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Preparation and Structure of a Tubular Addition Polymer: A True Synthetic Nanotube

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Supporting Information

ABSTRACT: The structure of a synthetic nanotube prepared by the solid-state polymerization of a stacked column of diacetylene-based macrocycles has been determined. A polyether macrocycle monomer with two parallel diacetylene functionalities was prepared. Its crystal structure revealed that the compound crystallizes with structural parameters suitable for topochemical polymerization. Slow annealing of a single crystal for 35 days brought about a single-crystal-to-single-crystal polymerization resulting in the first experimentally determined structure of a tubular addition polymer.

Carbon nanotubes are widely regarded as the prototypical and star players in today's nanotechnology revolution.[1,2] These marvels of chemistry are readily available in kilogram quantities, and potential applications abound. Single-walled carbon nanotubes have a diameter of essentially one nanometer but can have lengths in the millimeter range. From a structural point of view, it is difficult to imagine a better molecular tube.

Chemists have considered this a challenge as they have made many attempts to design and synthesize their own imaginative versions of tubular molecules. In the nanoworld, the structures have often been based upon the ideas of molecular self-assembly and supramolecular chemistry. Numerous tubular structures have been prepared by the self-assembly of a wide variety of substrates. Macrocyclic peptides, carbohydrates, and many purely synthetic monomers form tubular structures via hydrogen bonds.[3−5] Various molecules and polymers have been found to coil naturally into helical structures with a tubular core.[6,7] Aromatic macrocycles have been designed to self-assemble via $\pi-\pi$ stacking to give tubes.[8,9] Tubular structures held together by covalent bonds have been formed from cyclodextrins threaded on to a polyethyleneglycol chain.[10] Ghadiri used olefin metathesis to dimerize peptide macrocycles, yielding short tubular structures.[11]

One promising approach is the preparation of a diacetylene-based tubular addition polymer (Figure 1).[12] An advantage of tubular addition polymers is that they would be robust because of the continuous network of covalent bonds throughout the tubular network. This is a property that they would share with carbon nanotubes. However, a potential advantage of tubular addition polymers that would not shared with conventional carbon nanotubes is that they would be prepared by organic synthesis, which would allow for continuous structural variation for different applications.

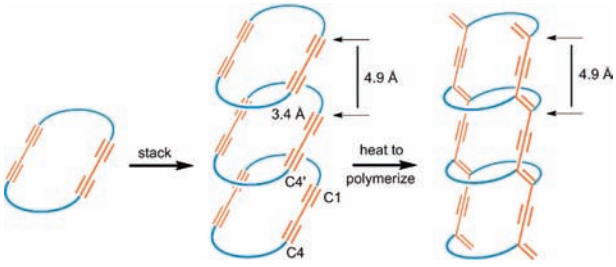

Figure 1. One possible route to a tubular polymer is via a topochemical polymerization of a diacetylene-containing macrocycle. For the reaction to proceed, the macrocycles would need to be spaced near the 4.9 Å expected for polymers with neighboring diacetylene C1−C4′ carbon atoms close to the van der Waals contact distance of 3.4 Å. The application of heat (or radiation) should bring about the polymerization.

What kind of monomer would be needed to give a tubular addition polymer? The obvious candidate would be a macrocycle, one that would self-assemble into a polymerizable stack. Since our own work has been focused on diacetylenes, we considered a macrocycle with a pair of diacetylene functionalities (Figure 1). The difficulty is controlling the spacing. For polymerization to take place, the monomers need to be spaced at a distance near 4.9 Å.

This approach is not new. All sorts of diacetylene macrocycles are known in the literature[12−15] The first reported attempt at macrocycle polymerization was by Vollhardt and Youngs,[13] but their system had a long repeat distance of over 6 Å. More recently, Shimizu[12] reported the polymerization of a diacetylene macrocycle that self-assembled via amide hydrogen bonds. Their spacing was 4.98 Å, very close to the ideal, but a loss of crystallinity prevented the determination of the polymer structure. Nagasawa[16] just reported the polymerization of various gels also formed from amide diacetylene macrocycles.

We designed a system based upon $\pi-\pi$ stacking of an aromatic system. A simple $\pi-\pi$ stack directly aligned in a direction perpendicular to an aromatic ring would give a van der Waals spacing comparable to that in graphite (3.4 Å). However, a slipped $\pi-\pi$ stack is much more common, and distances in excess of 4 Å are found. A number of aromatic derivatives of hexa-2,4-diyne-1,6-diol are known to stack at distances commensurate with the desired 4.9 Å spacing.[17] We reasoned that a macrocycle built from aromatic rings and hexa-2,4-diyne-1,6-diol might give such a stacking. This led us to

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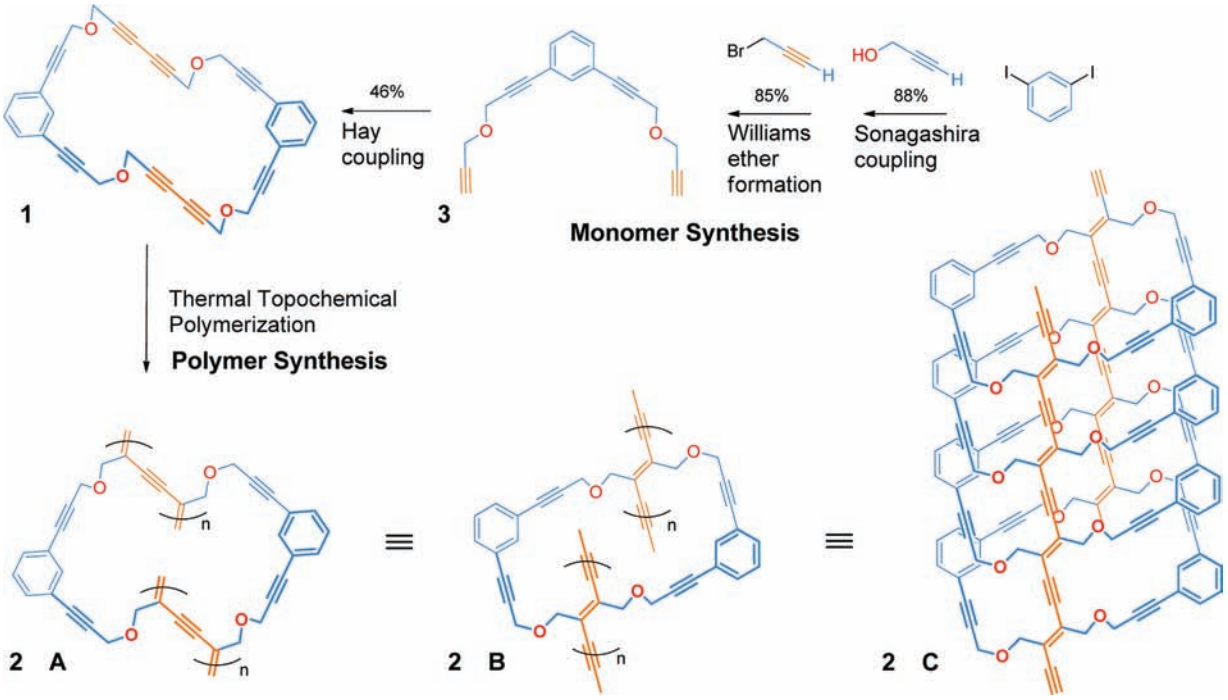

Figure 2. Synthesis of macrocycle **1** from readily available reagents. In the crystalline state, the compound undergoes a topochemical polymerization to give the tubular polymer **2**. Drawing **2 A** shows the original 34-atom macrocycle as it appears embedded within the polymer. After polymerization, a new and smaller 30- atom macrocycle **2 B** can also be identified. The final drawing **2 C** should be compared to the actual structure determined by single-crystal X-ray diffraction (Figure 3D).

design compound **1**, a 34-atom macrocyclic ether with two potentially polymerizable diacetylene functionalities.

Compound **1** was synthesized in three steps from relatively common starting materials (Figure 2). The difficult step was the last step, where the terminal diacetylene **3** was subjected to a cyclic dimerization using a copper-catalyzed oxidative Hay coupling to give the desired macrocycle **1** in 46% yield. A smaller 10% yield of the cyclomonomer was isolated, a small amount of the cyclic trimer was characterized, and the rest of the yield was likely polymeric material. The overall yield of compound **1** starting from 1,3-diiodobenzene was 34%.

The next step in the project required the preparation of single crystals of sufficient size and quality for a single-crystal X-ray diffraction study. A number of solvent systems were investigated, the best turning out to be 1:1 methylene chloride/hexane. Slow evaporation of a solution of **1** in this mixed solvent at room temperature gave pale-orange needles. When the evaporation was carried out at an elevated temperature of 40°, some of the crystals had an initial orange-red color (Figure 3A) but in a short time developed a darker color with a blue cast. Subsequent experiments showed that these two different crystalline forms were two different polymorphs of macrocycle **1**.

Single-crystal X-ray diffraction experiments revealed that the crystals formed at room temperature were monoclinic (Figure 3B), with the molecules of macrocyclic monomers **1** stacked in accordance with the design shown in Figure 1. The repeat distance of 5.09 Å was longer than the ideal repeat distance of 4.9 Å but within the range reported for other successful polymerizations.[18] Indeed, the crystals were very sensitive to heat. Gentle heating (50 °C) rapidly converted the crystals to an amorphous (and nondiffracting) state. When the crystals were kept at room temperature, they became completely amorphous in about 30 days. These transformations were accompanied by a color change to a deep-red, nearly black color. Crystals were examined on the X-ray diffractometer at various stages as the crystallinity was lost, but no structural change could be detected before the crystals became amorphous.

Differential scanning calorimetry (DSC) studies of **1** showed a single exothermic event at 106 °C consistent with a solid-state polymerization reaction. The cooling and reheating curves of the polymerized material were featureless, indicating a nonreversible solid- state change.

The crystals of **1** grown at 40 °C, the second polymorph, belong to the triclinic space group $P\bar{1}$ The molecules of the triclinic form had a different molecular conformation than the molecules of the original monoclinic form, but they had a similar stacked structure (Figure 3C). The molecular repeat distance in the triclinic form was 4.84 Å, quite close to the ideal value of 4.9 Å. Even though the repeat distance within the triclinic polymorph was a bit closer to the ideal value, the triclinic crystals were somewhat more robust than the monoclinic crystals. Initial experiments showed that the triclinic crystals were stable at room temperature but rapidly became amorphous upon heating to 50 °C.

In previous work with noncyclic diacetylenes, we found that slow annealing of a diacetylene monomer crystal at a relatively low temperature can bring about a single-crystal-to-single-crystal polymerization that is otherwise unobservable.[19] Following this idea, one particularly well formed crystal of the triclinic polymorph of **1** was chosen, and the monomer structure was verified using single-crystal X-ray diffraction. The crystal was then subjected to slow annealing at 40° in a temperature-controlled oven. At various intervals the crystal was removed from the oven and returned to the diffractometer, and the structure was redetermined. Signs of polymerization could be seen after 3 days of heating, as additional peaks

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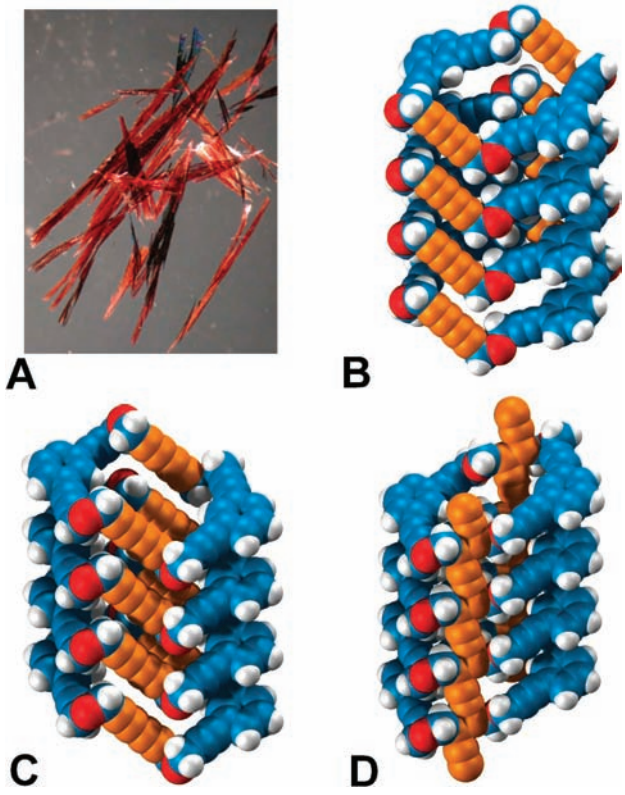

Figure 3. (A) Freshly formed crystals of the triclinic polymorph of macrocycle **1** grown at 40°. Upon sitting, these crystals developed a darker blue cast. The longest crystals in the picture were about 2 mm long with a thickness of only a few hundredths of a millimeter. (B) Observed molecular stacking in the monoclinic form of monomer **1**. The repeat distance of 5.09 Å was longer than the ideal polymerization value of 4.9 Å. (C) Observed molecular stacking in the triclinic form of monomer **1**. The observed repeat distance of 4.84 Å was much closer to the ideal value. (D) Structure of polymer **2** obtained by slow annealing of the triclinic crystals at 40°.

appeared in the diffraction-determined electron density maps. As the heating continued day by day, the percentage of polymer could be seen to increase, accompanied by a decrease in monomer content as well as a decrease in crystal quality. After 35 days of annealing at 40 °C, the crystal was returned to the diffractometer for the 20th and last successful crystal structure determination. This final structural analysis of the annealed crystal showed only the desired polymer structure (Figure 3D). Because of a lack of data, the structure of polymer **2** was not of high quality, but the polymerization appeared to be substantially complete. Further heating of the crystal gave only a scattering of diffraction data so the annealing experiment was brought to an end.

The molecular structure of polymer **2** (Figure 3D) is in complete accordance with the design shown in Figure 1. The macrocyclic monomers underwent a double-addition polymerization reaction to give a tubular polymer. The inner cross section of an idealized monomer is a roughly 11 Å × 12 Å oval (or roughly a 1 nm circle), which is large enough for the monomer to hold a guest molecule within its interior. However, the molecules crystallize to form a tube with an empty interior, with the macrocycle adopting a conformation with a smaller 7.5 Å × 11.5 Å cross section (Figure 4A). Furthermore, the rings tilt when they stack, closing down the tube interior and bringing opposing methylene groups into contact (Figure 4B).

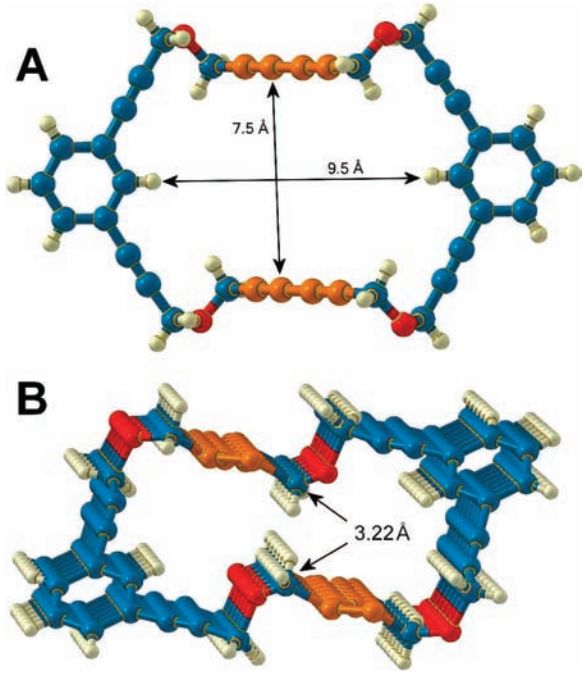

Figure 4. (A) The macrocycle monomers have a rectangular cross section of 7.5 Å × 9.5 Å. (B) The monomers stack at an angle such that the cross section of the tubular polymer **2** is reduced with a 3.22 Å contact between opposite methylene groups.

This is in keeping with the well-known principle "*Natura abhorret vacuum*":[20] one simply does not expect to find empty space within condensed matter. The molecular tilting is expected from a packing perspective, because direct stacking of flat molecules would bring atoms into direct "bump to bump" contact. Tilting removes these unfavorable contacts and also brings the neighboring C1 and C4′ atoms into the close contact needed for the polymerization step (Figure 1).

It is interesting that two polymorphs of monomer **1** were isolated. The conformations of the molecules in the two polymorphs are different. Each has inversion symmetry with four independent ether C−O bonds. In the monoclinic polymorph, three of these bonds are gauche and one is anti. In the triclinic polymorph, all four independent C−O bonds are gauche. Despite this major conformation difference, both polymorphs have the molecules stacked in accordance with the parameters needed for the polymerization. The monoclinic form has a longer repeat distance of 5.09 Å versus a distance of 4.84 Å in the triclinic form. The important neighboring C1−C4′ contact between potential reacting atoms (3.7 Å) is shorter in the monoclinic structure than in the triclinic structure (3.9 Å). The "ideal" distances are 4.9 Å for the repeat and 3.4 Å for the contact. Both the monoclinic and triclinic forms appear to undergo the polymerization reaction, but only for the triclinic form is this a crystal-to-crystal process. The repeat distance appears to be the most important parameter. An incommensurate monomer−polymer repeat distance would naturally lead to more crystal motion and presumably be more likely to yield an amorphous solid.[18]

Freshly made samples of **1** rapidly acquired color indicative of the polymerization even though the amount of polymer was at a level not detected by the single-crystal X-ray studies. However, evidence of this initial polymerization could be seen in a Raman spectrum of a fresh sample, which showed the two

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strong resonance-enhanced bands characteristic of polydiacetylenes.[12] The Raman spectrum of the fully polymerized crystals of **2** showed these two bands, at 1484 and 2095 cm^{-1}, at a much greater intensity.

Once the polymerization occurred, we found the crystals to be totally insoluble in a wide range of standard solvents. One would expect an isolated tube to be a flexible molecule able to incorporate solvent or other small molecules within the interior. Because of the complete lack of solubility, we have not yet been able to verify this hypothesis. The synthesis of **2** is straightforward from readily available starting materials, and more soluble analogues should be possible using similar synthetic methodology. Soluble analogues should have the open void space that would increase the potential applicability of molecular tubes.[21]

Should one call polymer **2** a synthetic nanotube? We believe so. The interior is 1 nm across in the long direction, and the outer dimensions are about 1 nm × 2 nm; the length is indeterminately long. In an idealized conformation, the tubes would have a roughly circular cross section of about 1 nm, very similar to that of a single-walled carbon nanotube.

The significance of this new polymer is that it is the first example of a structurally characterized tubular addition polymer and that a general strategy for synthesizing any tubular polymer has been confirmed. One can imagine that the power of organic synthesis may lead to similar polymers that can be tailor-designed for a wide range of applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization details, Raman spectra of **1** and **2**, DSC study of **1**, color photographs of crystals of **1** and **2**, representations of the molecular conformations of **1**, and CIF files for the two polymorphs of monomer **1** and the structure of polymer **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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