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Synthesis of the Stable Ordered Conjugated Polymer Poly(dibromodiacetylene) from an Explosive Monomer

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Abstract: *Dibromobutadiyne is an extremely unstable compound that explodes at room temperature, even under inert atmosphere. This instability has limited the studies of dibromobutadiyne almost entirely to spectroscopic characterization. Here we report an approach to control the reactivity of dibromobutadiyne, via topochemical reaction in cocrystals, leading to the ordered polymer poly(dibromodiacetylene), PBDA. At low temperatures (−15 to −18°C), dibromobutadiyne can form cocrystals with oxalamide host molecules containing either pyridyl or nitrile side groups, in which halogen bonds align the dibromobutadiyne monomers for topochemical polymerization. The cocrystals with the bis(nitrile) oxalamide host undergo complete ordered polymerization to PBDA, demonstrated by solid-state MAS-NMR, Raman, and optical absorption spectroscopy. Once formed, the polymer can be separated from the host; unlike the monomer, PBDA is stable at room temperature.*

Dibromobutadiyne was first reported in 1930 as an extremely unstable and explosive compound.[1] At room temperature, it decomposes explosively in seconds, although it is stable in solution below −30 °C when kept in the dark.[2] Research on dibromobutadiyne has thus been quite limited.[2,3] More generally, bromoalkynes are highly reactive and unstable. Two years ago, Frauenrath and co-workers reported the first clean solid-state reactions of a bromodiyne and a related bromotriyne.[3b] They discovered that in single crystals, these glycosylated bromopolyynes each undergo an unprecedented multistep dimerization/rearrangement. However, the more common solid-state reaction of diynes, namely the polymerization to form a polydiacetylene (PDA), has not been reported previously for any bromodiyne. Likewise, there are very few examples in the literature of bromine-containing polymers, and the ones that have been reported have saturated backbones with bromine substituents on the side arms, rather than directly bonded to the backbone.[4] We describe here the controlled, ordered polymerization of the explosive monomer dibromobutadiyne (C_4Br_2), providing a conjugated polymer containing only carbon and bromine, the first PDA with bromine substituents.

The solid-state polymerization of diynes is a well-established reaction that provides a path to the highly ordered PDAs, in which the conjugated backbone contains alternating double and triple carbon–carbon bonds. Polymerization of crystalline monomers provides PDAs with excellent optical and electronic properties, leading to many different applications, including colorimetric,[5] chemical[6] and biological sensors,[7] as well as nanoelectronics.[8]

Achieving a high degree of polymerization in a solid-state reaction requires an appropriate spatial arrangement of the monomers. As discovered by Wegner[9] and further described by Baughman,[10] if diynes are aligned properly in the solid state at a distance commensurate with the repeat distance in the target polymer, they can polymerize topochemically (according to their arrangement in space). However, few diynes will align appropriately by themselves for this reaction. For diynes that do not self-organize in this way, Fowler and Lauher have developed a host–guest approach to make topochemical polymerization possible.[11] The oxalamide functional group forms self-complementary hydrogen bonding networks with a repeat distance (4.9–5.0 Å) that corresponds to the spatial repeat required for 1,4-topochemical polymerization. Using non-covalent interactions between the diyne as guest and an appropriate oxalamide host, Fowler and Lauher have shown that the hydrogen bonding of the oxalamides can determine the repeat distance of the diyne monomers, aligning them for polymerization.

In 2006, we reported the first and only synthesis of a PDA with single-atom side groups—polydiiododiacetylene (PIDA),[12] prepared by the host–guest approach using halogen bonding, the non-covalent interaction between a halogen atom (Lewis acid) and a Lewis base. Diiodobutadiyne forms cocrystals with host **4** or **6** (Figure 1) that are well aligned, allowing for spontaneous polymerization at room temperature.[12,13] The abundance of transition metal-catalyzed coupling reactions led us to explore PIDA as a precursor to other PDAs via post-polymerization modification. However, the iodine atoms of PIDA are extremely labile, and the polymer undergoes deiodination (carbonization) under mild conditions, including room-temperature reaction with amines or other bases.[14] PIDA is therefore not an appropriate substrate for post-polymerization coupling to make new PDAs.

Fortunately, polydibromodiacetylene (PBDA) should be much more stable than PIDA, offering the possibility of post-polymerization reaction. In model studies in our lab, *trans*-dibromoalkenes have shown to be much more resistant to dehalogenation than *trans*-diiodoalkenes.[15] Dibromoalkenes

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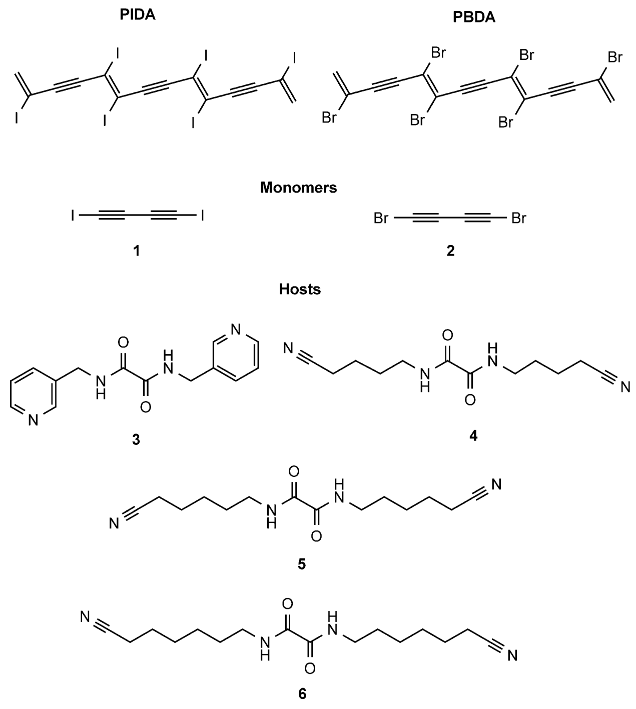

Figure 1. PIDA, PBDA and monomer **1** and **2**, with Lewis-basic host molecules **3**–**6**.

have been used previously as substrates for transition metal-catalyzed coupling reactions.[16] However, the preparation and ordered polymerization of dibromobutadiyne represents a significant challenge. As described above, the monomer is highly unstable and requires special handling. In addition, bromine is both less electrophilic and less polarizable than iodine, leading to much weaker halogen-bonding interactions. Dibromobutadiyne is therefore a particularly challenging substrate for assembly of ordered cocrystals.

Our approach to the preparation of dibromobutadiyne cocrystals uses bis(pyridyl)oxalamide and bis(nitrile)-oxalamide hosts **3**, **4**, **5** and **6**. Due to the stronger halogen bonding to pyridine, bis(pyridyl)oxalamide **3** was tried first. Cocrystals were prepared in a cold bath at -15 °C to slow the decomposition of dibromobutadiyne (**2**). A variety of solvents, including THF, dichloromethane, chloroform, methanol, acetonitrile, acetone, toluene and ethyl acetate, were tested, but in each case, host **3** and guest **2** precipitated out as separate solids. However, in a mixture of dichloromethane and methanol at -15 °C, blue crystals were observed (Figure 2 A). Dichloromethane and methanol form an 8:1 azeotrope, with boiling point of 38 °C, compared to 40 °C for dichloromethane and 65 °C for methanol alone.[17] In the azeotrope, the host is much more soluble than in dichloromethane alone, while monomer **2** is more stable than in methanol alone. In addition, the lower boiling point of the azeotrope accelerates crystal formation, reducing decomposition of monomer.

Monomer **2** and host **3** form a cocrystal in a 1:1 ratio (Figure 2 B), with a repeat distance (5.05 Å) that is slightly longer than ideal for topochemical polymerization. Kept in the freezer for as long as a month, these cocrystals undergo only limited reaction; they do not change color, and X-ray diffraction indicates that compound **2** continues to be present primarily as monomer. Upon warming to room temperature, the cocrystals change from purple to black, indicating increased polymerization. The Raman spectrum (Figure 2 D), a sensitive tool for detecting the conjugated enyne chain of a PDA, demonstrates the presence of polymer. However, X-ray diffraction on warmed samples has been unsuccessful, suggesting increased mosaicity in the material.

The partial success in preparing cocrystals of compounds **2** and **3** encouraged us to pursue cocrystals with bis(nitrile)oxalamide hosts **4**, **5** and **6**. To try to form cocrystals, host **4**, **5** and **6** were each mixed with diyne **2**, in a range of solvents including THF, dichloromethane, chloroform, methanol, acetonitrile, acetone, toluene and ethyl acetate. Regardless of conditions, hosts **4** and **6** were found in each case to precipitate separately from monomer **2**, accompanied by rapid decomposition of the diyne. In most solvents, host **5** also precipitated on its own. However, in dichloromethane at -18 °C, host **5** and diyne **2** together form deep blue cocrystals. Even in the freezer, these crystals slowly turn from deep blue-purple to a dark brown. With slow warming to 20 °C over 24 h, the crystals instead change color from blue-purple to a coppery, metallic appearance (Figure 2 C), which according to our previous experience suggests a high degree of polymerization.[12,13]

A comparison of the Raman spectra of **2**·**3** and **2**·**5** cocrystals (Figure 2 D,E) shows excitation occurring at the same energies in each sample (1030, 1441, and 2104 cm^{-1}), consistent with the polymer PBDA. However, the spectrum obtained from the **2**·**5** cocrystal demonstrates lower background fluorescence, greater peak intensities, and an enhanced signal to noise ratio, further support for an increased degree of polymerization.

Solid-state NMR studies confirm that the copper-colored cocrystals with host **5** contain fully polymerized PBDA. In solid-state cross-polarization magic-angle-spinning (CP-MAS) ^{13}C NMR experiments (Figure 3 B), the slowly warmed **2**·**5** cocrystals show only two peaks besides those for host **5**: a sharp peak at 103 ppm and a broader, partially overlapping signal at 108 ppm (Figure 3 B), corresponding to the alkyne and bromoalkene carbons of the polymer PBDA, respectively. These chemical shifts are consistent with what is observed in PIDA (alkyne peak at 110 ppm) and in previously reported bromoalkenes (100–110 ppm).[18] In the solid state, coupling to the quadrupolar bromine nucleus broadens the peak corresponding to the alkene carbon. Monomer **2**, which in solution has NMR peaks at 66.7 and 39.0 ppm,[2b] is not visible in the spectrum, indicating that the sample is $>90\%$ polymerized.

CP-MAS NMR can also shed light on the partially polymerized cocrystals of monomer **2**, both those that contain host **3** that have been allowed to react as fully as possible and those that contain host **5** but have been kept at low temperature to prevent complete polymerization. Interestingly, these samples give very different NMR signatures.

Upon warming to room temperature, the cocrystals with pyridyl host **3** turn black, and their Raman spectrum matches PBDA, although at lower intensity than the warmed **2**·**5**

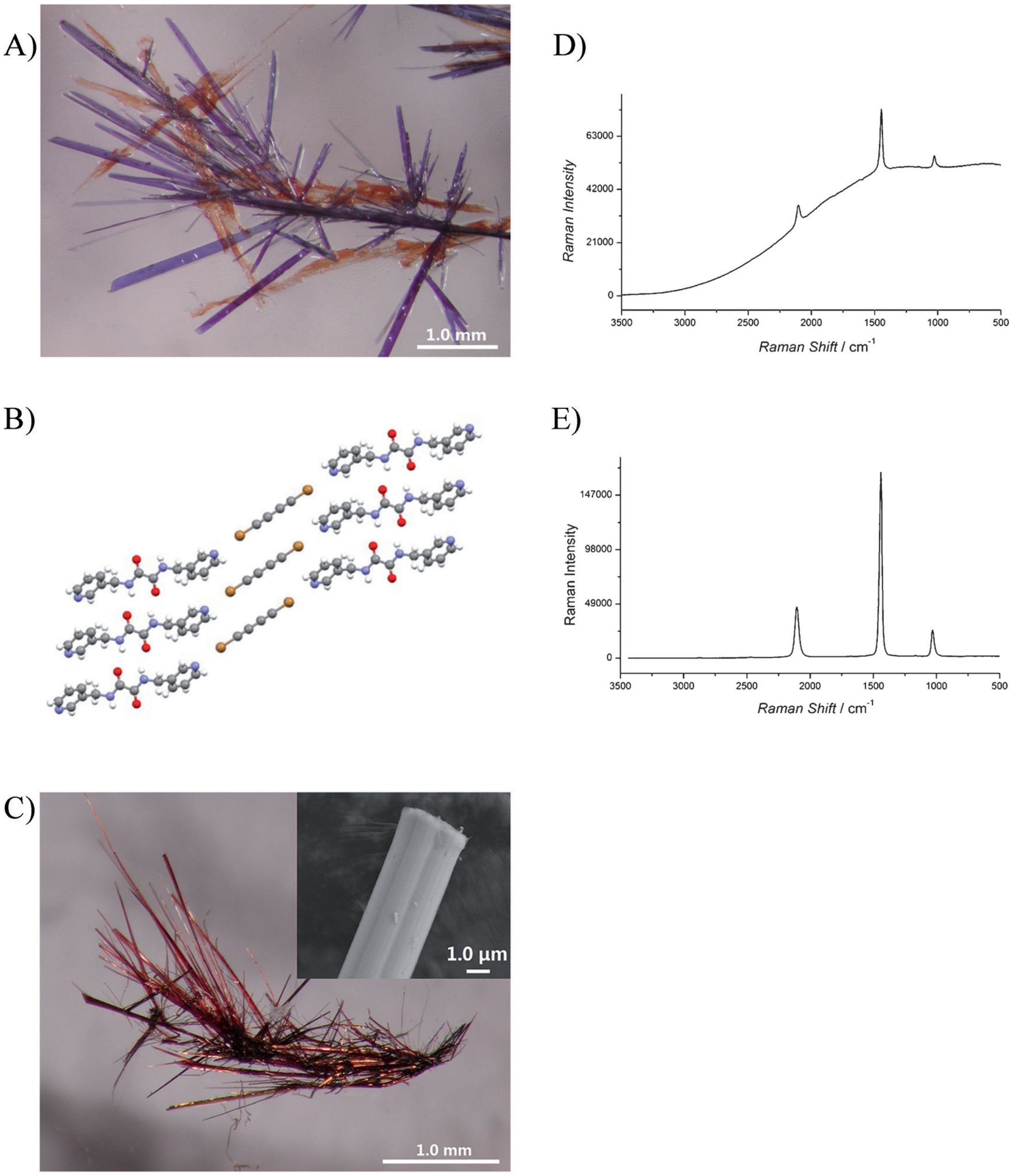

Figure 2. A) Morphology of cocrystal **2**·**3**. B) Structure of cocrystal **2**·**3** determined by X-ray diffraction. C) Morphology of cocrystal PBDA·**3**. D) Raman spectrum of cocrystal **2**·**3** after warming to 20 °C. E) Raman spectrum of cocrystal PBDA·**5**.

cocrystals. Consistent with these observations, these crystals give a CP-MAS NMR spectrum which clearly shows the presence of both polymer (peaks at 103 and 108 ppm) and monomer (67 ppm). Possible oligomeric intermediates are not readily discernable.

In contrast, low-temperature solid-state ^{13}C CP-MAS NMR experiments on the **2**·**5** cocrystals suggest a different polymerization pattern (Figure 3 C). These cocrystals were examined at −20 °C, after storage for several days at −15 °C. Over those few days, they had already undergone partial color change, with some of the sample turning dark brown and some still deep purple. The NMR spectrum of this sample does not show the presence of either monomer or PBDA, but instead contains a broad set of signals covering the range of 60–90 ppm. This broad envelope is consistent with partially reacted oligomers.

The difference in behavior between cocrystals with pyridyl host **3** and nitrile host **5** can be attributed to the differing amount of strain associated with polymerization in these crystals. The presence of monomer in the warmed **2**·**3** cocrystals indicates a barrier to initiating the reaction. Once started, reaction continues through enough steps to produce material with the same NMR signature as the polymer. In contrast, in the cocrystals with nitrile host **5**, even at low

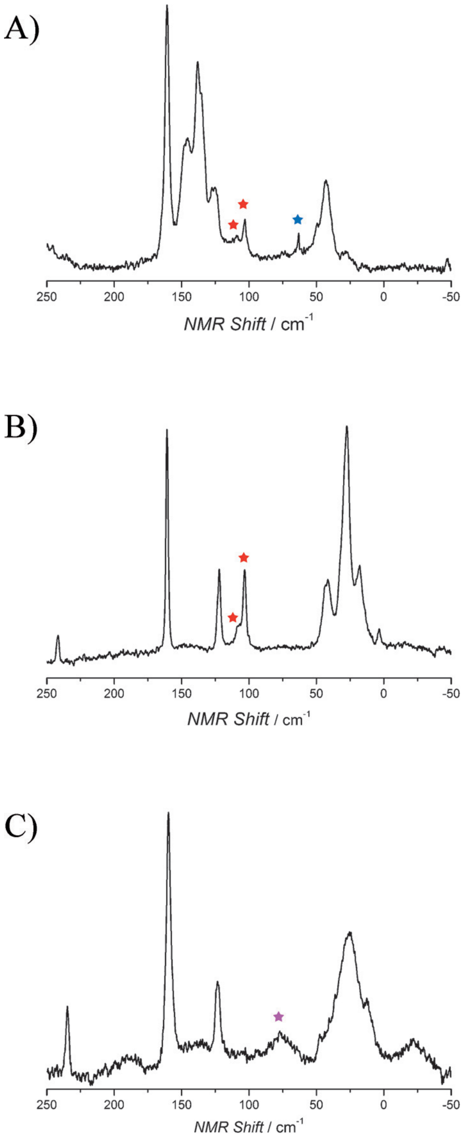

Figure 3. CP-MAS ^{13}C NMR of cocrystals. A) Cocrystal **2·3** after warming to 20 °C in atmosphere. B) Cocrystal **2·5** after warming to 20 °C in atmosphere. C) Cocrystal **2·5** held at < -10 °C in freezer; spectrum acquired at -20 °C. Red stars represent polymer peaks, blue star represents monomer peak, and purple star represents partially reacted material.

temperature, the monomers all react to form oligomeric species, well before individual chains are long enough to appear as PBDA in the NMR spectrum.

Once prepared, PBDA can be isolated from the cocrystal by dissolving away host **5** in dichloromethane to leave insoluble shiny green fibers (Figure 4 A). Raman and NMR data (Figure 4 B,C) confirm that this material is indeed the polymer PBDA. Mass balance experiments indicate isolation of 87 % of the expected polymer, providing a lower bound on the degree of polymerization in the sample.[19] As hoped, poly(dibromodiacetylene) is significantly more stable than poly(diiododiacetylene). PBDA is stable to shock pressure and mild heating, and chemically tolerant to the addition of many bases, including pyridine and triethylamine.

In conclusion, we have prepared the stable conjugated bromine-substituted polymer poly(dibromodiacetylene) by taming and directing the reactivity of the explosive monomer dibromobutadiyne. Future effort will focus on exploring the properties of this new, extremely simple polymer and examining it as a precursor to other polydiacetylenes via post-polymerization modification.

Experimental Section

*Safety note: Dibromobutadiyne (**2**) is explosive at room temperature.* To reduce risks from explosion, compound **2** was prepared only in quantities of less than 200 mg. Dibromobutadiyne should be used immediately, or kept in solution at ≤ 0 °C or as a solid at ≤ −40 °C. When the diyne was prepared, it was immediately mixed with host solutions, pipetted into an evaporating dish cooled to −78 °C and transferred to the chiller.

General procedure for growing crystals: The crystallization experiments were performed in a Fisher Scientific Isotemp Refrigerated/Heated Bath Circulator. The circulator was filled with a cooling bath of water and ethylene glycol (50:50 v/v), which has a freezing point of −30 °C. After the bath was cooled to −15 °C, an evaporating dish containing a solution of diyne **2** and host was placed in the circulator, so that the bottom of the evaporating dish was just below the surface of the bath. To block ambient light, the evaporating dish was covered with aluminum foil, poked with holes to promote evaporation.

After cocrystals form in the cold bath, the crystals must be rinsed with pentane to remove excess monomer from the surface. Otherwise, excess diyne can quickly decompose, and potentially explode, when warmed.

Dibromobutadiyne (**2**): To a 250 mL round-bottom flask were added 1,4-bis(trimethylsilyl)-1,3-butadiyne (0.10 g, 0.5 mmol), *N*-bromosuccinimide (0.19 g, 1.1 mmol), $AgNO_3$ (0.17 g, 1.0 mmol), and acetone (100 mL). The round-bottom flask was wrapped with aluminum foil, and the mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo at 0 °C, and the mixture was poured into cooled pentane (200 mL). A short silicon plug (pentane) was used to remove excess catalyst and byproduct. Solvent was removed in vacuo while holding the sample at 0 °C, resulting in a white flaky solid. Caution: the flaky solid melts and decomposes in seconds at room temperature; therefore, keep it cold and use it immediately after it is prepared.

Oxalamide hosts **3**–**6** were prepared according to literature procedures.[20]

Cocrystal **2·3**: X-ray quality cocrystals were grown by dissolving guest **2** (≈ 30 mg, 0.14 mmol) and host **3** (15 mg, 0.056 mmol) in 3 mL of CH_2Cl_2/MeOH (10:1 to 19:1), which was then allowed to evaporate slowly at −15 °C for 3 days. Once the cocrystals formed, they were warmed slowly to room temperature over 1 day.

Cocrystal **2·5**: Cocrystals were grown by dissolving guest **2** (≈ 30 mg, 0.14 mmol) and host **5** (15 mg, 0.054 mmol) in 3 mL of CH_2Cl_2, which was then allowed to evaporate slowly at −18 °C for 2 days. Once the cocrystals formed, half were transferred to the freezer and held at −15 °C until they could be examined by MAS-NMR at −20 °C. The other half were warmed slowly to room temperature over 1 day and stored for 7 days, then examined by MAS-NMR at room temperature.

X-Ray diffraction: Crystals were selected and mounted on glass fibers using epoxy cement. Each crystal was centered, and the X-ray intensity data were measured on an Oxford Gemini A diffractometer with graphite-monochromated Mo irradiation. The structures were solved by direct methods and refined by using full-matrix least-squares methods (SHELX97).

MAS-NMR: Solid-state ^{13}C NMR spectra were acquired with a Varian Infinity-plus 500 spectrometer, operating at 125.68 and

499.79 MHz for ^{13}C and ^{1}H respectively, and a Varian double-resonance T3-type MAS probe assembly configured for 4 mm (outside diameter) rotors. Spinning rates of 13–15 kHz, a 50 kHz transverse ^{1}H field, and a linear ramp of the ^{13}C field of ± 7 kHz about the first sideband match condition were used for the $^{13}C\{^{1}H\}$ CP-MAS experiments. The $^{1}H \rightarrow {}^{13}C$ contact time was 10 ms and the relaxation delay was 2 s. The ^{13}C chemical shifts are reported with respect to the methylene carbon of adamantane, taken to be +38.5 ppm. Fully relaxed ^{13}C single-pulse MAS-NMR spectra were taken at a 14 kHz spinning rate with direct excitation by a 4-μs pulse (90° pulse was 5 μs) and 500 s relaxation delay. The ^{13}C T1 of PBDA was estimated to be 90 s, from the inversion-recovery null-point method. Typically, a 50–70 kHz ^{1}H decoupling field was applied during acquisition.

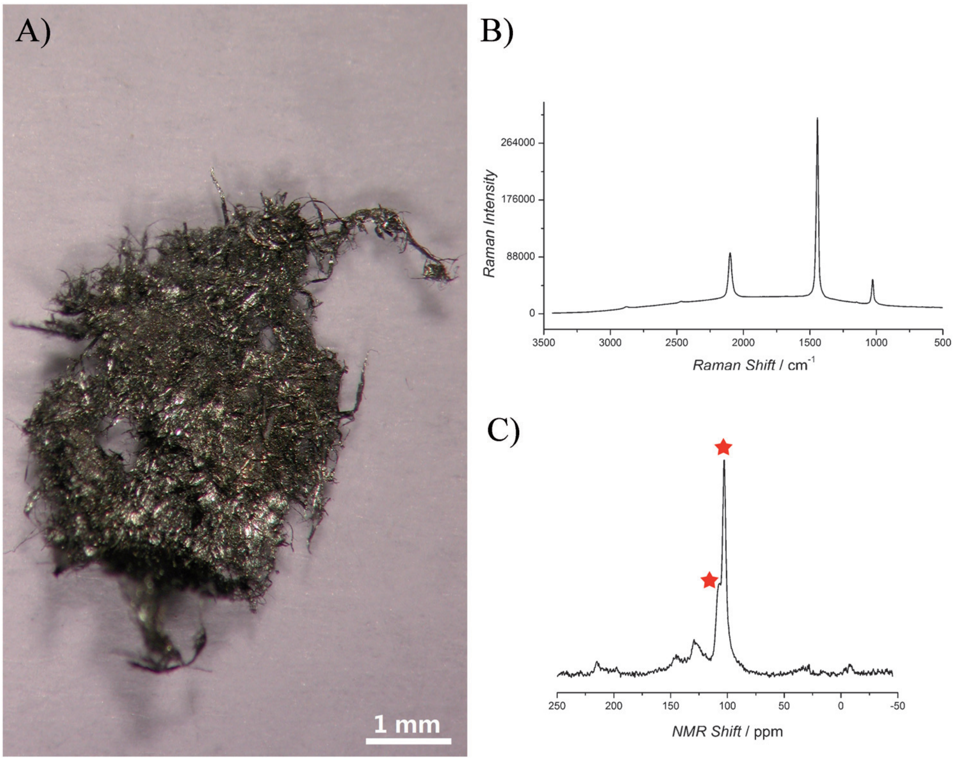

Figure 4. A) Morphology of the isolated PBDA. B) Raman spectrum of the isolated PBDA. C) solid-state ^{13}C direct-excitation MAS NMR spectrum of isolated PBDA. Red stars present polymer peaks.

Raman: Raman microspectroscopy was performed using a Thermo Nicolet Almega dispersive Raman spectrometer coupled to a microscope with infinity-corrected optics. The spectrometer employs a 785 nm class I laser, and the data were collected using a 10x objective lens and an aperture of 25 μm, yielding a spot size of approximately 3 μm. Individual samples were analyzed with 32 or 64 scans of 1 s duration at 10% laser power. The data were then processed and analyzed using the Omnic software suite (Nicolet, USA).

CCDC 981914 contains the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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