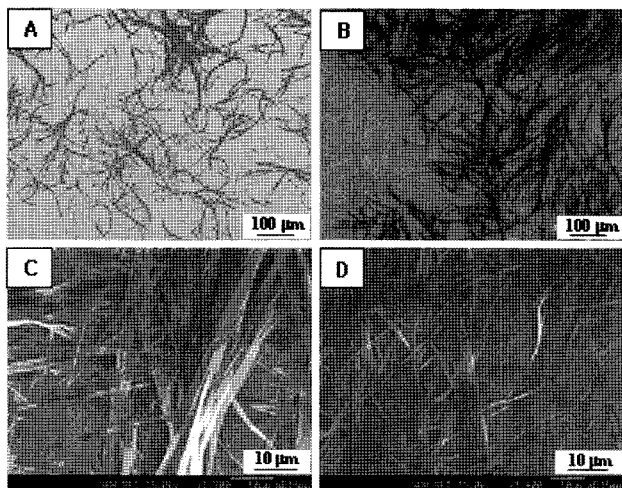


Figure 1. Optical (A and B) and SEM (C and D) images of PCDA-IPA-derived self-assembled diacetylene ribbons obtained before (A and C) and after (B and D) UV irradiation (254 nm, 1 mW/cm², 1 min).

lated in this way show that the diacetylene assemblies exist as microfibers. As expected, UV irradiation (254 nm, 1 mW/cm², 1 min) of this self-assembled diacetylene monomer produces blue-colored microwires associated with the formation of conjugated ene-yne grouping (Figure 1(B)). Close inspection of the SEM image of the material after irradiation (Figure 1(D)) reveals that no significant morphological change has occurred.

In order to determine the effect of solvent composition on the formation and morphology of the resulting diacetylene supramolecules, fiber formation with PCDA-IPA was carried out in solvent systems containing various ratios of H₂O-EtOH (Figure 2). PCDA-IPA is soluble at room temperature in pure EtOH and no precipitate forms. Fibers are formed upon cooling of heated solutions of PCDA-IPA in 20% H₂O-EtOH but they exist as bundles (Figure 2(A)). When the amount of water in the H₂O-EtOH solution is in the range of 30–50%, individual ribbons are formed as shown by the SEM images (Figure 2(B) and (C)). Interestingly, significantly shorter wires form when supramolecular assembly is conducted in 60% H₂O-EtOH (Figure 2(D)) as compared to those formed in 30–50% H₂O-EtOH. Increasing the relative amount of water above 60% retards wire formation and results in the build-up of amorphous aggregates. Only amorphous aggregates are produced when fiber formation is attempted in pure H₂O. The above observations indicate that the fiber length can be manipulated to a degree by changing the solvent system used. Thus, if relatively long fibers are desired, self-assembly in 30–50% H₂O-EtOH is recommended, whereas shorter wires can be prepared by using 60% H₂O-EtOH system.

In order to probe the fluorescent properties of PDA wires, a white solid precipitate formed upon cooling a solution of

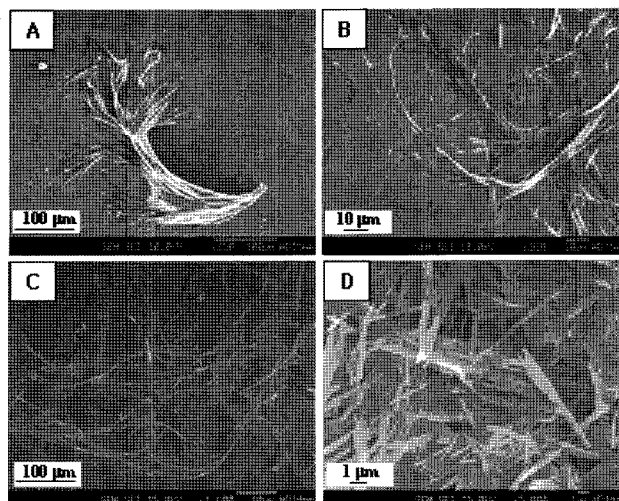


Figure 2. SEM images of PCDA-IPA-derived polymerized solid precipitates obtained in EtOH solutions containing 20 (A), 30 (B), 50 (C), and 60% (D) of H₂O (UV irradiation: 254 nm, 1 mW/cm², 1 min).

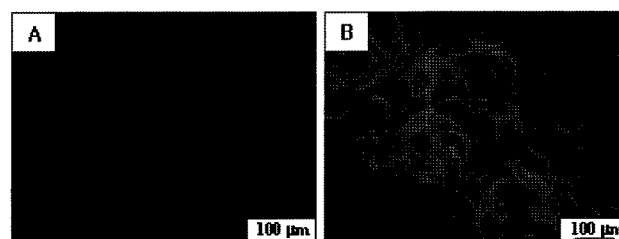


Figure 3. Fluorescence microscopic images of self-assembled (30% H₂O-EtOH) and polymerized (UV irradiation: 254 nm, 1 mW/cm², 1 min) PCDA-IPA observed before (A) and after (B) heating (100 °C, 1 min).

PCDA-IPA in 30% H₂O-EtOH was irradiated with 254 nm UV light (1 mW/cm²) for 1 min. As expected, UV-irradiation results in the generation of blue-colored PDAs. A glass slide containing a drop of the blue-colored suspension was heated at 100 °C for 1 min. This promoted the blue-to-red color transition of the PDAs. In Figure 3 are shown fluorescent microscopic images of the PDAs generated in this manner before and after heat treatment. As expected, no image appears from the sample obtained before heating (Figure 3(A)). In contrast, fluorescence images are clearly observed from the thermally-treated, red-colored fibers (Figure 3(B)). The heat-induced nonfluorescent-to-fluorescent change shows that polymerized diacetylene fibers are fluorescent in their ‘red-phase’, much in the same way that they are in immobilized vesicles.¹⁰ We believe that the stress-induced fluorogenic properties of PDA microfibers will be applicable to the development of PDA-based fiber sensor systems.

Conclusions

We have developed a simple strategy for the preparation

of fluorogenic polydiacetylene fibers. The diacetylenic isophthalic acid PCDA-IPA was found to form microfibers when warm aqueous ethanolic solutions are cooled to room temperature. Irradiation of the self-assembled diacetylene wires with 254 nm UV light afforded blue-colored polydiacetylene wires, as evidenced by optical, fluorescence and scanning electron microscopic analyses. Relatively long polymer ribbons (ca. 100 μm) were obtained when 30-50% H₂O-EtOH solvent systems are used while much shorter wires (< 10 μm) form in 60% H₂O-EtOH. Thus, wire lengths can be varied by changing solvents. Importantly, the nonfluorescent polymerized ribbons were transformed to fluorescent PDAs upon heating. The observations made in this effort should be useful in the development of new and interesting PDA-based materials.

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