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Pressure induced topochemical polymerization of diiodobutadiyne: a single-crystal-to-single-crystal transformation†

Hongjian Jin,[a] Anna M. Plonka,[b] John B. Parise[ab] and Nancy S. Goroff*[a]

Diiodobutadiyne forms cocrystals with bis(pyridyl)oxalamides, based on halogen bonds between the pyridine groups of the host and the iodoalkynes of the guest. These interactions align the diyne for topochemical polymerization to form poly(diiododiacetylene) or PIDA. To induce polymerization, the crystals are subjected to pressures of 3.5 GPa or above. Previously, we reported spectroscopic evidence of this pressure-induced polymerization, but attempts to recover single crystals after pressure treatment were unsuccessful. Here we present direct structural evidence of clean single-crystal to single-crystal polymerization in these cocrystals. The structure of the polymer cocrystal was solved from single-crystal diffraction data and is supported by high pressure *in situ* Raman spectroscopy. Careful analysis of the structural changes suggests that increasing pressure changes the packing of host molecules, and that the flexibility of the pyridine ring orientation enables the polymerization. The new sigma bonds of the polymer form at the expense of the halogen bonds in the starting cocrystal; after polymerization, the iodine atoms are no longer ideally located for strong halogen bonding with the host.
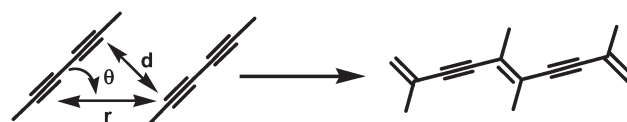
Introduction

Polydiacetylenes (PDAs) are conjugated polymers with alternating double and triple bonds making up a one-dimensional π system. These polymers, formed in the solid state, often have large molecular weights and highly planar structures, earning them consideration as "molecular wires". The high degree of polarizability along the one-dimensional π system gives PDAs significant multiphoton absorption cross-sections.[1–3] PDAs also exhibit great sensitivity to their environment, switching between a red fluorescent state and a blue non-emissive state. With a variety of side chains, PDAs are potential materials for optical applications including optical switches, optical limiters, and chemo and biosensors.[4–6] Despite these promising properties, the synthesis of polydiacetylenes remains a challenge. PDAs are prepared by regioselective 1,4-polymerization of assembled diynes in the solid state. In solution, monomer diynes undergo random 1,2- or 1,4-polymerization, creating a disordered material. However, diynes are found to polymerize cleanly with 1,4-regiochemistry in the solid state, if they are aligned properly, namely with a repeat distance (r) of 4.9–5.0 Å, matching the repeat in the polymer, and a tilt angle (θ) of 45°, which together determine the distance (d) from C1 of one monomer to C4 of the neighboring monomer (C1–C4′) at approximately 3.5 Å (Scheme 1).[7,8]

Fowler and Lauher have developed a host–guest strategy that extends the range of diynes that align appropriately for the topochemical polymerization.[9–11] Oxalamides such as compounds **3** and **4** (Fig. 1) form 1-dimensional networks of self-complementary hydrogen bonds at the desired repeat distance of 4.9–5.0 Å.[12] In cocrystals with diyne monomers, additional non-covalent interactions between the host pyridine groups and hydrogen bond-donating guests transmit this repeat distance from the hosts to the diynes, promoting polymerization of the monomer diynes.

Hosts **3** and **4** can also be used to align diynes containing halogen-bond donor groups, in particular diiodobutadiyne (**1**). There is a long history of using halogen bonding to influence crystal packing.[13–16] Iodoalkynes such as monomer **1** are good Lewis acids, forming halogen bonds with bases in solution[17–23]

[a] *Department of Chemistry, Stony Brook University, Stony Brook, NY 11794-3400, USA. E-mail: Nancy.goroff@stonybrook.edu; Fax: +1-631-632-1335; Tel: +1-631-632-8356*

[b] *Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100, USA*

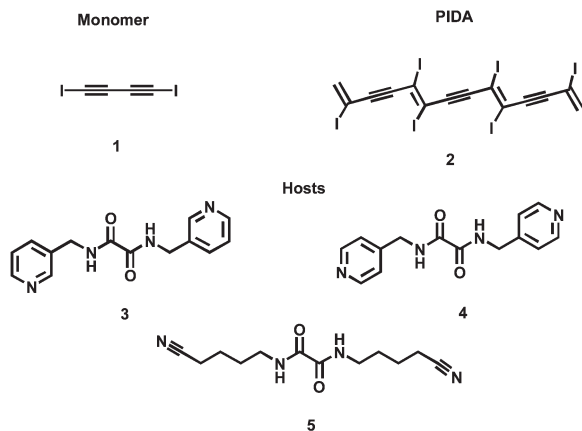† CCDC 910540. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce26851a

Scheme 1 Alignment of diynes for topochemical polymerization. Optimal values for 1,4 polymerization are r = 4.9–5.0 Å, θ = 45°, d = 3.5 Å.[7,8]

Monomer

PIDA

1

2

Hosts

3

4

5

Fig. 1 PIDA and monomer, shown with host molecules.

and in the solid state.[15,24] Using halogen bonding to align monomer **1**, we can produce poly(diiododiacetylene), PIDA, a bare conjugated polymer wire containing only iodine-atom side groups.[25,26]

Previously we have reported the successful synthesis of diiodobutadiyne cocrystals with hosts **3–5**.[26,27] The cocrystals with host **5** undergo spontaneous polymerization to form PIDA in a single-crystal-to-single-crystal transformation, at room temperature in ambient light.[25,26] The **1·3** and **1·4** cocrystals, on the other hand, are much less reactive, and attempts to induce polymerization by irradiation with visible or UV light or by heating lead only to partial reaction and increased mosaicity.[27] In these cocrystals, steric interactions between the pyridine rings and neighboring iodine atoms appear to interfere with clean polymerization. However, the polymerization of diiodobutadiyne can be induced in these materials, especially the **1·3** cocrystals, by application of hydrostatic pressure.[28] Subjecting samples in a multi-anvil press to pressures above 3 GPa leads to material which is >90% polymerized, according to solid-state MAS NMR. Nonetheless, the polymer chain length in this partially polymerized cocrystal was unknown, because we were unable to attain a single-crystal-to-single-crystal (SCSC) polymerization.

In new pressure studies, by monitoring the Raman spectrum during the experiment, we have now achieved the polymerization of diiodobutadiyne in a **1·3** cocrystal, as a single-crystal-to-single-crystal transformation. Our report focuses on the crystal structure of the PIDA·**3** cocrystal, further supported by *in situ* Raman microscopy. In comparison, we show that the **1·4** cocrystal undergoes only partially transformation, due to the less favorable spatial arrangement of the diiodobutadiyne molecules.

Experimental

Preparation of bis(pyridyl)oxalamide/diiodobutadiyne cocrystals (1·3 and 1·4)

X-ray quality cocrystals of diiodobutadiyne with host **3** or host **4** were obtained by slow evaporation from a solution of guest and host (molar ratio 1 : 1) in methanol at room temperature, over two days, according to the procedure described previously.[15]

High-pressure Raman spectroscopy

For each monomer cocrystal sample, a single crystal and a ruby chip for pressure calibration were loaded, with fluorinert as a pressure-transmitting medium, into a Merril–Basset diamond anvil cell (DAC) equipped with 600 μm cullet diamonds. Pressure was calibrated, based on measuring the optical shift of ruby R1 and R2 fluorescence lines, and was increased up to 3.5 GPa for the **1·3** cocrystal and up to 5.4 GPa for the **1·4** cocrystal. Unpolarized Raman spectra were collected with a WITec alpha300R confocal microscopy system. The Raman microscope images were collected at the highest pressure attained for each cocrystal. A frequency-doubled Nd:YAG laser, with a wavelength of 532 nm, was used as the excitation source and was focused onto the sample in the DAC with an optical microscope, producing a laser-beam size of ~650 nm at the sample. The scattered light was collected in a back-scattering geometry and analyzed by a UHTS 300, f/4, 300 mm focal-length spectrometer, equipped with a 600 lines mm^{-1} grating and a thermoelectrically-cooled charge-coupled device detector. All measurements were taken at room temperature.

Single-crystal X-ray diffraction of polymer cocrystal

After the high-pressure experiment, the PIDA cocrystal with host **3** was recovered and mounted on a CryoLoop for single-crystal data collection. Reflections were collected at low temperature (100 K), using a four-circle kappa Oxford Gemini diffractometer equipped with an Atlas detector ($\lambda = 0.71073$ Å) with 1° ω scans. The raw intensity data were collected, integrated and corrected for absorption effects using CrysAlis PRO software. All of the non-hydrogen atoms were refined with anisotropic displacement parameters. The pyridine rings of the host were constrained to be planar, and hydrogen atoms were added to the structure using geometrical constraints. The crystallographic details can be found in Table 1.

Results and discussion

High pressure Raman spectroscopy

The pressure-induced polymerization of diiodobutadiyne in the cocrystals with hosts **3** and **4** was followed *via in situ* Raman microscopy. For the crystal with host **3**, the color changed rapidly, indicating ongoing polymerization. At a pressure of 1.1 GPa, the crystal turned blue, and the observed Raman spectrum indicated the appearance of weak modes associated with the presence of polymer (Fig. 2). After increasing pressure to 3.5 GPa, the color of the crystal changed homogeneously to black with a copper-like sheen, and the modes at 970 cm^{-1}, 1389 cm^{-1} and 2043 cm^{-1} reached their maximum intensity.

At this pressure, the Raman intensities were mapped; the images covering the spectral range of the polymer modes show

Table 1 Crystallographic data and structural refinement details of **2·3** cocrystal

Empirical formula	$C_{18}H_{14}I_2N_4O_2$
Formula weight	572.13
Collection temperature (K)	100
Wavelength (Å)	0.71073
Space group	$P\bar{1}$
a (Å)	4.9330(3)
b (Å)	8.4214(5)
c (Å)	12.3642(8)
α (°)	100.542(5)
β (°)	82.986(5)
γ (°)	97.144(5)
Volume (Å^3)	498.45(5)
Z	1
Calculated density (g cm^{-3})	1.906
Absorption coefficient (mm^{-1})	3.174
$F(000)$	272.0
Crystal size (mm)	$0.15 \times 0.05 \times 0.03$
θ range of data collection (°)	3.83–26.37
Index range	$-6 \leqslant h \leqslant 6$
	$-10 \leqslant k \leqslant 10$
	$-15 \leqslant l \leqslant 15$
Collected reflections	13 901
Independent reflections	2038
R_{int}	0.0794
Completeness to θ_{max}	99.8%
Data/restraints/parameter	2038/15/118
R_1 (on F_o, $I > 2\sigma(I)$)	0.0673
wR_2 (on F_o^2, $I > 2\sigma(I)$)	0.2064
Goodness of fit	1.050

that the polymerization takes place over the whole crystal. At the end of the pressure experiment, the sample was recovered and subjected to X-ray diffraction analysis, which confirmed full polymerization, as well as the single-crystal character of the sample.

The **1·4** cocrystal was examined *via* similar experiments. However, for this material, the color change and the
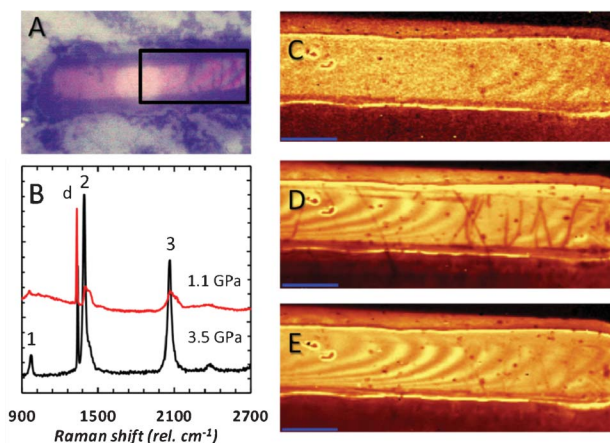

Fig. 2 *In situ* high-pressure Raman experiment on polymerization of diiodobutadiyne in **1·3** cocrystal. (A) Crystal inside the DAC at a pressure of 3.5 GPa, as seen in reflected light; purple color is sheen, not real color of the crystal; black rectangle indicates the area chosen for Raman images. (B) Raman spectra at 1.1 GPa (red) and 3.5 GPa (black), normalized to diamond peak (d). Raman images within the spectral range of (C) first polymer mode (120–920 cm^{-1}) (D) second polymer mode (1355–1420 cm^{-1}) (E) third polymer mode (2000–2125 cm^{-1}). Blue bar represents 15 µm.
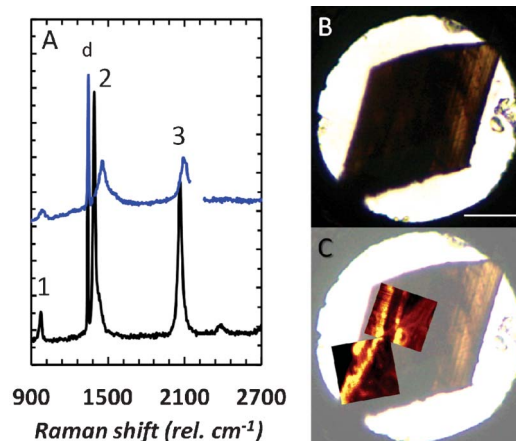

Fig. 3 *In situ* high-pressure Raman experiment on polymerization of diiodobutadiyne in cocrystal with host **4**. (A) Raman spectrum of cocrystal with host **4** at 5.4 GPa (blue) compared to spectrum of cocrystal with host **3** at 3.5 GPa, normalized to diamond peak (d). (B) Crystal inside the DAC as seen in transmitted light at 5.4 GPa. Notice heterogeneity of the black color, indicating partial polymerization. (C) The same crystal with overlaid Raman picture, within the spectral range of second polymer mode (1400–1600 cm^{-1}).

appearance of polymer-related modes started at higher pressure. The polymer modes were not visible until 5.4 GPa and the intensity was significantly lower than in the case of the **1·3** cocrystal (Fig. 3A). In addition, the black color was not homogeneously distributed, as seen in the optical microscope image (Fig. 3B), indicating that the polymerization was incomplete. The Raman microscope images collected at 5.4 GPa (Fig. 3C) and X-ray analysis of the recovered crystal both confirmed the presence of primarily monomer, even after subjecting the sample to this much higher pressure.

Structural changes and polymerization mechanism

The X-ray analysis demonstrates that the **1·3** cocrystal pressed to 3.5 GPa maintains single-crystal character, while monomer **1** is transformed into the polymer PIDA (Fig. 4). Upon polymerization, however, the unit cell parameters change significantly. The a parameter in the starting crystal is equivalent to the repeat distance between monomer molecules
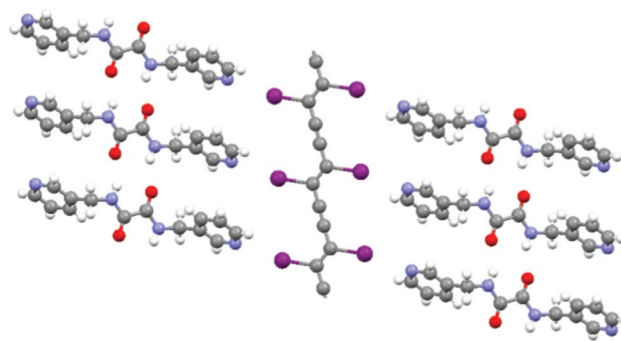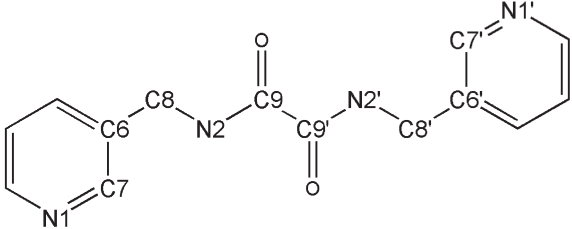

Fig. 4 The structure of fully polymerized polydiiodobutadiyne with host **3** determined by single crystal X-ray diffraction. Purple spheres represent iodine, grey – carbon, red – oxygen, blue – nitrogen, and white – hydrogen.

Table 2 Comparison of the geometrical parameters of the monomer[18] and PIDA in cocrystals with host **3** (numbering of atoms consistent with polymerized sample)

	Fresh sample	Polymerized sample
Selected angles (°) and distances (Å) from host 3		
N2–C9–C9′	114.13	112.19
C8–N2–C9	123.37	122.56
C6–C8–N2	113.71	113.99
N1···I1	2.828	3.026
N1–I1–C1	169.67	161.44
I1···I1′′ (r)	5.109	4.933
C8···C8′	6.195	6.148
C6···C6′	7.981	8.022
Pyridine-chain dihedral angle	75.64	80.71
Unit cell parameters (Å, °, Å³)		
a	5.109	4.933
b	8.604	8.421
c	11.779	12.364
α	96.189	100.542
β	99.644	82.986
γ	103.855	97.144
Volume	490.3	498.4

(r, I1···I1′′), while in the final crystal it corresponds to the polymer repeat; this distance decreases from 5.11 Å in fresh samples[21] to 4.93 Å after polymerization, very similar to the PIDA repeat of 4.94 Å, seen in the cocrystal with host **5**. At the same time, the cell length c increases from 11.78 Å[28] to 12.28 Å, while cell parameter b decreases slightly (Table 2). This change implies release of the structure along the c direction, accompanied by contraction along the a and b directions (Fig. 5).

In addition, after polymerization, the cell angles α, β and γ each change, with β in particular transforming from an obtuse angle of 99.6° to an acute angle of 83.0° (Table 2). As shown in Fig. 5, this shift represents significant movement of each stack of pyridyl hosts relative to one another, as the monomers come
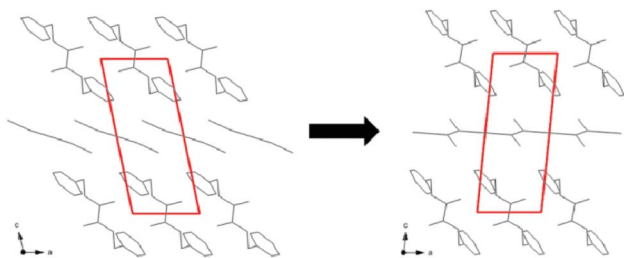

Fig. 5 Transformation of the unit cell after polymerization, 010 view showing the large change in the β angle.
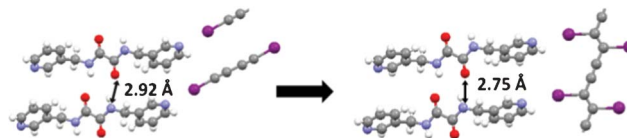

Fig. 6 The change of distance between host molecules after polymerization.

closer together and form polymer. After polymerization, the host molecules within each stack are packed more closely, with shorter hydrogen bonds. The hydrogen-bonding distance between host molecules, measured as the distance between N2 and O1′′, decreases from 2.92 Å to 2.75 Å (Fig. 6).

The changes in the crystal structure upon polymerization also affect the halogen bonding in the system. We can quantify the geometry of the halogen bond by measuring the N1–I1–C1 angle and N1···I1 distance. Structural analysis indicates that the halogen bonds in the product cocrystal are weaker than in the starting crystal, with the N1···I1 distance increasing from 2.83 Å to 3.03 Å and the N1–I–C angle decreasing from 169.7° to 161.4° (Fig. 7).

Comparison of the **1·3**, **1·4** and **1·5** cocrystals demonstrates that the spatial distribution in the initial cocrystals plays a vital role in the topochemical polymerization of diiodobutadiyne. While the **1·5** cocrystal polymerizes at ambient pressure and temperature, the **1·3** cocrystal polymerizes at 3.5 GPa, and the **1·4** cocrystal undergoes only partial polymerization at 5.4 GPa. Compared with the **1·3** cocrystal, the **1·5** cocrystal has a similar tilt angle (51 vs. 53°) and a similar C1–C4′′ distance (3.90 vs. 3.88 Å) but a shorter repeat distance (5.11 vs. 4.98 Å), favouring the polymerization. At the same time, the **1·4** cocrystal has a shorter repeat distance (5.02 Å) than the **1·3** cocrystal, but a significantly greater tilt angle (65°) and a longer C1–C4′′ distance (4.89 Å), hindering polymerization. Thus, these systems confirm the integral importance of both repeat distance and tilt angle in determining the success of diyne polymerization.

In addition to the crystal structures described above, which are based on recovered crystals after the pressure experiment, we have also attempted to acquire in situ X-ray diffraction data on a **1·3** cocrystal sample within the diamond anvil cell. The measured diffraction intensities were great enough to index the crystal and confirm that the unit cell after the observed change in color matched that of the polymer, rather than the monomer cocrystal. However, the low symmetry of the structure and obstruction from the DAC resulted in a very small coverage of the diffraction sphere (24%), coupled with weak intensities of the spots, preventing a full solution of the crystal structure. Synchrotron X-ray diffraction experiments,
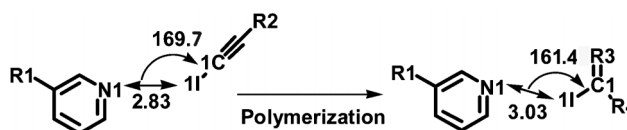

Fig. 7 Halogen bond geometry changed after polymerization. The distance unit is Å and angle unit is °.

using a beam of shorter wavelength and much higher intensity than in the laboratory diffractometer, may in the future be able to overcome these limitations.

Conclusion

Pressure is an especially effective method for introducing energy into a crystal system without disrupting the crystalline matrix. In cocrystals with bis(pyridyl)oxalamide **3**, diiodobutadiyne (**1**) polymerizes to the polymer PIDA at 3.5 GPa, while persisting as a single crystal. As far as we are aware, this is the first reported case of a pressure-induced single-crystal-to-single-crystal polymerization. The success of the polymerization depends on the alignment of the monomers in the cocrystal, *via* halogen bonds with the oxalamide host.

Acknowledgements

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