

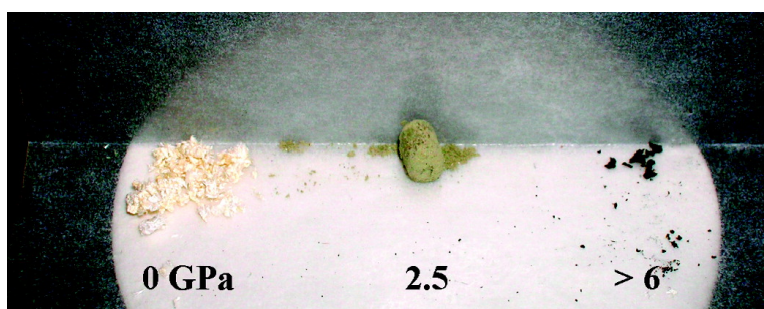
Article

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Pressure-Induced Polymerization of Diiodobutadiyne in Assembled Cocrystals

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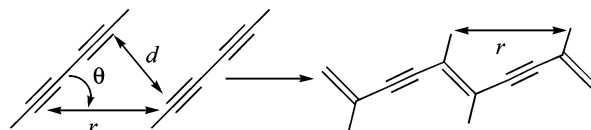
Abstract: Diiodobutadiyne forms cocrystals with bis(pyridyl)oxalamides in which the diyne alignment is near the ideal parameters for topochemical polymerization to the ordered conjugated polymer, poly-(diiododiacetylene) (PIDA). Nonetheless, previous efforts to induce polymerization in these samples via heat or irradiation were unsuccessful. We report here the successful ordered polymerization of diiodobutadiyne in these cocrystals, by subjecting them to high external pressure (0.3–10 GPa). At the lower end of the pressure range, the samples contain primarily monomer, as demonstrated by X-ray diffraction studies, but some polymerization does occur, leading to a pronounced color change from colorless to blue and to the development of intense Raman peaks at 962, 1394, and 2055 cm^{-1} , corresponding to the poly-(diacetylene). At higher pressures, the samples turn black and contain primarily polymer, as determined by solid-state NMR and Raman spectroscopy. Both density functional theory calculations (B3LYP/LanL2DZ) and comparisons to authentic samples of PIDA have confirmed the data analysis.

Introduction

Poly(diacetylenes) (PDAs) are conjugated polymers with alternating double and triple bonds along the polymer backbone. Their unidimensional π systems make them excellent multiphoton absorbers, leading to large third-order nonlinearities.^{1–3} Such nonlinear absorptions make PDAs potential components in all-optical switches, optical limiters, and high-resolution photore-sists.⁴ However, the applications for PDAs have been limited by the difficulties of synthesis.

The preparation of a poly(diacetylene) generally requires assembly of the monomer diynes in an appropriate arrangement for topochemical polymerization. In solution, polymerization leads to a mixture of 1,2- and 1,4-reaction, creating a disordered material. However, the monomers can polymerize cleanly if they are held in alignment in the solid state (Scheme 1).^{5,6} To effect this polymerization, the monomers must sit at a translational repeat distance that matches the polymer repeat (~ 5.0 Å) and

Scheme 1. Alignment of Diynes for Topochemical Polymerization^a



^a Optimal values for 1,4-polymerization are $r = 4.9\text{--}5.0$ Å, $\theta = 45^\circ$, and $d = 3.5$ Å.⁶

at a tilt angle of $\sim 45^\circ$, bringing C1 of one monomer to within van der Waals distance (~ 3.5 Å) of C4 of the neighboring monomer. In some cases, appropriately aligned monomer crystals will polymerize spontaneously under ambient light at room temperature. Polymerization can also be initiated by UV or γ -ray irradiation or by heating. Pressure has been reported as a method for inducing polymerization of solid-state diynes in a relatively small number of cases.^{7–12}

Fowler and Lauher have extended the range of accessible poly(diacetylenes) by preparing host molecules such as **3** and **4** (Figure 1), which will form cocrystals with a variety of

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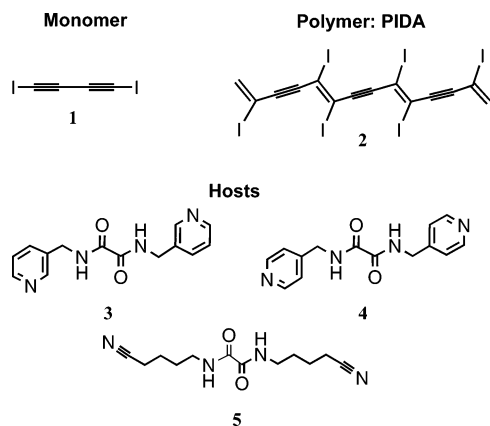


Figure 1. Diiodobutadiyne (**1**) can be aligned for polymerization to form PIDA (**2**) in the presence of oxalamide hosts such as **3–5**.

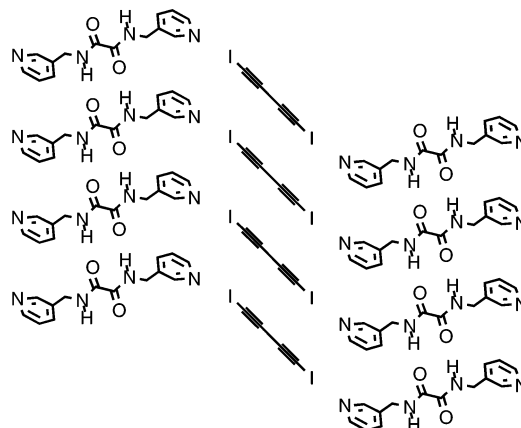
diynes.^{13,14} In these cocrystals, the oxalamides of the host create a one-dimensional hydrogen-bonding network with a repeat distance of 4.9–5.1 Å, while the pyridine rings interact with the diyne guest, transmitting the repeat parameter to the diyne. Oxalamides **3** and **4** were originally designed to align diynes containing carboxylic acid end groups.

Recently, we began studying poly(diiiododiacetylene), PIDA (**2**), a unique conjugated polymer that consists of a carbon backbone and iodine-atom side groups.^{15,16} PIDA has the potential to provide new routes for poly(diacetylene) synthesis, via transition metal-catalyzed coupling reactions at the iodinated positions. Such couplings may provide access to previously unavailable poly(diacetylenes), namely those without side groups that can guide alignment.

In addition, by the simplicity of its structure, PIDA may provide insights into the optical and electronic properties of PDAs more broadly. For example, poly(diacetylenes) are generally either blue or red in the solid state, but some PDAs can undergo reversible transitions between the two color phases. Such color transitions have been a long-standing focus of study^{17,18} and are believed to result from variations in planarity of the conjugated backbone caused by steric interactions and packing forces on the side chains.^{19,20} In addition, aggregation has been proposed to play a role in the color transitions, which are also observed to a lesser degree in PDA solutions or suspensions.^{21,22} PIDA has no side groups to provide steric repulsion and, therefore, presents an important test case for future studies examining the inherent electronic and optical properties of the PDA backbone.

In our first efforts to prepare PIDA, we demonstrated that diiodobutadiyne (**1**) will assemble with host **3** or **4** via “halogen

Scheme 2. Bis(pyridyl)oxalamide Hosts Align Diyne **1** via Nitrogen–Iodine Halogen Bonds



bonds”, the Lewis acid–base interactions between nucleophilic nitrogen and electrophilic iodine, as shown in Scheme 2.¹⁵ The resulting cocrystals have repeat distances appropriate for ordered topochemical polymerization (5.11 Å for **1·3** and 5.02 Å for **1·4**). In the cocrystals with host **3**, the tilt angle (51°) is also near the ideal value, so that the intermolecular C1–C4′ distance is relatively small (3.90 Å). In the **1·4** cocrystals, the tilt angle is large enough (65°) that C1 of one monomer is closer to C2 of the neighboring diyne than to C4 (4.65 vs 4.88 Å), but previous experience has demonstrated that repeat distance is more important than C1–C4′ distance in determining the success of diyne polymerization.²³ Despite the promising alignment of monomer **1** in these cocrystals, previous attempts to induce ordered polymerization in these materials by heat, UV irradiation, or γ rays have been unsuccessful.

Modified host **5** provides one route around these difficulties. In cocrystals with bis(nitrile) oxalamide **5**, diiodobutadiyne (**1**) polymerizes spontaneously to form PIDA (**2**) in a single-crystal to single-crystal transformation.¹⁶ The polymer cocrystals produced with host **5** have a coppery color and metallic sheen. However, the nitrile–iodine halogen bond is significantly weaker than the pyridine–iodine interaction, making it challenging to obtain large quantities of the PIDA·**5** cocrystals. In addition, oxalamide **5** is significantly more difficult and expensive to prepare than bis(pyridyl) hosts **3** and **4**. Studying PIDA as a precursor to other polymers and as a potentially useful material in its own right requires ample quantities of the polymer.

We have therefore returned to the cocrystals with pyridyl hosts **3** and **4** as sources of PIDA, examining pressure as a means to induce polymerization. There have been several reports of pressure-catalyzed polymerization of diynes.^{7,8,24–26} Pressure has been particularly useful in cases where steric bulk in the side groups impeded heat or light-induced polymerization.^{7,8} At Stony Brook’s COMPRES facility, we have access to equipment that can reach pressures as high as 10 GPa. We report here the

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Figure 2. Powdered samples of the **1·3** cocrystal, before pressing (left), after pressing to 3 GPa in a multianvil press (center), and after pressing to 6 GPa (right).

successful polymerization of diiodobutadiyne upon subjecting the cocrystals to pressures of 0.3–10 GPa.

Results and Discussion

Subjecting **1·3** or **1·4** cocrystals to pressure results in an immediate and readily apparent color change. In cocrystals of monomer **1** and host **3** in a diamond-anvil cell (DAC), this change occurs as soon as pressure is applied (0.3 GPa), with the crystals shifting from transparent and colorless to blue and opaque. With further increases in pressure, the crystals darken steadily to black. In cocrystals of diyne **1** with host **4**, the color change occurs more suddenly and at higher pressure, starting near 2.8 GPa. In single-crystal DAC studies of **1·4** cocrystals, a distinct blue color can be observed appearing first at a single point in the crystal and spreading throughout the material. As with the **1·3** cocrystals, pressing the material to higher pressures leads to further darkening. Each of the observed color changes is irreversible: if at any point the pressure is removed, the blue or black color remains. In addition, examination of pressed single crystals with polarized light demonstrates that the color has significant anisotropy, suggesting that it comes from an aligned chromophore in the sample.

Larger powdered samples were prepared using a multianvil press, in which the pressure was estimated from the oil pressure in the hydraulic ram. Not unexpectedly, the estimated pressures at which reaction begins in the large volume apparatus and in the DAC are different, due to differences in sample particle size, increased shear in the large volume case, and changes in hydrostaticity above and below the freezing point of fluorinert in the DAC. However, the qualitative behavior remains the same as in the single crystals: after a sample is pressed to 3 GPa, the powder is green (**1·3**) or blue (**1·4**). At 6 GPa, the powder is black (Figure 2).

X-ray Diffraction Studies. The color changes appear in single-crystal samples, subjected to high pressures in a diamond-anvil cell, and in powdered samples, pressed in a multianvil apparatus. Studies with single crystals allowed us to examine changes in structure and crystallinity as a function of pressure. As described above, diyne **1** forms initial cocrystals with the 3-pyridyl host **3** that match the expected parameters for polymerization well (Figure 3A). Both the repeat distance and the C1–C4' distance are within the desired range. Upon pressing of a single crystal to 1 GPa (blue), X-ray diffraction indicates that the sample still contains monomer, with a unit cell very similar to the original crystal. However, crystal quality decreases, with fewer data points measured and a significant increase in the *R*-values. Higher pressures lead to an increase in the mosaicity of the crystals, preventing further analysis by single-crystal X-ray diffraction.²⁷

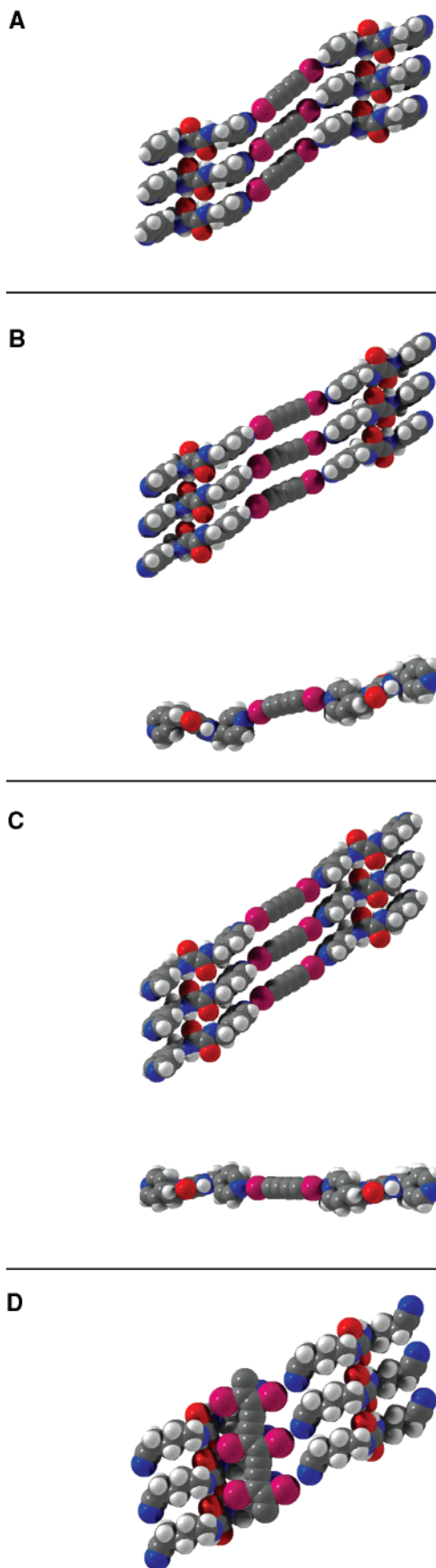


Figure 3. Crystal structures of the cocrystals as determined by X-ray diffraction: (A) **1·3** before pressing; (B) **1·4** before pressing (side and top views); (C) **1·4** after pressing to 3 GPa (side and top); (D) **2·5** polymer cocrystal.

As discussed above, cocrystals of 4-pyridyl host **4** with diyne **1** have an initial structure that is farther from the desired parameters for polymerization, with a tilt angle of 65° and a C1–C4' distance of 4.88 Å (Figure 3B). Upon pressing of a single crystal to 3 GPa (blue), again X-ray diffraction gives no evidence for polymerization. However, the X-ray diffraction data reveal that the crystal has undergone a phase change to a new polymorph, in which one arm of the host has rotated (Figure 3C, top view). This bicycle-like motion brings the two pyridine rings of the host parallel to one another, creating a new inversion center at the midpoint of the diyne and another between adjacent hosts. In this more symmetric polymorph, the C1–C4' distance does not change significantly, decreasing slightly to 4.73 Å. As with the **1**·**3** cocrystals, the black material that results from higher pressures no longer diffracts as a single crystal.

Raman Spectroscopy. While the X-ray diffraction data suggest only slight changes in the cocrystal structure upon initial pressing, Raman spectroscopy provides a different picture. Raman spectra of the initial cocrystals (Figure 4A,C) contain identifiable peaks corresponding to diyne **1** and the oxalamide host **3** or **4**. A **1**·**4** single-crystal was subjected to 2.8 GPa in the diamond anvil press and then used for both Raman and X-ray diffraction studies. This sample provided the X-ray structure shown in Figure 3C, indicating primarily monomer. Nonetheless, the Raman spectrum of the same sample (Figure 4D) shows dramatic changes from the spectrum before pressing (Figure 4C). In the partially pressed sample, there are three new peaks visible, at 962, 1398, and 2059 cm^{-1} . These peaks have much greater intensity than the initial Raman scatterings from host and monomer, drowning out any signal from these species. The cocrystals with the more promising host **3** demonstrate similar changes upon pressing. Figure 4B shows the Raman spectrum of a **1**·**3** cocrystal pressed to 2.5 GPa, containing the same three high-intensity peaks (962, 1394, and 2055 cm^{-1}). We have also obtained the Raman spectrum of a known sample of polymer **2**, prepared using bis(nitrile) oxalamide host **5** (Figure 4E), and it is very similar to the observed Raman spectra (peaks at 971, 1415, and 2072 cm^{-1}).

The seemingly contradictory Raman and X-ray diffraction data on the partially pressed crystals can be reconciled by considering the difference in sampling methods for the two techniques. While X-ray diffraction captures the average structure of the sample, Raman will detect the strongest scatterer, weighted by concentration in the sample. Poly(diacetylenes) such as PIDA give very strong Raman signals due to the delocalized bonding of the polymer backbone. In the partially pressed **1**·**4** cocrystals, even a small amount of PIDA can dwarf the Raman signal from monomer and host. Density functional calculations on PIDA oligomers of varying lengths have confirmed that the three characteristic Raman peaks due to the poly(diacetylene) backbone increase exponentially in intensity as the oligomer length increases.²⁸ The Raman and X-ray data together therefore suggest the presence of some polymer (or oligomeric intermediates) in a crystal that contains primarily monomer.

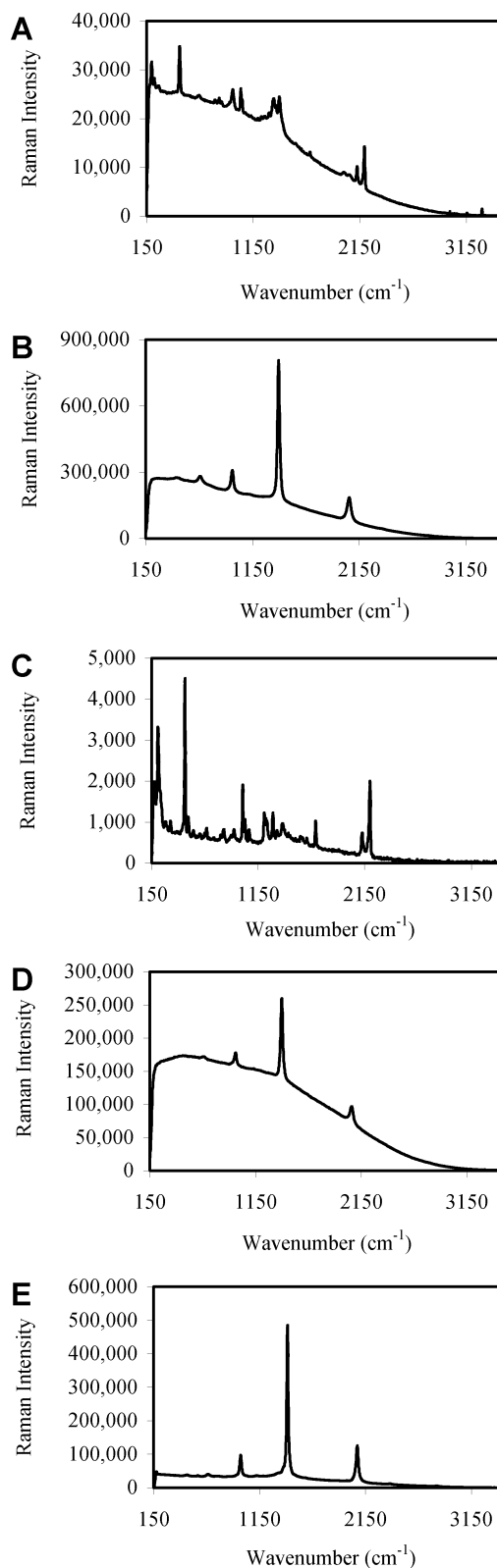


Figure 4. Raman spectra of the cocrystals: (A) **1**·**3** before pressing; (B) **1**·**3** after pressing to 2.8 GPa; (C) **1**·**4** before pressing; (D) **1**·**4** after pressing to 3 GPa; (E) **2**·**5** polymer cocrystal.

(27) Powder diffraction studies on the pressed samples are still possible, but the powder diffraction data are dominated by scattering from the iodine atoms in the crystal. High-resolution powder diffraction experiments are therefore required to obtain any information about the polymerization. These experiments are now underway.

(28) See Table S1, Supporting Information.

¹³C CP-MAS NMR Studies. To gain further information on the composition of the partially pressed samples, as well as the black material pressed to >6 GPa, we have carried out solid-state ¹³C MAS NMR studies. A ramped cross-polarization pulse

sequence was used to enhance detection of the nonprotonated carbon atoms of monomer **1** and polymer **2**.²⁹ The α -carbons give very broad signals in the solid-state MAS NMR spectra because they are bonded to iodine atoms: The 100% abundant iodine-127 nuclei are associated with large quadrupole moments, and thus the ^{13}C – ^{127}I dipolar coupling cannot be completely removed by MAS, resulting in characteristic, field-dependent peak splitting or line broadening. This effect is well established for ^{13}C – ^{14}N dipolar coupling.³⁰

Figure 5 shows the ^{13}C MAS-NMR spectra of the cocrystals of **1** with **3** and **4** as powdered samples, both before and after pressing to >6 GPa. The larger scale powder samples for these experiments were prepared in a multianvil press. In the cocrystals with 3-pyridyl host **3**, the peaks corresponding to the monomer diyne (blue arrows at 18 and 80 ppm) disappear almost completely upon pressing. At the same time, two new peaks appear, a sharp resonance at 110 ppm and a broader resonance centered at 89 ppm (red arrows). The cocrystal of **1** with 4-pyridyl host **4** also includes these two new peaks after pressing, but the stronger signals observed in these cocrystals are still from the monomer. The two newly observed peaks can be compared to the ^{13}C NMR spectrum of the polymer in cocrystals with host **5**, shown in Figure 5E. This spectrum includes a sharp peak at 110 ppm, attributed to the β -carbon, and a broad peak at ~ 81 ppm, corresponding to the α -carbon. The difference in chemical shift for the α -carbon in Figure 5B,D, compared to Figure 5E, is expected, as it results from a difference in the strength of the Lewis acid–base interaction of the iodine atoms of PIDA with the pyridyl vs nitrile hosts.^{31,32} Computational modeling on PIDA oligomers (GIAO-B3LYP/LanL2DZ) suggests that the Lewis acid–base effect increases the chemical shift of the pyridine-complexed polymer by about 9 ppm compared to an isolated polymer strand, while the interaction with a nitrile, at the angle observed in the **2**·**5** cocrystals, will have a negligible effect on the α -carbon chemical shift.³³

Integration of the monomer and polymer peaks in Figure 5B,D provides an estimate of the degree of polymerization. In Figure 5B, the monomer α -carbon peak is difficult to differentiate from the noise in the spectrum, but the sharper β -carbon peak is more readily analyzed. On the basis of relative integration of the peaks at 80 and 110 ppm in Figure 5B, the cocrystal with host **3** contains $>90\%$ polymer after pressing. In contrast, the cocrystal with host **4** reaches only $\sim 55\%$ polymerization, as calculated from both the α - and β -carbon peaks. Powdered samples subjected to lower pressures give ^{13}C MAS-NMR spectra that include the peaks assigned both to monomer and to polymer; the spectra clearly indicate decreasing concentration of monomer and increasing concentration of polymer as the pressure increases, consistent with the color changes and Raman spectroscopy. The degree of polymerization can be estimated only to within approximately 10%, because of the relatively low signal-to-noise ratios in the spectra, but they give a qualitative picture of the effect of pressure.

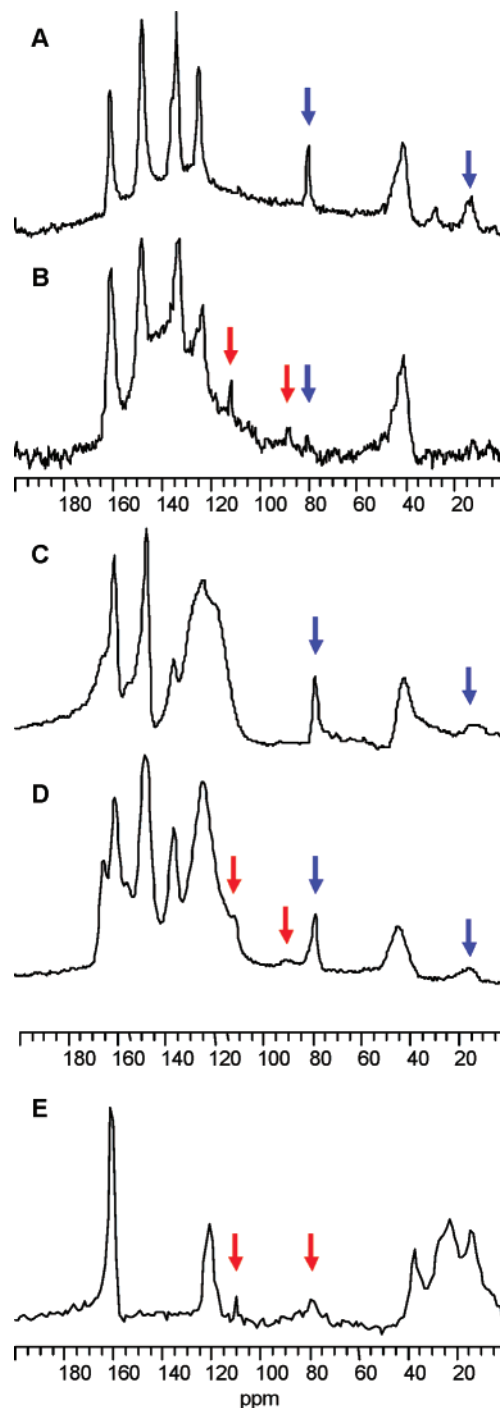


Figure 5. CP-MAS ^{13}C NMR Spectra of the cocrystals: (A) **1**·**3** before pressing; (B) **1**·**3** after pressing to >6 GPa; (C) **1**·**4** before pressing; (D) **1**·**4** after pressing to >6 GPa; (E) **2**·**5** polymer cocrystal. Blue arrows indicate peaks corresponding to monomer **1**; red arrows indicate peaks corresponding to polymer **2**.

An important consideration in analyzing the NMR data is the fact that any paramagnetic (high-spin) intermediates that form during the polymerization process may be NMR silent. We note, however, that the NMR spectra are not consistent with high concentrations of paramagnets: no line broadening, increases in sideband intensities of the host resonances, or noticeable reductions in spin–lattice relaxation times were observed. Further experiments using electron spin resonance (ESR) spectroscopy will address the question of high-spin intermediates.

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(33) Calculated structures and chemical shifts can be found in the Supporting Information.

Role of Pressure in the Polymerization. Why should high pressures induce polymerization in these cocrystals? In the simplest model, pressure favors the polymer cocrystal over the monomer because the polymer is more compact. If the volume of the unit cell decreases upon polymerization, applied pressure will increase the relative stability of the product. However, the irreversibility of the reaction under all tested conditions suggests that the observed increase in degree of polymerization as the pressure increases represents a change in the kinetics of the reaction, more than a thermodynamic effect. Applied pressure lowers the barrier to reaction, presumably for the same reason that it stabilizes the product.

In the case of the **1•3** cocrystals, polymerization begins immediately as soon as the pressure is applied. It is possible that even at these lower pressures, the polymerization can be driven to completion by longer reaction times or increased temperatures. In the case of the less well aligned **1•4** cocrystals, no reaction is observed until after a pressure-induced phase change to the new polymorph shown in Figure 3C, which has a 3% smaller volume than the initial cocrystal. Once this polymorph is formed, the reaction proceeds steadily as the pressure is increased, much like in the **1•3** cocrystals.

In both systems, polymerization is accompanied by an increase in mosaicity of the crystals, suggesting some mismatch between the monomer and polymer crystal lattices. The polymer that is produced has the characteristic blue color of PIDA, but the samples with the highest degree of polymerization appear black and opaque, unlike the highly reflective material formed in the single-crystal transformation of cocrystals with bis(nitrile) host **5**.¹⁶ The polymer chains may therefore be shorter than in the previously prepared PIDA. At the same time, the excellent

match in Raman and NMR spectra between the materials suggests that the chains are long enough to exceed the effective conjugation length for the polymer, so that electronic properties of the two materials should be similar. The greater solubility of the (bis)pyridyl hosts **3** and **4** will make it easier for us to isolate PIDA for further study.

Conclusions

The experiments described here support using high pressure as a method to access PIDA, allowing us to begin studying the materials properties of this unique polymer. Consistent with the structures of the initial monomer-host cocrystals, polymerization of diyne **1** is particularly facile starting from cocrystals with bis(3-pyridyl)oxalamide host **3**. Both ESR and high-resolution powder diffraction experiments may provide further insights into the mechanism of the reaction, at the same time that we use it to prepare PIDA samples for study.

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Supporting Information Available: Full experimental and computational details and crystallographic data for the pressed **1•4** cocrystal. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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