Poly(diiododiacetylene): Preparation, Isolation, and Full Characterization of a Very Simple Poly(diacetylene)

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Abstract: Poly(diiododiacetylene), or PIDA, is a conjugated polymer containing the poly(diacetylene) (PDA) backbone but with only iodine atom substituents. The monomer diiodobutadiyne (**1**) can be aligned in the solid state with bis(nitrile) oxalamide hosts by hydrogen bonds between oxalamide groups and weak Lewis acid–base interactions (halogen bonds) between nitriles and iodoalkynes. The resulting cocrystals start out pale blue but turn shiny and copper-colored as the polymerization progresses. The development of a crystallization methodology that greatly improves the yield of PIDA to about 50% now allows the full characterization of the polymer by X-ray diffraction, solid-state ^{13}C MAS NMR, Raman, and electron absorption spectroscopy. Comparison of a series of hosts reveals an odd–even effect in the topochemical polymerization, based on the alkyl chain length of the host. In the cocrystals formed with bis(pentanenitrile) oxalamide (**4**) and bis(heptanenitrile) oxalamide (**6**), the host/guest ratio is 1:2 and the monomer polymerizes spontaneously at room temperature, while in the case of bis(butanenitrile) oxalamide (**3**) and bis(hexanenitrile) oxalamide (**5**), where the host and guest form cocrystals in a 1:1 ratio, the polymerization is disfavored and does not go to completion. The topochemical polymerization can also be observed in water suspensions of micrometer-sized **6·1** cocrystals; the size distribution of these microcrystals, and the resulting polymer chains, can be controlled by sonication. Completely polymerized PIDA cocrystals show a highly resolved vibronic progression in their UV/vis absorption spectra. Extensive rinsing of the crystals in organic solvents such as methanol, THF, and chloroform separates the polymer from the soluble host. Once isolated, PIDA forms blue suspensions in a variety of solvents. The UV/vis absorption spectra of these suspensions match the cocrystal spectrum, without the vibronic resolution. However, they also include a new longer-wavelength absorption peak, associated with aggregation of the polymer chains.

Introduction

Conjugated organic polymers have attracted great interest for their electronic and optical properties and for potential applications including organic light-emitting diodes (OLEDs),[1–3] field-effect transistors,[4] and chemical and biological sensors.[5,6] Poly(diacetylenes) (PDAs) are a widely investigated class of conjugated polymers composed of an alternating poly(ene-yne) structure. The nonlinear optical properties resulting from this quasi-one-dimensional π system make PDAs excellent multiphoton absorbers.[7–9] In addition, they are good candidates for sensing materials; many PDAs undergo a visible color change in response to environmental perturbations like temperature, pH, and ligand–receptor interactions.[10–13]

Recently, we reported the first preparation of poly(diiododiacetylene), or PIDA, a poly(diacetylene) with single iodine atom substitutents.[14] Compared with other PDAs that have been reported, PIDA has a nearly unadorned backbone and therefore offers the potential for new insights into the inherent optical and electronic properties of PDAs without side-chain interference. In addition, PIDA can be considered as an iodinated carbyne, and thermally or electrically induced carbon–iodine bond dissociation may provide a route from PIDA to structurally homogeneous and fully characterized linear carbyne. PIDA also represents a potent precursor for general PDA preparation via post-polymerization modification at the iodinated sites.

Because of the simplicity of its structure, PIDA can provide insights into the color transitions observed in other PDAs, which

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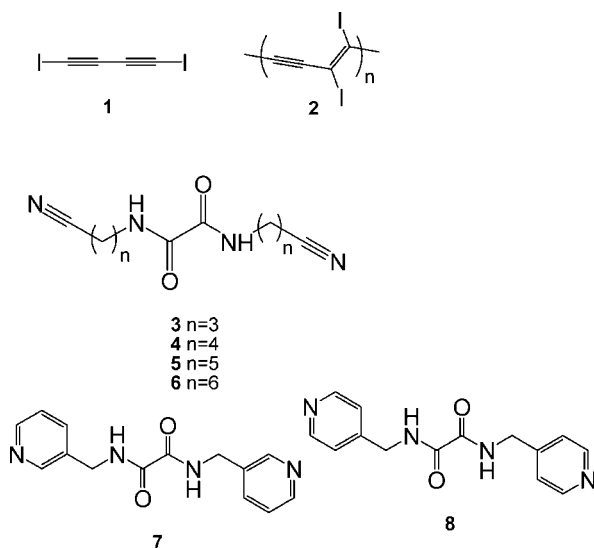(14) Sun, A. W.; Lauher, J. W.; Goroff, N. S. *Science* **2006**, *312*, 1030–1034.

Figure 1. Diiodobutadiyne (**1**) may be aligned by Lewis-basic hosts **3**−**8** for topochemical polymerization to form PIDA **2**.

have been attributed to side-chain-induced conformational changes in the PDA backbone.[15] Chromatic changes in PDAs in response to environmental stimuli have served as the basis for the majority of PDA-based sensing materials. However, to elucidate the mechanisms of the color and emission changes in PDA materials has proven to be a great challenge. Studies have shown that the factors affecting the chromic state and the susceptibility to chromic change of PDA materials include rotational changes in the polymer backbone,[15] changes in the structure of the side-chain assembly,[16] and hydrogen-bonding interactions at the side-chain head-groups.[10,17] The aggregation states and the transition of the polymer backbone from extended rod-like segments to discrete coils[18] further confuse discussion of the interplay between the conjugated polymer backbone and the ensemble material structure in determining the observed optical properties. PIDA has no side chains, presenting an important test case in the study of PDA optical properties.

The preparation of PDAs requires assembly of the monomer diynes in an appropriate arrangement, either on their own or by interaction with cocrystallizing agents, to favor the head-to-tail 1,4-polymerization.[19,20] To align monomer diiodobutadiyne (**1**) with the required spacing for this topochemical polymerization, we use host−guest supramolecular scaffolds based on halogen bonds, the Lewis acid−base interactions between **1** and functionalized Lewis bases (see Figure 1). In our report of the first preparation of PIDA,[14] bis(pentanenitrile) oxalamide (**4**) was employed to produce cocrystals with monomer **1**, in which **1** spontaneously polymerizes at room temperature. However, preparing large quantities of PIDA proved challenging due to the insolubility of the host and the relatively weak halogen bonds between the host and guest. Bispyridyl oxalamides **7** and **8** also form cocrystals with **1** based

Scheme 1. Synthesis of Hosts **4**−**6**
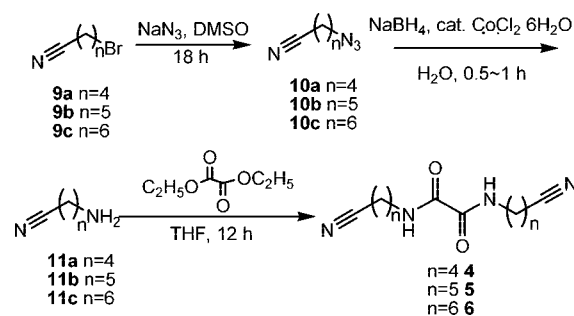
on the stronger pyridine−iodine halogen bonds, but in these cocrystals the monomers are even harder to polymerize. Although PIDA can be obtained by subjecting cocrystals **7·1** and **8·1** to high pressure of 3−6 GPa,[21] the increased mosaicity of the crystals and the complexity of the pressure method limit the potential for further studies and applications of PIDA.

We report here a new methodology for preparing cocrystals of **1** with host **4**, as well as hosts **5** and **6**, so that PIDA crystals with well-defined structures can be produced reliably and in large quantities. This development makes it realistic to carry out studies of the unique optical, electronic, and chemical properties of the material and to explore using PIDA as a starting material for the synthesis of novel PDAs, especially those without any appropriate "handle" to control their solid-state assembly for topochemical polymerization. This paper presents new conditions for the formation of PIDA via single-crystal-to-single-crystal topochemical polymerization and a more comprehensive characterization of PIDA than was previously possible.

Results and Discussion

Synthesis of Hosts and Guest. Hosts **4**−**6** were prepared from amines **11a**−**c** (see Scheme 1) as described previously for host **4**.[14] The route to the amines was altered slightly from the previously reported method, replacing H_2O/triphenylphospine reduction of azide **10**[22] with a cobalt(II) chloride-catalyzed sodium borohydride reduction because of the mild reaction conditions, high chemoselectivity, and efficiency of this method.[23] The monomer diiodobutadiyne (**1**) was prepared in one step from commercially available 1,4-bis(trimethylsilyl)-butadiyne by silver nitrate-catalyzed iodination with *N*-iodo-succinimide.[24]

Preparation of Host−Guest Cocrystals. In previous attempts, crystallization of monomer **1** with host **4** gave crystals of varying quality and polymer yield. Investigation of a variety of crystallization techniques revealed the importance of removing all particulate impurities from the solution at the start of the recrystallization. In the optimized method, the host is first dissolved in methanol, and then diyne **1** is added to make a 1:1 or 1:2 host/guest ratio. The solution is subjected to centrifugation and then decanted and transferred to a shallow crystallization dish. The dish is covered with needle-punctured aluminum foil,

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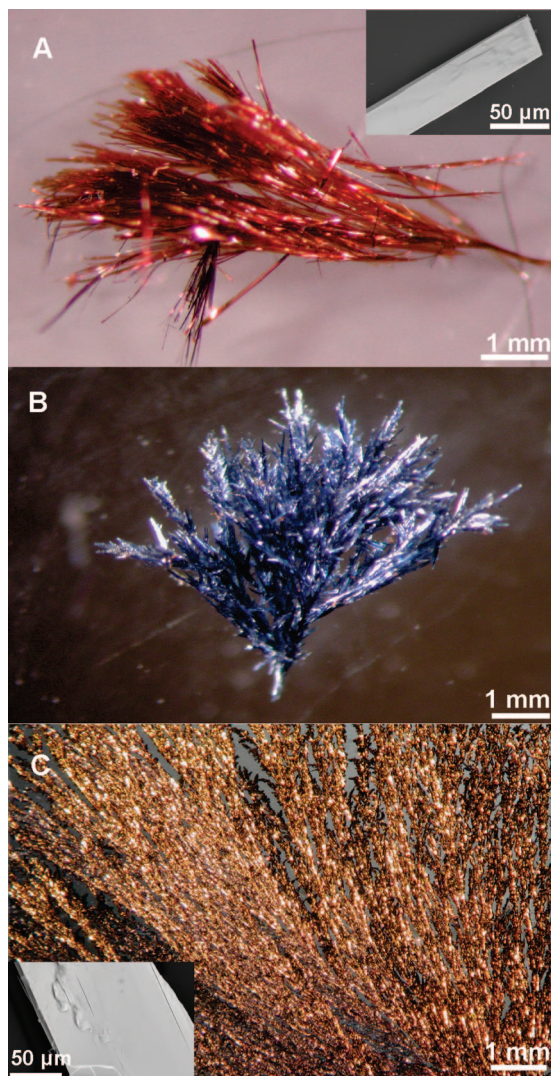(24) Gao, K.; Goroff, N. S. *J. Am. Chem. Soc.* **2000**, *122*, 9320−9321.

Figure 2. Microscopic images of host−guest cocrystals from hosts **4** (A), **5** (B), and **6** (C). Insets in panels A and C are SEM images of corresponding cocrystals.

and the methanol is allowed to evaporate slowly. Blue crystals appear when all the solvent has evaporated. For cocrystals with hosts **4** and **6**, a 1:2 ratio works best, and the initially formed blue crystals become shiny and copper- or gold-colored after about 1 week at room temperature. In the case of host **4**, some of the cocrystals are highly reflective and copper-colored even at the start. With host **5**, a 1:1 ratio is better, leading to blue crystals that turn dark over time but never become shiny (Figure 2).

Single-Crystal-to-Single-Crystal Topochemical Polymerization. The improvements in the crystallization method increase the reliability and yield for the production of cocrystals. The first crystals isolated upon evaporation of solvent from a solution of diyne **1** and host **4** include some copper-colored, shiny material. These highly reflective crystals tend to be the largest and highest quality among those isolated, and their structure matches our previous report for the **4·2** cocrystals. The blue crystals that make up the bulk of the material are not of X-ray quality. However, during a week at room temperature, the blue crystals steadily darken in color, finally becoming shiny and very similar in appearance to previously isolated copper-colored crystals (Figure 2A). The cocrystals look like filaments, with
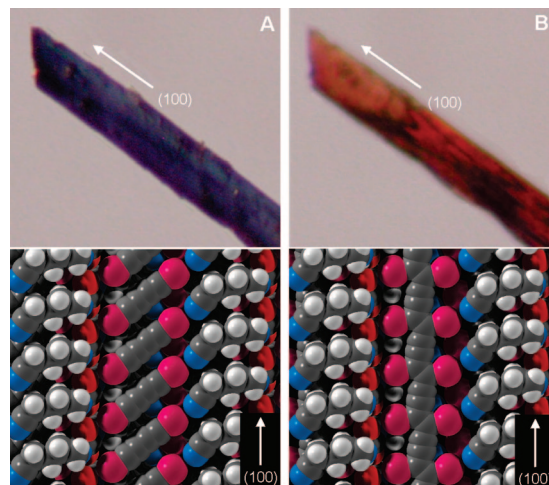

Figure 3. (A) Blue single crystal grown from a solution of diyne **1** and host **4** at 4 °C. (B) The same crystal, which turned shiny and copper-colored after staying at room temperature for 1 week. The corresponding crystal structures are shown below.

the long dimension corresponding to the (100) axis, the direction of polymer growth. The slow evaporation of solvent from a solution of diyne **1** and host **5** or **6** produces similar blue crystals but in greater yields, which we attribute to the longer side chains and the resulting better solubility of the hosts. No highly reflective material is isolated initially from either system. The pale blue cocrystals made with host **5** (Figure 2B) turned dark gray after staying at room temperature for 1 week, while those made with host **6** transformed to a shiny gold color under the same conditions, very similar to the cocrystals made with host **4**. Scanning electron microscopy (SEM) images of the gold crystals made with host **6** reveal that they have very smooth surfaces, with one dimension (010) much smaller than the other two dimensions (inset, Figure 2C).

To identify the structure of the blue material produced with host **4**, crystals were grown at 4 °C, thereby reducing the solvent evaporation rate. The blue crystals acquired under these conditions are similar in appearance to those grown at room temperature, but they are larger, allowing for structural determination by X-ray diffraction. Diffraction studies demonstrate that these initial cocrystals contain primarily the monomer (Figure 3A), analogous to the polymer cocrystals. In the **4·1** cocrystals, half the iodine atoms of **1** are halogen-bonded to the nitrile nitrogen atoms, and half are in close contact with the oxalamide oxygens. Compared to those in the polymer cocrystals, the halogen bonds of the monomer have a more favorable geometry, with an N−I−C angle of 177° and an O−I−C angle of 164° (compared to 165° and 131°, respectively, in the polymer cocrystal, Figure 4). These observations match our expectation that the arrangement of host and guest in the cocrystal is determined by interactions of the monomer, before polymerization begins.

Note that the blue color of the initial cocrystal indicates the presence of some polymer. Weiser has demonstrated that PDAs forming in a monomer crystal can be observed by UV/vis absorption at very low mole fractions, $<10^{-5}$.[25] Initially, the polymerization concentration is too low to be detected by X-ray diffraction, but it is still observable by the eye. During a week at room temperature, these crystals undergo a transition in

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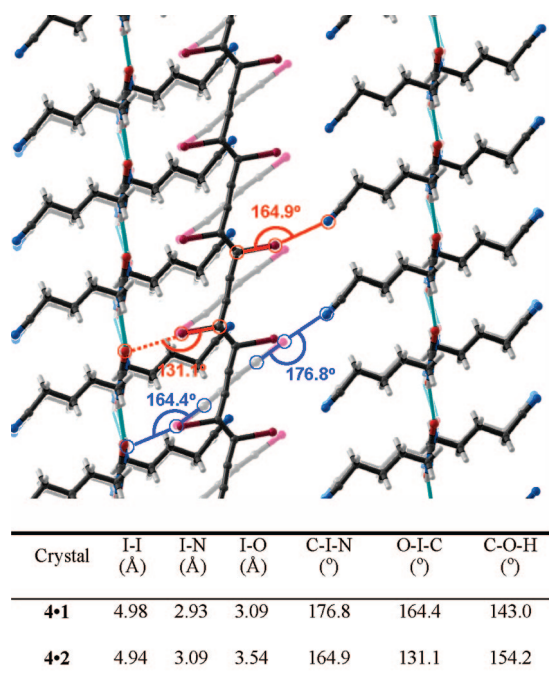| Crystal	I–I (Å)	I–N (Å)	I–O (Å)	C–I–N (°)	O–I–C (°)	C–O–H (°)
4·1	4.98	2.93	3.09	176.8	164.4	143.0
4·2	4.94	3.09	3.54	164.9	131.1	154.2

Figure 4. The lighter background shows the structure of the monomer diiodobutadiyne cocrystal; the bold foreground drawing shows the structure of the resulting PIDA. The symbols in the figure represent the halogen bond angle changes between guest and host (blue, monomer; red, polymer; dashed line, pointing out of the plain). The table below summarizes the changes in the crystal structure upon polymerization.

appearance from opaque blue to copper-colored and highly reflective, with a concurrent transformation in the crystal structure to the previously observed PIDA cocrystal. This single-crystal-to-single-crystal topochemical polymerization is shown in Figure 3, while Figure 4 indicates the intermolecular changes that occur as a result of the polymerization. As the mole fraction of polymer nears 100%, the crystals take on a characteristic metal-like appearance.

Within the **4·1** cocrystals, the repeat distance of aligned monomers is 4.98 Å, the C4–C1′ contact distance is 3.88 Å, and the molecular tilt angle is 52°. After polymerization, the repeat distance shortens to 4.94 Å. The topochemical polymerization occurs spontaneously at room temperature, requiring relatively little atomic motion, other than movement of the carbon atoms that are directly involved in the bonding changes, as demonstrated in Figure 4.

Efforts to determine the structures of the cocrystals obtained with host **5** and **6** by X-ray diffraction have been inconclusive. The mosaicity of the cocrystals prevents complete analysis, but the diffraction data do provide well-defined unit cells of both cocrystals, allowing us to determine the ratio of host to guest in each case. In the case of cocrystal **5·1**, assuming a host/guest ratio of 1:1, the measured non-hydrogen atomic volume is 19.1 Å^3, and the calculated density is 1.94 Mg/m^3, both values that match well with those for previous fully determined cocrystals. In contrast, the unit cell parameters of cocrystal **6·2** suggest a 1:2 ratio of host and guest within the cocrystal; the non-hydrogen volume (22.0 Å^3) and calculated density (2.02 Mg/m^3) for a 1:2 stoichiometry are both consistent with those observed in cocrystal **4·2** (Table S1, Supporting Information). Within cocrystal **6·2**, the iodine atoms are resolvable, and they are consistent with the proposed all-planar polymer structure.

^{13}C MAS NMR. The insolubility of the PIDA cocrystals makes it difficult to characterize them by solution-phase NMR. However, magic-angle spinning NMR (MAS NMR) techniques allow for NMR characterization of the solid samples, particularly the cocrystals formed with hosts **5** and **6** that cannot be identified completely by X-ray diffraction. The ^{13}C MAS NMR spectrum of cocrystal **4·1**, characterized previously by X-ray diffraction, contains peaks at 161.2, 122.6, 39.2, 29.2, 24.6, and 16.7 ppm (corresponding to the host) and at 80.0 ppm (monomer β-carbon), while the signal for the α-carbon of the monomer, a broad peak in the range of 10–20 ppm,[21] is hidden by the host methylene carbon peaks, as shown in Figure 5A. The spectrum of polymer cocrystal **4·2** exhibits two new peaks at 110.6 and 80.1 ppm, attributed to the β (sp) and α (sp^2) carbons of PIDA, respectively (Figure 5B). The polymer α-carbon has a chemical shift very similar to that of the monomer β-carbon, but it is much broader because of the interaction of the α-carbon with the quadrupolar iodine atom.

Using these ^{13}C NMR spectra as reference, we can determine the composition of the cocrystals formed with hosts **5** and **6**. The spectrum of the dark blue, week-old cocrystals with host **5**, as shown in Figure 5C, does not include clear resonances corresponding to either monomer or polymer carbons. Instead, there is a very broad peak or collection of peaks in the range of 70–100 ppm. After heating of the dark cocrystals in vacuum at 30 °C for 1 month, the NMR spectrum shows a new resonance at 110 ppm and a broader signal centered at 81 ppm (Figure 5D). The cocrystals with host **5** evidently polymerize very slowly at room temperature, turning dark gradually. Heating the samples increases the rate of polymerization, but the crystals do not regain crystallinity. Figure 5E shows the NMR spectrum of the gold cocrystals with host **6**, with one peak at 109.6 ppm and another double-peak signal centered at 85.0 ppm. The reason is not yet clear for this splitting in the peak attributed to the α-carbon, but this double peak integrates at a ratio of ∼1:1 with the peak at 110 ppm, corresponding to the β-carbon, indicating the formation of fully polymerized PIDA within the cocrystals.

Raman Spectroscopy. Raman spectroscopy is a sensitive tool for identifying the alternating ene-yne structure of poly(diacetylenes). Figure 6 shows the progressive change in the Raman spectrum of cocrystals with host **4** over the course of the topochemical polymerization of **1**. The Raman spectrum of the initial blue **4·1** cocrystals has a relatively low scattering intensity, shown as the blue spectrum in Figure 6. The band at 1413 cm^{-1}, corresponding to a carbon–carbon double bond stretching mode, indicates the presence of some polymer, consistent with the crystals' blue color. After staying at room temperature for 3 days, when the crystals have turned deeper blue and have an approximately 50% degree of polymerization, as determined by X-ray diffraction, the Raman scattering intensity has increased greatly, and three major bands are visible at 962, 1415, and 2067 cm^{-1}, corresponding to the carbon–carbon single bond, double bond, and triple bond stretches, respectively (ν(C–C), ν(C=C), and ν(C≡C)). When the crystals have polymerized fully, gaining a coppery appearance, the Raman intensity (red spectrum, Figure 6) increases to about 100 times that of the initial spectrum. Here, ν(C–C) is found at 971 cm^{-1}, ν(C=C) is at 1415 cm^{-1}, and ν(C≡C) is at 2071 cm^{-1}.

These observations are consistent with the increased concentration of polymer **2** within these cocrystals. The polymer itself exhibits a very strong Raman spectrum because of the large polarizability of the PDA backbone. Initially, the cocrystals contain only small amounts of polymer. As the reaction
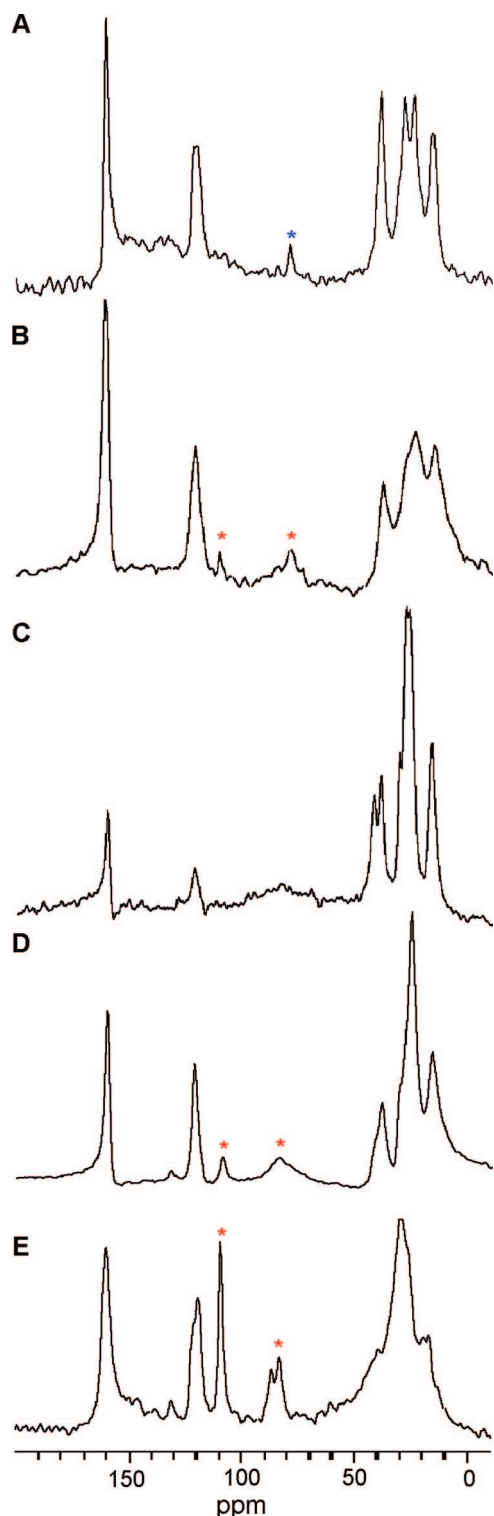
Figure 5. Solid-state ^{13}C NMR spectra of cocrystals: (A) cocrystal **4·1**; (B) cocrystal **4·2**; (C) black cocrystals prepared with host **5**; (D) cocrystals from panel C after being heated under vacuum at 30 °C for 1 month; and (E) gold cocrystals with host **6**. Blue asterisk marks the peak for monomer **1**; red asterisks mark signals for PIDA **2**.

proceeds, the spectrum for the polymer increases in intensity. However, the energies of the Raman scattering peaks do not change significantly, indicating that the observed signal, even at the start, comes from the low concentration of polymer in the sample. The scattering from the polymer dwarfs any signal
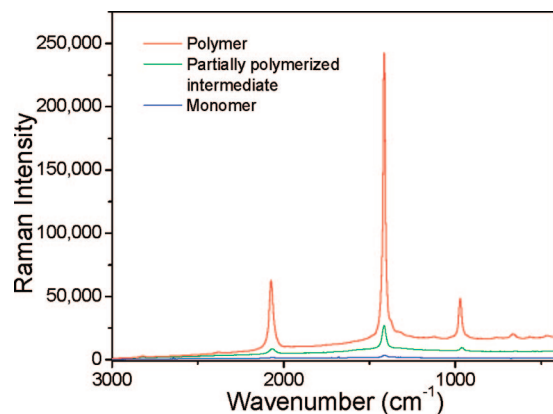
Figure 6. Raman spectra of monomer (blue), partially polymerized (green), and polymer (red) cocrystals made by host **4**.

Table 1. Odd−Even Effect of Host Side Chain Lengths on Topochemical Polymerization of Guests **1**

host[a]	color[b]	host−guest stoichiometry	repeat distance (Å)	spontaneous polymerization
3	brown to dark	1:1	5.25	no
4	blue to coppery	1:2	4.94	yes
5	blue to dark	1:1	5.07	no
6	blue to gold	1:2	4.89	yes

[a] Host compound numbers, corresponding to the number of CH_2 groups in the host side chains. [b] Color transitions of cocrystals staying at room temperature for 1 week.

from the less polarizable monomer or short intermediate oligomers.

Odd−Even Effect on Topochemical Polymerization. The results of the X-ray diffraction, ^{13}C MAS NMR, and Raman spectroscopy studies demonstrate an odd−even effect based on the length of the alkyl chains in the host molecules (see Table 1). Host **3** forms cocrystals with monomer **1** in a ratio of 1:1, and the repeat distance of packed monomers in these cocrystals is 5.25 Å.[14] These brown cocrystals turn dark and decompose at room temperature, with the Raman spectrum showing no evidence of polymerization (Figure S5, Supporting Information). The cocrystals of host **5** with diyne **1** have the same host−guest stoichiometry of 1:1. Their initial blue appearance indicates that polymer chains have been formed at low concentration in a monomer matrix. These **5·1** cocrystals turn dark at room temperature but do not gain the metallic appearance characteristic of a high degree of polymerization. Only after the cocrystals have been heated for an extended period can the polymer be detected by ^{13}C MAS NMR. As demonstrated by the increase in mosaicity of the crystals, the host does not provide an ideal scaffold for single-crystal-to-single-crystal polymerization of monomer **1**.

In contrast, the cocrystals with hosts **4** and **6**, which each contain an even number of methylene groups in their alkyl side chains, have a stoichiometry of two monomers for every host molecule. These cocrystals undergo spontaneous topochemical polymerization as single crystals. Odd−even effects have been reported previously in the polymerization and chromism of PDA materials.[26−28] Our results provide a new example in which the alkyl chain's parity determines the packing of host and guest

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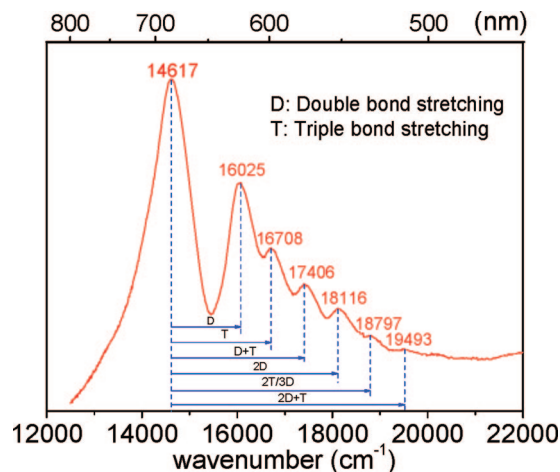
Figure 7. UV/vis absorption spectrum of gold **6·2** cocrystals, plotted as a function of wavenumber.

in the cocrystals and the success of the desired polymerization. When the host has an odd number of methylene groups in each alkyl chain, each iodine atom in the guest forms a halogen bond with a terminal nitrogen of the guest, as designed. When the number of methylene groups in each host side chain is even, the stoichiometry shifts to 2:1, and one iodine atom in each guest is in close contact with a host carbonyl oxygen. The interaction between iodine and oxalamide oxygen is not likely to provide significant stabilization, given that the carbonyls are also simultaneously acting as hydrogen-bond acceptors. Therefore, the difference in observed stoichiometry must come from different spatial requirements for the odd vs even hosts.

Electron Absorption Spectroscopy. An important method to characterize the formation of the PDA backbone is UV/vis absorption spectroscopy. The layered morphology of PIDA cocrystal **6·2** (Figure 2C) provides a very good substrate to measure the electronic absorption spectrum of the polymer where the individual PIDA strands are completed planar and isolated from one another. Figure 7 shows the absorption spectrum of gold **6·2** crystals plotted as a function of wave-number (cm^{-1}). On this frequency scale, the major absorption peak at 684 nm corresponds to an energy of 14 617 cm^{-1} (1.8 eV), consistent with the $\pi-\pi^*$ transition of the polymer backbone. This transition is followed by a detailed vibrational progression, resulting from exciton coupling to the double-bond ($D \approx 1400$ cm^{-1}, as determined by Raman) and triple-bond ($T \approx 2100$ cm^{-1}) stretching modes, and an extended high-energy tail, attributed to free motion of excitons along the chain.[25]

Similar vibronic progressions have been observed in the reflectance spectra of substituted PDAs and the derived absorption spectra from these measurements.[29] Weiser, Schott, and co-workers have also observed some vibrational overtones in the absorption spectra of PDA chains diluted in a monomer matrix.[30] However, to our knowledge, this is the first directly acquired absorption spectrum of a fully polymerized PDA to show this detailed vibronic resolution. The low energy of the
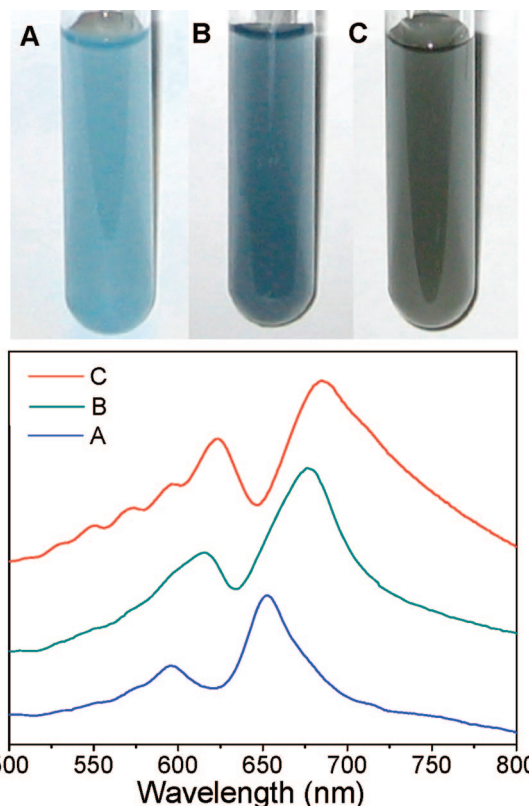
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Figure 8. Absorption spectroscopic change of a water suspension of cocrystals made with host **6**. (A) Blue **6·1** cocrystals dispersed in water. (B) Water suspension from panel A turns dark blue after 3 days at room temperature. (C) Suspension from panel A appears dark gray after 6 days at room temperature.

major absorption in the UV/vis spectrum of the cocrystals and the highly resolved vibronic satellites are consistent with PIDA's highly planar structure. The clean, detailed spectrum indicates that each of the polymer chains has the same geometry and environment, without significant interchain interactions. Previously, such a well-resolved PDA spectrum could only be approached by theoretical models.[31] According to theoretical studies by Weiser and co-workers,[25,29,32] vibronic progressions in optical spectra of PDA crystals derive from the high polarizability of the singlet excitons, which are also responsible for the large nonlinear susceptibility $\chi^{(3)}$ observed in PDAs.

Topochemical Polymerization in Microcrystal Suspensions. To investigate the polymerization process, we examined the spectroscopic changes in water suspensions of the **6·1** cocrystals (Figure 8). Cocrystals of monomer **1** and host **6** can be dispersed into water to form quasi-homogeneous microcrystalline suspensions. The blue curve in Figure 8 shows the absorption spectrum of the suspension formed when blue crystals made with host **6**, determined by Raman spectroscopy to contain primarily monomer (Figure S7, Supporting Information), were dispersed in water (Figure 8A). The major absorption peak at 650 nm and the vibrational satellite at 594 nm suggest the presence of oligomers or polymer chains, dilute in a monomer crystal matrix at a mole fraction that cannot be detected by X-ray diffraction or NMR. The blue suspension turns darker in color after 3 days

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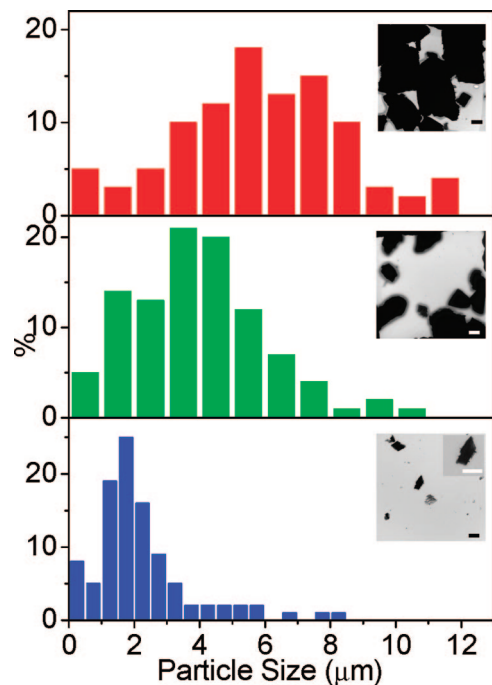
Figure 9. Size distributions of microcrystalline particles obtained by dispersing **6·1** cocrystals in water via sonication over varying times: red, 30 min; green, 60 min; blue, 120 min. Insets are typical SEM images of the particles after the corresponding treatment (scale bars are 2 μm).

at room temperature (Figure 8B), and the two major absorption peaks shift to 679 and 621 nm. These changes indicate an increase in the effective conjugation length of the polymer as the reaction progresses within the microcrystalline particles. After 3 more days, the absorption spectrum of the suspension shows a maximum absorption peak at 689 nm and a clearly resolved vibronic progression (Figure 8C). The excellent match between the absorption spectra of the water suspension and solid crystals indicates complete topochemical polymerization within the suspended particles.

Formation of these water suspensions, before polymerization, can also be used to control the size distribution of the resulting polymer cocrystals.[33–35] Transmission electron microscopy (TEM) images of the micrometer-sized monomer cocrystals demonstrate that the particle size decreases as the sonication time increases. Figure 9 indicates the size distributions of the particles, based on a statistical comparison of over 100 particles for each. When blue **6·1** cocrystals are initially dispersed in water by sonication, individual particles exceed the TEM dimensions. After 30 min of sonication, the cocrystals are broken into particles with average diameters of 5 μm. Further sonication results in smaller size and a finer dispersion of the particles. For example, after 120 min of sonication, most particles have diameters of approximately 2 μm, and they are dispersed more evenly throughout the suspension. Topochemical polymerizations of PDAs in optimal crystalline lattices have been shown to proceed quantitatively, spanning the length of each
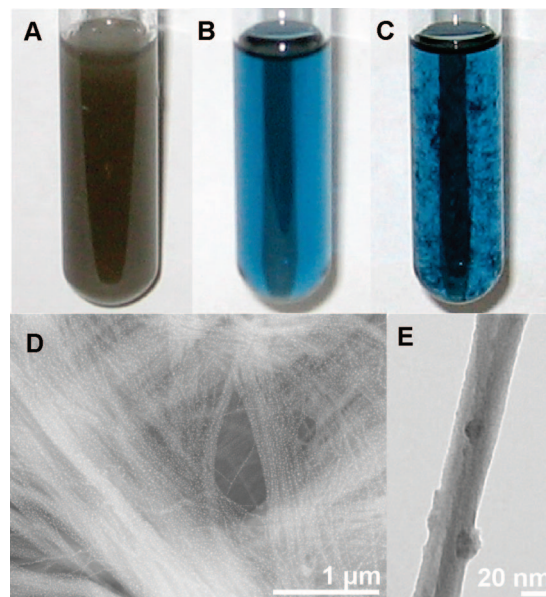

Figure 10. Suspensions and aggregates of PIDA. (A) Gold **6·2** cocrystals dispersed in H$_2$O. (B) Suspension of isolated PIDA (**2**) in THF. (C) Suspension from panel B after 2 h at room temperature, with visible aggregation. (D) SEM image of PIDA aggregates. (E) TEM image of a PIDA fiber with a diameter of about 20 nm.

microcrystal.[36,37] Because PIDA is formed here in a single-crystal-to-single-crystal transformation, the particle size should be directly related to the resulting polymer length, providing a route to control the molecular weight distribution of the polymer.

Isolation and Aggregation of PIDA. Although an oxalamide host is necessary to form PIDA, the polymer can be separated from the host after the polymerization. The gold **6·2** cocrystals can be dispersed in water (Figure 10A) or organic solvents such as methanol, THF, or chloroform. The host oxalamide **6** is insoluble in water but much more soluble in organic solvents. After extensive sonication and rinsing, these solvents give a clear blue suspension, which is fully depleted of host **6**, as judged by FTIR spectroscopy (Figure 10B; see Figure S9, Supporting Information, for details). The blue suspensions start out transparent but begin to show visible aggregates after minutes or hours without sonication (Figure 10C). SEM and TEM images (Figure 10D,E) of drop-cast fibers from a THF suspension demonstrate that these fibers have diameters of approximately 10−50 nm, suggesting aggregates of hundreds of individual polymer strands. The aggregation of PIDA is not surprising, given expected favorable interactions between the electron-rich π backbone of the polymer and the Lewis-acidic iodine atom side groups.

The removal of host, and subsequent aggregation of polymer, can be followed by UV/vis absorption spectroscopy. Figure 11A shows the absorption spectra of several different suspensions, each prepared using fully polymerized gold cocrystals of PIDA and host **6**. The red spectrum was measured using an aqueous suspension, such as that pictured in Figure 10A. This spectrum is indistinguishable from the previously measured spectrum of gold **6·2** cocrystals in the solid state (Figure 7). If the gold **6·2**

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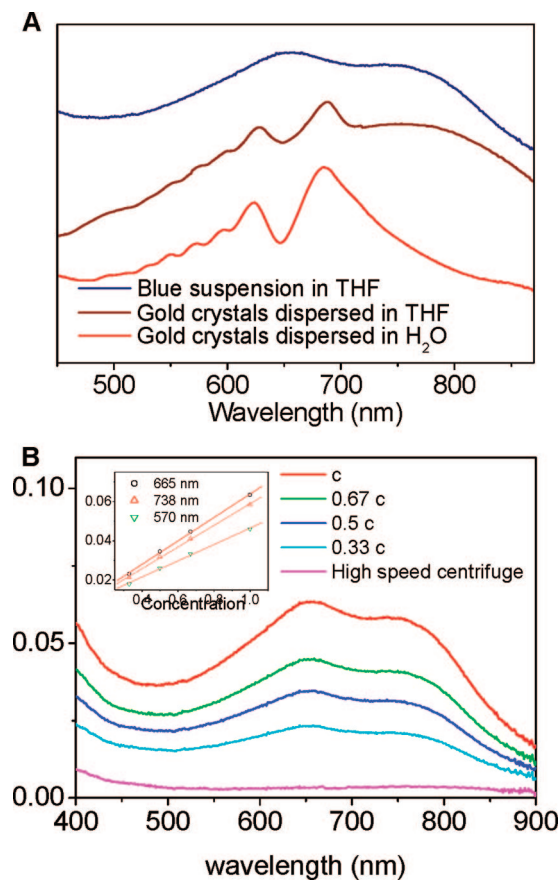
Figure 11. (A) UV/vis absorption spectra of suspensions of gold-colored **6·2** cocrystals: red, aqueous suspension of **6·2** cocrystals, as pictured in Figure 10A; brown, **6·2** cocrystals immediately after dispersing in THF; blue, host-depleted PIDA suspension in THF, as pictured in Figure 10B. (B) Absorption spectra of the host-depleted PIDA in THF, measured at a series of relative concentrations (c, $0.67c$, $0.50c$, $0.33c$) prepared by successive dilution. Inset: Plot of absorbance at several different wavelengths vs relative concentration.

cocrystals are dispersed in an organic solvent such as methanol, THF, or chloroform, the spectrum quickly takes on a different appearance. As shown in the brown curve in Figure 11A, the initial spectrum upon forming the suspension in THF (or the other organic solvents) includes a new broad shoulder at about 750 nm and a simultaneous broadening of the shorter-wavelength vibronic satellites. After removal of the host by sonication and rinsing, as described above, the UV/vis spectrum loses all vibrational definition, and the long-wavelength absorption becomes more prominent.

The appearance of the absorbance at longer wavelength can be attributed to a new lower-energy exciton generated by either

increase of conjugation length or interchain aggregation. We do not have complete X-ray diffraction data on PIDA in the **6·2** cocrystals to determine unambiguously that the polymer backbone is fully planar, but our other spectroscopic studies (Raman and MAS NMR) indicate that the polymer in these crystals is indistinguishable from the material in the **4·2** cocrystals. Thus, it seems most likely that the UV/vis spectrum of the gold cocrystals, with its λ_{max} at approximately 690 nm, represents the polymer in a completely planar conformation. We believe interchain interactions, demonstrated in the SEM and TEM images, are the most reasonable explanation of the observed low-energy absorption.

To test the stability of these aggregates, we examined the UV/vis absorption behavior upon dilution of the suspensions. Figure 11B shows the UV/vis spectrum of the initial host-depleted suspension, as well as the spectra after successive dilution. Plots of the absorption at multiple wavelengths as a function of relative concentration (inset, Figure 11B) obey Beer's law, indicating that the aggregates are not in dynamic equilibrium under these conditions. However, high-speed centrifugation (10 000 rpm, 1 h) leads to removal of the absorbing particles, confirming that the blue sample is a suspension, rather than a true solution.

Conclusion

The isolation of PIDA from the host molecules allows us to explore further applications and properties of this minimally substituted poly(diacetylene). For example, we will explore the transformation of PIDA into other functionalized PDAs via transition-metal-catalyzed couplings. We will also examine the possibility of reductive dehalogenation of PIDA to give linear carbon structures, i.e., the elusive carbyne. In addition, the ability to prepare PIDA in aqueous suspensions gives us an effective method to control the molecular weight distribution of the polymer. PIDA has potential as a useful material in its own right, and we will continue to study its physical, chemical, optical, and electronic properties.

Supporting Information Available: Complete experimental and characterization information for hosts **4**−**6** and the resulting cocrystals, including crystallographic data in CIF format for cocrystals **4·1** and **4·2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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