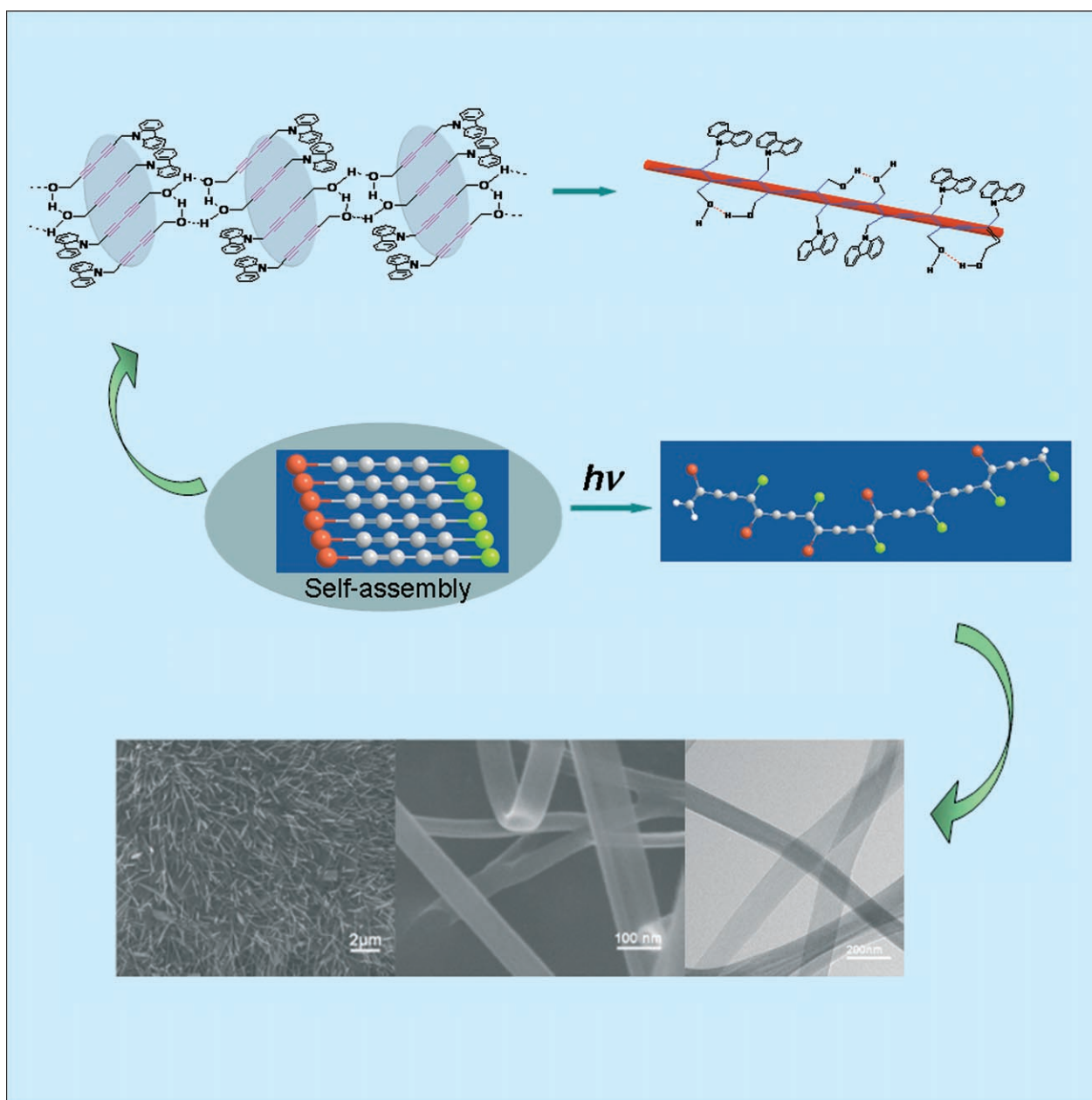# FOCUS REVIEWS

Progress in Polydiacetylene Nanowires by Self-Assembly and Self-Polymerization

Weidong Zhou, Yuliang Li,* and Daoben Zhu*[a]

Abstract: In recent years, there has been immense interest in studying nanoscale aggregate structures derived from various polydiacetylenes (PDAs). The motivation for this is not only to understand the fundamental aggregate structures at different scales, but also to explore their potential for future technological applications. PDAs have been made sensitive to external stimuli such as light and chemical entities by incorporating a spectroscopically active moiety or a receptor unit as the head group of the PDA molecule. This makes them suitable for applications such as sensing and actuating. Furthermore, owing to the delocalization of π-conjugated electrons, PDAs have been exploited as good candidates for organic nonlinear optical materials. This Focus Review highlights some of the instructive work done by various groups to develop well-defined one-dimensional assembly systems with a highly structural aspect ratio, which can be directly imaged by microscopic techniques.

Keywords: nanowires · polydiacetylenes · polymerization · polymers · self-assembly

1. Introduction

Molecules with a one-dimensional (1D) projection show the most potential as materials for nanodevices. π–π-Conjugated (semiconducting) polymers are by far the most promising functional polymers in view of their applications in less-expensive and flexible electronic devices. For example, polypyrrole nanowires were synthesized by electrodeposition for pH sensors,[1] polyphenylenevinylene nanowires were synthesized by nanolithography for light-emitting materials,[2] sharp conical volcano-like polypyrrole nanostructures were formed for field-emission applications,[3] and so on. Polydiacetylenes (PDAs), a type of conjugated polymer, attract considerable attention owing to their quasi-1D electronic structures, quick and large nonlinearity responses, and very fast photoconduction properties.[4] PDA nanowires as a type of conductive material have shown their importance in interconnecting molecular devices in molecular electronics systems.[5,6] Furthermore, PDA systems can also work as chemical sensors because they undergo a visible color change (blue→red) in response to a variety of environmental perturbations such as temperature, pH, and ligand–receptor interactions.[6]

[a] W. Zhou, Prof. Y. Li, Prof. D. Zhu
    Key Laboratory of Organic Solids
    Center for Molecular Sciences, Institute of Chemistry
    Chinese Academy of Sciences
    Beiijng, 100080 (China)
    Fax: (+86)10-826-16-576
    E-mail: ylli@iccas.ac.cn
          zhudb@iccas.ac.cn

2. Self-Assembly Process and Mechanism

Diacetylene polymerization occurs only when it is in a highly ordered state (i.e., topochemical or solid-state polymerization).[7–9] It requires an optimal packing of the diacetylenic units to allow propagation of the linear chain through the ordered phase. When the system is extremely well-ordered and the extent of polymerization is high, the potential for application is enhanced because polymerization does not alter the morphology. The packing of monomers is determined by the side groups attached to the diacetylene units, thus it can be tailored by choosing the appropriate substituents or head groups. The key structural factors for a diacetylenic-lipid system include the total chain length, the position of the diacetylenic unit within the chain, and the chemical nature of the head group. Interactions between neighboring molecules via their head groups are especially important for the propagation of induced 1D ordered nanostructures. When diacetylene polymerization occurs in the middle of an alkyl chain, highly organized self-assembled systems in which the diacetylene groups are aligned as a band form. Unlike polydiacetylene itself, these materials are rather tractable, especially if a linear superstructure is required.
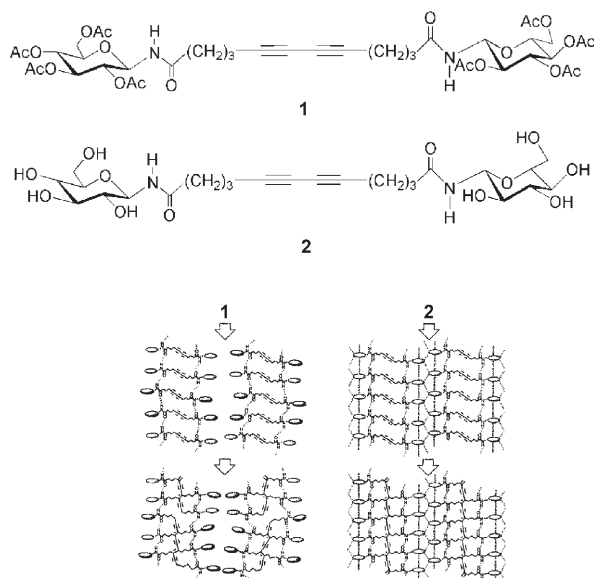
Various 1D ordered nanostructures have been constructed from the polymerization of diacetylene in the past decade, such as nanorods, -wires, -planes, helical ribbons, and so on. The general explanations suggested for the driving force of the self-assembly and the mechanisms of the aggregation process are hydrogen bonding, hydrophobic interactions, and π–π stacking. On the basis of this important point, the aggregation of PDAs can be classified into these three categories.

FOCUS REVIEWS

2.1. Assembly by Hydrogen Bonding

Hydrogen bonds are ideal secondary interactions for constructing supramolecular architectures as they are highly selective and directional. In nature, beautiful examples of these properties are present in DNA and proteins. Hydrogen bonds are formed when a donor (D) with an available acidic hydrogen atom interacts with an acceptor (A) carrying available nonbonding lone-pair electrons.[9] In the past three decades, hydrogen bonding, as a very useful driving force for the construction of supramolecular systems, has been widely used for the design of various molecular aggregates. In many cases, the introduction of strong hydrogen-bonding moieties, such as amide or urea groups, was shown to be instrumental in the structuring and stabilization of these assemblies. To date, a large variety of functional PDA 1D nanostructures has been constructed through multiple hydrogen bonds.

The structures of bisglucoside bolas with a stiff core have been widely studied in the field of supramolecular self-as-sembly owing to the potential introduction of multiple hydrogen bonds and hydrophile interaction. The structure of stiff diacetylene groups with bisglucoside bolas and their self-assembly behavior have been described by Masuda and co-workers.[10] The peracetylated derivative **1** (Scheme 1) formed an organogel from boiling ethyl acetate/n-hexane mixed solvent upon cooling to room temperature. In contrast, **2** produced fibrous assemblies from aqueous solution on addition of THF by vapor diffusion. TEM revealed the formation of nanowires with widths of 6–20 nm for **1** and more than 50 nm for **2**. Powder X-ray diffraction studies revealed that fibers derived from **2** displayed a higher molecular packing order than those from **1**. These differences were ascribed to the formation of stronger, multiple hydrogen bonds in **2** (Scheme 1). Under UV irradiation, both gels turned red due to covalent polymerization, which did not change their morphologies.

Scheme 1. Molecular structure and proposed molecular packing order in the self-assembled and polymerized diacetylenes a) **1** from EtOAc/n-hexane and b) **2** from H$_2$O/THF.

Weidong Zhou was born in 1981 in Shandong, China. He is currently studying at the Institute of Chemistry, Chinese Academy of Sciences (ICCAS) as a joint-course graduate student under the guidance of Prof. Yuliang Li.

Yuliang Li is a Professor at the Institute of Chemistry, Chinese Academy of Sciences. His research interests lie in the fields of functional organic molecular systems, covalent and noncovalent supramolecular self-assembly systems, and fullerene chemistry, with particular focus on the design and synthesis of photoelectroactive organofullerenes and nanoscale and nanostructural materials.

Daoben Zhu was born in Shanghai, China (1942). He completed his graduate study at the East China Univ. of Science and Technology (1968). He is Prof. and Director of the Organic Solids Laboratory of the Institute of Chemistry, Chinese Academy of Sciences (academician in 1997). His research interests include molecular materials and devices. He has contributed much to the development and promotion of research institutions and academic societies in China and is currently Vice-President of the Chinese Chemical Society and the Chinese Materials Society.

Abstract in Chinese：

近几年来，一维聚合物纳米线逐渐成为研究的一个热点，它具有纳米微粒结构的特征，又有纳米结构组合引起的新的效应。在众多共轭聚合物中，聚联乙二炔因其准一维的电子结构，大而快的非线性响应和良好的光电导性质而格外引人注目。利用非共价力诸如氢键，亲水一疏水作用和π堆积作用自组装是制备有机纳米线的有效方法。本文从这三个方面讲述了聚联乙二炔纳米线的制备及其性质研究。

Cholesteryl moieties have been widely used in various self-assembly systems owing to the existence of strong intermolecular van der Waals interactions. Tamaoki et al. reported a diacetylene dicholesteryl ester **3** with urethane linkages, which polymerized in the organogel state to form a stable blue organogel containing PDA nanowires[11] (Figure 1).
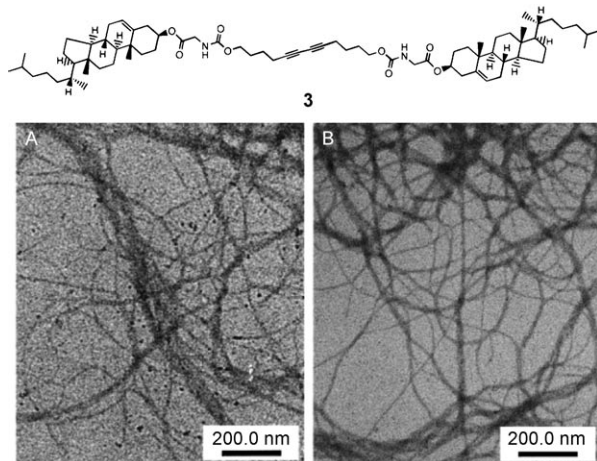

Figure 1. Molecular structure and energy-filtering (EF) TEM images of cyclohexane gel containing **3**. A) Unirradiated; B) photoirradiated with UV light from a high-pressure Hg lamp. (Reprinted with permission from reference [11]. Copyright 2000 American Chemical Society.)

This gelator employed two classic secondary interactions: hydrogen bonds among the urethane moieties and van der Waals interactions among the cholesteryl moieties. When the urethane group in **3** was replaced with a trimethylene group, neither gel formation nor polymerization in the crystalline phase occured.[12] It has been interpreted that intermolecular hydrogen bonding between urethane groups on both sides of the diyne groups in **3** stabilizes the gel and makes the stacking model in the gel state preferable for 1,4-addition.

As an extended work, Nagasawa et al. synthesized various diacetylene cholesteryl esters with two urethane linkages[13] to study the relationship between the properties and chemical structures of the aggregation state. Most of these compounds formed organogels in cyclohexane, and some compounds gelatinized in hexane, diethyl ether, *N,N*-dimethylformamide, and ethanol. The gel aggregates formed linear three-dimensional networks, and the fibers had widths in the range of 20–50 nm, which did not exhibit any obvious change after UV irradiation. Hydrogen bonding from the urethane groups was considered to be the main driving force of gel formation, which was further stabilized by the strong van der Waals interactions from the cholesteryl moieties. Furthermore, the lengths and structures of the spacers affected the gelation and polymerization process.

To exploit the function of the PDA further, we synthesized compounds **4a** and **4b** to study and compare their aggregation-state and photoelectric properties.[14] As shown in

Figure 2, compound **4a** with a hydroxy tail polymerized to form large-scale orderd nanowires with widths of 50–120 nm and lengths of several microns; this process is driven by π-
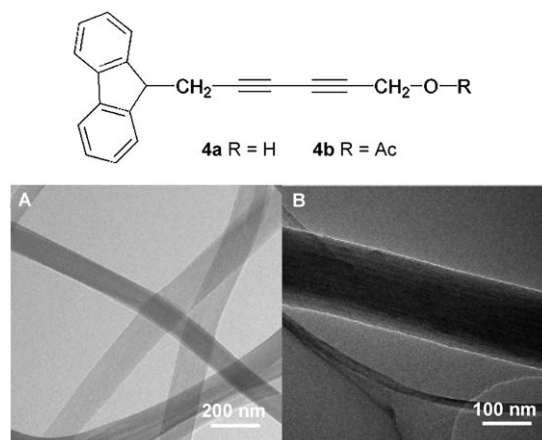

Figure 2. Molecular structure of **4a** and **4b** and TEM images of A) poly-**4a** nanowire and B) a single poly-**4a** nanowire. (Reprinted with permission from reference [14]. Copyright 2005 American Chemical Society.)

stacking and hydrogen-bonding interactions. However, the ester derivative **4b** could not form nanowires under the same conditions, thus certifying the crucial effect of hydrogen bonding for the formation of nanowires. Significantly, the nanowires showed excellent field-emission properties; this presents a new opportunity to exploit conducting polymer nanowires. The work function of the poly-**4a** nanowires is around 3.05 eV, which is much smaller than that of graphite (4.34 eV), thus demonstrating that the PDA nanowires have great potential as a competitive candidate for field emitters.

2.2. Assembly by Hydrophile–Hydrophobe Interactions

The self-assembly of biologically based amphiphiles into potentially useful nanostructures has been the subject of intense study in recent years. Fibrous assemblies formed from synthetic amphiphiles have recently provided a wide variety of well-defined and intriguing nano- and microstructures.[15] In most cases, these systems consist of a chiral hydrophilic head group such as phospholipid or amino acid and an achiral lipid moiety that can self-assemble in an aqueous environment.

Phospholipids containing diacetylene moieties in their hydrocarbon chains have been extensively studied for their ability to self-assemble into tubule or helical wire structures from aqueous and aqueous/alcohol solvents.[16] These helical structures have attracted interest due to potential applications in controlled-release, electroactive composite, and multifunctional materials. 1,2-Bis(10,12-tricosadiynoyl)-*sn*-glycero-3-phosphocholine (**6**; Figure 3) was shown to form hollow microtubules with lengths of 50–200 μm and an average diameter of approximately 0.5 μm.[16a] Svenson and Mes-
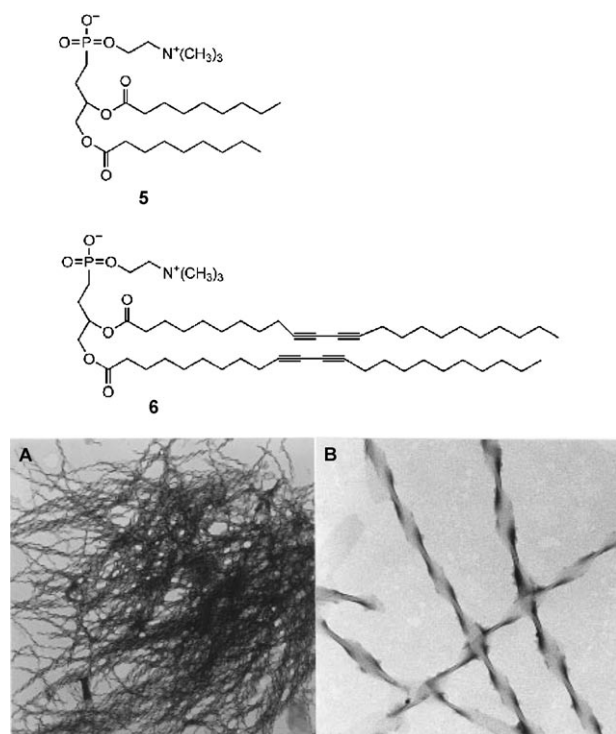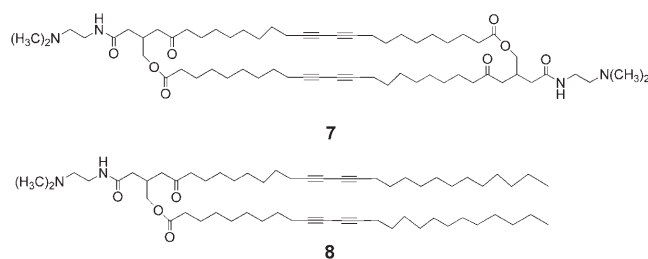
5

6

7

8

Figure 3. Molecular structure of **5** and **6** and TEM images of a 1:1 mixture of **5** and **6** (12.0 mM total lipid concentration) after 24 h at ambient temperature. A) Low-magnification image showing helical ribbon aggregates emanating in all directions from a dense entangled core. B) High-magnification image showing the helical nature of the ribbons and their apparent fusion at junctions. (Reprinted with permission from reference [17]. Copyright 1999 American Chemical Society.)
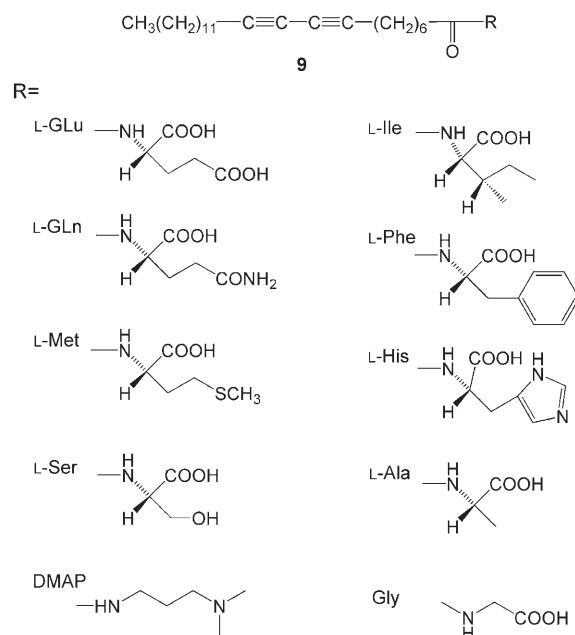
alcohol solution. Lipid **8** has the same head group as **7**, but the fatty acyl groups are not anchored at both ends; it therefore formed helices and tubules[5a] from a chloroform/ethanol/water mixture. On the other hand, lipid **7** formed very uniform flat strips or sheets under similar conditions. The inability of **7** to form helices and tubules was supported by theoretical models that explained the origin of curvature in bilayer systems.[20] Under acidic conditions, colored ribbons and liposomes formed in the presence of metal ions. Furthermore, the polymerized strips were extremely fluorescent and could be detected by fluorescence spectroscopy.

Various amino acid terminated diacetylenic lipids have been synthesized to study their aggregation microstructures (Scheme 2).[21] The observed morphologies for the micro-

$$CH_3(CH_2)_{11}-C\equiv C-C\equiv C-(CH_2)_6-\!\!\!\!\!\!\!\begin{array}{c}\\\|\\O\end{array}\!\!\!\!\!\!-R$$

9

R=

L-GLu, L-GLn, L-Met, L-Ser, DMAP, L-Ile, L-Phe, L-His, L-Ala, Gly

Scheme 2. Molecular structures of the amino acid terminated lipids from **9**.

sersmith reported that an equimolar mixture of **5** and **6** in aqueous solution formed nanotubules with diameters of 50–60 nm and lengths of up to 100 μm after incubation at ambient temperature for several hours[17] (Figure 3). Continued incubation of the nanotubule suspension at ambient temperature caused a gradual transformation of the nanotubules into a lipid–gel phase consisting of interconnected helical wires. The transformation rate from nanotubule to helical wire was dependent on the lipid concentration, and suspensions of higher lipid concentration transformed more rapidly than less-concentrated solutions. However, the transformation to helical wires could be completely prevented by storing the nanotubule suspension at 4°C. Significantly, polymerization under UV irradiation induced the destruction of the nanotubules and formation of an interconnected lamella, which indicated a spontaneous nanotubule-to-ribbon transformation triggered by polymerization of **6**.

Diacetylenic lipids **7** and **8** with terminal amine units gave typical amphiphilic structures, which were first polymerized by UV irradiation to form organic conductive materials and then metallized to form thin lamellar differentially conductive arrays.[18, 19] The driving force of the assembly was mainly ascribed to the hydrophobic interaction of the long lipid tail rather than the hydrogen bonds of the amide unit, given the highly polar assembly environment of the water/

structures, which include tubule, helix, ribbon, sheet, braided fiber, and planar platelet, strongly depended on the chemical structures of the head groups. Among them, Gln–PDA formed ribbon-shaped microstructures (Figure 4), and only planar platelets were obtained for Glu–PDA, Phe–PDA, Gly–PDA, and Met–PDA, even though their head groups are chiral. For Gln–PDA, His–PDA, and Ile–PDA, well-de-
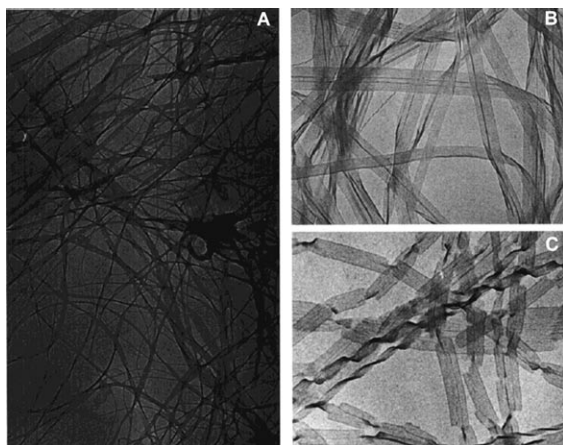
Figure 4. TEM images of the microstructures of Glu–PDA and Gln–PDA. A) Glu–PDA; B) and C) Gln–PDA. The scale bar is 0.6 µm. (Reprinted with permission from reference [21]. Copyright 2000 American Chemical Society.)

10

Figure 5. Molecular structure and TEM images of poly-**10** (0.15 mg mL^{-1}). (Reprinted with permission from reference [5b]. Copyright 2001 American Chemical Society.)

fined helical assemblies were readily obtained. Significantly, Ser–PDA formed open-ended tubular assemblies. It was claimed that molecular chirality, electrostatic interactions, and hydrogen-bonding interactions in the head-group region determined the formation of microstructures with twisted features: nonchiral molecules do not form curved structures, although the presence of chiral groups did not necessarily result in the formation of helix structures. Furthermore, the degree of hydration of the different amino acids in aqueous phase could be another controlling factor, as a large hydrophilic head group can cause curvature, as observed by Fuhrhop and Boettcher.[22] The polymerized lipid microstructures exhibited a blue-to-red color transition in response to thermal and pH changes, similar to that observed for related bilayer vesicles. The microstructures of lipids with hydrophobic head groups are more sensitive to pH changes than those of lipids with hydrophilic head groups.[22,23]

Another simple case, given by Song et al., formed ribbon-like microstructures with lengths of tens to hundreds of microns in both polymerized and unpolymerized forms of **10**[5b] (Figure 5). Polymerization of the diacetylenes did not appear to change the morphology of the material. Tubular structures were observed as segments of some helical ribbons, apparently resulting from higher regional helicity. Extensive experiments[24,25] and theoretical treatments[26] of the lipid microstructures have been attempted to explain the formation of tubular or helical morphologies. Most theories emphasize the principle of chiral packing. Schnur et al. postulated that when bilayer chiral amphiphilic lipids aggregate, they first form large strips with sharply separated domains.[24] When the original aggregate is larger than the favored ribbon width, such aggregates would then break up along the domain edge to form ribbons that are free to twist into helices by the chiral-packing effect. Helical ribbons may further fuse into tubular structures to reduce edge energy. Significantly, upon increasing the pH, all helical ribbons and flat sheets frayed into thin nanofibers accompa-
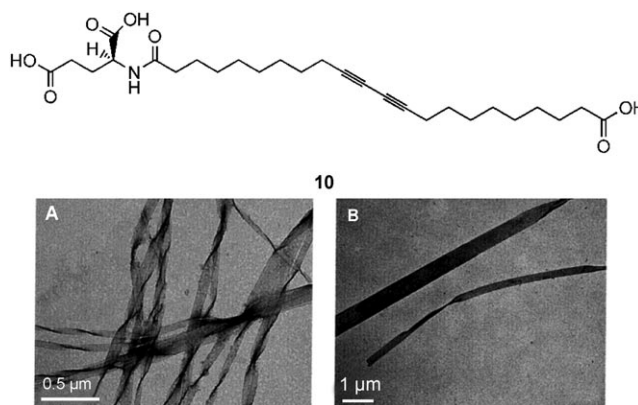
nied by a sharp blue-to-red chromatic transition. The CD spectra of poly-**10** before and after base treatment shows a dramatic loss in molar ellipticity, indicating the loss of chiral microstructures (helical ribbons and tubes) during the transformation.

2.3. Assembly by π–π Stacking

π–π Stacking is another useful way to construct plastic materials with applications in electronics. Furthermore, functionalization of disk-shaped aromatic molecules with hydrocarbon chains has been shown to be a useful method to influence π–π stacking and to create 1D electronic materials.

Fibrous PDA microcrystals have also been prepared successfully by Oikawa et al. through the reprecipitation method[27] (Figure 6), and their applications in nonlinear op-
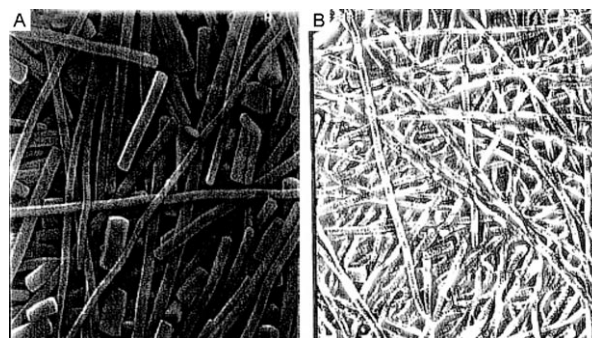

Figure 6. SEM images of fibrous microcrystals of poly-**11** formed in A) the absence and B) the presence of sodium dodecylsulfate by the reprecipitation method.

tical (NLO) devices were explored.[28] A possible scheme for the formation of fibrous microcrystals was also proposed. In the first stage, amorphous particles of **11** formed with the diffusion of the solvent from its droplets dispersed in the surrounding aqueous medium. Meanwhile, a portion of

11

12a M = 2H
12b M = Cu
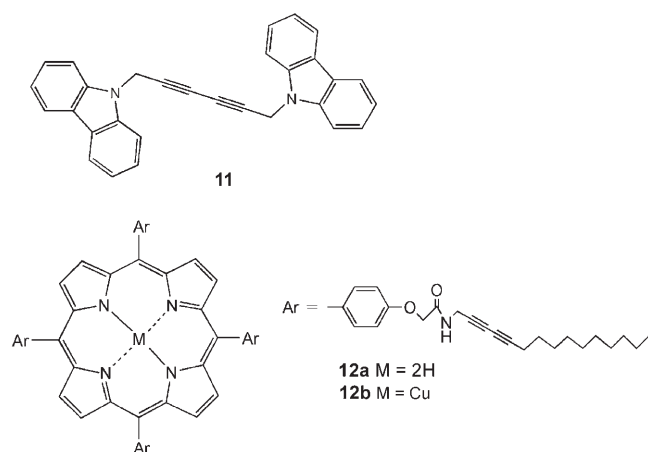
these particles microcrystallized. The microcrystals then acted as a substrate when the amorphous particles of **11** bound epitaxially on their surface. Through repetition of this process, 1D fibrous microcrystals of **11** eventually grew. The diacetylene microcrystals turned into blue PDA microcrystals through solid-state polymerization under UV irradiation. In particular, it was found that the electronic absorption peak positions for the PDA microcrystals were shifted to the short-wavelength region with decreasing crystal size.

Well-defined Ag-coated poly-**11** nanowires were also constructed for the improvement of NLO susceptibility by a simple silver-mirror reaction under aqueous conditions[29] (Figure 7) The structure of the Ag colloid coating poly-**11**
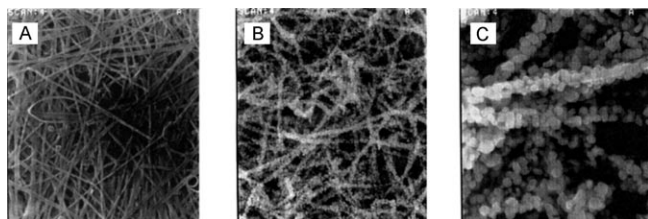

Figure 7. SEM images of microcrystals of poly-**11** A) before and B) after the silver-mirror reaction. C) Magnified image of B).

was not destroyed by ultrasonication, which indicates that the binding between silver and poly-**11** is not electrostatic attachment but strong adsorption. On the other hand, coating with Au through the reduction of tetrachloroauric acid ($HAuCl_4$) failed. This difference in coating between Ag and Au was ascribed to the electrostatic interaction between metal ions and the ζ potential of the microcrystal surface.

The combination of diacetylene units as polymerizable monomers with other 1D aggregates were also constructed to obtain a linear supramolecular architecture.[30] Compound **12b** successfully triggered molecular aggregation to lead to the formation of very transparent gels in cyclohexane and decahydronaphthalene (decalin) with fibrous networks, although **12a** did not act as a gelator. In the 1D gel tissue,

molecules adopted an H-type aggregation mode in which amide–amide hydrogen bonding and porphyrin π stacking work efficiently. By using this material as a photopolymerization template, unimolecularly segregated PDA nanowires were easily obtained. Furthermore, the thickness of the fibers was consistent with the molecular width of **12b**, which explains the fact that **12b** molecules are arranged in a 1D structure, the diacetylene units of which are photopolymerized in situ. In addition, each unimolecularly polymerized PDA fiber was elongated to more than several micrometers in length without any defect.

3. Conclusions

This review has covered some of the developments in the field of polydiacetylene nanowires to probe the underlying mechanism of their formation. They are potentially useful new materials for a variety of applications, including optical waveguides, nonlinear optics, and the fabrication of biosensors and novel photoelectric materials. Therefore, greater emphasis needs to be given to the understanding of the intricate organization of these organic nanowires and their properties so as to exploit more rational approaches for their application.

Acknowledgements

[1] M. Yun, N. V. Myung, R. P. Vasquez, C. Lee, E. Menke, R. M. Penner, *Nano Lett.* **2004**, *4*, 419.

[2] A. Noy, A. E. Miller, J. E. Klare, B. L. Weeks, B. W. Woods, J. J. DeYoreo, *Nano Lett.* **2002**, *2*, 109.

[3] I. Kymissis, A. I. Akiwande, *Appl. Phys. Lett.* **2003**, *82*, 2347.

[4] M. Nisoli, V. Pruneri, V. Magni, S. De Silvestri, G. Delleoiane, D. Comoretto, C. Cuniberti, J. Le Moigne, *Appl. Phys. Lett.* **1994**, *65*, 590.

[5] a) G. J. Wang, R. I. Hollingsworth, *Langmuir* **1999**, *15*, 6135; b) J. Song, Q. Cheng, S. Kopta, R. C. Stevens, *J. Am. Chem. Soc.* **2001**, *123*, 3205.

[6] a) *Polydiacetylenes: Synthesis, Structure, and Electronic Properties*, Vol. 102, (Eds.: D. Bloor, R. R. Chance), Martinus Nijhoff Publishers, Boston, **1985**; b) *Polydiacetylenes* (Ed.: H.-J. Cantow), Springer-Verlag, New York, **1984**; c) M. F. Shostakovskii, A. V. Bogdanova, *The Chemistry of Diacetylenes*, John Wiley & Sons, New York, **1974**.

[7] a) G. Wegner, *Makromol. Chem.* **1972**, *154*, 35–48; b) H. Bassler, V. Enkelmann, H. Sixl, *Advances in Polymer Science*, Vol. 63, Springer-Verlag, Berlin, **1984**.

[8] a) H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem.* **1988**, *100*, 117; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 113–158; b) B. Tieke, G. Wegner, *Topics in Surface Chemistry* (Eds.: E. Kay, P. S. Bagus), Plenum Press, New York, **1978**, pp. 121–134; c) D. F. O'Brien, T. H. Whitesides, R. T. Klingbiel, *J. Polym. Sci. Polym. Lett. Ed.* **1981**, *19*, 95–101; d) J.-H. Fuhrhop, P. Blumtritt, C. Lehmann, P. Luger, *J. Am. Chem. Soc.* **1991**, *113*, 7437–7439; e) T. Kim, K. C. Chan, R. M. Crooks, *J. Am. Chem. Soc.* **1997**, *119*, 189–193; f) J. H. Georger, A.

Singh, R. R. Price, J. M. Schnur, P. Yager, P. E. Schoen, *J. Am. Chem. Soc.* **1987**, *109*, 6169–6175; g) K. Inoue, Y. Ono, Y. Kanekiyo, K. Hanabusa, S. Shinkai, *Chem. Lett.* **1999**, 429–430.

[9] a) J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791–804; b) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105* (4), 1491–1546; c) L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101* (12), 4071–4098.

[10] a) T. Shimizu, M. Masuda, *J. Am. Chem. Soc.* **1997**, *119*, 2812–2818; b) M. Masuda, T. Hanada, K. Yase, T. Shimizu, *Macromolecules* **1998**, *31*, 9403–9405; c) M. Masuda, T. Hanada, Y. Okada, K. Yase, T. Shimizu, *Macromolecules* **2000**, *33*, 9233–9238.

[11] N. Tamaoki, S. Shimada, Y. Okada, A. Belaissaoui, G. Kruk, K. Yase, H. Matsuda, *Langmuir* **2000**, *16*, 7545–7547.

[12] a) N. Tamaoki, A. Parfenov, A. Masaki, H. Matsuda, *Adv. Mater.* **1997**, *9*, 1102; b) N. Mizoshita, T. Kutsuna, K. Hanabusa, T. Kato, *Chem. Commun.* **1999**, 781.

[13] J. Nagasawa, M. Kudo, S. Hayashi, N. Tamaoki, *Langmuir* **2004**, *20* (19), 7907–7916.

[14] H. Gan, H. Liu, Y. Li, Q. Zhao, Y. Li, S. Wang, T. Jiu, N. Wang, X. He, D. Yu. , D. Zhu, *J. Am. Chem. Soc.* **2005**, *127* (36), 12452–12453.

[15] a) J.-H. Fuhrhop, W. Helfrich, *Chem. Rev.* **1993**, *93*, 1565–1582; b) J.-H. Fuhrhop, T. Wang, *Chem. Rev.* **2004**, *104* (6), 2901–2938; c) N. Nakashima, S. Asakuma, T. Kunitake, *J. Am. Chem. Soc.* **1985**, *107*, 509–510; d) J. H. Fuhrhop, P. Schnieder, J. Rosenberg, E. Boekema, *J. Am. Chem. Soc.* **1987**, *109*, 3387–3390; e) S. B. Lee, R. R. Koepsel, A. J. Russell, *Nano Lett.* **2005**, *5*, 2202–2206; f) M. S. Spector, A. Singh, P. B. Messersmith, J. M. Schnur, *Nano Lett.* **2001**, *1*, 375–378.

[16] a) P. Yager, P. E. Schoen, *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 371; b) M. A. Davies, B. R. Ratna, A. S. Rudolph, *Langmuir* **1994**, *10*, 2872; c) M. S. Spector, J. V. Selinger, A. Singh, J. M. Rodriguez, R. R. Price, J. M. Schnur, *Langmuir* **1998**, *14*, 3493, and references therein; d) B. N. Thomas, C. R. Safinya, R. J. Plano, N. A. Clark, *Science* **1995**, *267*, 1635.

[17] S. Svenson, P. B. Messersmith, *Langmuir* **1999**, *15*, 4464–4471.

[18] G. Wang, R. I. Hollingsworth, *Langmuir* **1999**, *15*, 3062.

[19] G. Wang, R. I. Hollingsworth, *Adv. Mater.* **2000**, *12*, 12.

[20] U. Seifert, J. Shillcock, P. Nelson, *Phys. Rev. Lett.* **1996**, *77*, 5237.

[21] Q. Cheng, M. Yamamoto, R. C. Stevens, *Langmuir* **2000**, *16*, 5333–5342.

[22] J.-H. Fuhrhop, C. Boettcher, *J. Am. Chem. Soc.* **1990**, *112*, 1768.

[23] Q. Cheng, R. C. Stevens, *Langmuir* **1998**, *14*, 1974.

[24] a) J. M. Schnur, *Science* **1993**, *262*, 1669–1676; b) J. M. Schnur, B. R. Ratna, J. V. Selinger, A. Singh, G. Jyothi, K. R. K. Easwaran, *Science* **1994**, *264*, 945–947.

[25] a) J.-H. Fuhrhop, P. Schnieder, J. Rosenberg, E. Boekema, *J. Am. Chem. Soc.* **1987**, *109*, 3387–3390; b) D. S. Chung, G. B. Benedek, F. M. Konikoff, J. M. Donovan, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 11341; c) J. S. Chappell, P. Yager, *Chem. Phys. Lipids* **1991**, *58*, 253.

[26] a) J. V. Selinger, F. C. MacKintosh, J. M. Schnur, *Phys. Rev. E* **1996**, *53*, 3804–3818; b) B. N. Thomas, C. M. Lindemann, N. A. Clark, *Phys. Rev. E* **1999**, *59*, 3040–3047; c) P.-G. de Gennes, *C. R. Acad. Sci. Paris* **1987**, *304*, 259; d) T. C. Lubensky, J. Prost, *J. Phys. II* **1992**, *2*, 371; e) W. Helfrich, J. Prost, *Phys. Rev. A* **1988**, *38*, 3065; f) Z.-C. Ou-Yang, J.-X. Liu, *Phys. Rev. A* **1991**, *43*, 6826; g) P. Nelson, T. Powers, *Phys. Rev. Lett.* **1992**, *69*, 3409.

[27] H. Oikawa, T. Oshikiri, H. Kasai, S. Okada, S. K. Tripathy, H. Nakanishi, *Polym. Adv. Technol.* **2000**, *11*, 783–790.

[28] a) H. Katagi, H. Kasai, S. Okada, H. Oikawa, H. Matsuda, Z-F. Liu, H. Nakanishi, *Jpn. J. Appl. Phys.* **1996**, *35*, L1364; b) H. Katagi, H. Kasai, H. Kamatani, S. Okada, H. Oikawa, H. Matsuda, H. Nakanishi, *J. Macromol. Sci. Pure Appl. Chem.* **1997**, *A34*, 2013; c) H. Matsuda, S. Yamada, E. V. Keuren, H. Katagi, H. Kasai, H. Kamatani, S. Okada, H. Oikawa, H. Nakanishi, E. C. Smith, A. K. Kar, S. Wherrett, *SPIE Proc.* **1997**, *2998*, 241.

[29] H. Katagi, H. Kasai, S. Okada, H. Oikawa, H. Matsuda, H. Nakanishi, *Polym. Adv. Technol.* **2000**, *11*, 778–782.

[30] M. Shirakawa, N. Fujita, S. Shinkai, *J. Am. Chem. Soc.* **2005**, *127* (12), 4164–4165.